Surface Analysis of Nanomaterials

(나노소재표면분석)

:Surface and Thin Film Analysis

(표면 및 박막분석)

장소: 공과대학 6호관 510호

시간: 목 (1-A, 1-B, 2-A, 2-B, 3-A, 3-B)

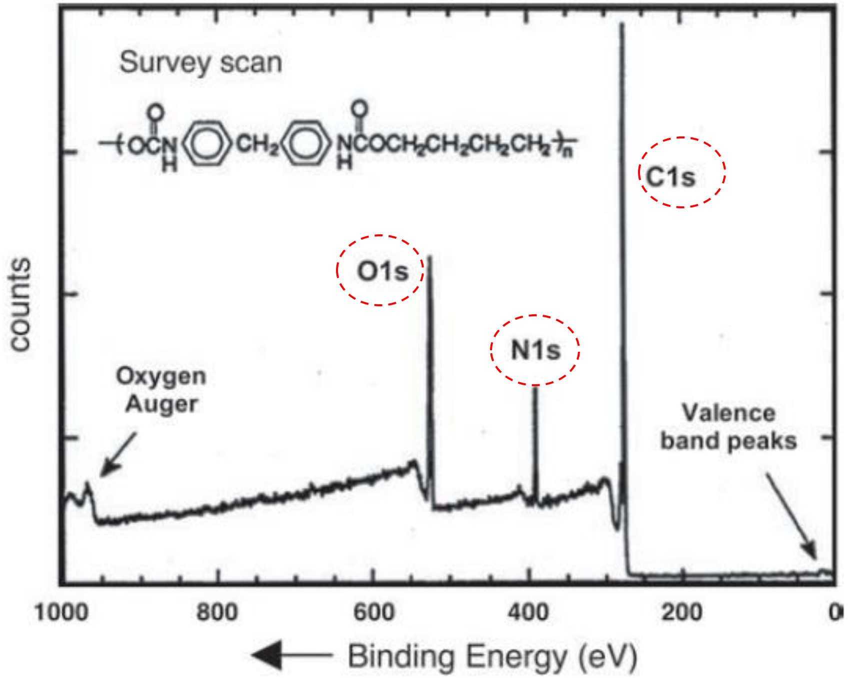
2. Electron Spectroscopy for Chemical Analysis

Electron Spectroscopy for Chemical Analysis

Spectral Features

The understanding and analysis of ESCA spectra

First, ESCA analyses are typically performed by taking a **wide scan** or **survey scan** spectrum, <u>often covering a range of 1100 eV</u>.



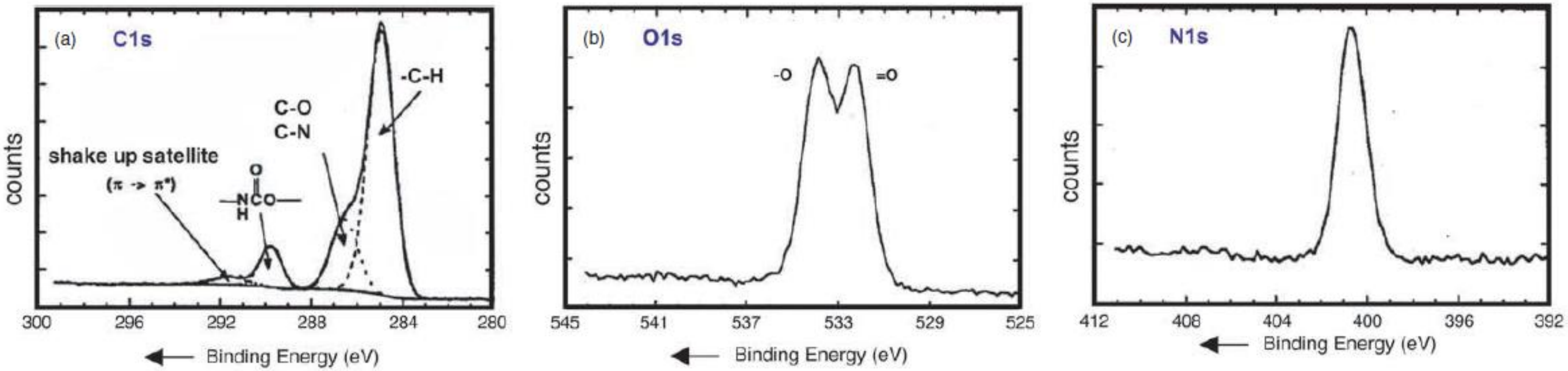
More detail scans
-> Oxygen
-> Carbon
-> Nitrogen

The ESCA survey scan of a hard-segment polyurethane

Electron Spectroscopy for Chemical Analysis

Spectral Features

Looking in more detail over smaller ranges (perhaps 20 eV) at specific features found in the wide scan spectrum

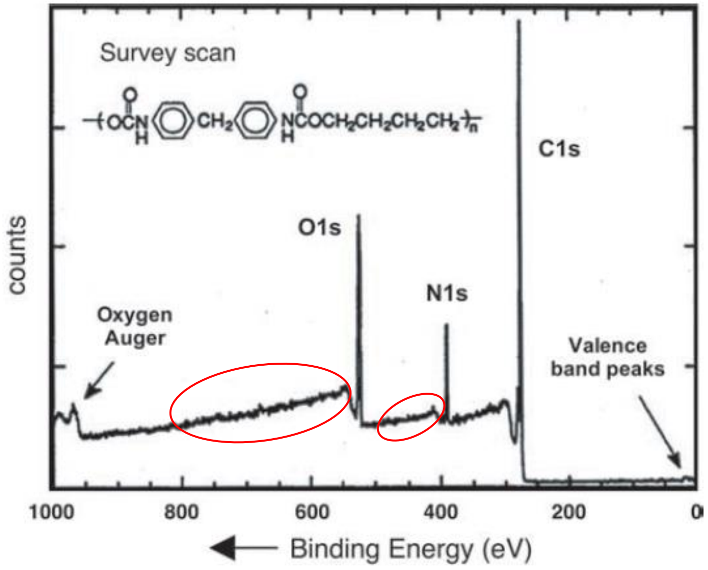


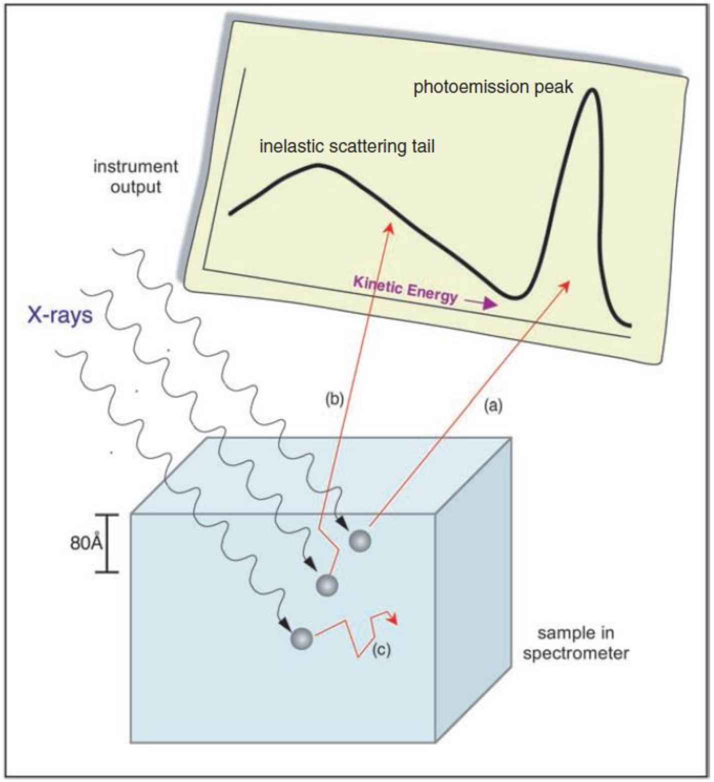
- From the Einstein equation, it is apparent that we could also plot it in terms of KE
- the KE of the emitted photoelectron is a precisely measured value. The binding energy is a calculated value computed from the KE
- The binding energy is a calculated value computed from the KE, the energy of the X-ray photon, the work function of the surface, and a correction term due to electrical charge accumulation on the surface.

Electron Spectroscopy for Chemical Analysis

Spectral Features

The background



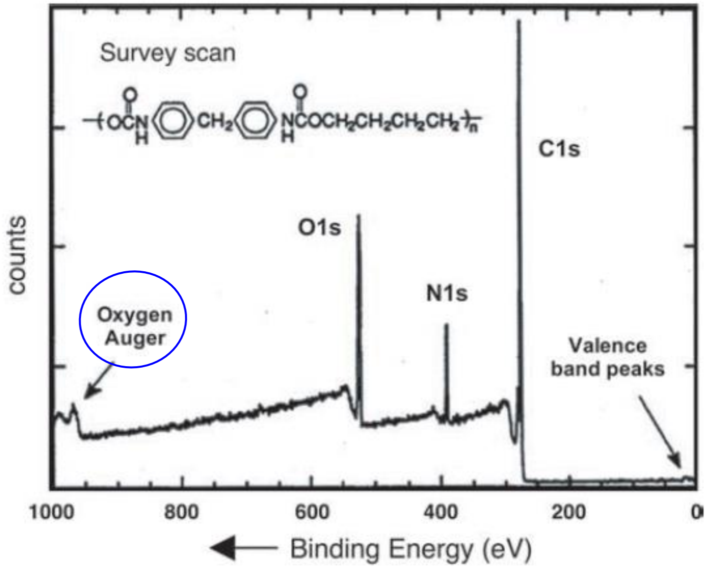


The number of counts attributed to the background will typically first increase abruptly and then decrease slowly with increasing binding energy (decreasing kinetic energy) above the photoemission peak → inelastic scattering

Electron Spectroscopy for Chemical Analysis

Spectral Features

The background



- Photoemission peaks associated with **core-level photoionization** events and X-ray-induced **Auger electron emission** peaks.

