Surface Analysis of Nanomaterials

(나노소재표면분석)

:Surface and Thin Film Analysis

(표면 및 박막분석)

장소: 공과대학 6호관 510호

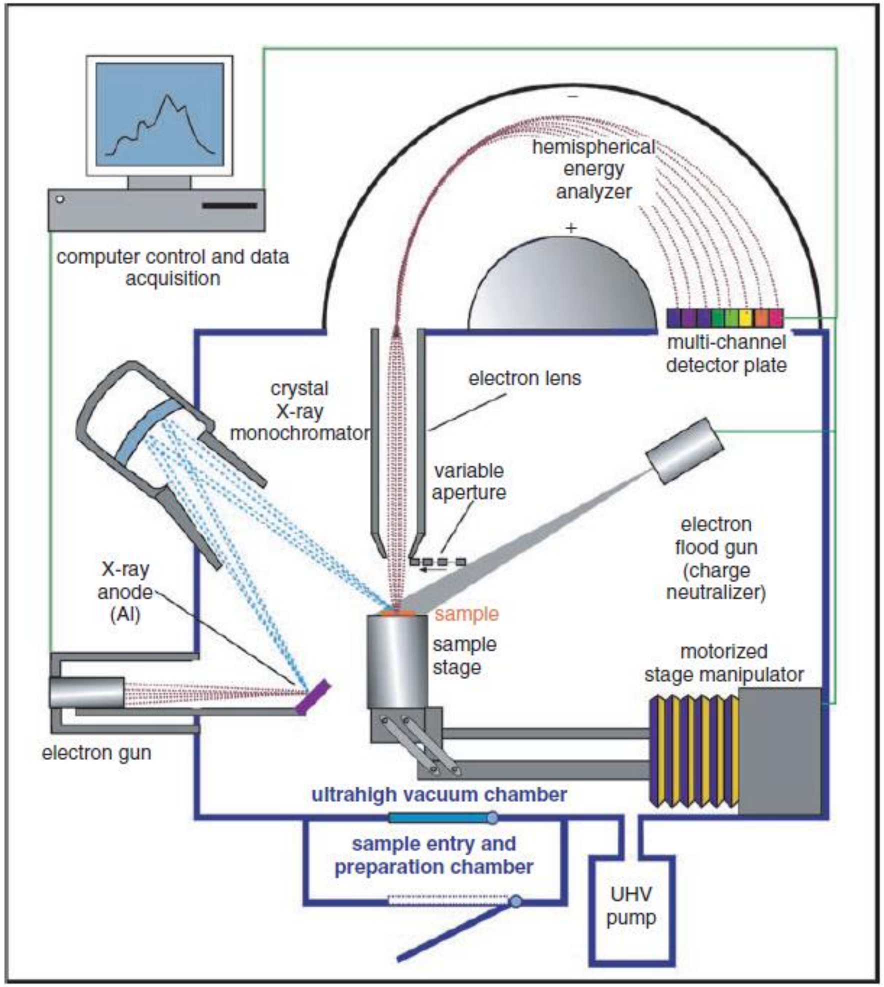
시간: 목 (1-A, 1-B, 2-A, 2-B, 3-A, 3-B)

2. Electron Spectroscopy for Chemical Analysis

Electron Spectroscopy for Chemical Analysis

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

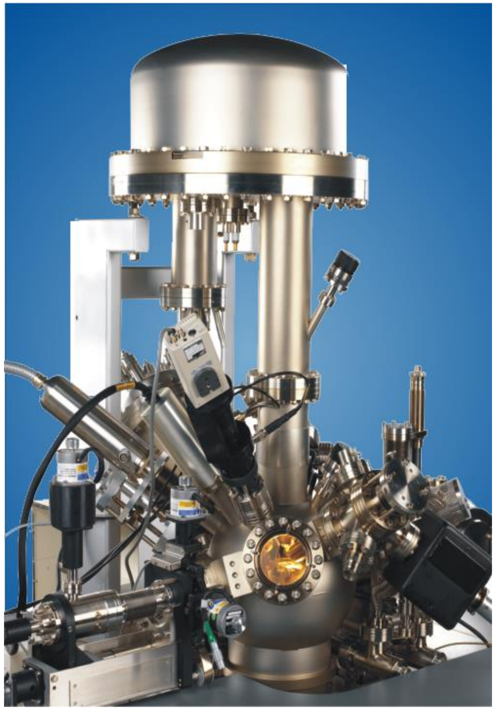
Electron Spectroscopy for Chemical Analysis

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.).

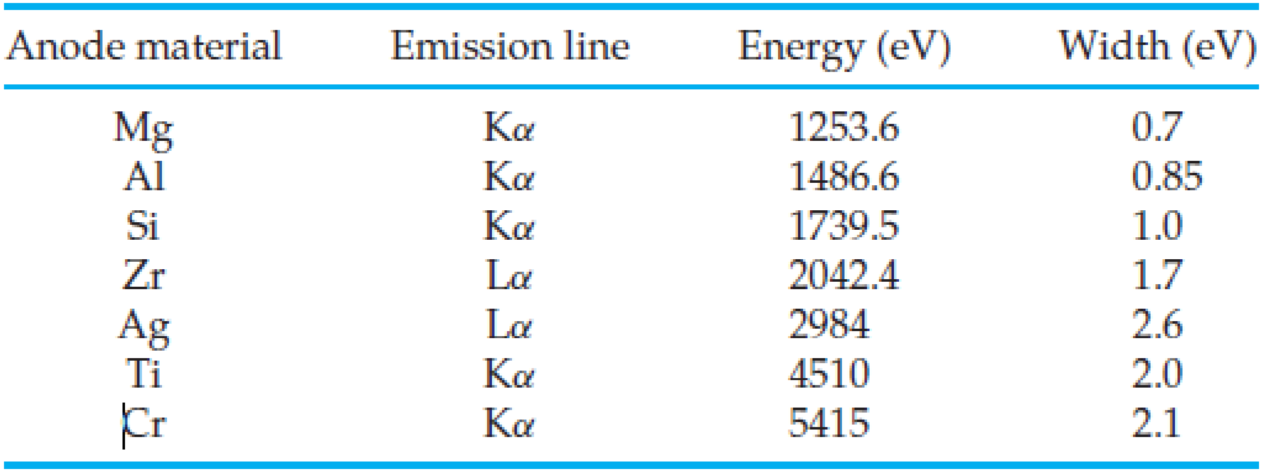
Electron Spectroscopy for Chemical Analysis

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)



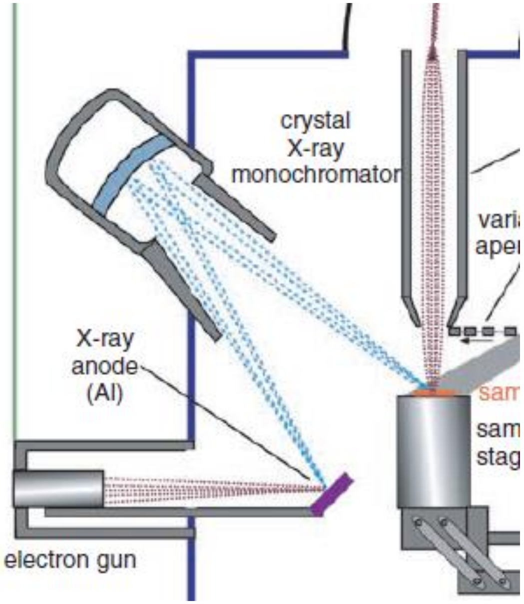
Anode material	Emission line	Energy (eV)	Width (eV)
Mg	Kα	1253.6	0.7
Al	Kα	1486.6	0.85
Si	Kα	1739.5	1.0
Zr	Lα	2042.4	1.7
Ag	Lα	2984	2.6
Ti	Kα	4510	2.0
Cr	Kα	5415	2.1

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

Electron Spectroscopy for Chemical Analysis

Instrumentation

Analyzers

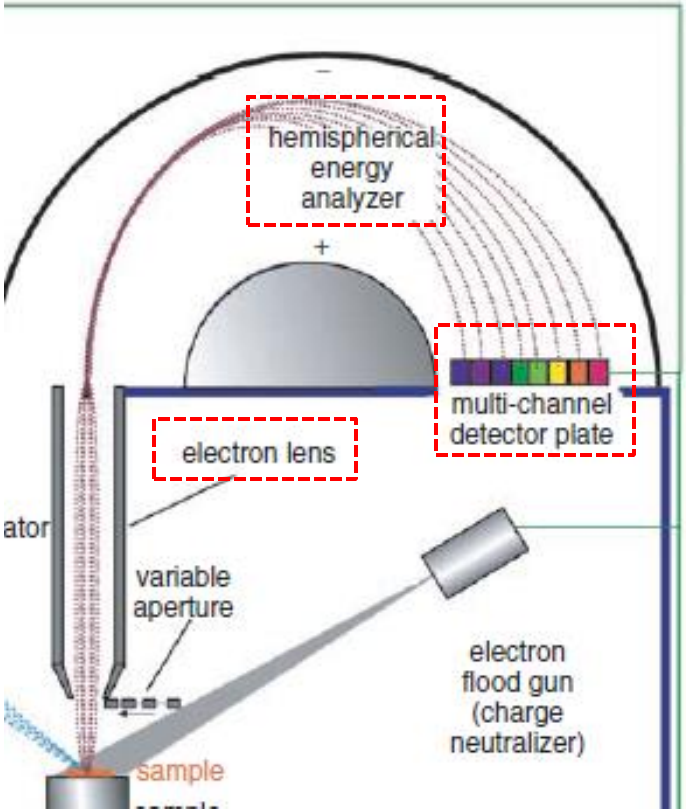
The analyzer system consists of three components:

1. the collection lens
2. the energy analyzer
3. the detector

1. the collection lens

- On most modern ESCA spectrometers, the lens system can collect photoelectrons from solid angles>20°. The higher the collection solid angle, the higher the number of photoelectrons collected per incident X-ray, which is generally advantageous.

- The increased collection angle is particularly important for samples that degrade upon exposure to X-rays, since the more efficient the detection system is (e.g. the more photoelectrons collected per X-ray) the more data that can be collected before the sample is damaged.



