

# Photoelectron Spectroscopy (PES)

## Highlights:

- ❑ In PES, kinetic energy of photoelectrons are determined to get their bonding energy, intensity, angular distributions and obtain the electronic structure.
- ❑ Working principle is based on [Einstein's photoelectric effect](#).
- ❑ Differs from conventional spectroscopic techniques, as it detects electrons not photon from the sample.

## Photoelectron Spectroscopy (PES)

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graph TD; PES[Photoelectron Spectroscopy (PES)] --- XPS[X-ray Photoelectron Spectroscopy (XPS)]; PES --- UPS[UV Photoelectron Spectroscopy (UPS)]; XPS --- AES[Auger electron spectroscopy (AES)]; UPS --- UPS_desc[Involves UV ionization of lower energy valence electrons]; XPS --- XPS_desc[Involves X-ray/electron gun ionization of high energy core electrons];
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**X-ray Photoelectron Spectroscopy (XPS)**  
**Auger electron spectroscopy (AES)**

Involves X-ray/electron gun ionization of high energy **core electrons**

**UV Photoelectron Spectroscopy (UPS)**

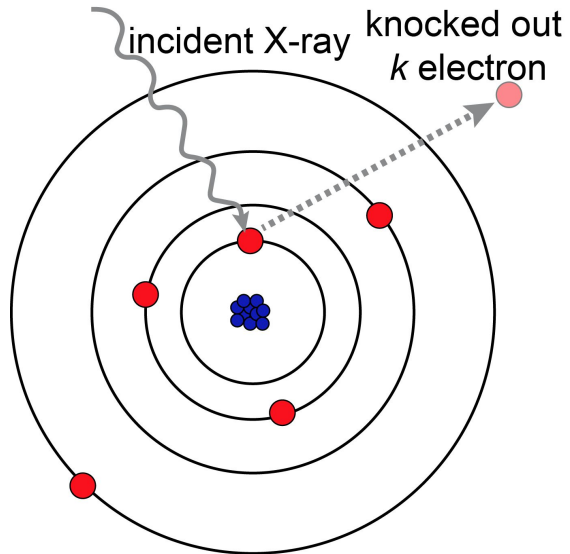
Involves UV ionization of lower energy **valence electrons**

# X-ray Photoelectron Spectroscopy (XPS)

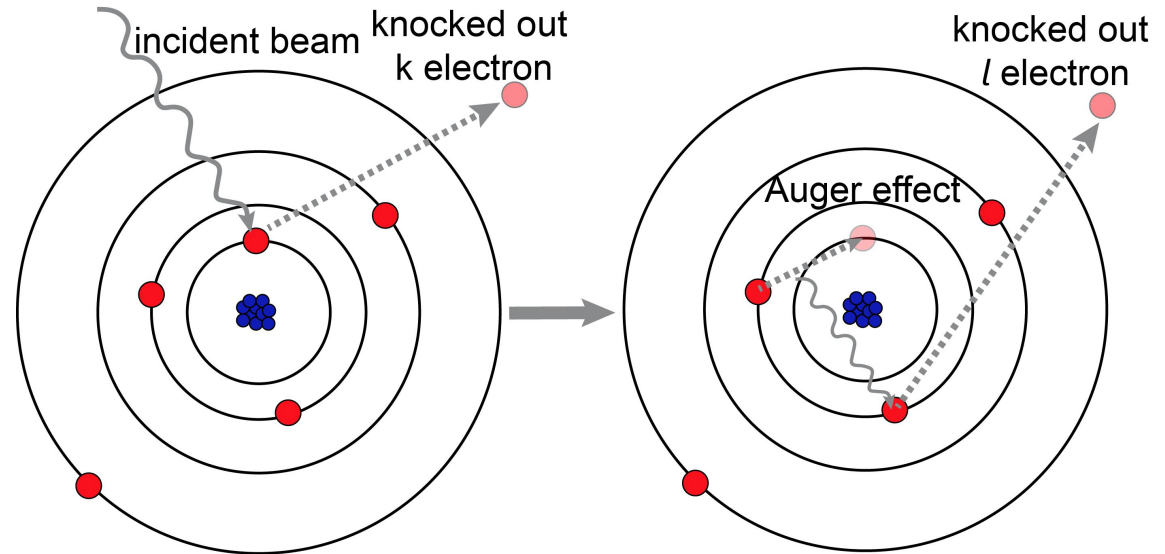
## Highlights:

- ❑ Also known as Electron Spectroscopy for Chemical Analysis (ESCA).
- ❑ Widely used in industry and engineering applications.
- ❑ It can give surface information and 1mm depth profiling.
- ❑ We can get electronic configuration, chemical composition, chemical state, surface texture and thin film properties of samples.

# X-ray Photoelectron Spectroscopy vs Auger electron spectroscopy



XPS = 1  $e^-$  emission process



AES = 2  $e^-$  emission process

## XPS

## AES

**Similarities:** Both XPS and AES based on photoelectric effect, can measure surface properties by recording the kinetic energy of an electron to determine its binding energy to extract useful chemical information.

X-ray is used for ionization

Electron beam is used

It's a 1 electron emission process

It's a 2-electron emission process

All sample types can be analyzed

Only conducting and semiconducting samples can be analyzed

Less sensitive, profile low sample size (1-10  $\mu\text{m}$  max) but data interpretation is easy

More sensitive, profile larger sample size (1-10 nm) but data interpretation is complicated

# Binding energy calculation

From Einstein's theory, formula for calculating the binding energy of the ejected electrons is:

$$\text{BE} = h\nu - \text{KE} - F$$

BE = Binding energy of the photoelectron

KE = Kinetic energy of the photoelectron

F = Work function of the spectrometer

# Sample preparation for XPS

- ❖ Sample can be prepared easily in powder or thin film or any other form. In general, glass or carbon tape is used for support.
- ❖ Removal of volatile organic compounds and moisture is done by exposing the sample in ultra-high vacuum (up to  $10^{-9}$  torr). This step prolongs the total measurement time.
- ❖ Compared to smooth and shiny surface, rough surface increases electron count. That's why sometimes rough paper is used for surface scratching for better Signal.