If binding energy referencing has been performed, peaks can be readily identified from their positions using **tabulations** of binding energy values

Electron Spectroscopy for Chemical Analysis

Spectral Features

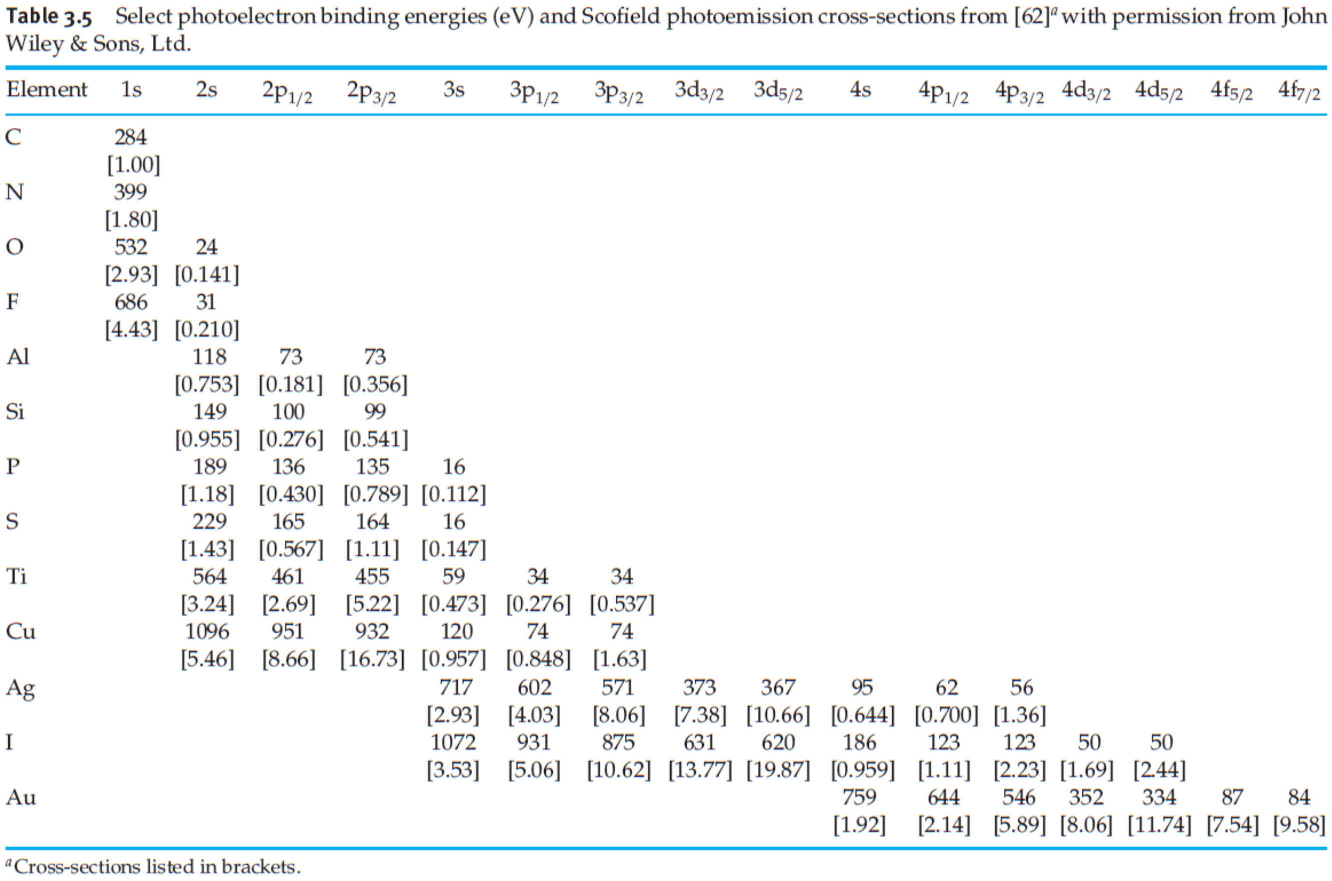


Table 3.5 Select photoelectron binding energies (eV) and Scofield photoemission cross-sections from [62][a] with permission from John Wiley & Sons, Ltd.

Element	1s	2s	$2p_{1/2}$	$2p_{3/2}$	3s	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$	4s	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	$4f_{5/2}$	$4f_{7/2}$
C	284 [1.00]															
N	399 [1.80]															
O	532 [2.93]	24 [0.141]														
F	686 [4.43]	31 [0.210]														
Al		118 [0.753]	73 [0.181]	73 [0.356]												
Si		149 [0.955]	100 [0.276]	99 [0.541]												
P		189 [1.18]	136 [0.430]	135 [0.789]	16 [0.112]											
S		229 [1.43]	165 [0.567]	164 [1.11]	16 [0.147]											
Ti		564 [3.24]	461 [2.69]	455 [5.22]	59 [0.473]	34 [0.276]	34 [0.537]									
Cu		1096 [5.46]	951 [8.66]	932 [16.73]	120 [0.957]	74 [0.848]	74 [1.63]									
Ag					717 [2.93]	602 [4.03]	571 [8.06]	373 [7.38]	367 [10.66]	95 [0.644]	62 [0.700]	56 [1.36]				
I					1072 [3.53]	931 [5.06]	875 [10.62]	631 [13.77]	620 [19.87]	186 [0.959]	123 [1.11]	123 [2.23]	50 [1.69]	50 [2.44]		
Au										759 [1.92]	644 [2.14]	546 [5.89]	352 [8.06]	334 [11.74]	87 [7.54]	84 [9.58]

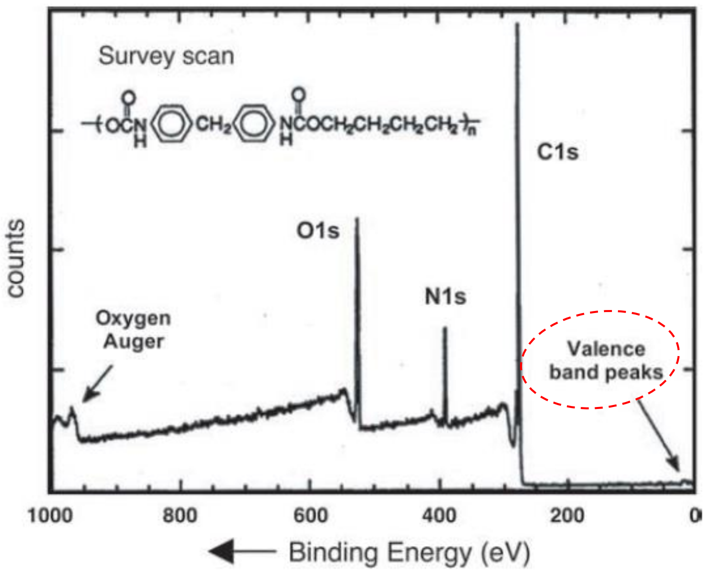
[a] Cross-sections listed in brackets.

the binding energies of a few select photoemission lines produced with Al $K\alpha$ irradiation (1487 eV)

Electron Spectroscopy for Chemical Analysis

Spectral Features

The background



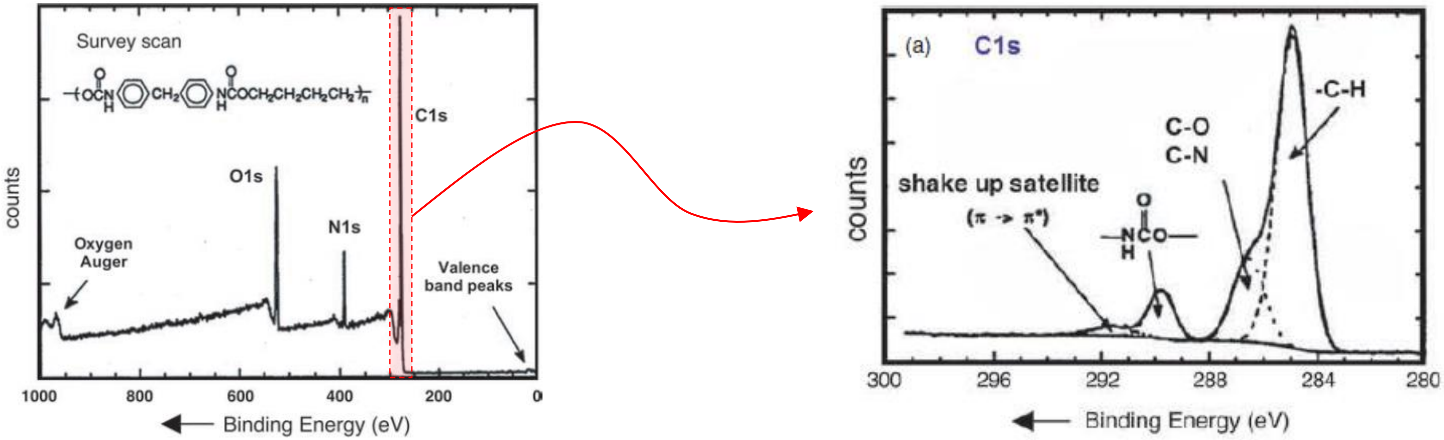
– The final feature to be discussed in thiswide scan spectrum is observed at low binding energies. The low–intensity features seen between 0 and 30 eV are due to photoemission of valence (outer shell) electrons

– Interpretation of these spectral features is often more complex than the core–level lines –> we will discuss this later.