Electron Spectroscopy for Chemical Analysis

Instrumentation

Analyzers

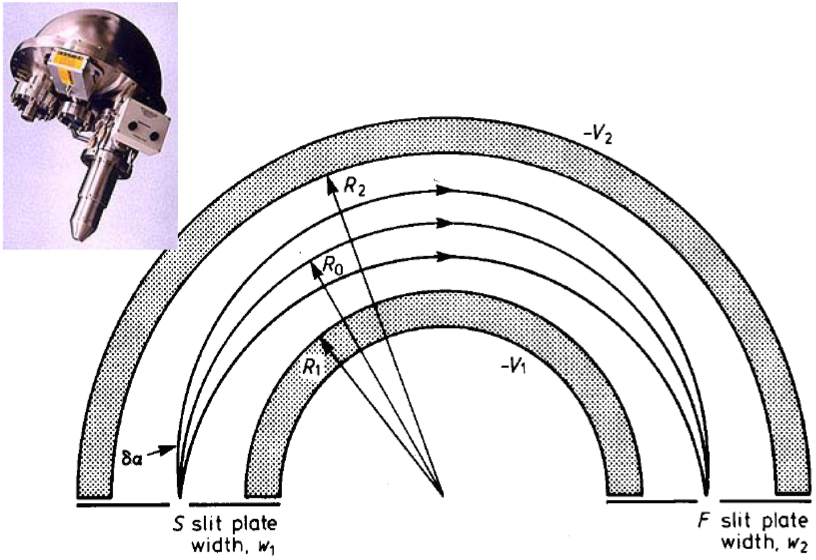
2. the energy analyzer

The most common type of energy analyzer used for ESCA experiments is the electrostatic hemispherical analyzer

It consists of two concentric hemispheres of radius R_1 and R_2.

A potential of V is placed across the hemispheres such that the outer hemisphere is negative and the inner hemisphere is positive with respect to the potential at the center line, $R_0 = (R_1 + R_2)/2$. The center line potential is known as the pass energy

Concentric hemispherical analyzer (CHA)



Electron Spectroscopy for Chemical Analysis

Instrumentation

Analyzers

2. the energy analyzer

pass energy

The center line potential is known as the pass energy. As noted previously, most ESCA experiments use a constant pass energy. This will maintain a constant absolute resolution, ΔE, for all photoelectron peaks, since the analyzer resolution is defined as $\Delta E/E$, where E is the energy of the electron as it passes through the analyzer

-> the signal intensity will also decrease at smaller pass energies

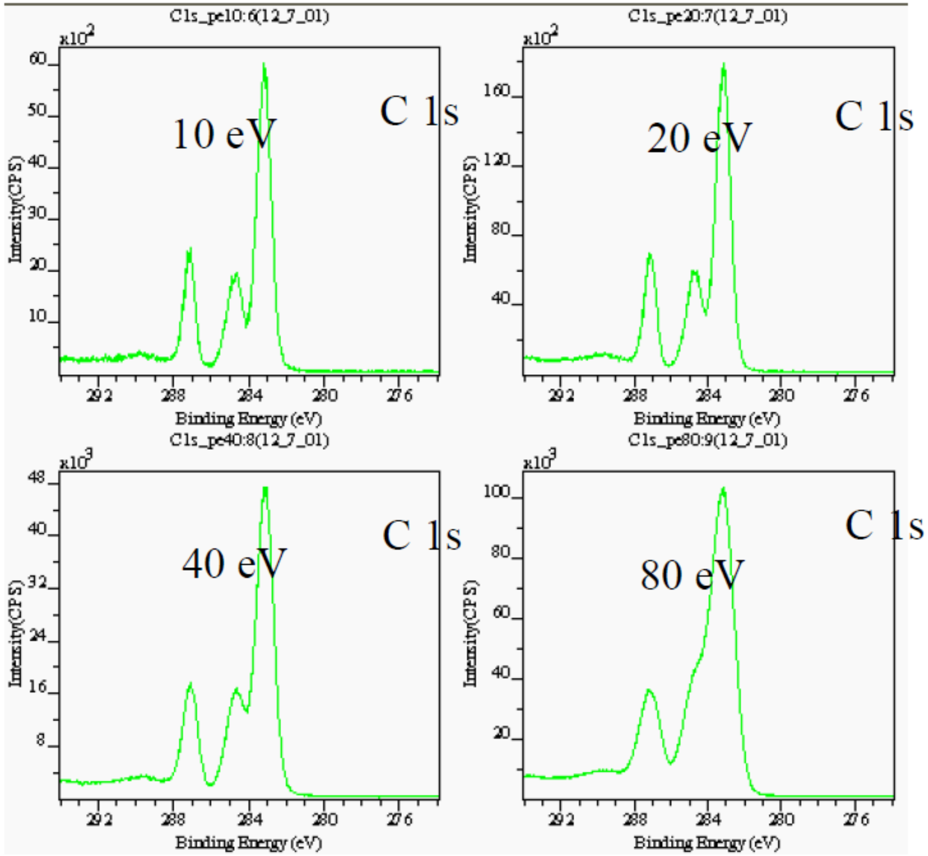
Electron Spectroscopy for Chemical Analysis

Instrumentation

Analyzers

2. the energy analyzer

PET : Polyethylene terephthalate



Different
Pass Energies
10-80 eV

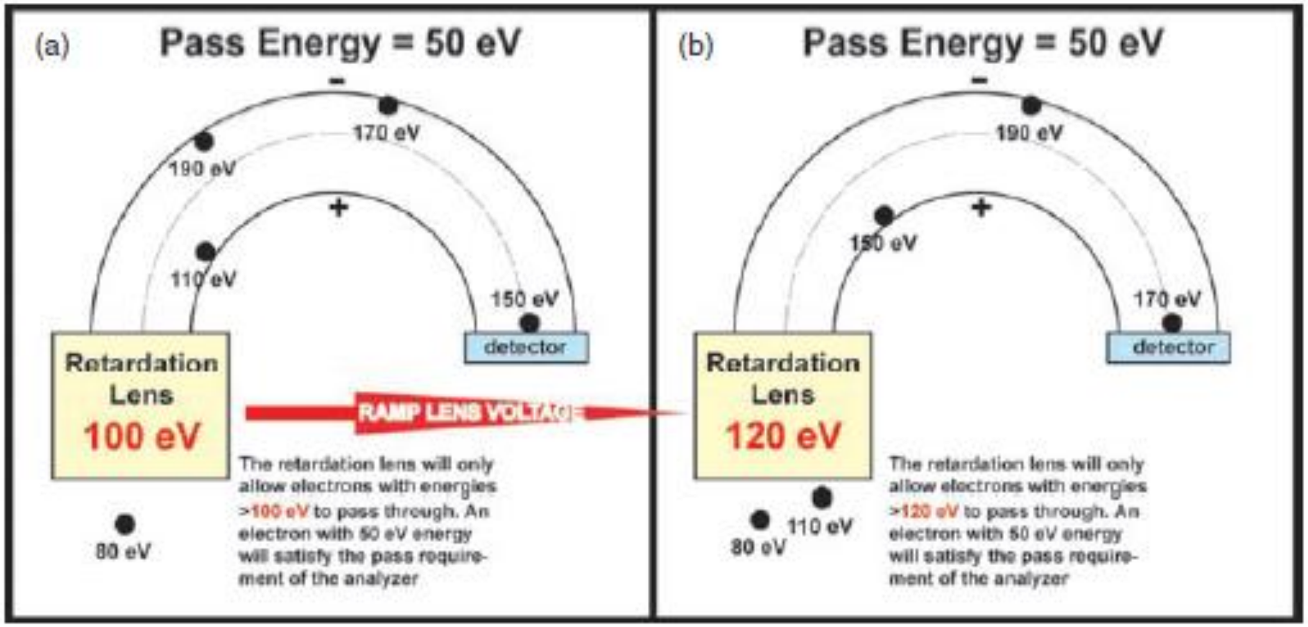
Electron Spectroscopy for Chemical Analysis

Instrumentation

Analyzers

3. Detector

– Since the electrons arrive at the analyzer exit with a range of energies, the most efficient means of detection is to use a multichannel array to count the number of electrons leaving the analyzer at each energy.



The retardation lens will only allow electrons with energies >100 eV to pass through. An electron with 50 eV energy will satisfy the pass requirement of the analyzer

The retardation lens will only allow electrons with energies >120 eV to pass through. An electron with 50 eV energy will satisfy the pass requirement of the analyzer

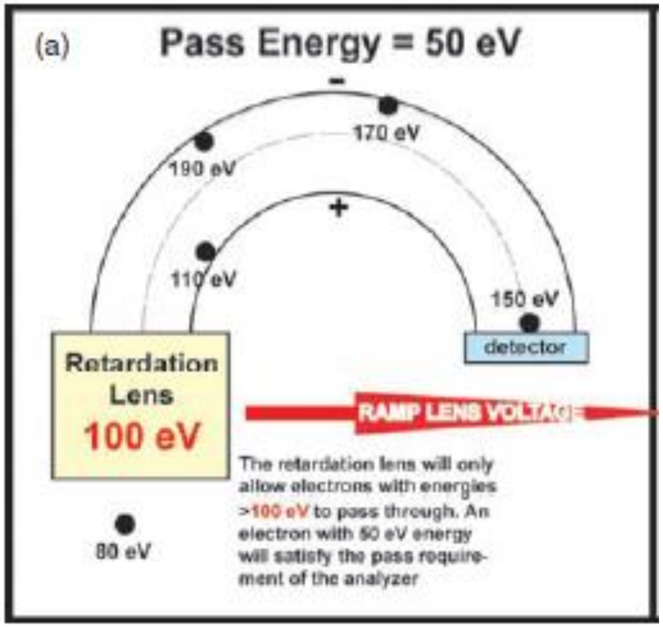
In both diagrams the analyzer pass energy is set to transmit electrons with a KE of 50 eV after retardation to the detector

Electron Spectroscopy for Chemical Analysis

Instrumentation

Analyzers

3. Detector



- The lens system in Figure (left) is set so only photoelectrons with KEs greater than 100 eV will be allowed into the analyzer and retarded.

- If a 150 eV photoelectron enters the lens it will be retarded to a KE of 50 eV, pass through the analyzer and strike the detector.

- Photoelectrons with KEs significantly great than 150 eV will pass through retardation lenses and strike the outer hemisphere of the analyzer since their KE after retardation in the lens is still greater than the 50 eV pass energy.

- Likewise photoelectrons with KEs significantly less than 150 eV, but still greater than 100 eV, will pass through the lenses and strike the inner hemisphere of the analyzer since their KE after retardation in the lenses is less than the 50 eV pass energy.

