Surface Analysis of Nanomaterials

(나노소재표면분석)

Surface and Thin Film Analysis (표면 및 박막 분석)

장소: E6, Room 116

시간: 월7A-8A, 수7A-8A

2. Electron Spectroscopy for Chemical Analysis

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

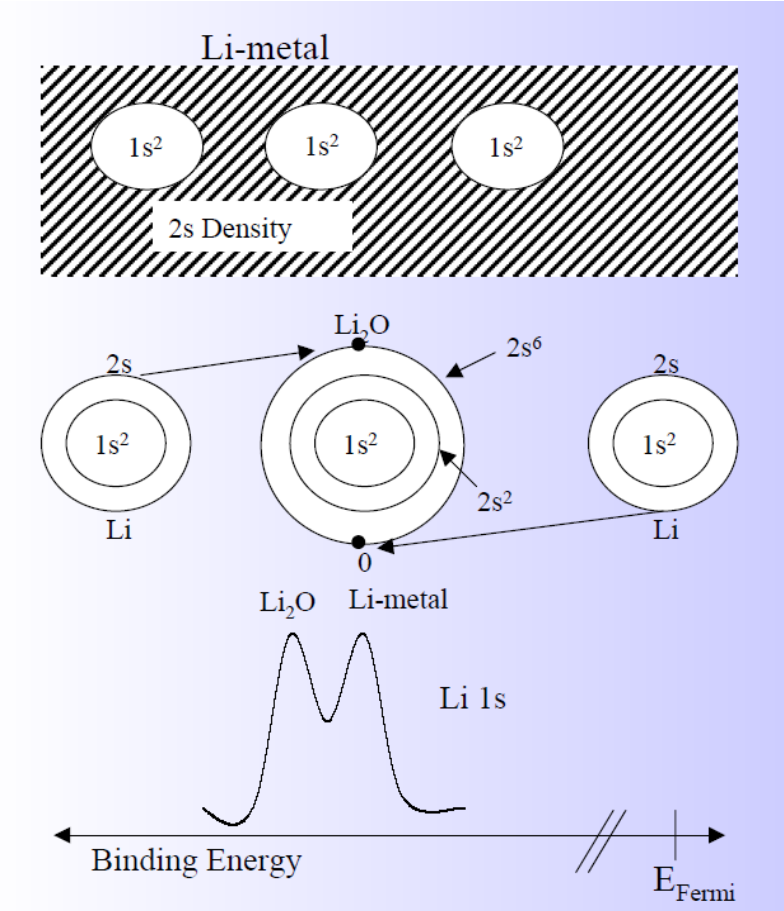
Withdrawal of valence electron charge (oxidation)--〉〉 increase in BE
Addition of valence electron charge --〉〉 decrease in BE

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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

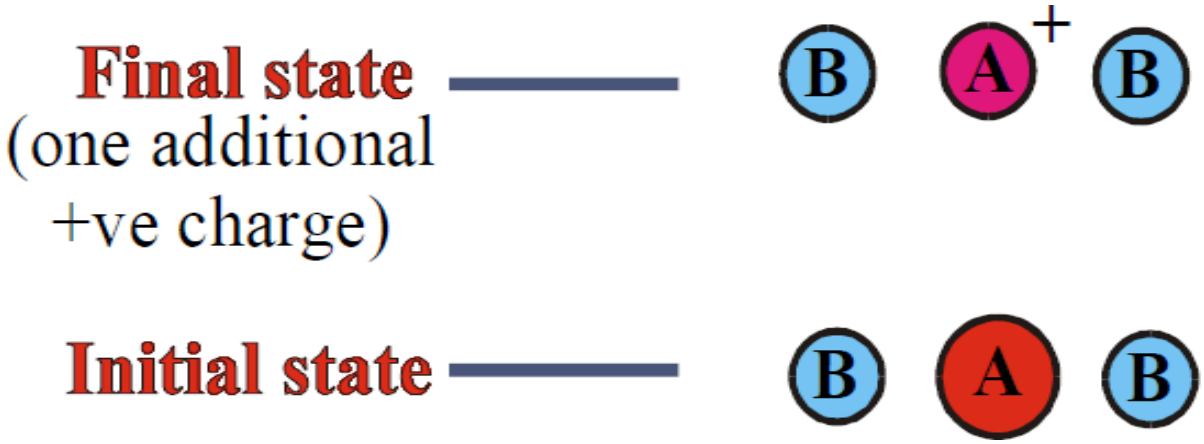
Binding Energy is higher because Li 2s electron density is lost to oxygen

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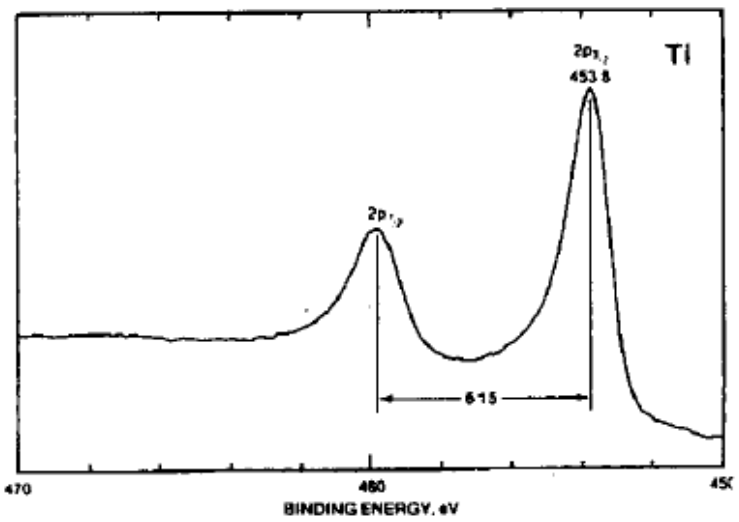
Photoemission Process can be thought of as 3 steps:

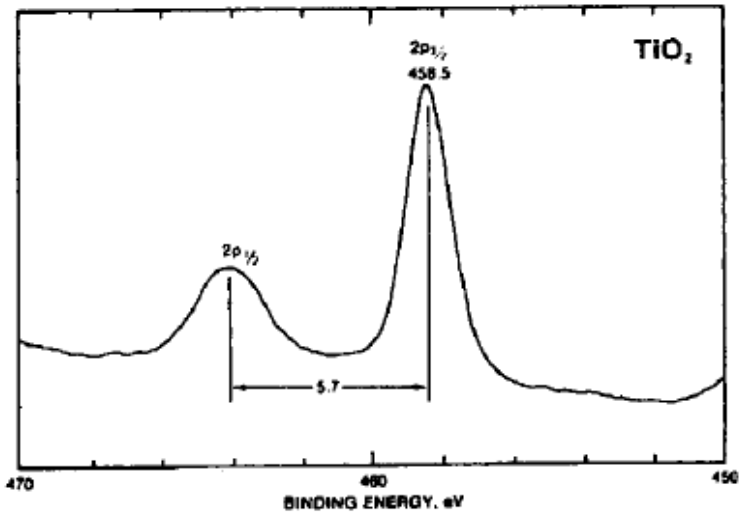
(a) Photon absorption and ionisation (initial state effects)
(b) Response of atom and creation of photoelectron (final state effects)
(c) Transport of electron to surface (extrinsic effects)



Electron Spectroscopy for Chemical Analysis

More about Chemical shift





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

Ti 2p1/2 and 2p2/3 chemical shift for Ti and Ti4+. Charge withdrawn Ti -> Ti4+ so 2p orbital relaxes to higher BE

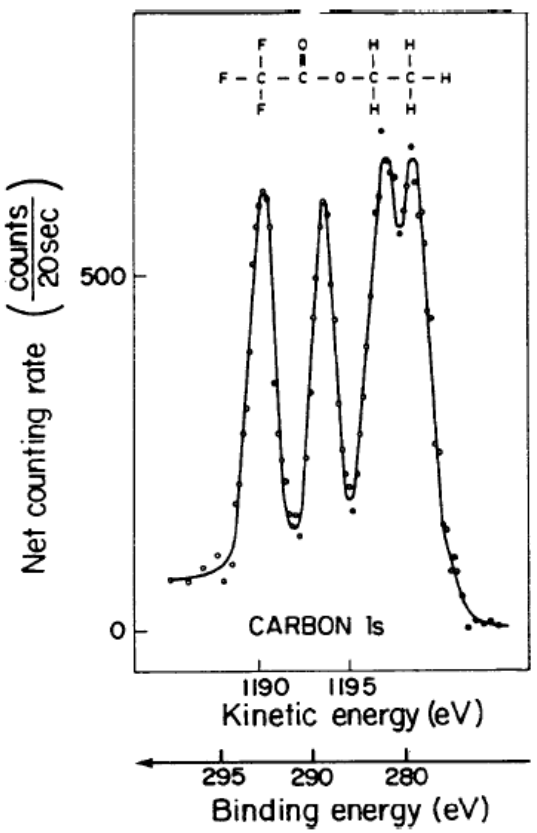
Note: Spin-orbital splitting(SOS) is approximately constant - confirming SOS is largely an initial state effect

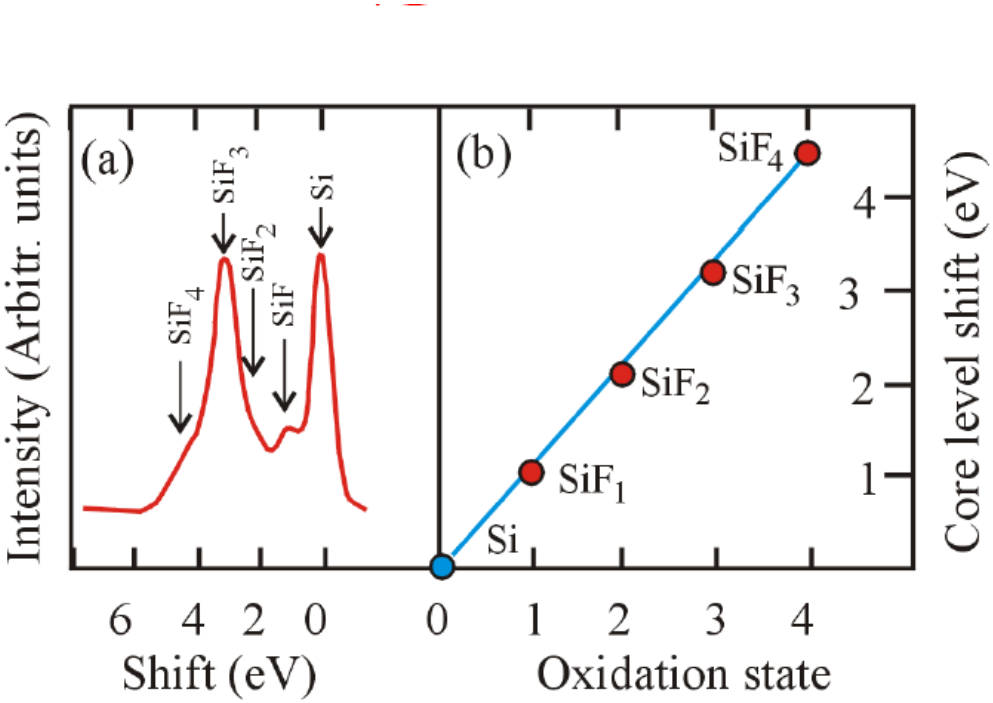
Chemical shift information very powerful tool for functional group, chemical environment, oxidation state.