Electron Spectroscopy for Chemical Analysis

Spectral Features

Additional Detail in the high-resolution ESCA spectra



- From the peak shape, it is apparent that this spectrum is composed of a number of subpeaks. These subpeaks, attributed to chemical shifts from atoms and groups bound to the carbons

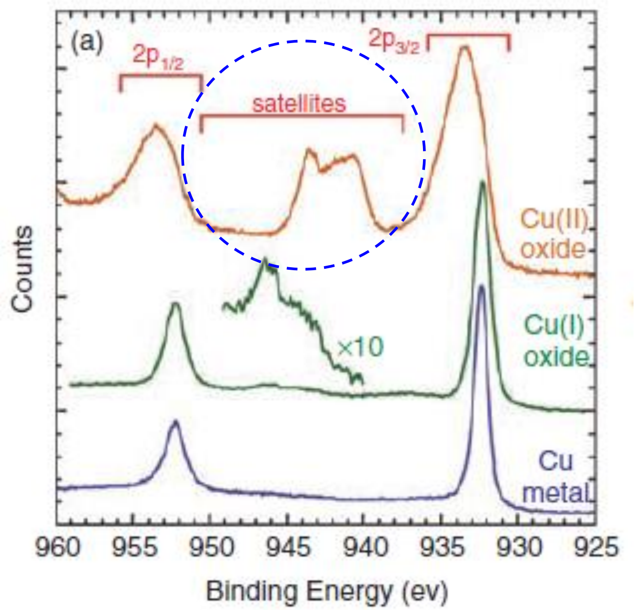
- Another feature is noted at 6.6 eV from the lowest binding energy (hydrocarbon) peak. This peak is referred to as a shake-up satellite. It represents photoelectrons that have lost energy through promotion of valence electrons from an occupied energy level (e.g. a π level) to an unoccupied higher level (e.g. a $\pi *$ level).

Electron Spectroscopy for Chemical Analysis

Spectral Features

“Shake-up peaks”

- Shake-up peaks (also called ‘loss peaks’ because intensity is lost from the primary photoemission peak) are most apparent for systems with aromatic structures, unsaturated bonds or transition metal ions



Examples of the Cu_2O and CuO shake-up satellites

Electron Spectroscopy for Chemical Analysis

Spectral Features

"Shake-off peak"

- If the departing photoelectron transfers sufficient energy into the valence electron to ionize it into the continuum, the photoemission loss peak is called a 'shake-off' peak

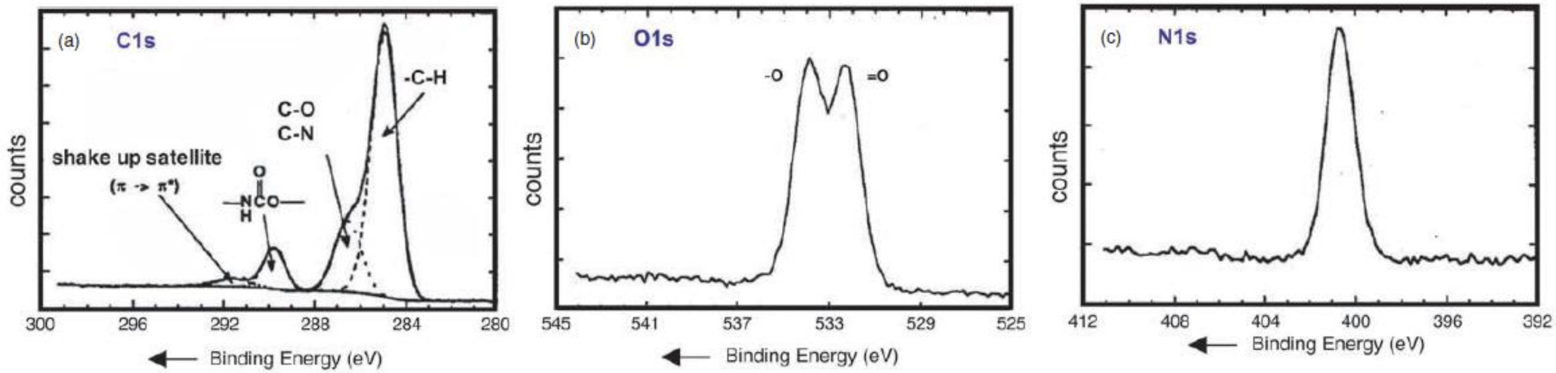
- The shake-off satellite peaks of the photoemission peak can have a wide range of possible energies (of course, always with a lower KE than the photoemission peak)

- This energetically broad feature is typically hidden within the background signal and is usually not detected or used analytically

Electron Spectroscopy for Chemical Analysis

Spectral Features

- High-resolution spectra of each of the features found in the wide scan spectrum are examined to extract maximum information.



- The information from a complete dataset **should be collaborative and not contradictory**

- For example, where **significant levels of oxygen** are seen in a wide scan spectrum of an organic polymer, subpeaks associated with **carbons bound to oxygen should be found in the high-resolution C_{1s} spectrum**

- the subpeaks in the O_{1s} spectrum should also have binding energies appropriate for oxygen-carbon functionalities

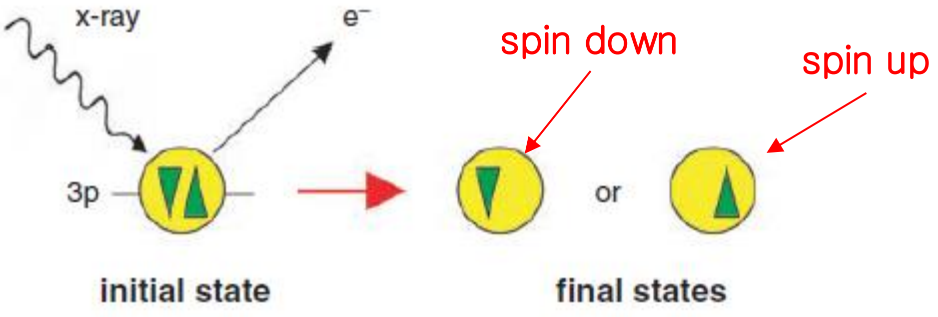
Electron Spectroscopy for Chemical Analysis

Spectral Features

About inorganic systems

⟶ Spin–orbit doublets, Multiplet splitting, Plasmon losses

“Spin–orbit doublets”



- The initial state and final states (after photoemission) for a pair of electrons in a 3p orbital

- Two energetically equivalent final states are possible, ‘**spin up**’ or ‘**spin down**’

Electron Spectroscopy for Chemical Analysis

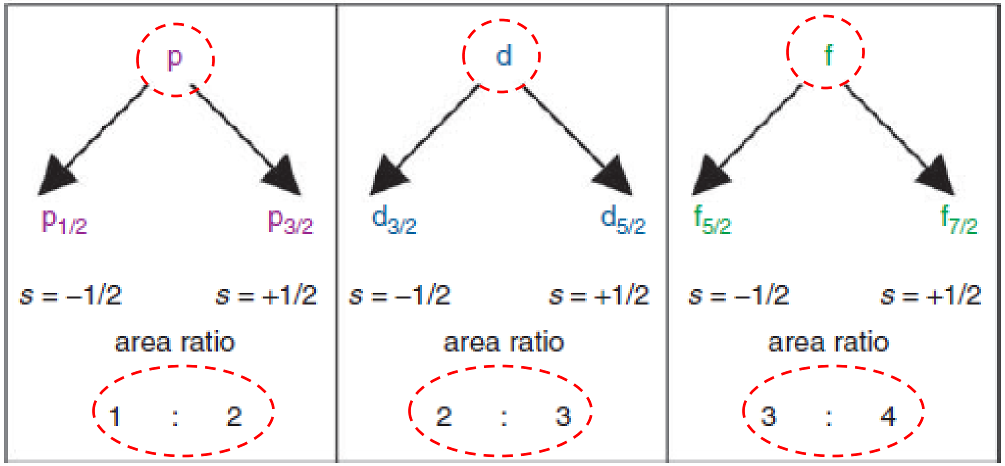
Spectral Features

"Spin–orbit doublets"

– If there is an open shell (quantum number 1 > 0, i.e. p, d, or f orbital) with two states of the same energy (orbital degeneracy), a magnetic interaction between the spin of the electron (up or down) and its orbital angular momentum may lead to a splitting of the degenerate state into two components

– This is called spin–orbit coupling or j–j coupling (j quantum number = 1 + s)

– The ratio of their respective degeneracies, $2j + 1$, determines the intensities of the components



Electron Spectroscopy for Chemical Analysis

Spectral Features

“Spin-orbit doublets”

Example, the $f_{5/2}$ and $f_{7/2}$ components of a gold 4f photoemission peak

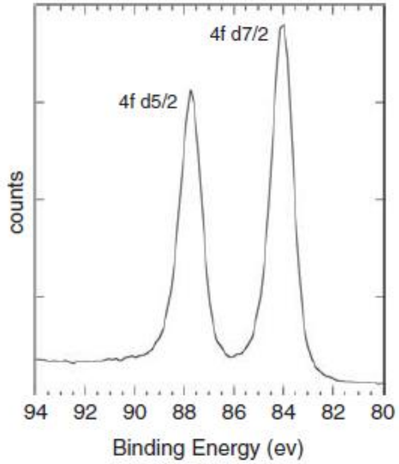


Figure 3.13 Spin–orbit coupling leads to a splitting of the gold 4f photoemission line into two subpeaks

The total 4f photoemission intensity for gold as used in quantitation is the sum of the two spin-orbit peaks. The trend for the doublet separation is $p > d > f$ within a given atom.

Electron Spectroscopy for Chemical Analysis

Spectral Features

"Multiplet (electrostatic) splitting"

- the **s orbital** photoemission from some transition metal ions (e.g. Mn^{+2}, Cr^{+2}, Cr^{+3}, Fe^{+3})

- A requirement for this splitting of the s photoemission peak into a doublet is that there be unpaired orbitals in the valence shells.

- Complex peak splittings can be observed in transition metal ions and rare earth ions when multiplet splitting occurs in p and d levels.