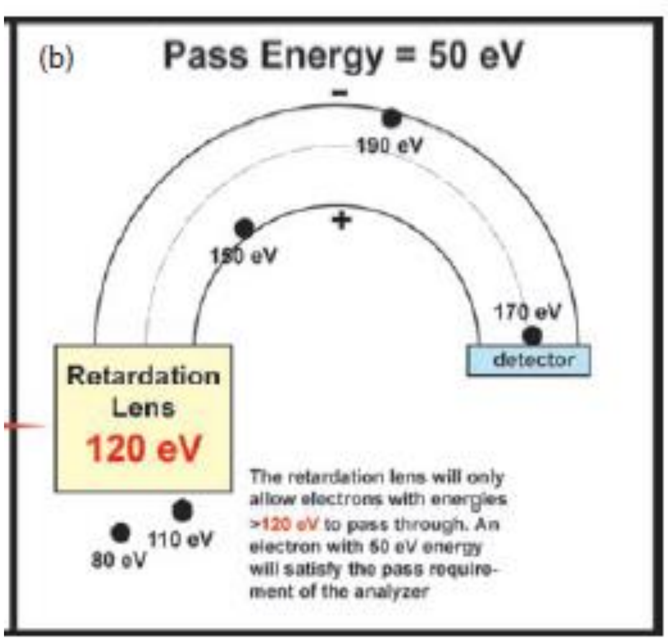
In both diagrams the analyzer pass energy is set to transmit electrons with a KE of 50 eV after retardation to the detector

Electron Spectroscopy for Chemical Analysis

Instrumentation

Analyzers

3. Detector



The retardation lens will only allow electrons with energies >120 eV to pass through. An electron with 50 eV energy will satisfy the pass requirement of the analyzer

- The lens setup has been changed so now only photoelectrons with KEs greater than 120 eV will be allowed into the analyzer and retarded.
- The 150 eV photoelectron will still pass through the lenses and be retarded.
- However, after retardation its KE will be significantly lower than 50 eV and it will strike the inner hemisphere.
- In Figure 3(left) photoelectrons with an initial KE of 170 eV will be passed through the lenses and be retarded to 50eV so they can pass through the analyzer.
- The higher energy photoelectrons (e.g. 190 eV) will pass through the lenses, but after retardation will still have KEs greater than 50 eV and will strike the outer hemisphere.

Electron Spectroscopy for Chemical Analysis

Spectral Quality

- The signal-to-noise (*S/N*) ratio and resolution are the most important properties to consider when evaluating spectral quality.

- The length of time it takes to reach a given *S/N* ratio at a given energy resolution is the important criterion

- The *S/N* of a spectrum can be increased by either increasing the scan time or decreasing the energy resolution

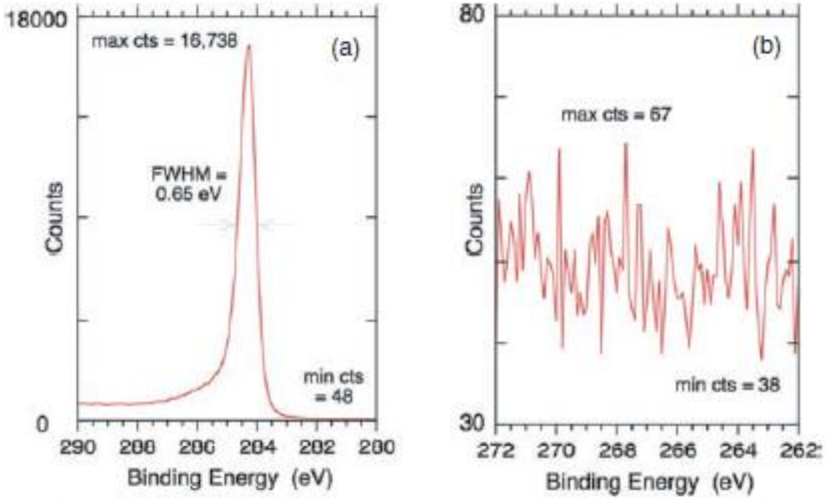


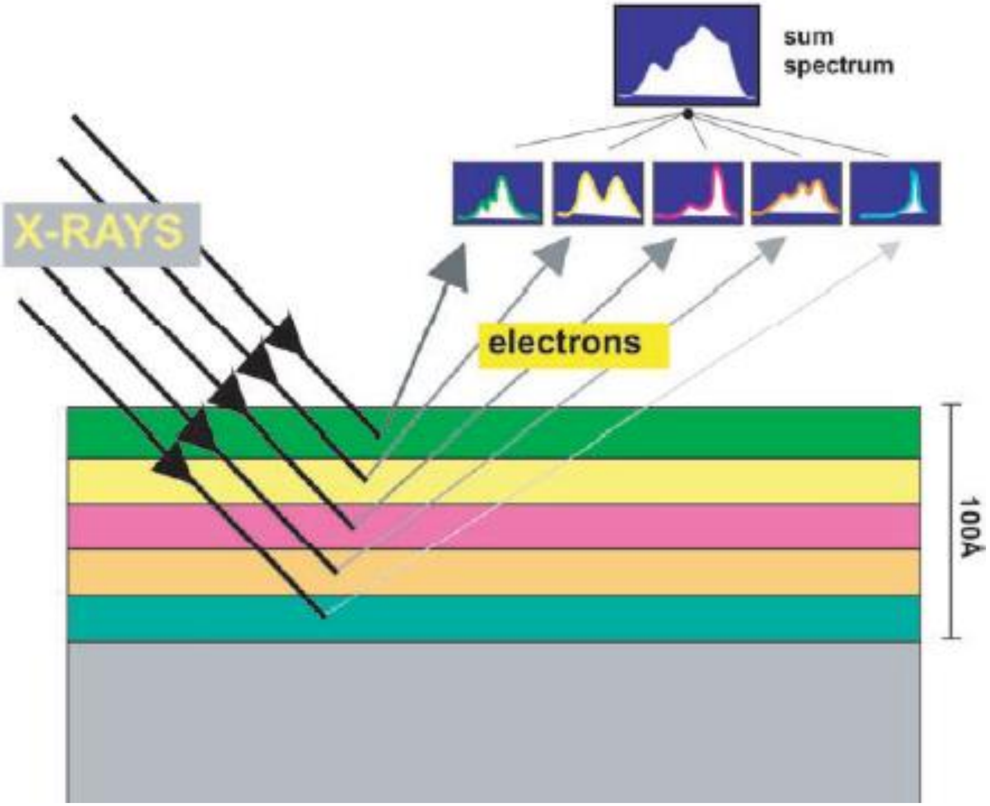
Figure 3.17 The (a) C_{1s} and (b) noise spectra from a graphite sample. The data in each region were acquired with the same scan parameters (time, eV/point, window, pass energy, etc.). These data, obtained after three minutes of scanning, have a peak-to-peak signal-to-noise ratio of 575 at an energy resolution of 0.65 eV

Electron Spectroscopy for Chemical Analysis

Depth Profiling

- The **sampling depth of ESCA is 10 nm** and the atomic dimensions are 0.3 nm, then the surface region could be composed of **~30 atomic layers**.

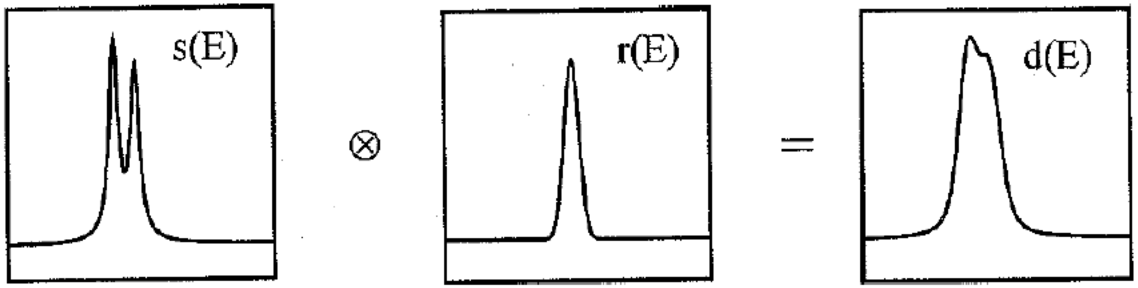
- The ESCA spectrum we obtain will be a convolution of the information from all the layers



Electron Spectroscopy for Chemical Analysis

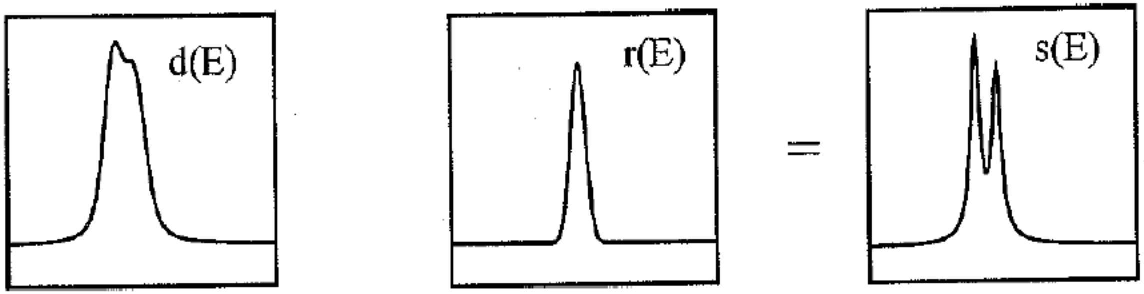
Depth Profiling

- The ESCA spectrum we obtain will be a convolution of the information from all the layers



Convolution

How to obtain high-resolution XPS spectra?