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts



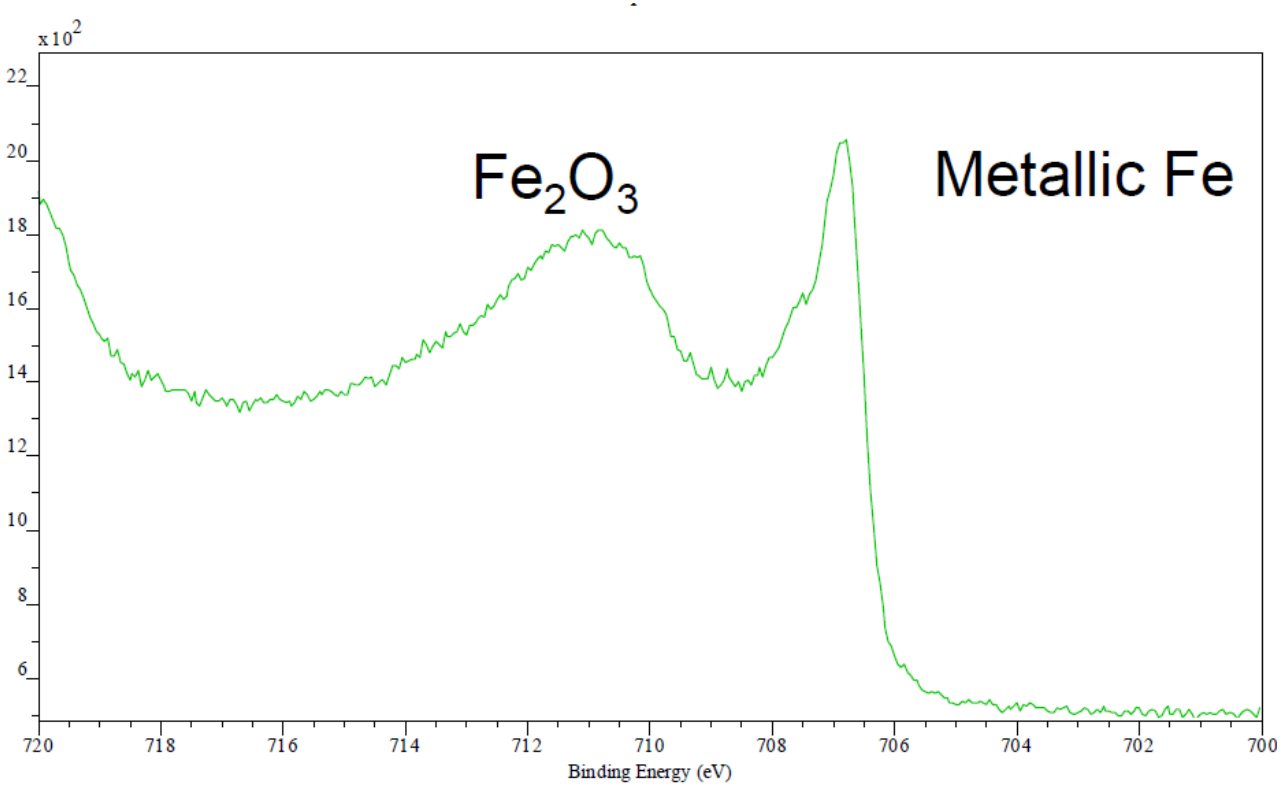


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More about Chemical shift

Examples of Chemical shifts

Detailed Iron 2p Spectrum of High Purity Iron

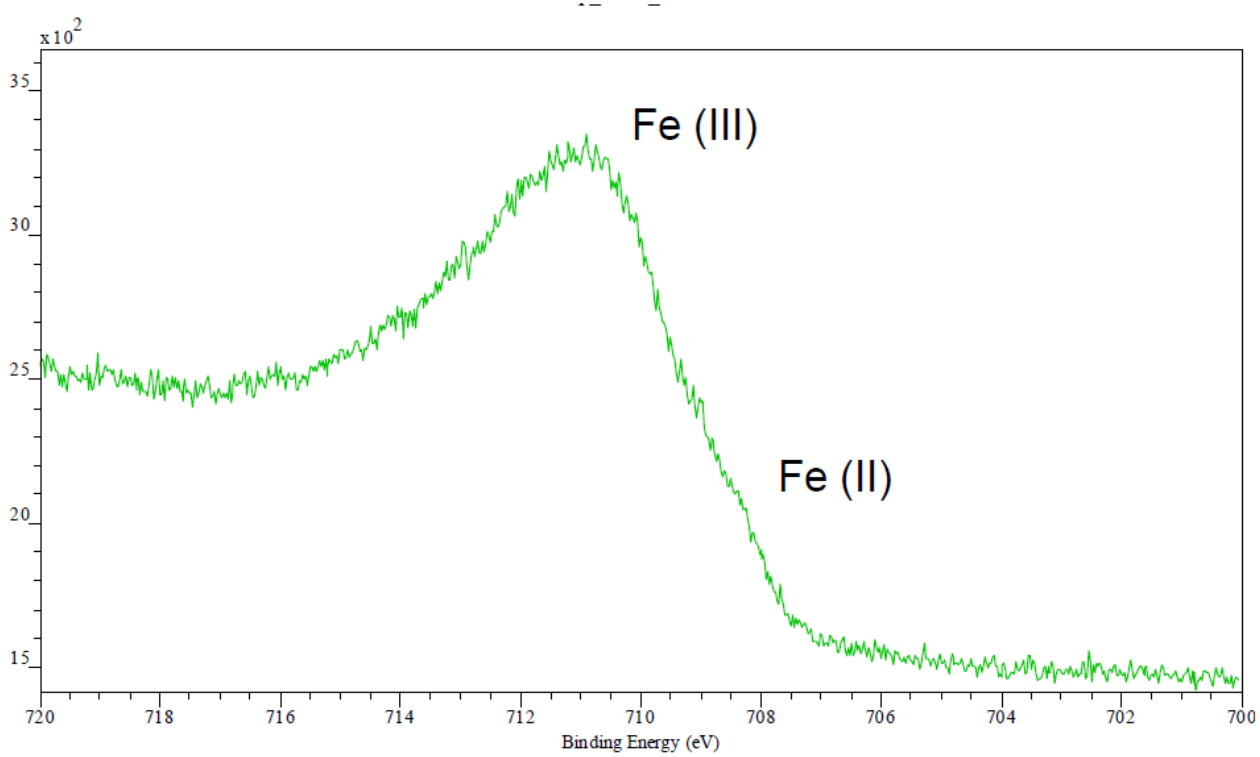


Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