Electron Spectroscopy for Chemical Analysis

Spectral Features

"Plasmon losses"

- The conduction electrons in metals, in contrast to being localized on each atom, have been likened to a 'sea' or continuum

- Characteristic **collective vibrations** have been noted for this continuum of electrons and are referred to as plasmon vibrations

- In some cases, the exiting photoelectron can couple with the plasmon vibrations leading to characteristic, periodic energy losses

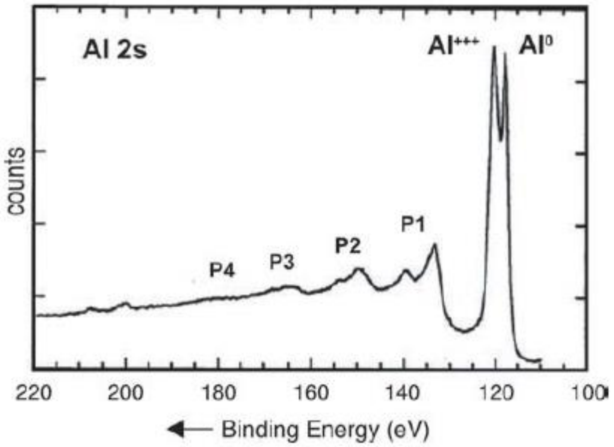


Figure 3.14 Plasmon loss peaks for the aluminum 2s photoemission peak

Electron Spectroscopy for Chemical Analysis

Spectral Features

A feature that is associated with the type of instrument is the **X-ray satellite**

Table (below) summarizes all features that are important both to understand the spectra obtained, and for enhancing the information content of the ESCA experiment

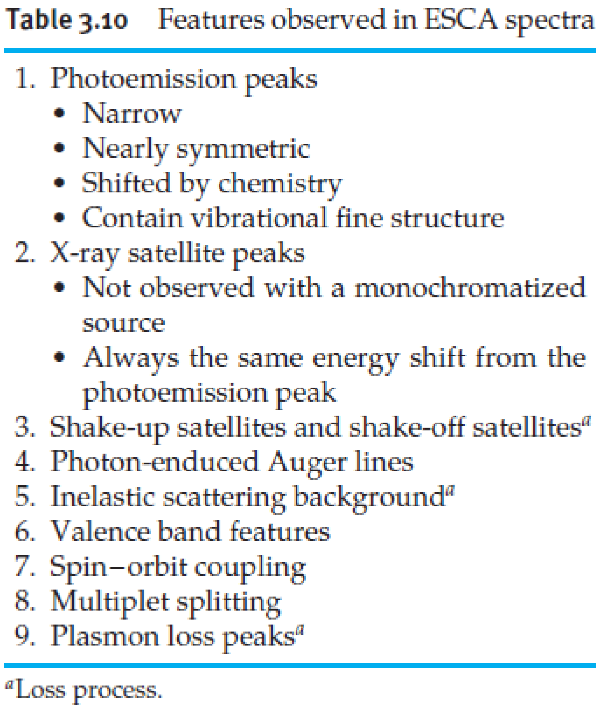


Table 3.10 Features observed in ESCA spectra

1. Photoemission peaks
   - Narrow
   - Nearly symmetric
   - Shifted by chemistry
   - Contain vibrational fine structure
2. X-ray satellite peaks
   - Not observed with a monochromatized source
   - Always the same energy shift from the photoemission peak
3. Shake-up satellites and shake-off satellites[a]
4. Photon-enduced Auger lines
5. Inelastic scattering background[a]
6. Valence band features
7. Spin–orbit coupling
8. Multiplet splitting
9. Plasmon loss peaks[a]

[a] Loss process.

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Chemical Effects in XPS

- Chemical shift: change in binding energy of a core electron of an element due to a change in the chemical bonding of that element.

Qualitative view

Core binding energies are determined by electrostatic interaction between it and the nucleus
Reduced by:
- the electrostatic shielding of the nuclear charge from all other electrons in the atom (including valence electrons)
- removal or addition of electronic charge as a result of changes in bonding will alter the shielding

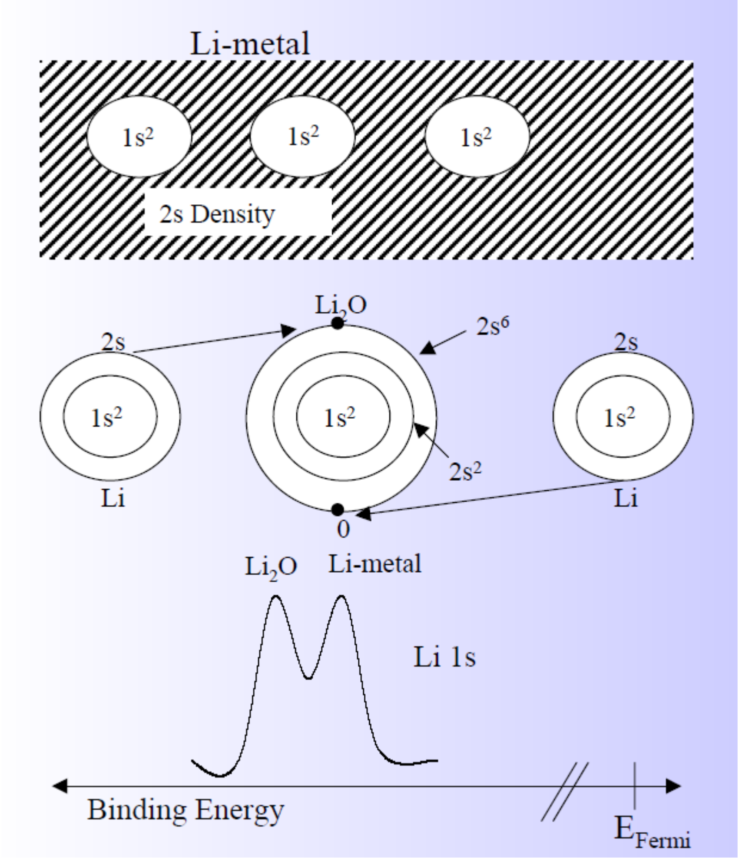
Withdrawal of valence electron charge (oxidation)-->> increase in BE
Addition of valence electron charge -->> decrease in BE

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Chemical Effects in XPS

Oxide Compared to Metal



Binding Energy is lower due to increased screening of the nucleus by 2s conduction by 2s electrons

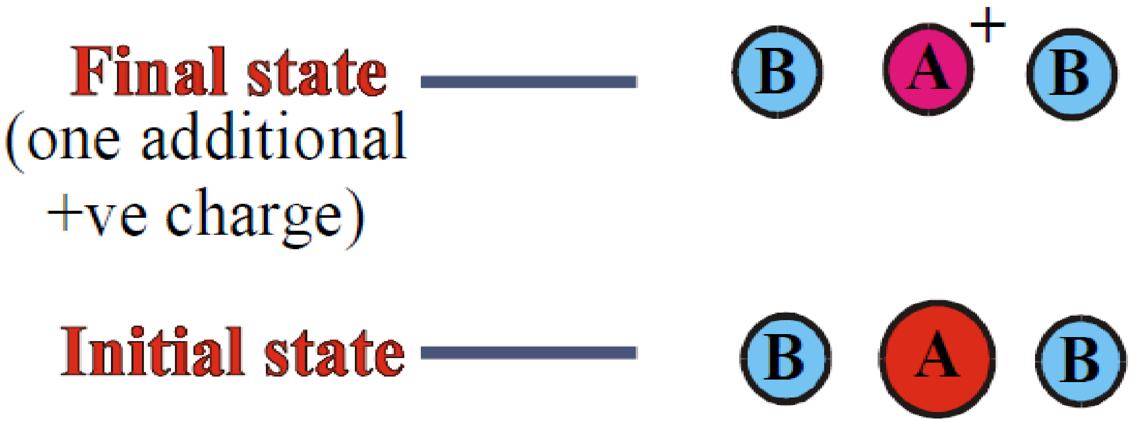
Binding Energy is higher because Li 2s electron density is lost to oxygen

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Photoemission Process can be thought of as 3 steps:

(a) Photon absorption and ionisation (initial state effects)
(b) Response of atom and creation of photoelectron (final state effects)
(c) Transport of electron to surface (extrinsic effects)



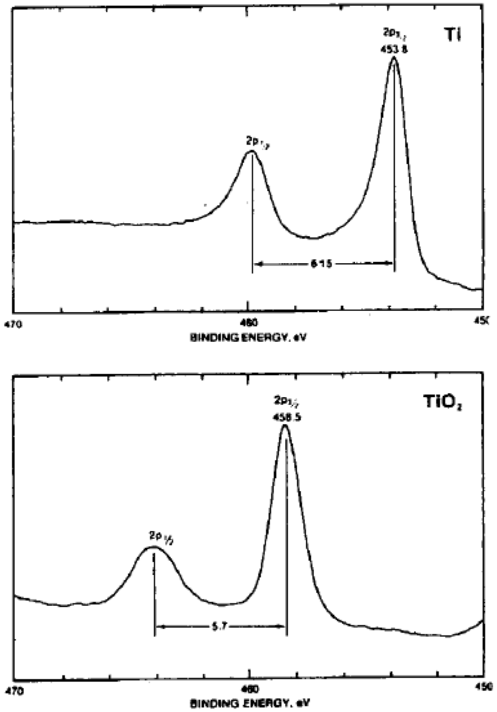
Final state
(one additional
+ve charge)

Initial state

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Usually chemical shifts are thought of as initial state effect (i.e. relaxation processes are similar magnitude in all cases)



Ti $2p_{1/2}$ and $2p_{3/2}$ chemical shift for Ti and Ti^{4+}. Charge withdrawn Ti → Ti^{4+} so 2p orbital relaxes to higher BE

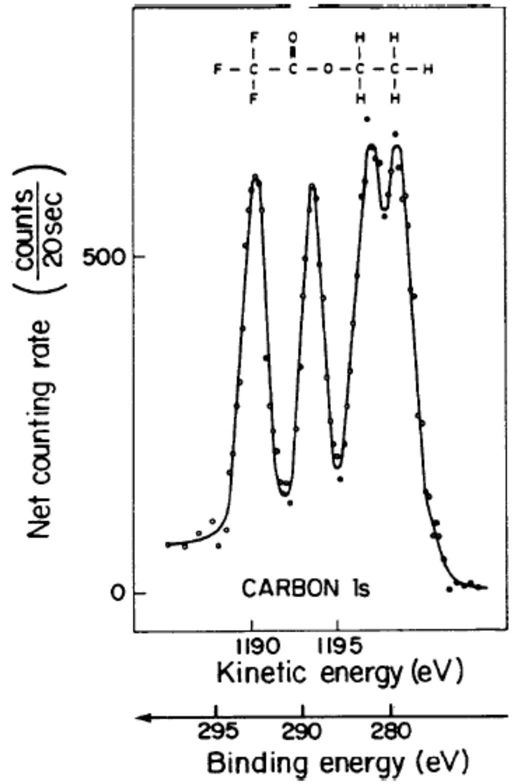
Note: Spin-orbit splitting is approximately constant - confirming SOS is largely an initial state effect