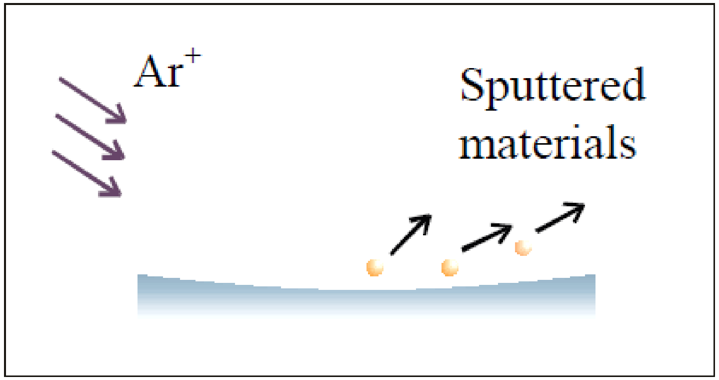


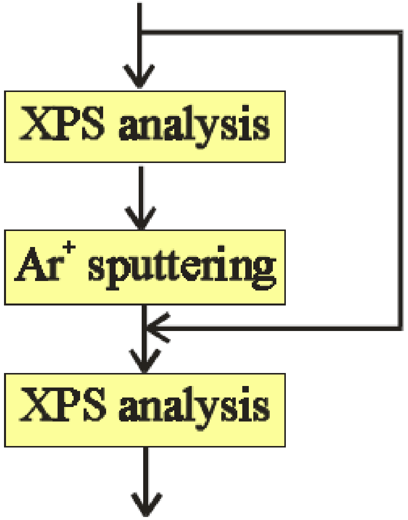
Deconvolution

Electron Spectroscopy for Chemical Analysis

Depth Profiling

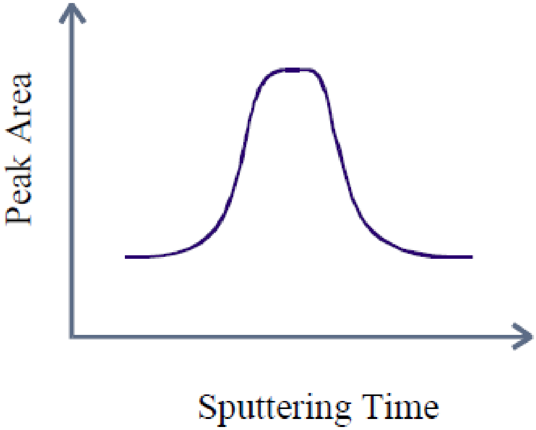
Conventional Depth profiling




XPS analysis

Ar^+ sputtering

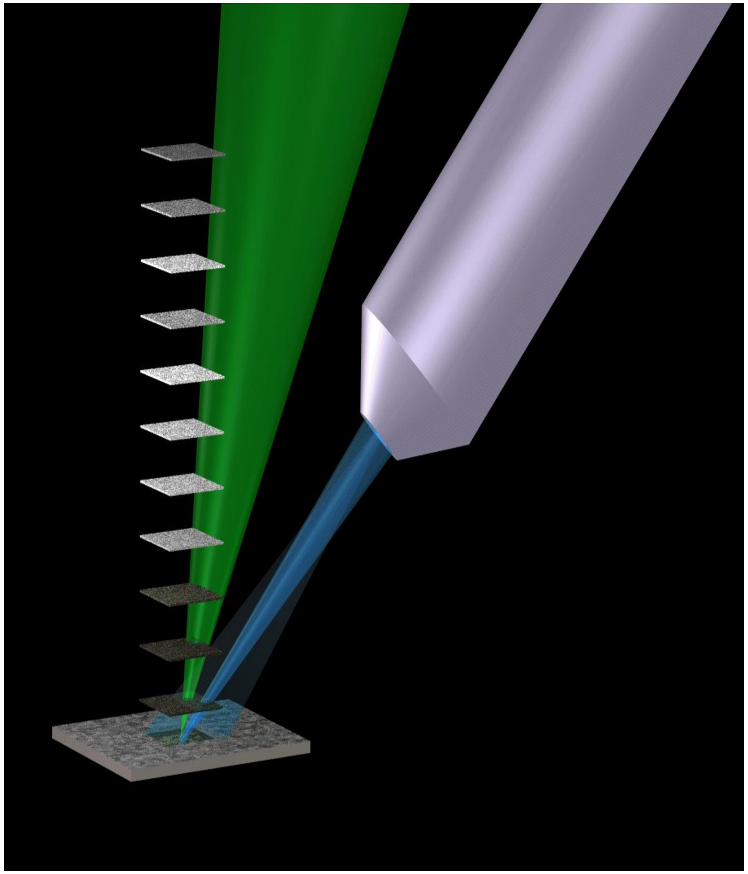
XPS analysis



Electron Spectroscopy for Chemical Analysis

Depth Profiling

Conventional Depth profiling

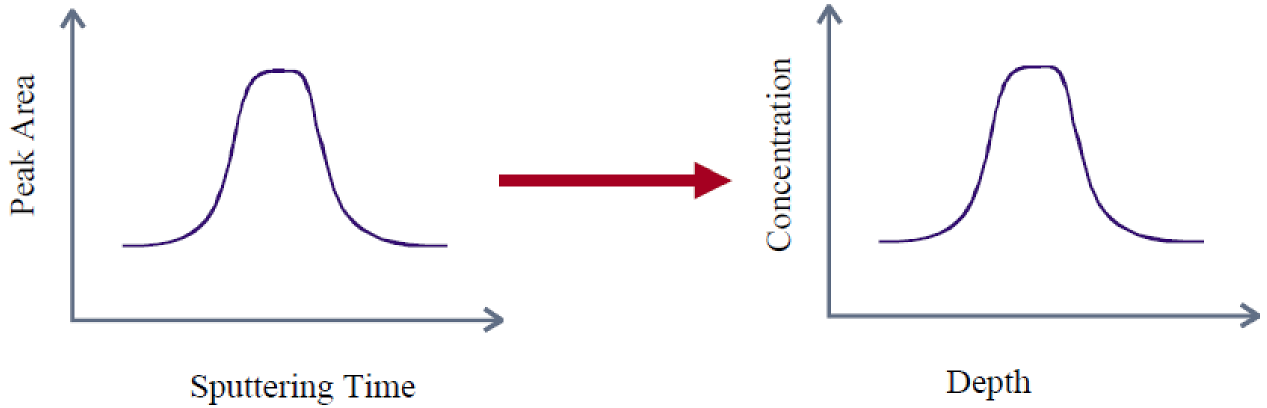


- Use of an ion gun to erode the sample surface and re-analyse
- Enables layered structures to be investigated
- Investigations of interfaces
- Depth resolution improved by:
  - Low beam energies
  - Small ion beam sizes
  - Sample rotation

Electron Spectroscopy for Chemical Analysis

Depth Profiling

Conventional Depth profiling



Calibration of depth scale

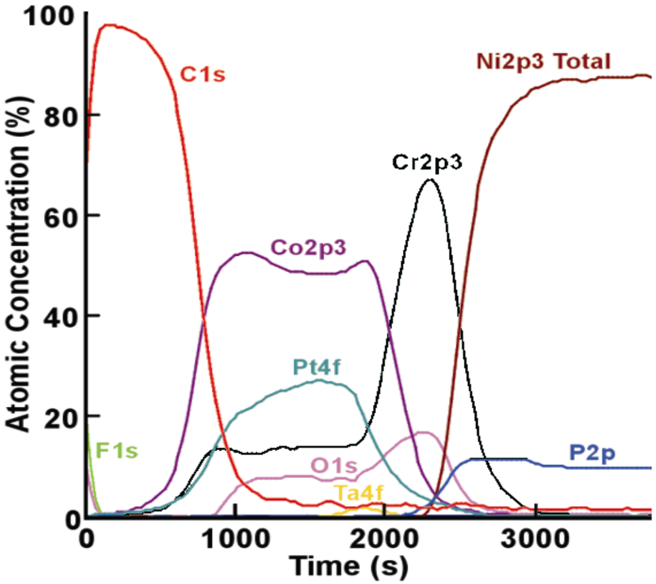
1. Sputtering rate determined from the time required to sputter through a layer of the same material of known thickness.

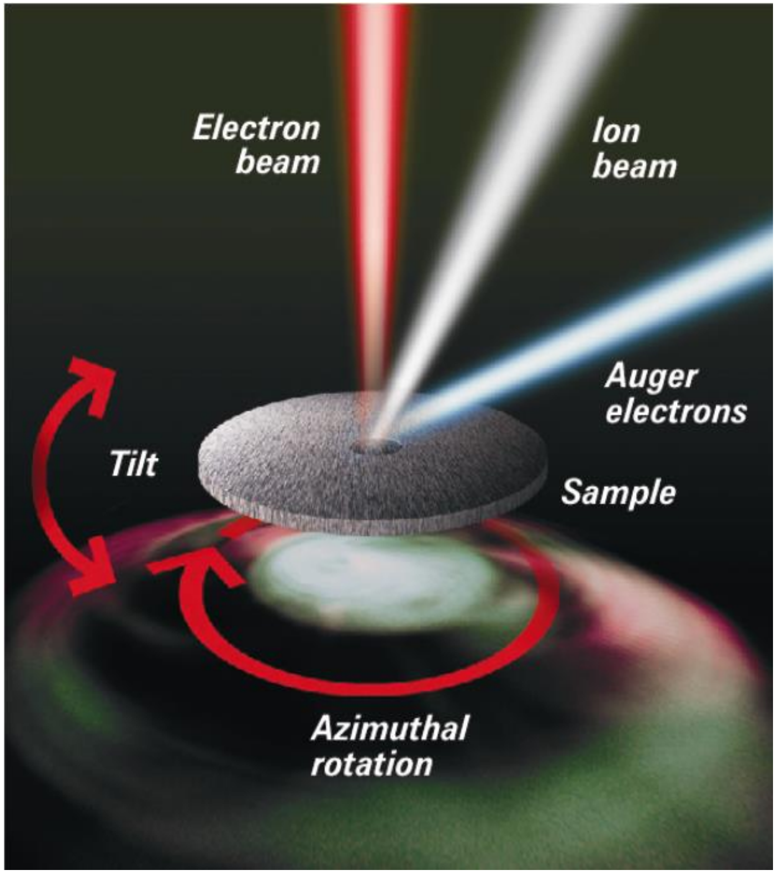
2. After the sputtering analysis, the crater depth is measured using depth profilometer. A constant sputtering rate is assumes.

Electron Spectroscopy for Chemical Analysis

Depth Profiling

Conventional Depth profiling





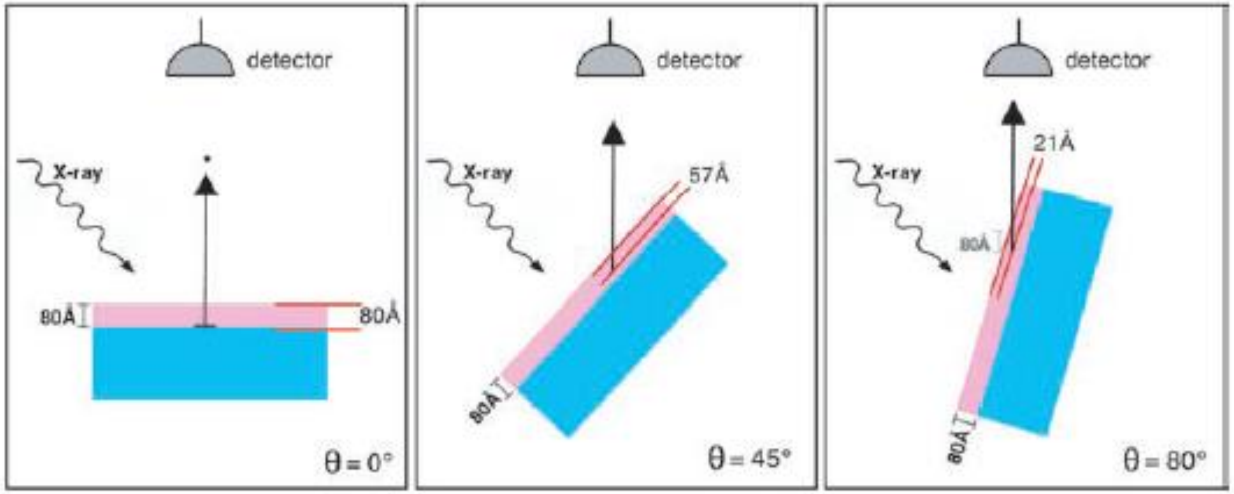
- Hard Disc Depth Profile:
  - Argon Ions
  - Low energy (1 keV)
  - Azimuthal Rotation
  - Non-linear Least Squares Fitting

Electron Spectroscopy for Chemical Analysis

Depth Profiling

Angular dependent ESCA

- As the sample angle to the analyzer entrance is increased, with the X-ray source and the analyzer kept in a fixed position, the photoelectrons originate from an increasingly surface localized zone



The sample angle, *θ*, is defined relative to the normal to the surface

- If data are acquired at photoelectron **take-off angles of, for example, 0°, 50°, and 80° from the surface normal**, three sets of ESCA data can be obtained that contain information about the composition as a function of depth.