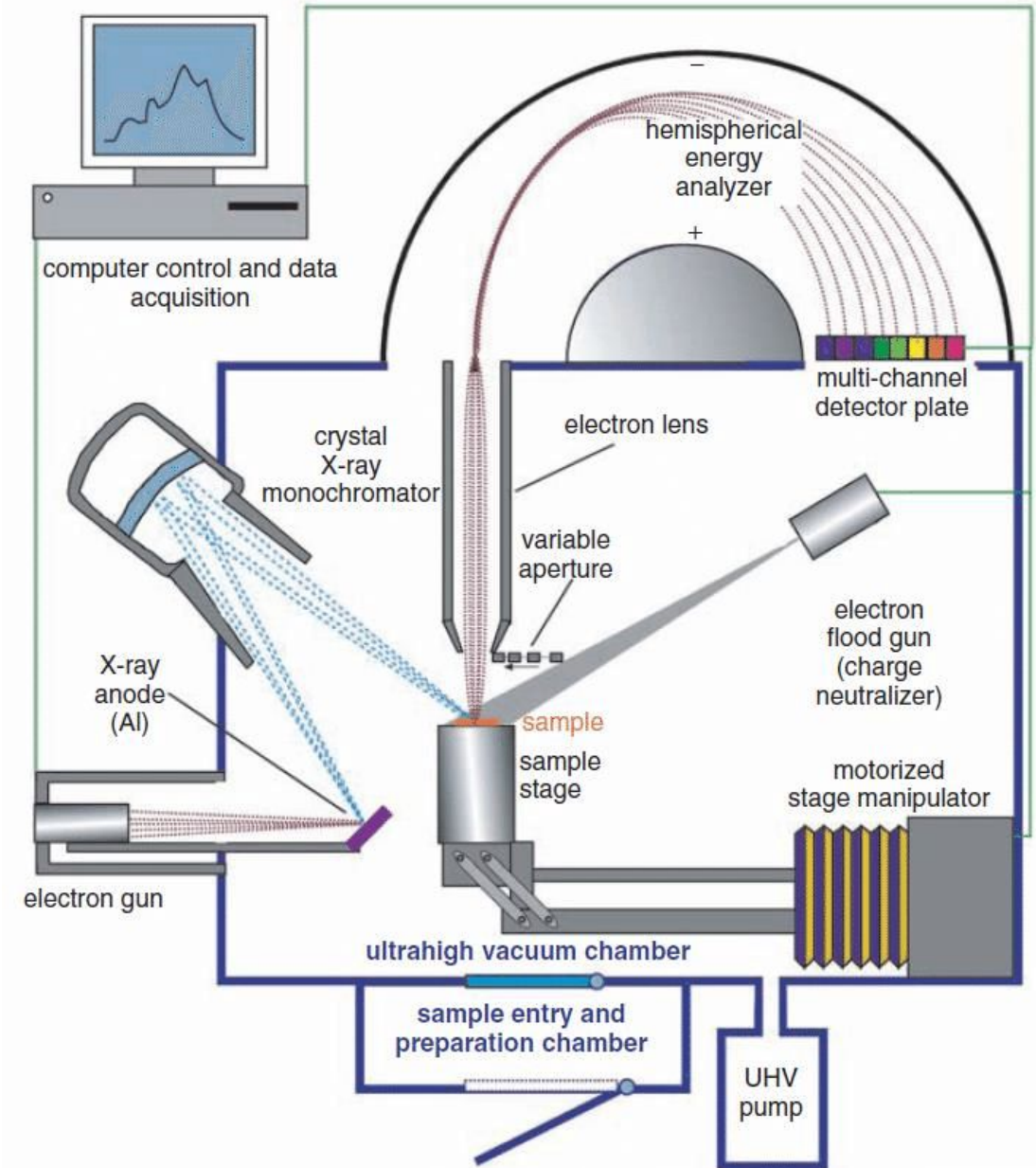
# Instrumentation setup

Monochromatic X-ray source: Al  $K\alpha$ ;  $h\nu = 1486$  eV

Mg  $K\alpha$ ;  $h\nu = 1253$  eV

Ultra-high vacuum chamber:  $10^{-9}$  Torr

Hemispherical energy analyzer: +vely charged plate inside to attract electron, -vely charged outer plate to guide charges in a circular path to the detector.



# Elemental shifts of XPS peaks

XPS peaks are plotted between number of collected electrons (unit as count per second) and binding energy of the collected electrons (expressed in eV)

Each element and its orbital has different binding energy for every electron present at that shell

The orbit which is closer to nucleus has higher binding energy, consequently the kinetic energy is lower

Element	Binding Energy (eV)		
	2p <sub>3/2</sub>	3p	Δ
Fe	707	53	654
Co	778	60	718
Ni	853	67	786
Cu	933	75	858
Zn	1022	89	933

Standard data of elements (obtained due to unique electron to nucleus attractive force for every element) helps us to identify desired elements present in the sample.