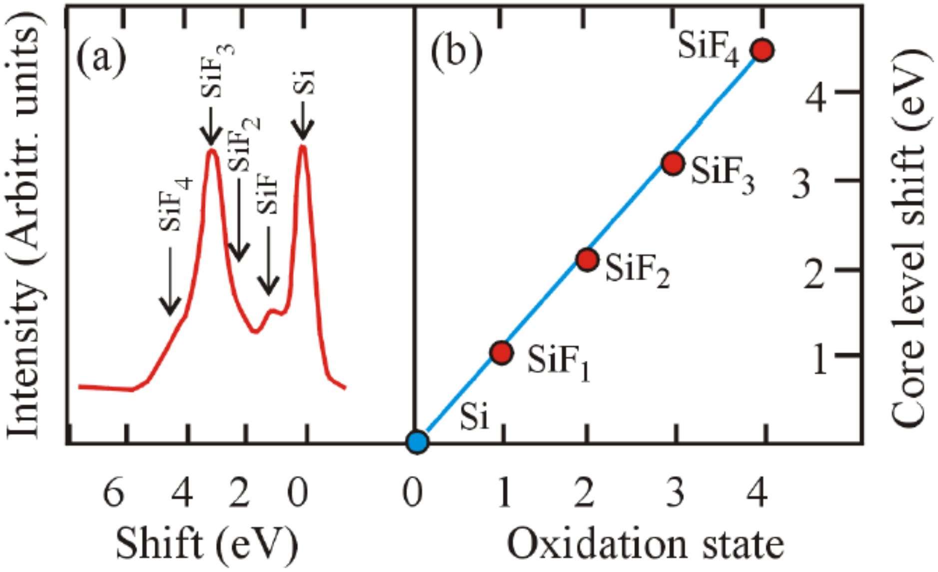
Chemical shift information very powerful tool for functional group, chemical enviroment, oxidation state

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts



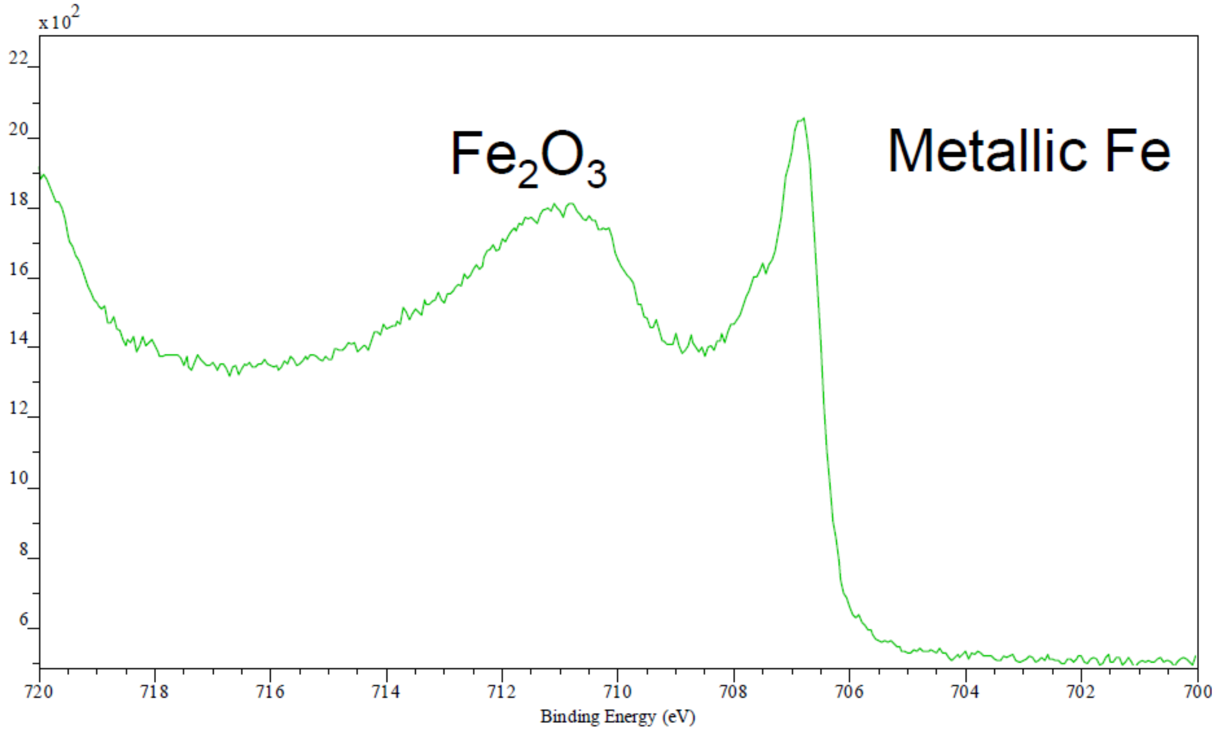


Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

Detailed Iron 2p Spectrum of High Purity Iron

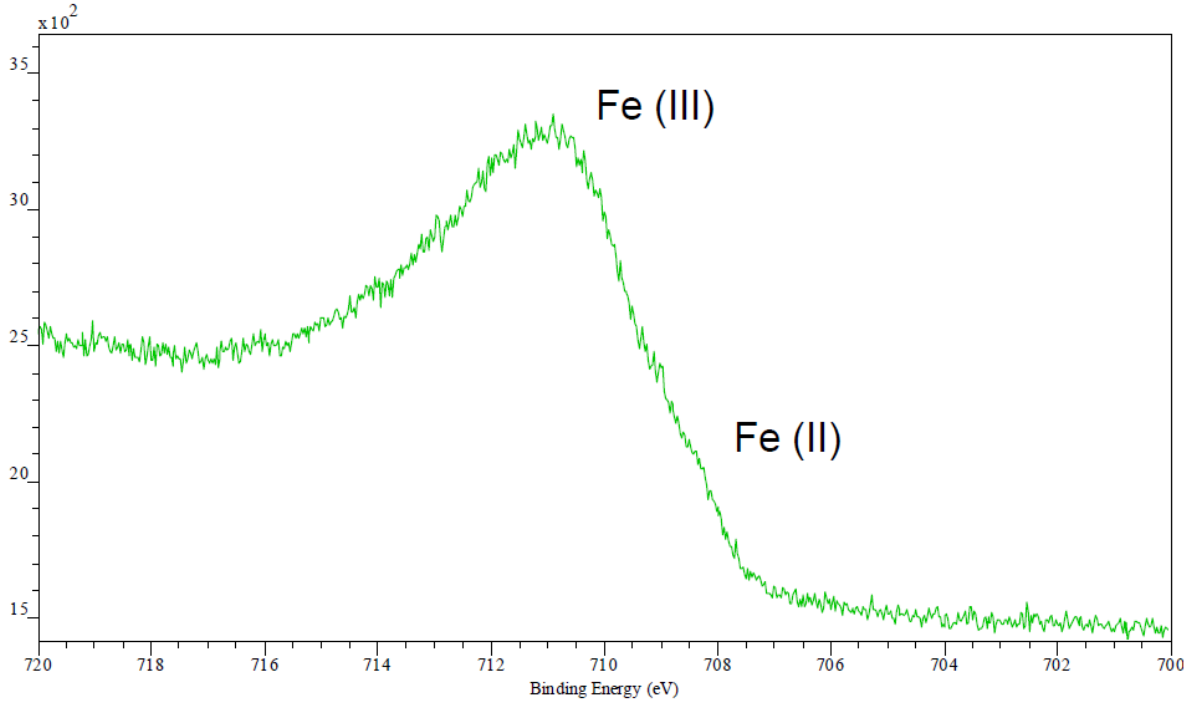


Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

Detailed Spectrum of Fe 2p line for Magnetite (partly oxidized)