Electron Spectroscopy for Chemical Analysis

Depth Profiling

Angular dependent ESCA

- The shape of this composition versus take-off angle curve can reveal much about the compositional organization of a surface

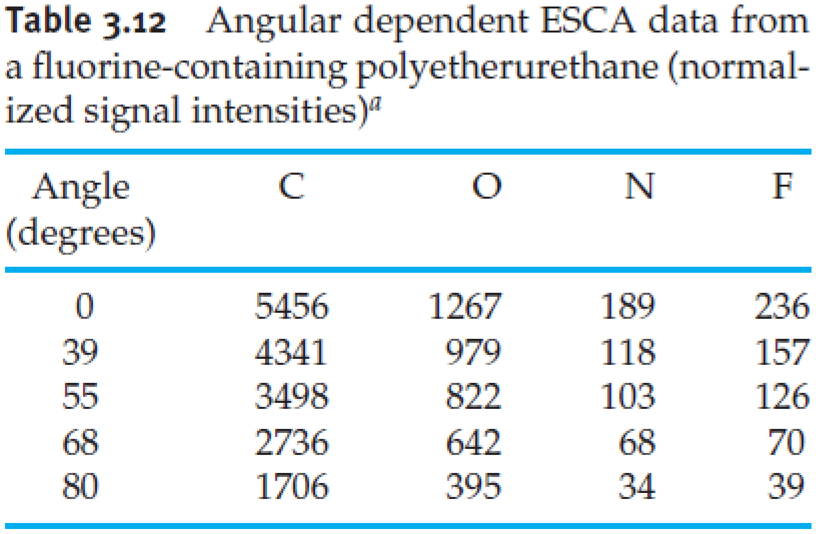


Table 3.12 Angular dependent ESCA data from a fluorine-containing polyetherurethane (normalized signal intensities)[a]

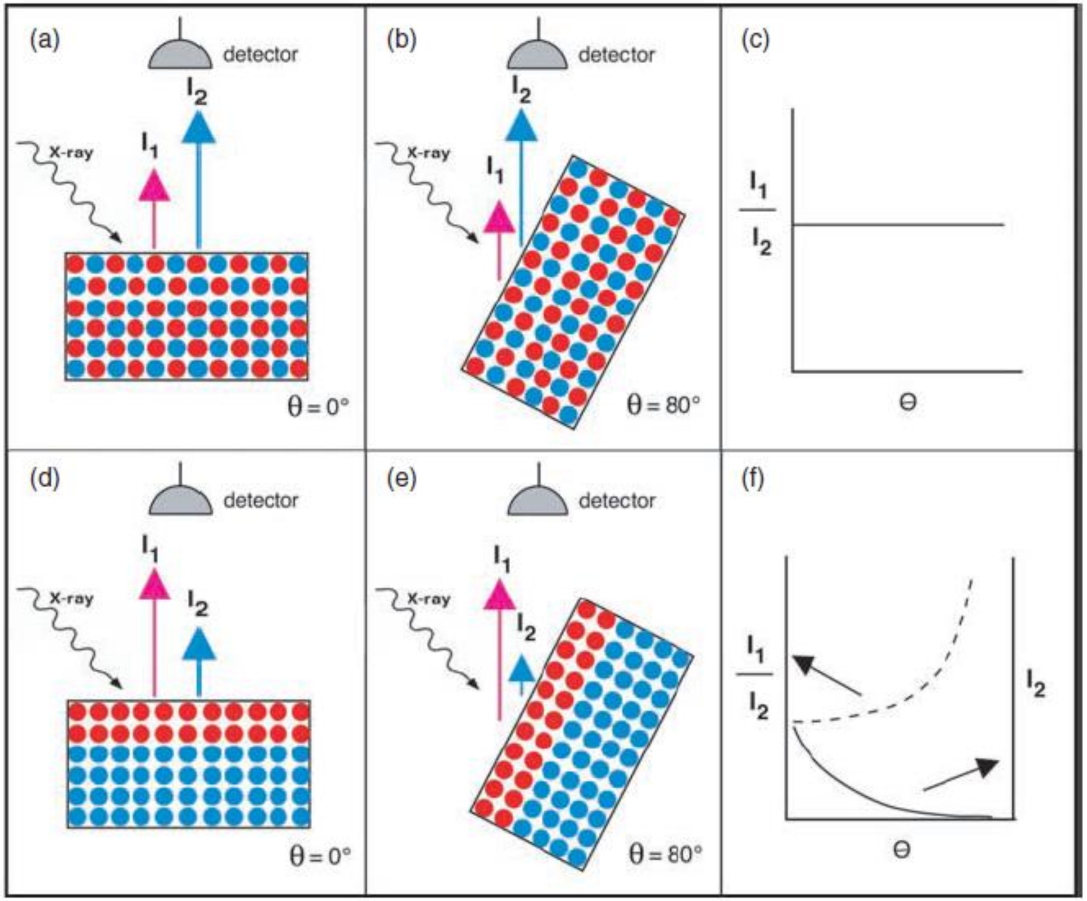
Angle (degrees)	C	O	N	F
0	5456	1267	189	236
39	4341	979	118	157
55	3498	822	103	126
68	2736	642	68	70
80	1706	395	34	39

- For accurate and meaningful depth profiles from angular dependent ESCA data, we assume that the surfaces and interfaces studied are molecularly smooth and that overlayers are of uniform thickness

Electron Spectroscopy for Chemical Analysis

Depth Profiling

Angular dependent ESCA



(c) Because <u>the ratio of intensities does not change with sample angle</u>, for a sample homogeneous in depth, a plot of the ratio of photoemission intensities (or the ratio of atomic percents) with sample angle will show zero slope

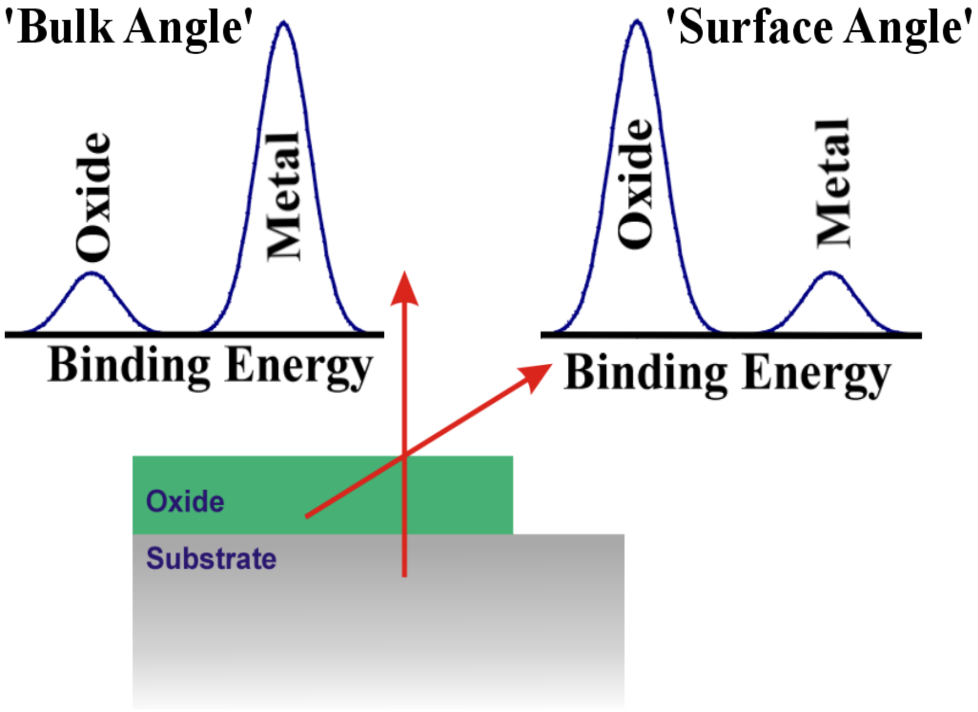
(f) a plot of <u>the ratio of the red atom photoemission intensity to the blue atom photoemission intensity with sample angle will increase in an exponential fashion with sample angle</u>. The photoemission from the blue atoms will decrease in intensity with increasing sample angle

Electron Spectroscopy for Chemical Analysis

Depth Profiling

Angular dependent ESCA

Depends Upon Take-Off Angle

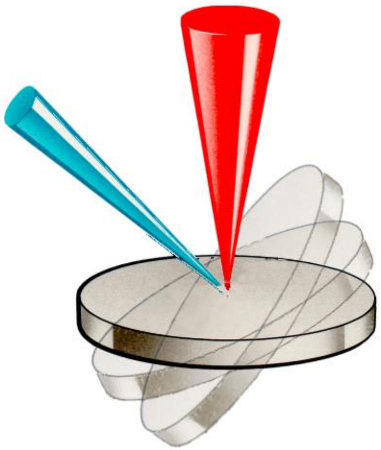


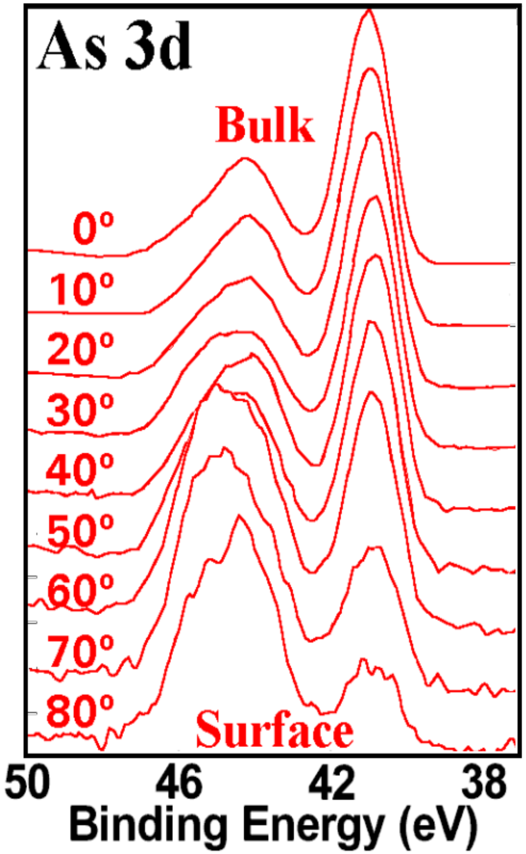
Electron Spectroscopy for Chemical Analysis