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

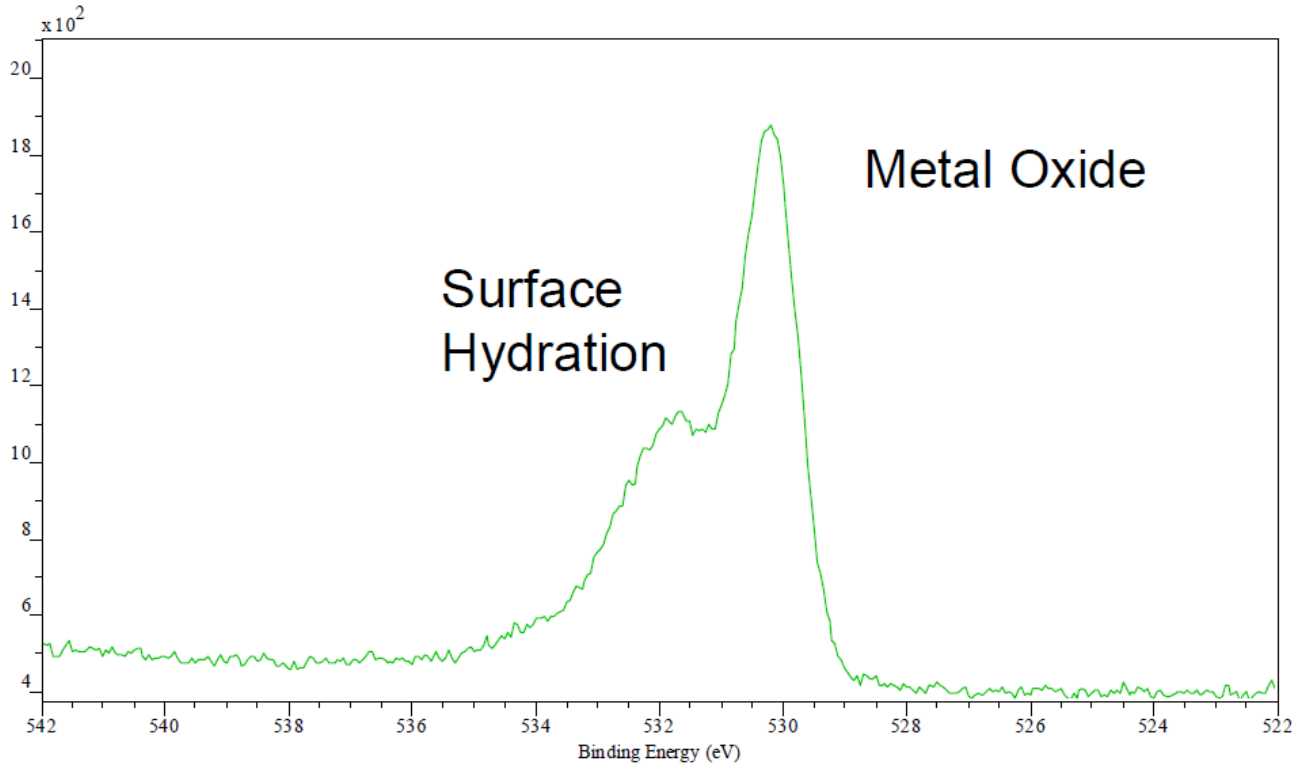


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More about Chemical shift

Examples of Chemical shifts

Detailed Oxygen 1s Spectrum



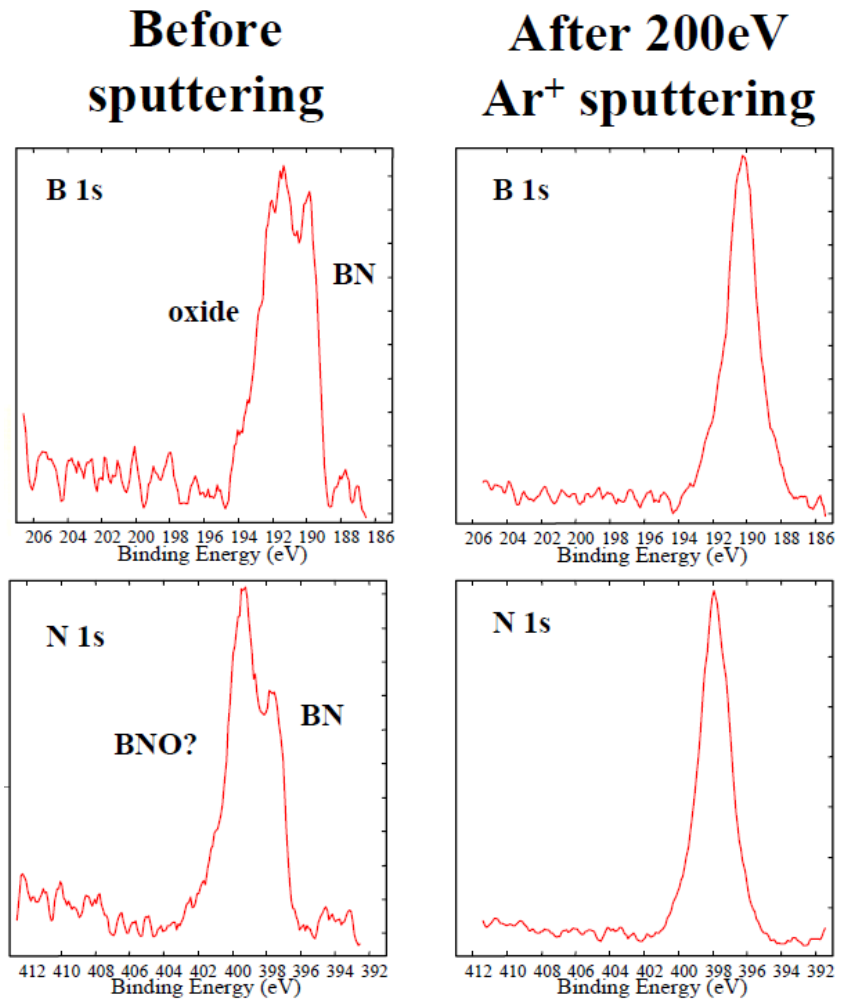
Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