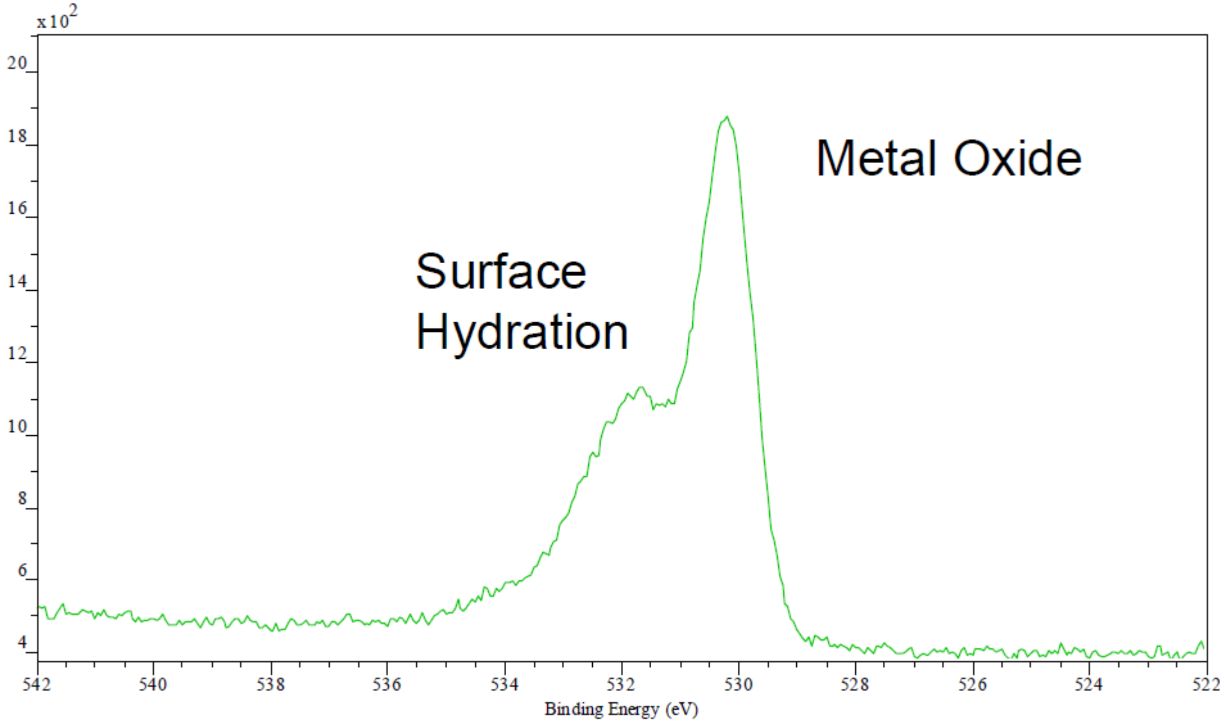


Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

Detailed Oxygen 1s Spectrum

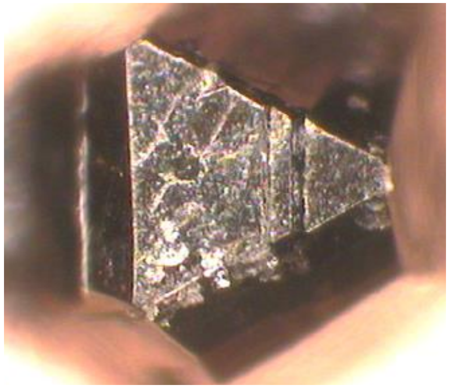


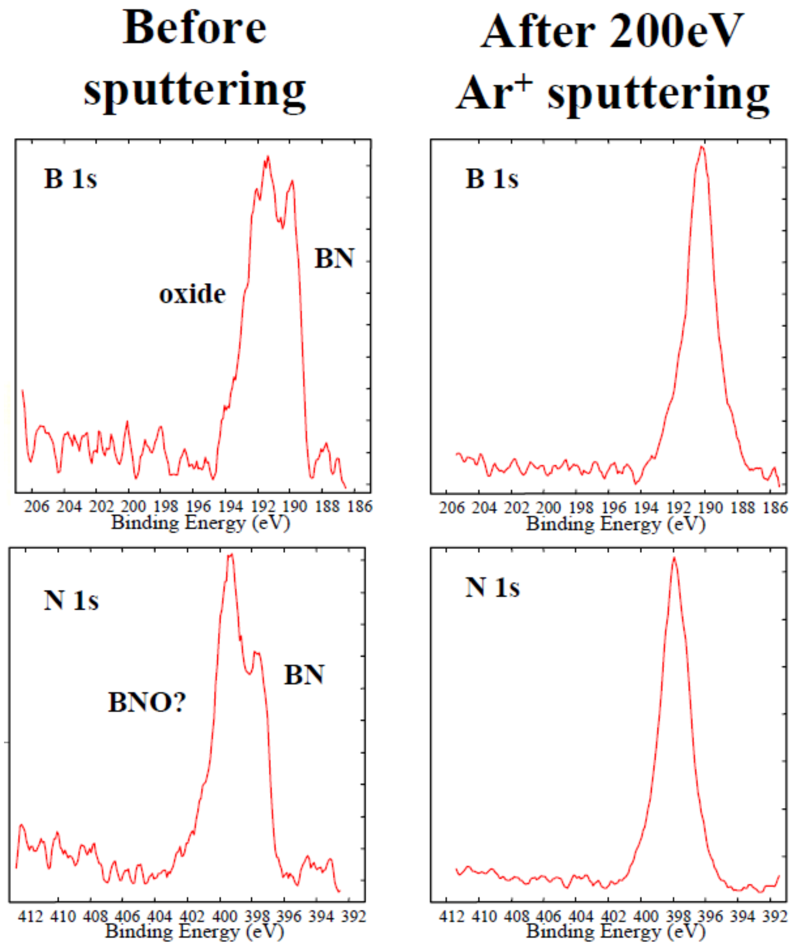
Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

Cubic – BN crystal



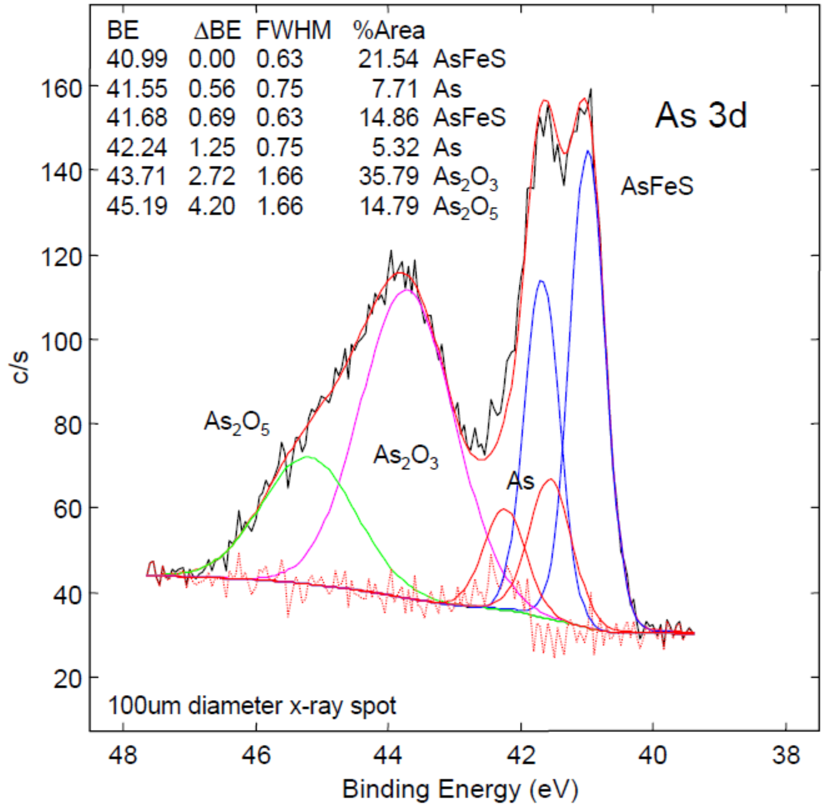


Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

High Resolution Spectra Arsenopyrite



BE	ΔBE	FWHM	%Area	
40.99	0.00	0.63	21.54	AsFeS
41.55	0.56	0.75	7.71	As
41.68	0.69	0.63	14.86	AsFeS
42.24	1.25	0.75	5.32	As
43.71	2.72	1.66	35.79	As_2O_3
45.19	4.20	1.66	14.79	As_2O_5

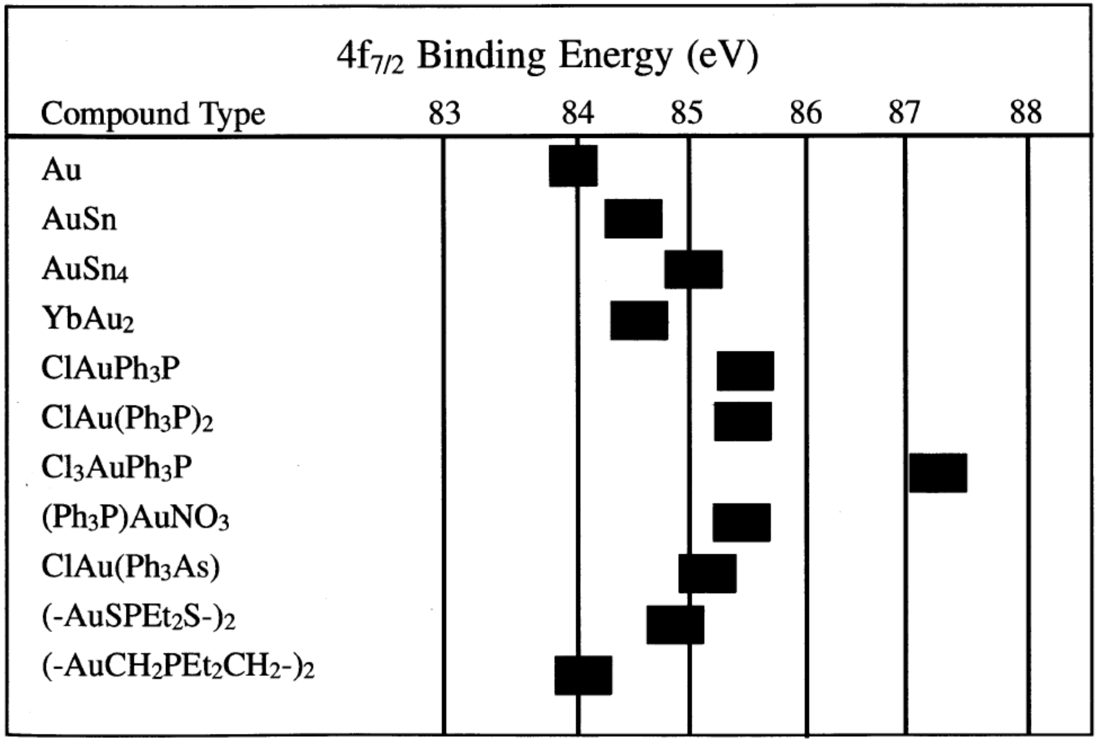
Arsenopyrite is an iron arsenic sulfide (FeAsS)

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

High Resolution Spectra Arsenopyrite



Electron Spectroscopy for Chemical Analysis

More about Chemical shift

X-ray Photoelectron Spectroscopy (XPS) reference page

http://www.xpsfitting.com/

X-ray Photoelectron Spectroscopy (XPS) Reference Pages

X-ray photoelectron spectroscopy (XPS or ESCA) curve fitting procedures, reference materials and useful notes are listed here to provide a starting point for the consistent interpretation of XPS spectra. These reference pages contain tips and techniques that are designed to help both the novice and advanced XPS user.