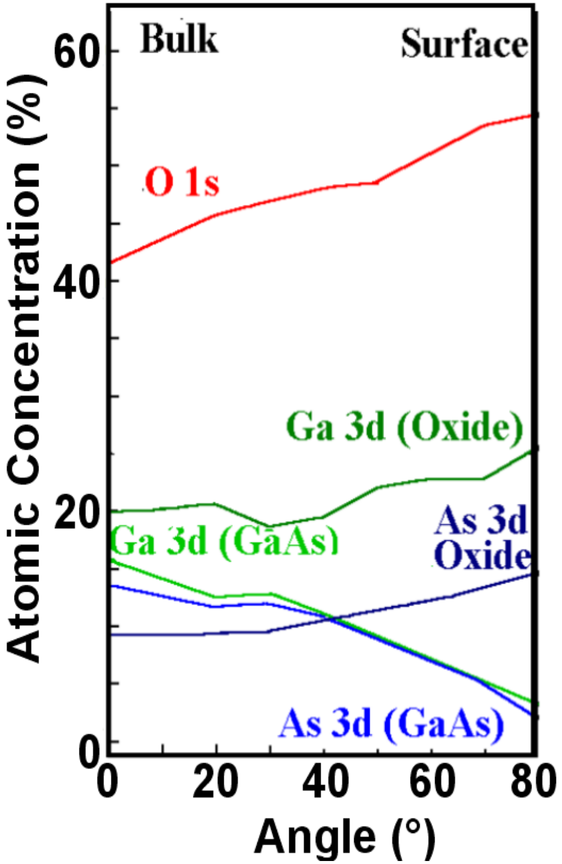
Depth Profiling

Angular dependent ESCA

Example. GaAs







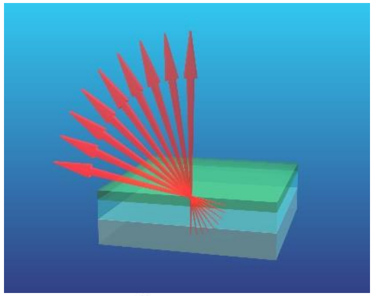
Electron Spectroscopy for Chemical Analysis

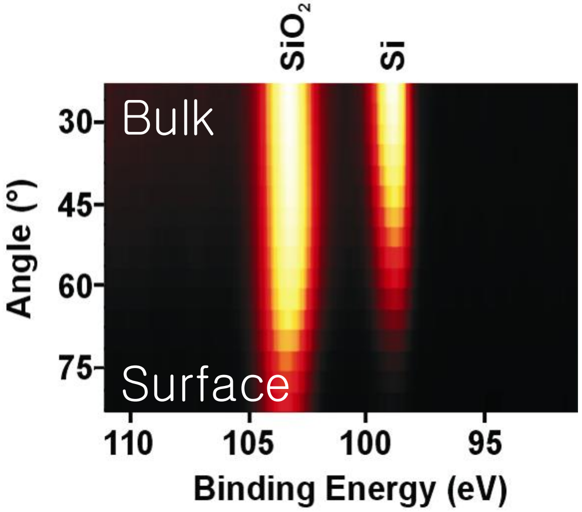
Depth Profiling

Angular dependent ESCA

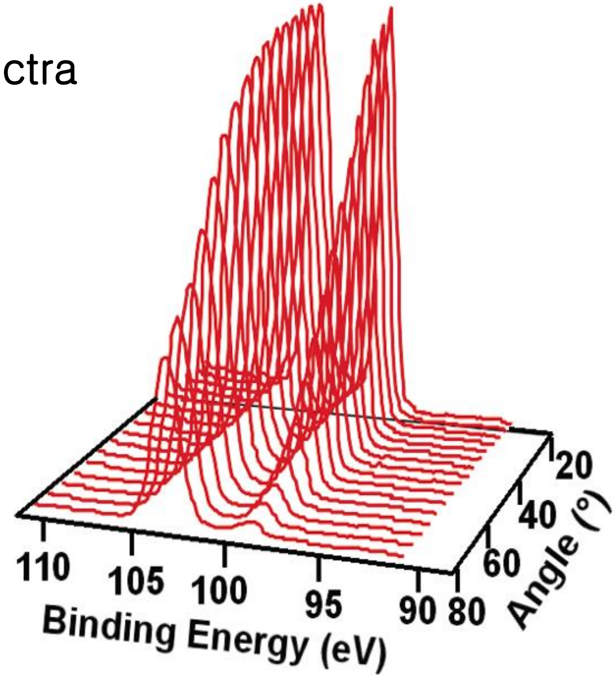
Example. Silicon wafer

- Full Range of angles collected simultaneously
- User selectable angle resolution (<=96 channels)





16 Spectra



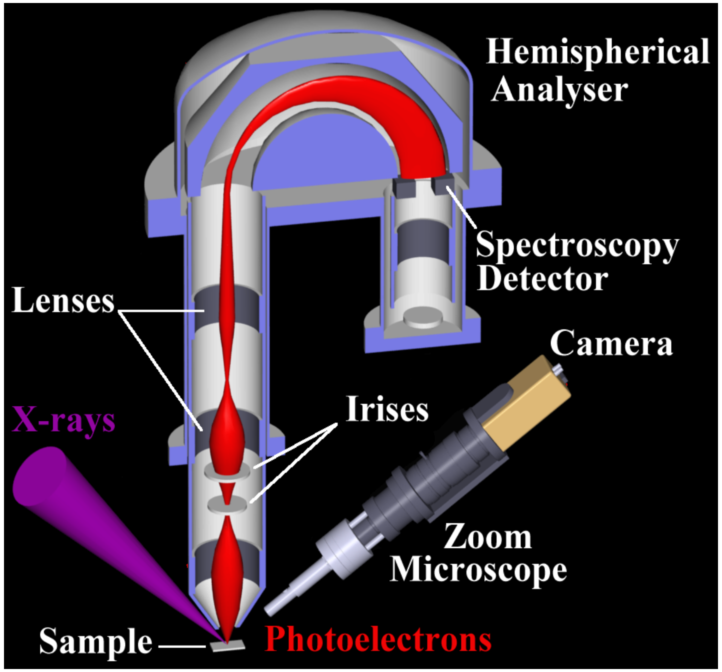
Electron Spectroscopy for Chemical Analysis

X-Y Mapping and Imaging

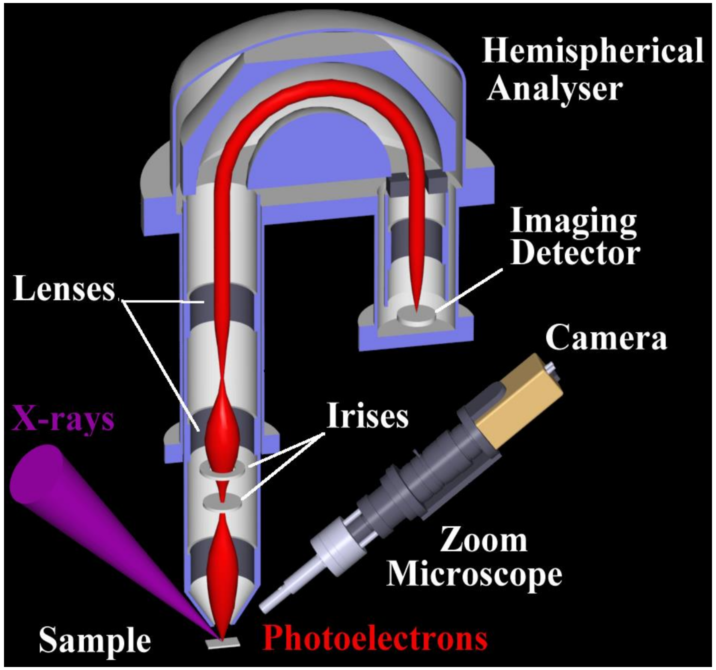
Parallel Imaging

– A method for image collection in which, at any given moment, data are collected from the entire field of view at a single energy

- Spectrum Acquisition



- Image Acquisition

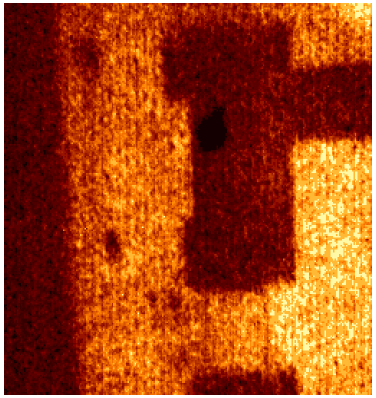


e.g. Parallel Imaging – ESCALAB 250

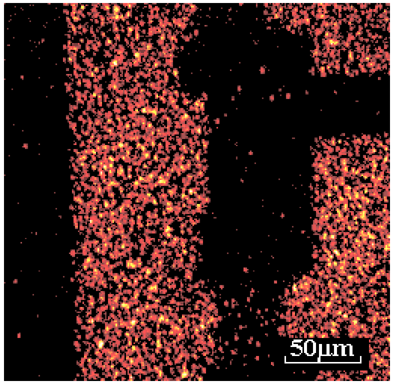
Electron Spectroscopy for Chemical Analysis