Cubic – BN crystal



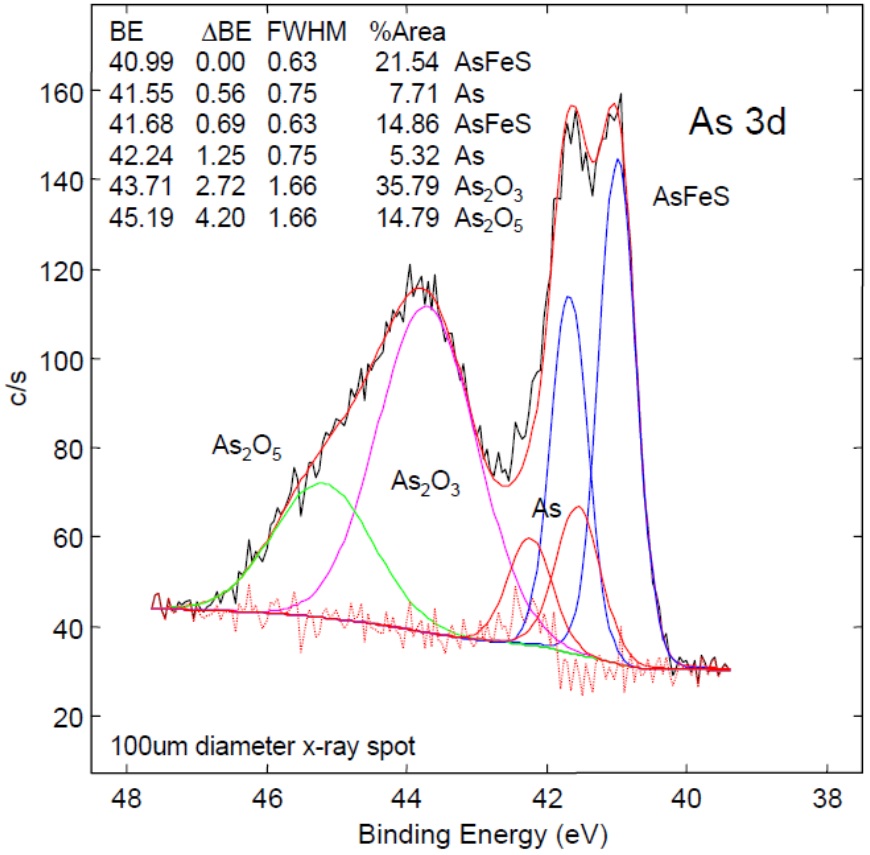


Electron Spectroscopy for Chemical Analysis

More about Chemical shift

Examples of Chemical shifts

High Resolution Spectra Arsenopyrite



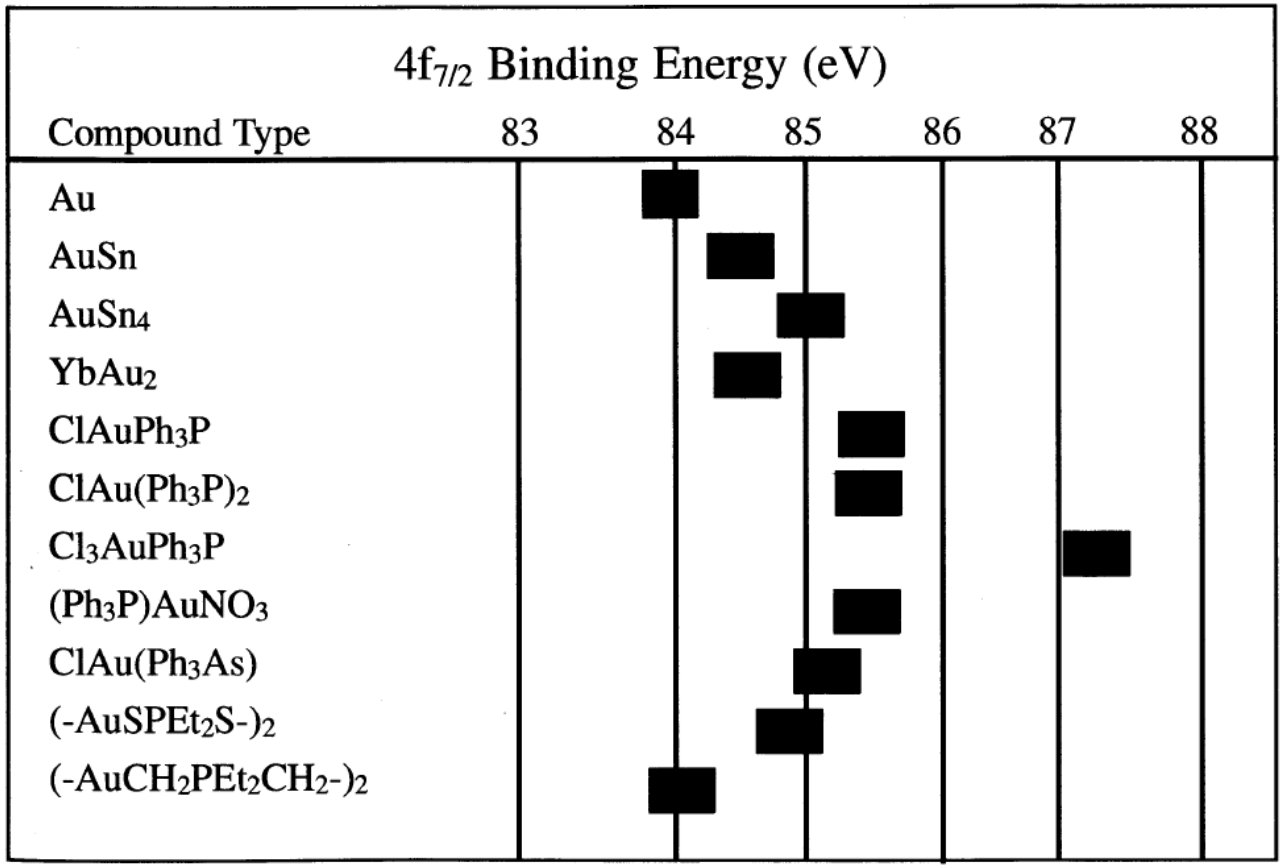
Arsenopyrite is an iron arsenic sulfide (FeAsS)