Showing posts with label **About This Site**. Show all posts

XPS Reference Pages

This site contains information gained from decades of X-ray photoelectron spectroscopy (XPS) analyses of an enormous variety of samples analyzed at Surface Science Western laboratories located at the University of Western Ontario. Originally this site was designed as a place for students and our clients to access valuable tips and information. It has since been opened to all those interested in the XPS technique. Summaries of literature data, relevant references and unpublished data taken of well characterized standard samples are presented. Also curve-fitting tips, instrument set-up tips (specifically for the Kratos AXIS Ultra and Kratos AXIS Nova), and CasaXPS tips pertaining to questions we normally get from our students and clients, and other odd bits of information are presented.

Element and Topic List

Click on each link below to retrieve curve-fitting details, binding energies, FWHM's, spin-orbit splitting values, references and other practical notes for that element. Other general topics are also available. Downloads can be obtained by clicking on the appropriate links.

- About This Site (1)
- Accuracy (1)
- Advanced Quantification (1)

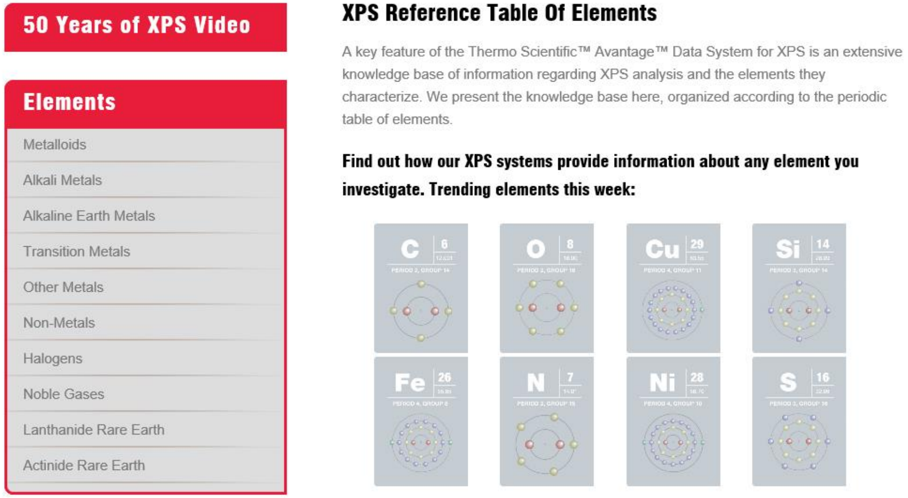
Electron Spectroscopy for Chemical Analysis

More about Chemical shift

X-ray Photoelectron Spectroscopy (XPS) reference page

https://xpssimplified.com/periodictable.php

XPS Elements Table



XPS Reference Table Of Elements

A key feature of the Thermo Scientific™ Avantage™ Data System for XPS is an extensive knowledge base of information regarding XPS analysis and the elements they characterize. We present the knowledge base here, organized according to the periodic table of elements.

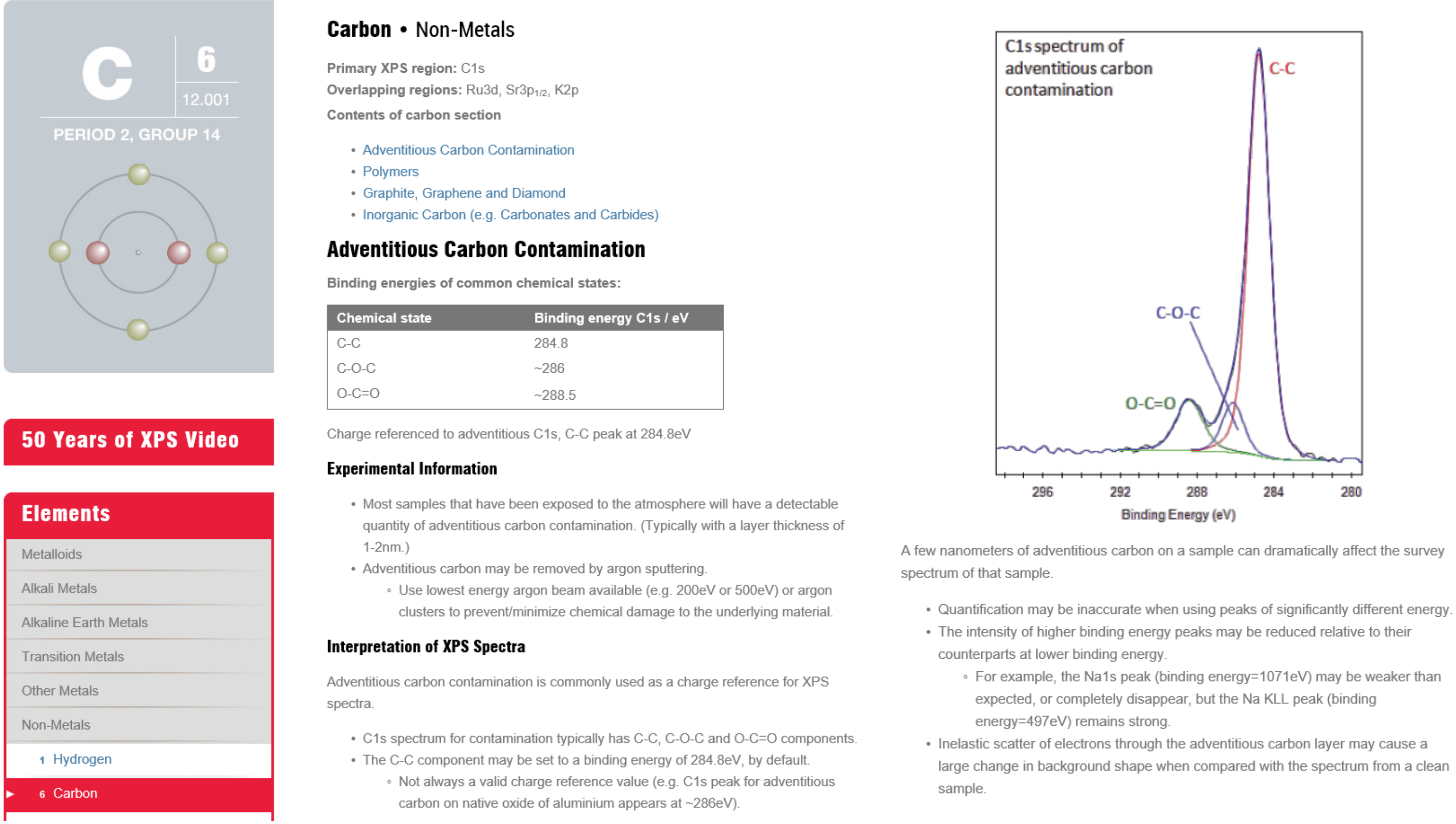
Find out how our XPS systems provide information about any element you investigate. Trending elements this week:

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

https://xpssimplified.com/periodictable.php

Example, **Carbon**



Carbon • Non-Metals

Primary XPS region: C1s
Overlapping regions: Ru3d, Sr3p$_{1/2}$, K2p
Contents of carbon section

- Adventitious Carbon Contamination
- Polymers
- Graphite, Graphene and Diamond
- Inorganic Carbon (e.g. Carbonates and Carbides)

Adventitious Carbon Contamination

Binding energies of common chemical states:

Chemical state	Binding energy C1s / eV
C-C	284.8
C-O-C	~286
O-C=O	~288.5

Charge referenced to adventitious C1s, C-C peak at 284.8eV

Experimental Information

- Most samples that have been exposed to the atmosphere will have a detectable quantity of adventitious carbon contamination. (Typically with a layer thickness of 1-2nm.)
- Adventitious carbon may be removed by argon sputtering.
  - Use lowest energy argon beam available (e.g. 200eV or 500eV) or argon clusters to prevent/minimize chemical damage to the underlying material.

Interpretation of XPS Spectra

Adventitious carbon contamination is commonly used as a charge reference for XPS spectra.

- C1s spectrum for contamination typically has C-C, C-O-C and O-C=O components.
- The C-C component may be set to a binding energy of 284.8eV, by default.
  - Not always a valid charge reference value (e.g. C1s peak for adventitious carbon on native oxide of aluminium appears at ~286eV).

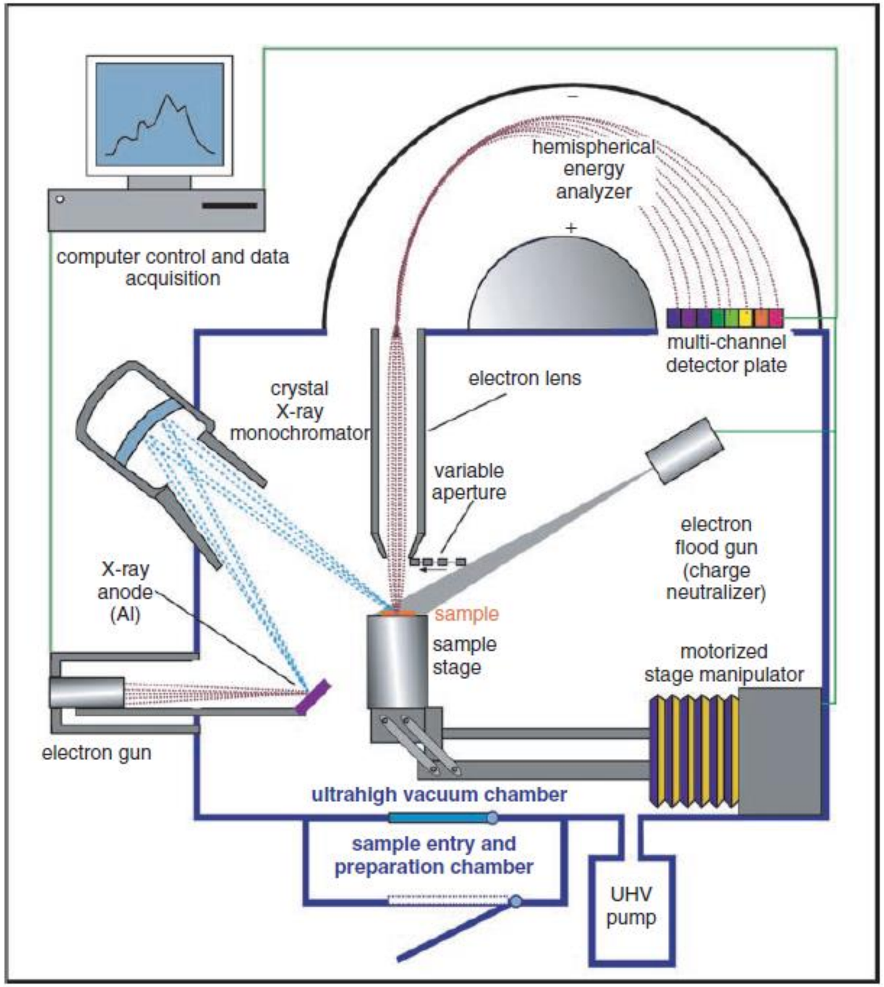
A few nanometers of adventitious carbon on a sample can dramatically affect the survey spectrum of that sample.