X-Y Mapping and Imaging

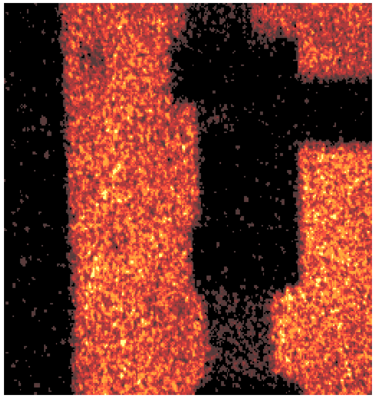
Parallel Imaging



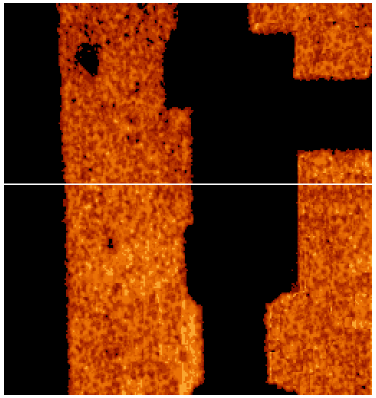
Flood Source Image
Real Time



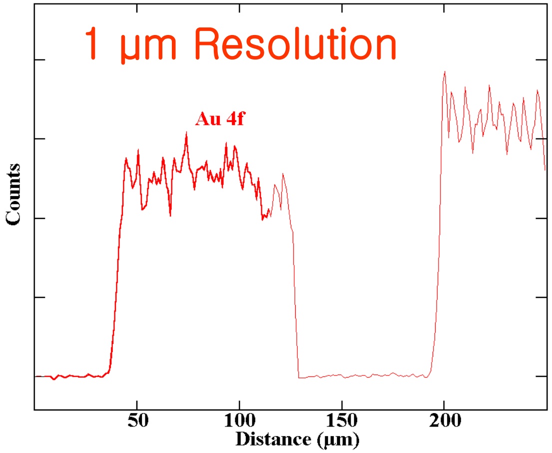
Au 4f Image – 6 seconds



Au 4f Image – 60 seconds



Au 4f Image –10 minutes



- Gold Tracks on Silicon
- Monochromated X-ray Source

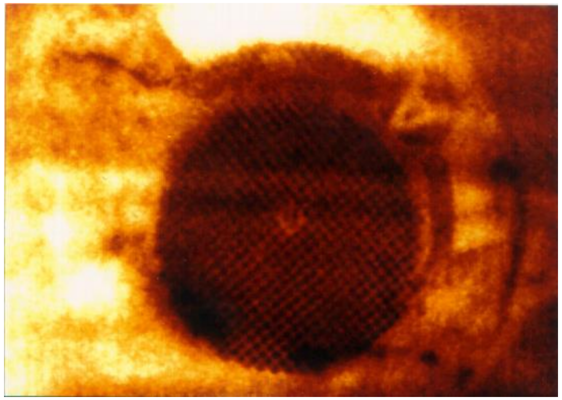
Electron Spectroscopy for Chemical Analysis

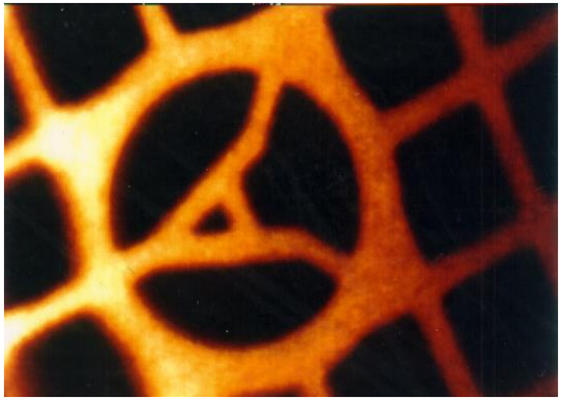
X-Y Mapping and Imaging

Parallel Imaging

- Wide Magnification Range 4 mm – 120 µm

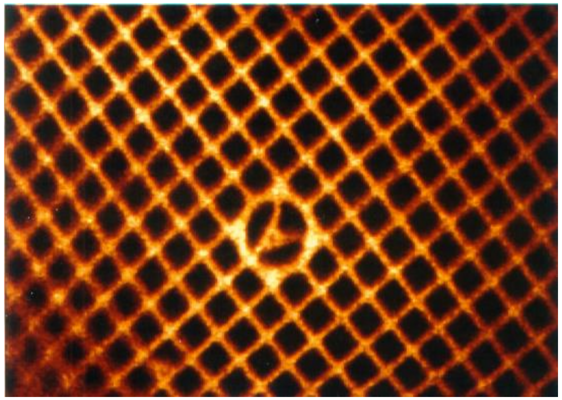
4 mm

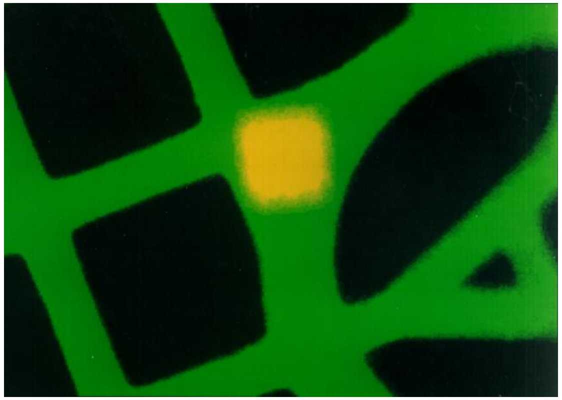




250 µm

1 mm





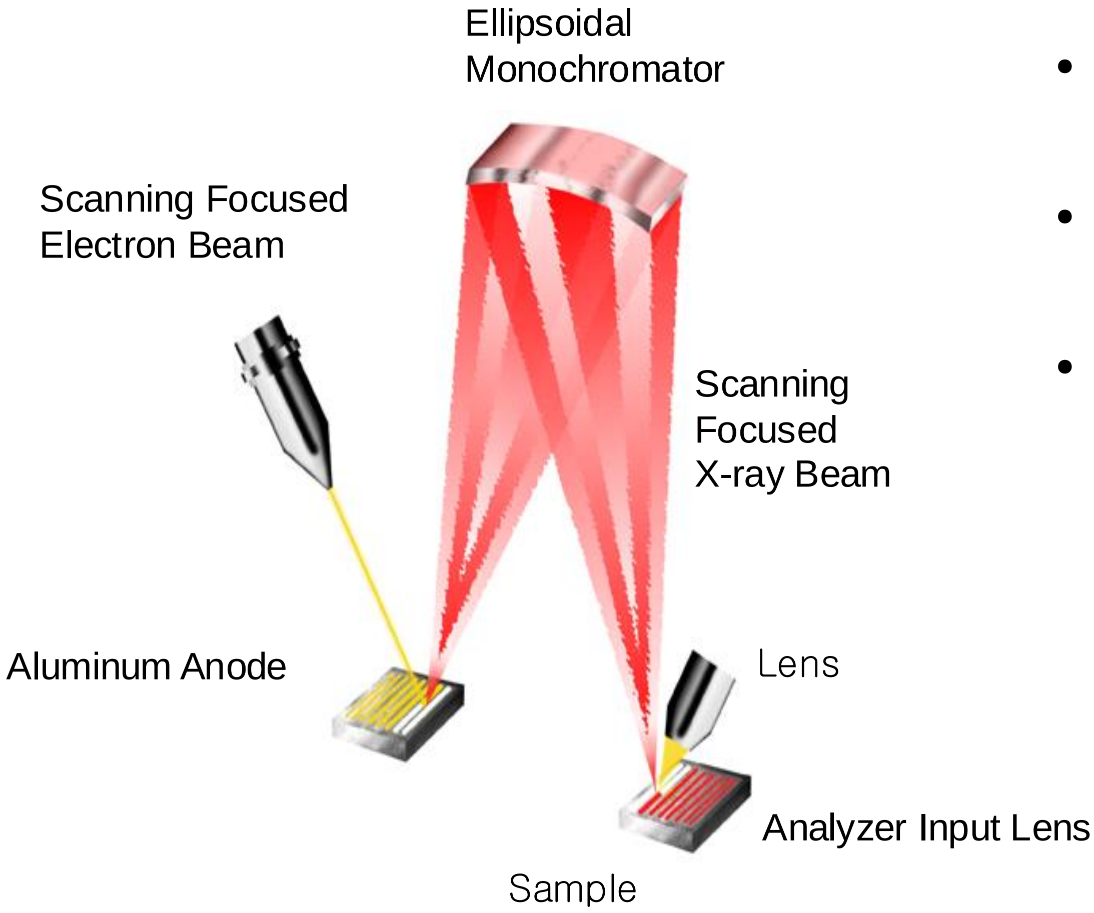
120 µm

and overlay of 15 µm lens defined micro-area

Electron Spectroscopy for Chemical Analysis

X-Y Mapping and Imaging

Stage Mapping



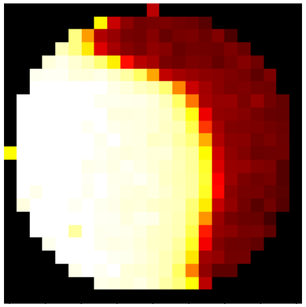
- Ultimate resolution
  - ~15 μm
- Field of View
  - ~1.5 mm x 0.4 mm
- Note
  - As the beam is scanned in the dispersive direction the X-ray energy and intensity changes – must be corrected in software.

Electron Spectroscopy for Chemical Analysis

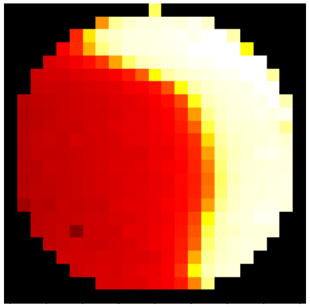
X-Y Mapping and Imaging

Stage Mapping

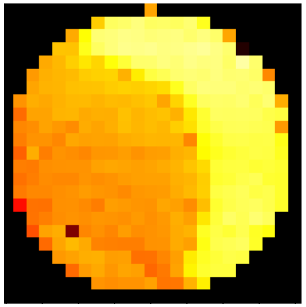
- Mixed Al_2O_3 HfO_2 layer deliberately grown to be non-uniform and mapped by XPS
- 379 Point Map from 200 mm Wafer



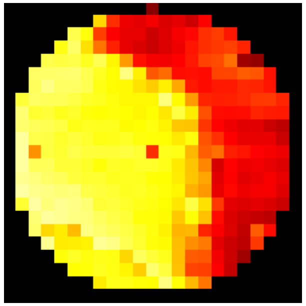
Al 2p



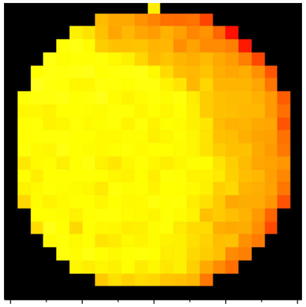
Hf 4f



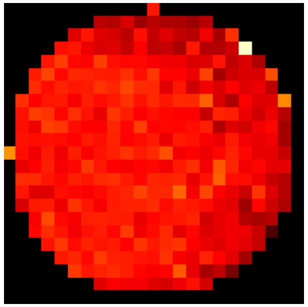
O 1s Low BE



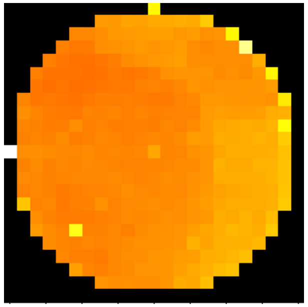
O 1s High BE



Si 2p Elemental



Si 2p Oxidised



C 1s

Electron Spectroscopy for Chemical Analysis

X-Y Mapping and Imaging

Comparison of Imaging Methods

	Parallel Imaging	Scanning Mono	Scanning Stage
Resolution	<3 μm	<15 μm	<15 μm
Field of View	120 μm to 4 mm	1.5 mm x 0.4 mm	Up to 300 mm
Speed	Fast	Medium	Slow
Additional Information	None	32 Channel snapshot	112 Channel snapshot 96 Channel ARXPS