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/

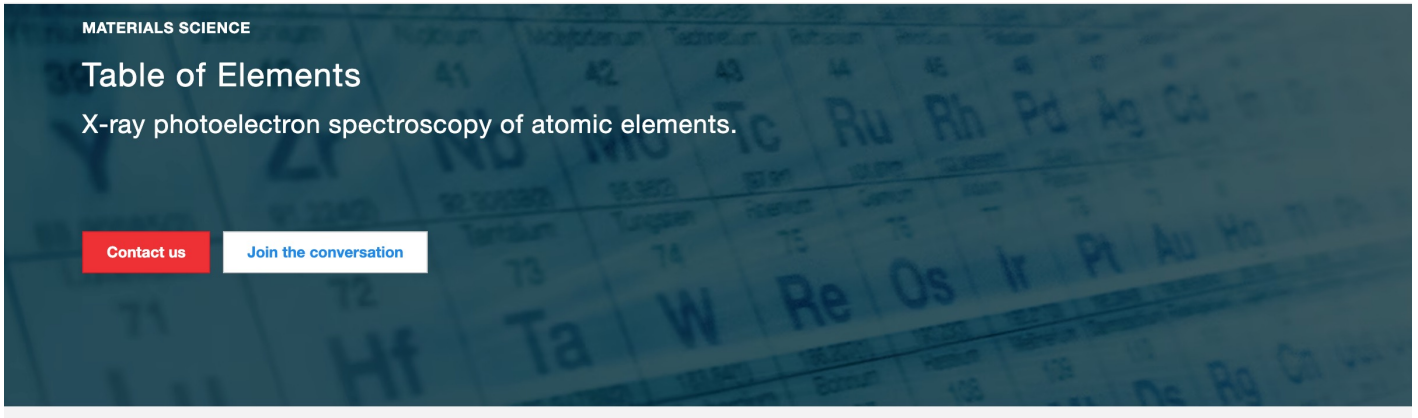


Electron Spectroscopy for Chemical Analysis

More about Chemical shift

X-ray Photoelectron Spectroscopy (XPS) reference page

https://www.thermofisher.com/kr/ko/home/materials-science/learning-center/periodic-table.html



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.

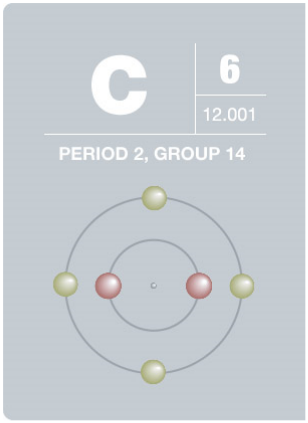
- Metalloid elements
- Non-metal elements
- Transition metal elements
- Lanthanide rare earth elements
- Alkali metal elements
- Alkaline earth metal elements
- Other metal elements
- Halogen elements
- Noble gas elements
- Actinide rare earth elements

Electron Spectroscopy for Chemical Analysis

More about Chemical shift

https://www.thermofisher.com/kr/ko/home/materials-science/learning-center/periodic-table/non-metal/carbon.html

Example, **Carbon**



50 Years of XPS Video

Elements

- Metalloids
- Alkali Metals
- Alkaline Earth Metals
- Transition Metals
- Other Metals
- Non-Metals
  - 1 Hydrogen
  - 6 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

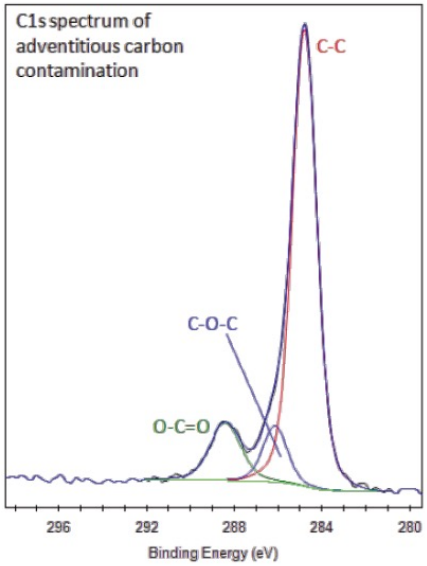
Experimental Information

- 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).



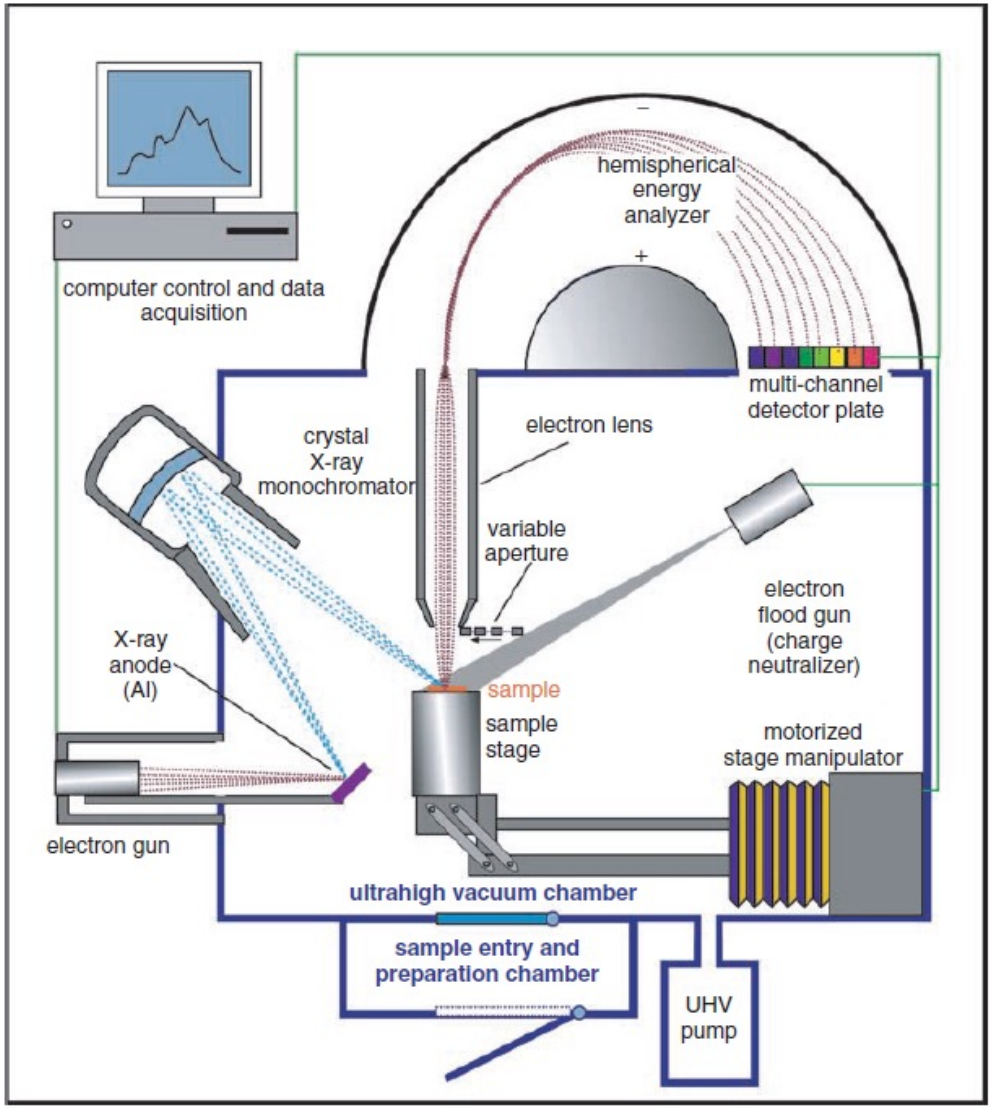
A few nanometers of adventitious carbon on a sample can dramatically affect the survey spectrum of that sample.