- Quantification may be inaccurate when using peaks of significantly different energy.
- The intensity of higher binding energy peaks may be reduced relative to their counterparts at lower binding energy.
  - For example, the Na1s peak (binding energy=1071eV) may be weaker than expected, or completely disappear, but the Na KLL peak (binding energy=497eV) remains strong.
- Inelastic scatter of electrons through the adventitious carbon layer may cause a large change in background shape when compared with the spectrum from a clean sample.

Electron Spectroscopy for Chemical Analysis

Instrumentation

The primary components that make up the ESCA instrument are the **vacuum system**, **X-ray source**, **electron energy analyzer**, and **data system**.



A schematic diagram of an ESCA spectrometer using a monochromatized X-ray source

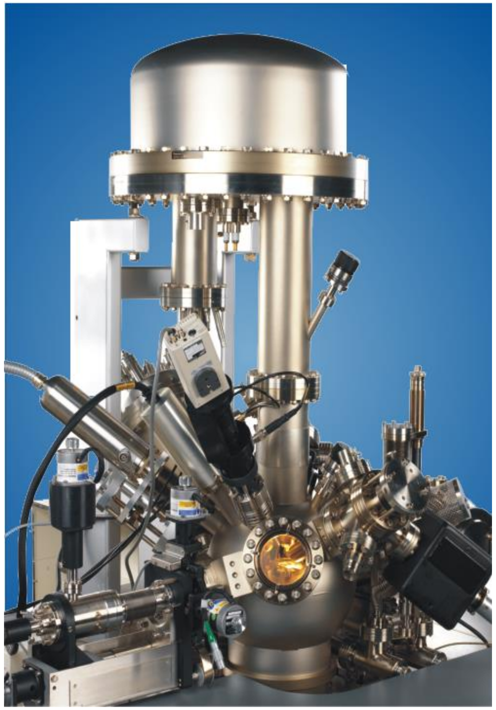
Electron Spectroscopy for Chemical Analysis

Instrumentation

Example

K-Alpha

ESCALAB 250



Electron Spectroscopy for Chemical Analysis

Instrumentation

Vacuum for ESCA analysis

The ESCA experiment must be conducted under vacuum for **three reasons**

- First, the emitted photoelectrons must be able to travel from the sample through the analyzer to the detectorwithout collidingwith gas phasemolecules.

→ 10^{-6}–10^{-7} torr; 1 torr = 133 Pa

- Second, some components such as the X-ray source require vacuum conditions to remain operational.

→ 10^{-6}–10^{-7} torr; 1 torr = 133 Pa

- Third, the surface composition of the sample under investigation must not change during the ESCA experiment.

→ The actual vacuum required will depend on the reactivity of the sample (e.g. metallic Na will require a better vacuum than PTFE). For most applications a vacuum of 10^{-10} torr is adequate. For studies on polymeric materials, good results can usually be obtained with a vacuum of 10^{-9} torr.

Electron Spectroscopy for Chemical Analysis

Instrumentation

Sample loading

- Samples are typically introduced into the analysis vacuum chamber via a load-lock or preparation chamber

- The load-lock is a small volume chamber that can be isolated from the analytical chamber and then backfilled to atmospheric pressure

- Sample manipulators typically have the capability to translate a sample in three directions and to rotate it in one or two directions.

- By coupling different sample mounting techniques with the manipulator capabilities and/or adding other components such as ion guns, a range of different ESCA experiments can be done (variable temperature, variable angle, multisample, destructive depth profiling, etc.).

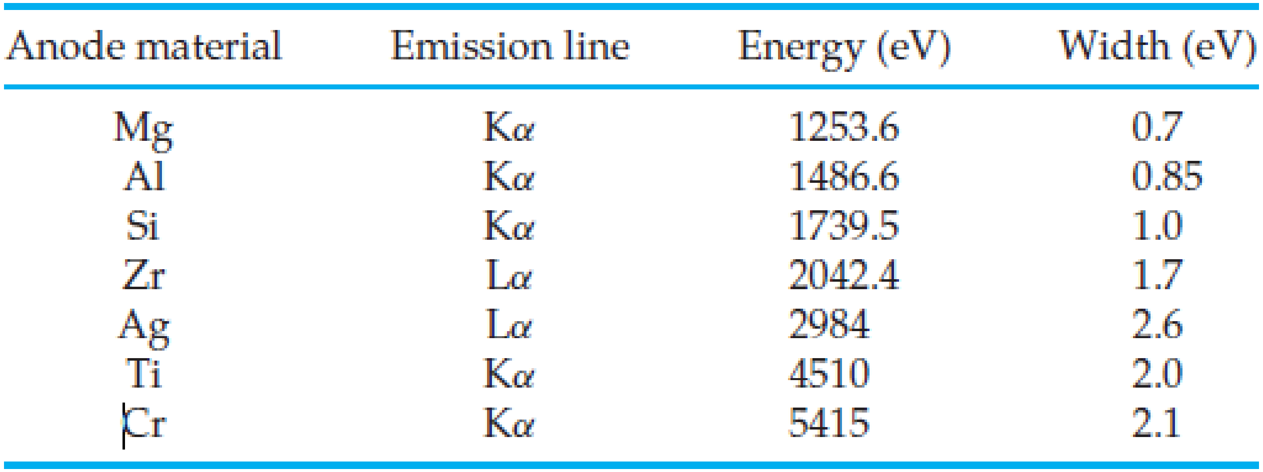
Electron Spectroscopy for Chemical Analysis

Instrumentation

X-ray Source

- X-rays for an ESCA experiment are usually produced by impinging a **high-energy (~10 keV) electron beam** onto a target.

- Common anodes along with the energies of their characteristic emission lines are listed in Table (below)



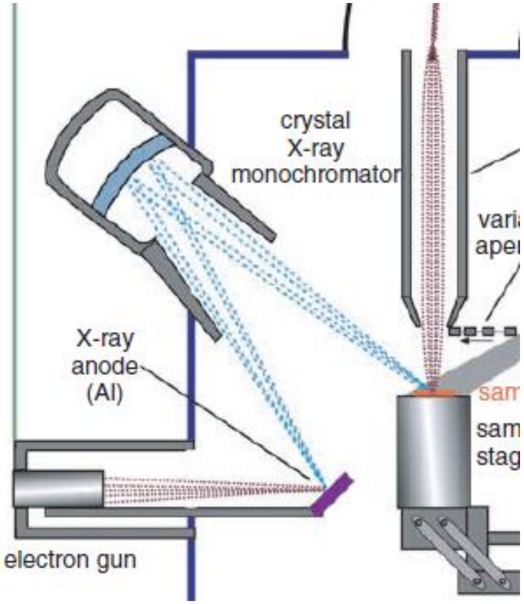
Anode material	Emission line	Energy (eV)	Width (eV)
Mg	Kα	1253.6	0.7
Al	Kα	1486.6	0.85
Si	Kα	1739.5	1.0
Zr	Lα	2042.4	1.7
Ag	Lα	2984	2.6
Ti	Kα	4510	2.0
Cr	Kα	5415	2.1

Electron Spectroscopy for Chemical Analysis

Instrumentation

X-ray Source

- A multi-anode configuration is used to provide two or more X-ray energies. Most spectrometers use only one or two anodes, with Al and Mg the most common for non-monochromatic sources and Al the most common for monochromatic sources.
- Since most of the incident electron energy is converted into heat, anodes are usuallywater cooled. This allows operation at higher power loads without significant degradation (e.g. melting).
- The best way to optimize single energy production is to use an X-ray monochromator. The most popular monochromatized source combines an Al anode with one or more quartz crystals.



Electron Spectroscopy for Chemical Analysis

Instrumentation

X-ray Source

- Most non-monchromatized sources illuminate a spot that is a few centimeters in diameter.

- In contrast, the monochromatized sources typically illuminate an area that is a few millimeters or smaller in diameter.

- With a focused electron gun and the quartz crystal used as both a **monochromator** and a focusing element, **spot sizes <50 μm in diameter** can be realized

- When used with a suitable monochromator, **synchrotron radiation** can provide a tunable source of high intensity, focused X-rays for photoemission experiments. With the use of zone plates **X-ray spot sizes <150nm** can be obtained

About Presentation

1. Presentation date
   -> 28th April (5 students)/ 12th May (5 students)

2. How long?
   -> 20 min long

3. Language
   -> Prefer English but Korean is also OK.

4. Subject and guideline
   -> All about XPS analysis that is related to your research topic.
   Please make your own presentation materials. Put introduction, how important it is, what and what kind of meaningful information they (when you review a paper) or you can get from the XPS analysis?, You can use your own data or review any paper that you have impressed.

End of Slide