Electron Spectroscopy for Chemical Analysis

X-Y Mapping and Imaging

Advantages of Stage Mapping

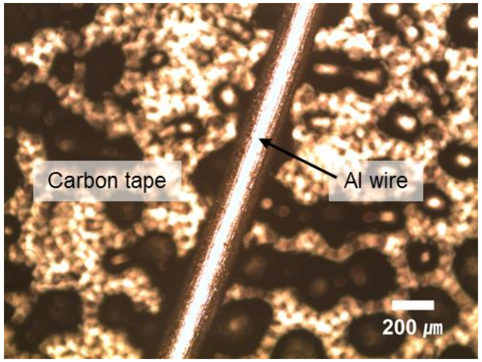
- Spatial resolution is determined only by the X-ray spot size
  - Constant throughout the acquisition
  - No degradation of the image quality at the edges
- Spectrum at every pixel allows
  - High-quality chemical state maps
  - Quantitative imaging
  - Thickness maps
- The spatial resolution is independent of the settings of the transfer lens
  - The spectrometer is always operated at its maximum transmission.
- The point on the sample being mapped is always in the optimum analysis position
  - There can be no changes in the sensitivity over the field of view.
- X-ray energy and intensity independent of position on the sample
  - No software corrections required
- Very large field of view possible (up to 60 x 60 mm for K-Alpha).

Electron Spectroscopy for Chemical Analysis

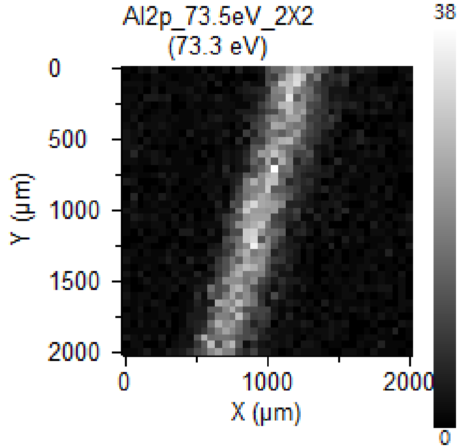
X-Y Mapping and Imaging

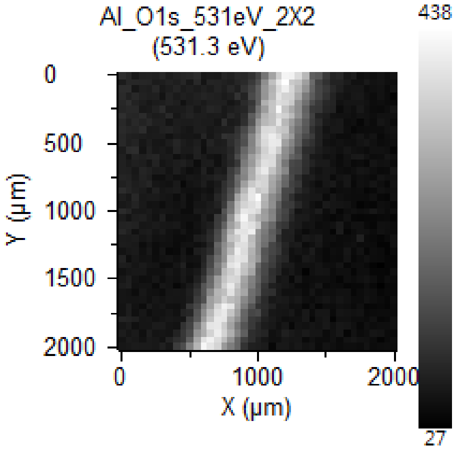
Examples

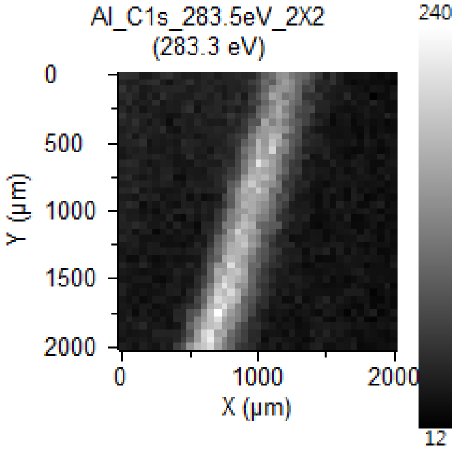
Al wire_XPS mapping

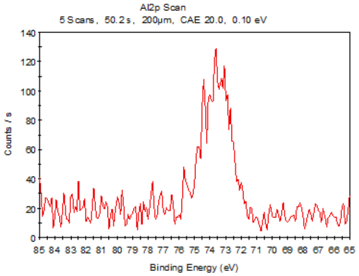


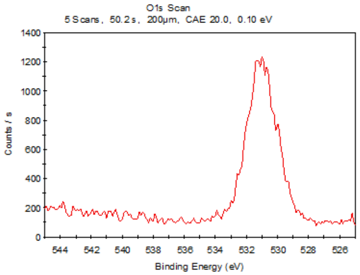
X-ray size : 200 ㎛
Area : 2 ㎜ × 2 ㎜
Step size : 50 ㎛
Point count : 1681 (41 × 41)
# of frames : 3
Time per Frames : 1 s
Center/Width
- Al2p : 73.5 / 2 eV
- O1s : 531 / 3 eV
- C1s : 283.5 / 2 eV

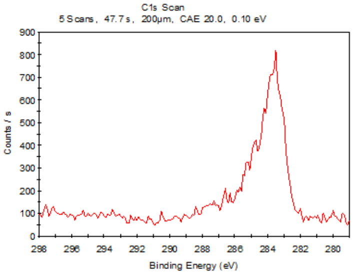

Al2p_73.5eV_2X2
(73.3 eV)


Al_O1s_531eV_2X2
(531.3 eV)


Al_C1s_283.5eV_2X2
(283.3 eV)


Al2p Scan
5 Scans, 50.2 s, 200µm, CAE 20.0, 0.10 eV


O1s Scan
5 Scans, 50.2 s, 200µm, CAE 20.0, 0.10 eV

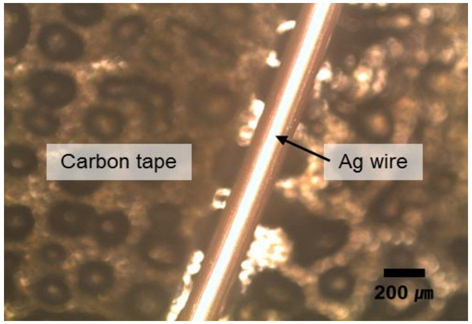

C1s Scan
5 Scans, 47.7 s, 200µm, CAE 20.0, 0.10 eV

Electron Spectroscopy for Chemical Analysis

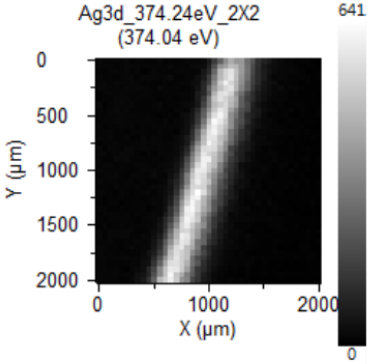
X-Y Mapping and Imaging

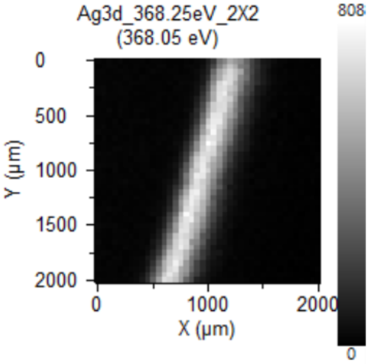
Examples

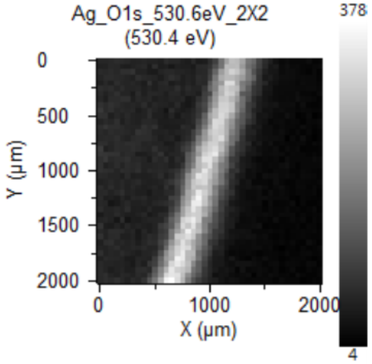
Ag wire_XPS mapping

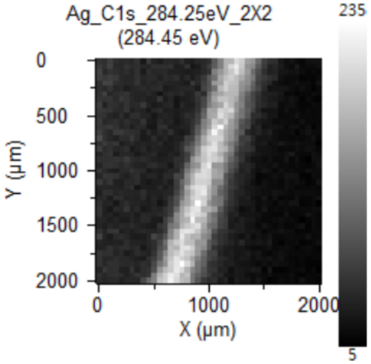


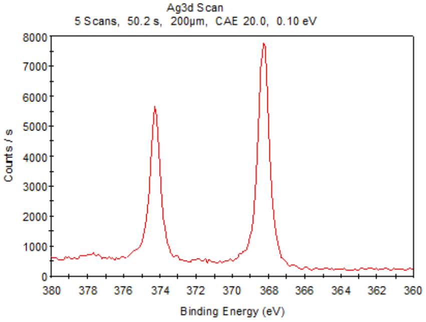
X-ray size : 200 ㎛
Area : 2 ㎜ × 2 ㎜
Step size : 50 ㎛
Point count : 1681 (41 × 41)
# of frames : 3
Time per Frames : 1 s
Center/Width
- Ag3d : 368.25 / 2 eV
- Ag3d : 374.24 / 2 eV
- O1s : 530.6 / 2 eV
- C1s : 284.25 / 2 eV

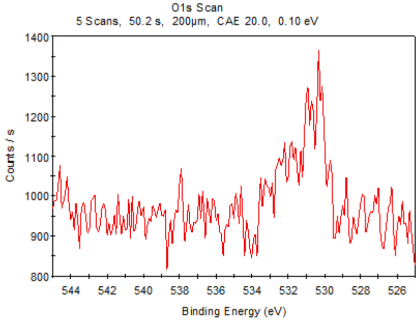


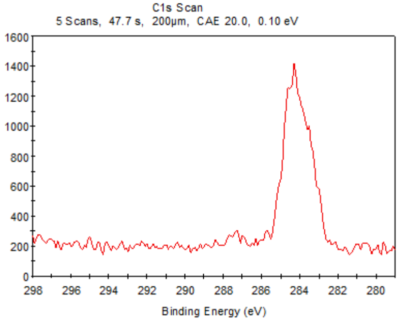












<Homework>

1. Plot XPS spectra of $CsPbBr_3$ on Gold foil
2. Deconvolute multiple peaks
3. Analysis atomic percentage

<Due date>

12th May / e-mail

<Reference>

1. Down load fitting program and raw data at APPND website
2. Watch follow link

https://www.youtube.com/watch?v=do1ZZP3yDrl

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.

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