- 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

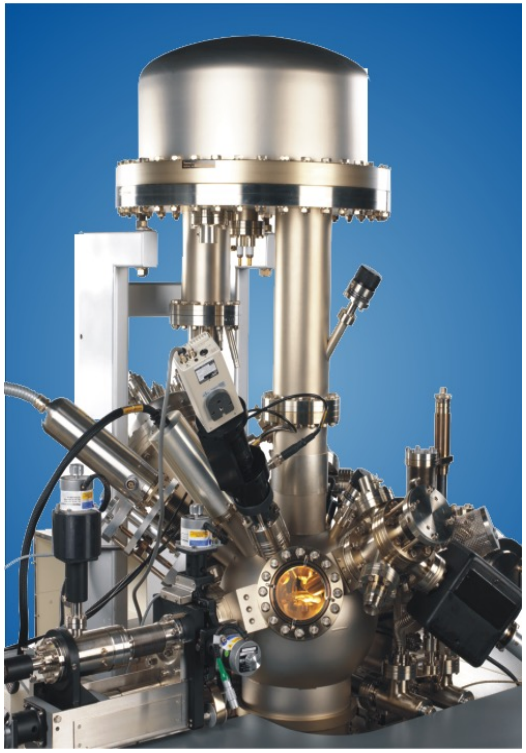
Instrumentation

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

X-rays are generated by bombarding a metallic anode with high-energy electrons. The energy of the emitted X-rays depends on the anode material and beam intensity depends on the electron current striking the anode and its energy.
Early XPS instruments were fitted with non-monochromatic X-ray sources because the sensitivity of the early instruments was low. Sensitivity and monochromator design have improved, and most XPS instruments include monochromators as standard equipment and non-monochromatic sources are optional.

X-ray monochromator

With a monochromated X-ray source, X-rays strike the parallel crystal planes at an angle θ and are reflected at the same angle. The distance travelled by the X-rays depends on the crystal plane at which they are reflected. If the distance between two crystal planes each reflecting X-rays is d, then the path length difference is $2d\sin\theta$. If this is equal to an integral number of wavelengths, then the X-rays interfere constructively. This effect produces the Bragg equation:

$$n\lambda = 2d\sin\theta$$

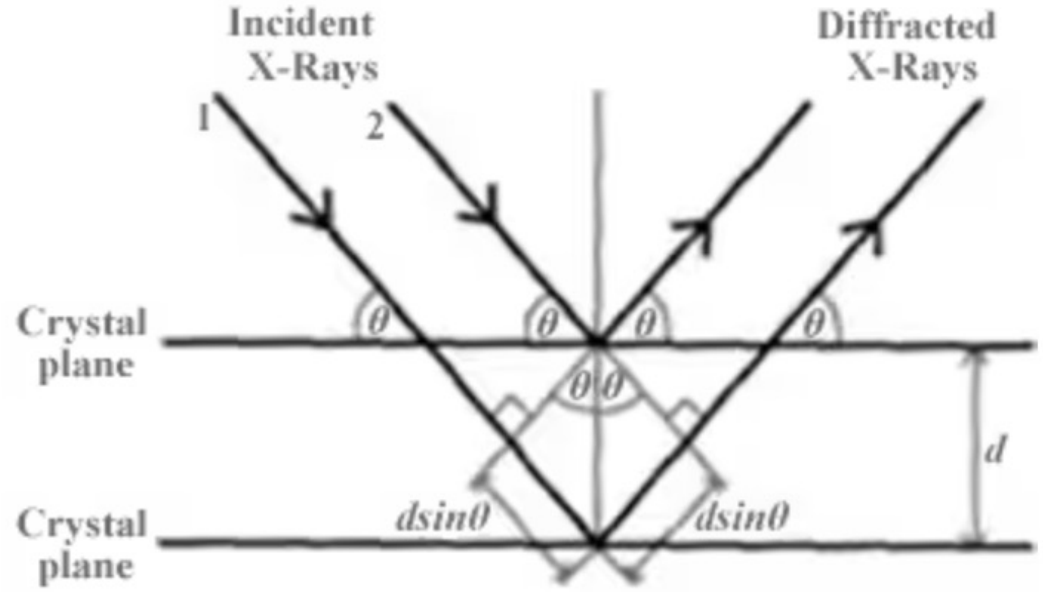
Where n = the diffraction order, λ = X-ray wavelength, d = the crystal lattice spacing and θ = the angle of diffraction (the Bragg angle).

Electron Spectroscopy for Chemical Analysis

Instrumentation

X-ray monochromator

The physical properties of quartz combined with its lattice spacing and availability as a single crystal, makes it the only material used for commercial X-ray monochromators in combination with Al K-alpha radiation. The quartz crystal is usually bent when it is used as an XPS monochromator.



Electron Spectroscopy for Chemical Analysis

Instrumentation

X-ray monochromator

- For the monochromators fitted to XPS Instruments, the radius of curvature is different in each direction (i.e., it is toroidally bent), which allows the X-rays to be focused and monochromated.

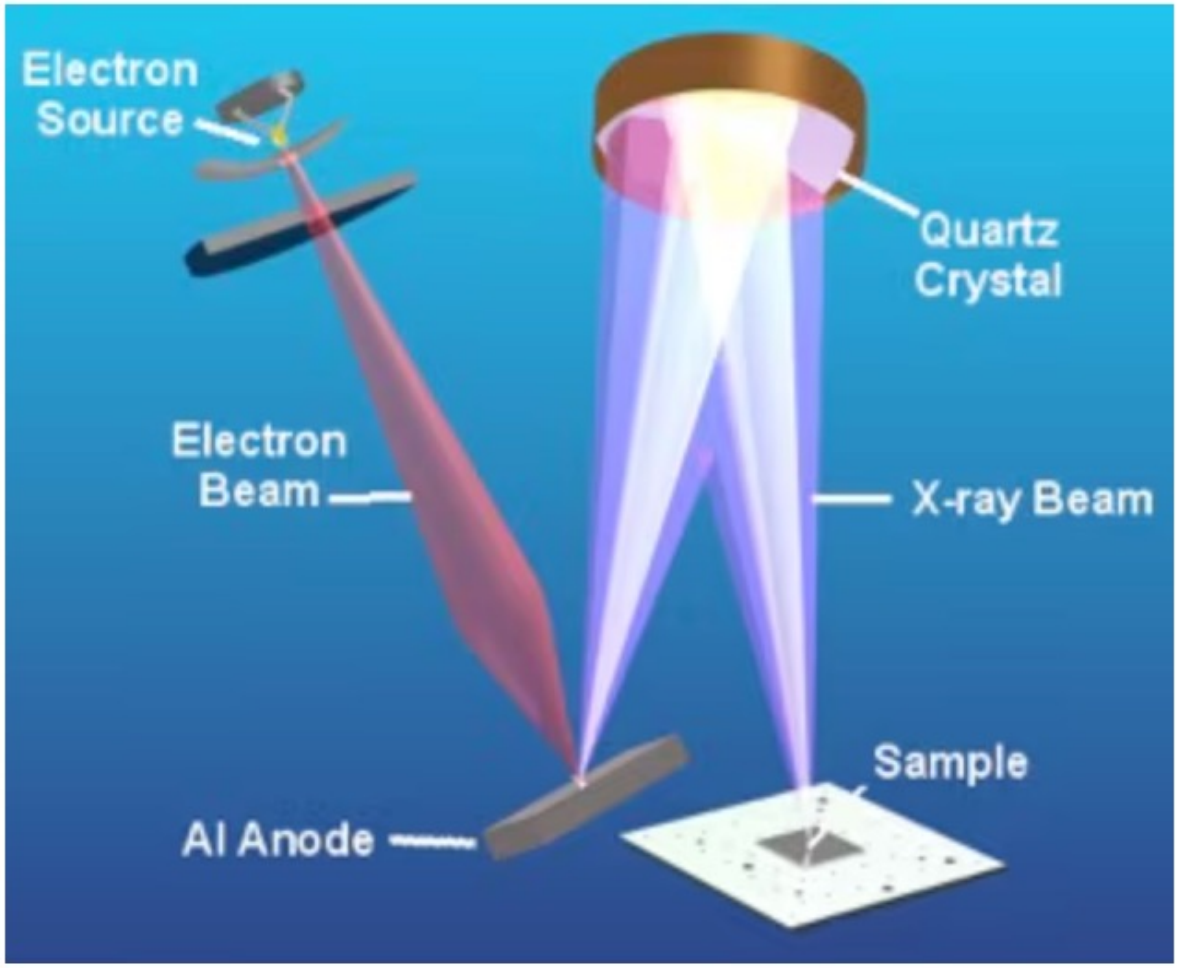
- Electrons are emitted from a bright source, such as LaB_6, and focused onto a water-cooled, aluminum anode. Some of the X-rays emitted from the anode are intercepted by the crystal and a monochromated beam of X-rays is focused onto the sample. The size of the X-ray spot at the sample is equal to the size of the electron beam spot on the anode. Therefore the analysis area can be controlled by controlling the electron beam spot size.

- X-rays produced in a twin-anode source have a wide X-ray line width, satellite X-ray peaks and a continuum of background radiation. All of these factors affect the quality of the XPS spectrum.

Electron Spectroscopy for Chemical Analysis

Instrumentation

X-ray monochromator



Electron Spectroscopy for Chemical Analysis

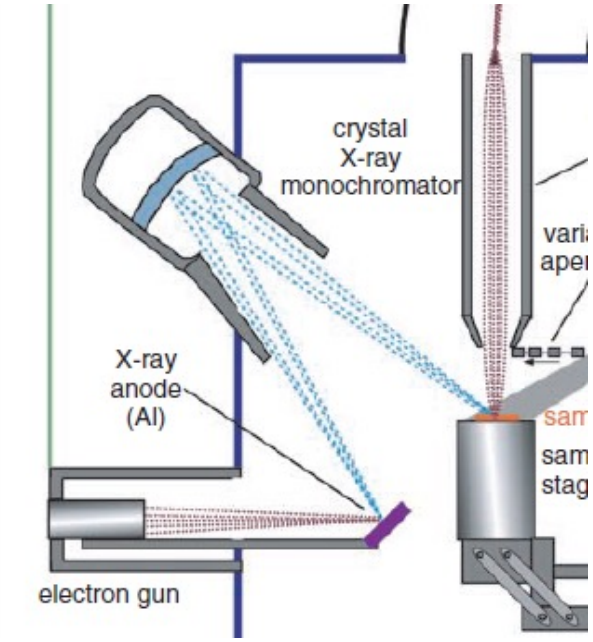
Instrumentation

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 photoemissionexperiments. With the use of zone plates **X-ray spot sizes 〈150nm** can be obtained

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