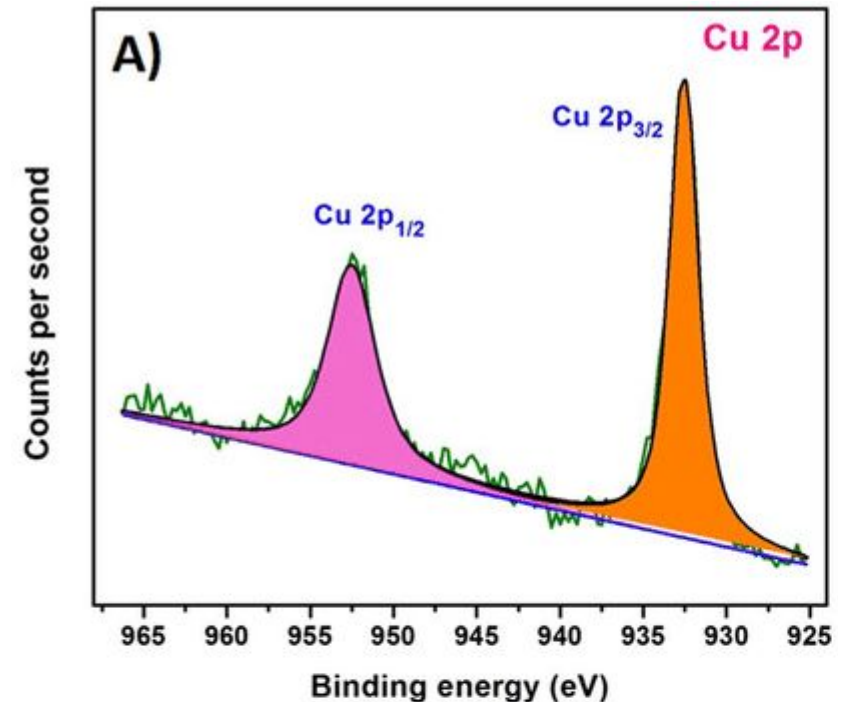
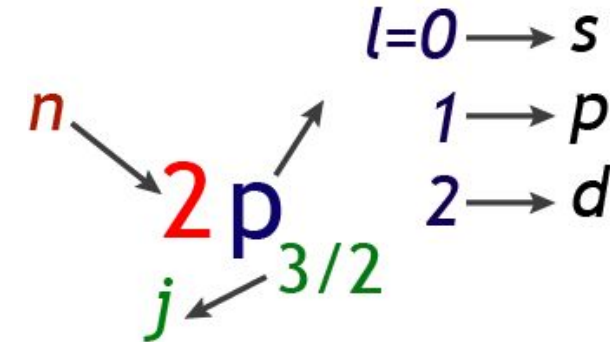
# Electronic effect of the XPS peak

The binding energy of the core electron is dependent on,

- ✓ Energy of the occupied shell
- ✓ Principle quantum number  $n$
- ✓ Orbital angular quantum number  $l$
- ✓ Spin angular quantum number  $s$
- ✓ Total angular quantum number  $j = l + s$

For p orbital,  $l = 1$ ,  $s = \pm 1/2$ ,  $j = 1/2, 3/2$

Subshell	$l$ values	$j$ values
s	0	1/2
p	1	1/2, 3/2
d	2	3/2, 5/2
f	3	5/2, 7/2





# Electronegativity effects on the chemical shifts : Carbon

<b>Functional Group</b>		<b>Binding Energy (eV)</b>
hydrocarbon	<u>C</u> -H, <u>C</u> -C	285.0
amine	<u>C</u> -N	286.0
alcohol, ether	<u>C</u> -O-H, <u>C</u> -O-C	286.5
Cl bound to C	<u>C</u> -Cl	286.5
F bound to C	<u>C</u> -F	287.8
carbonyl	<u>C</u> =O	288.0

# XPS of PET as an example

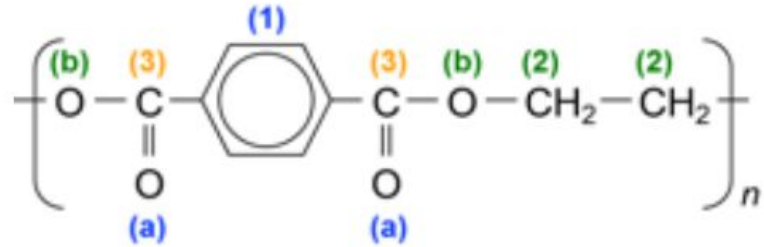


Figure 1. Structure of PET

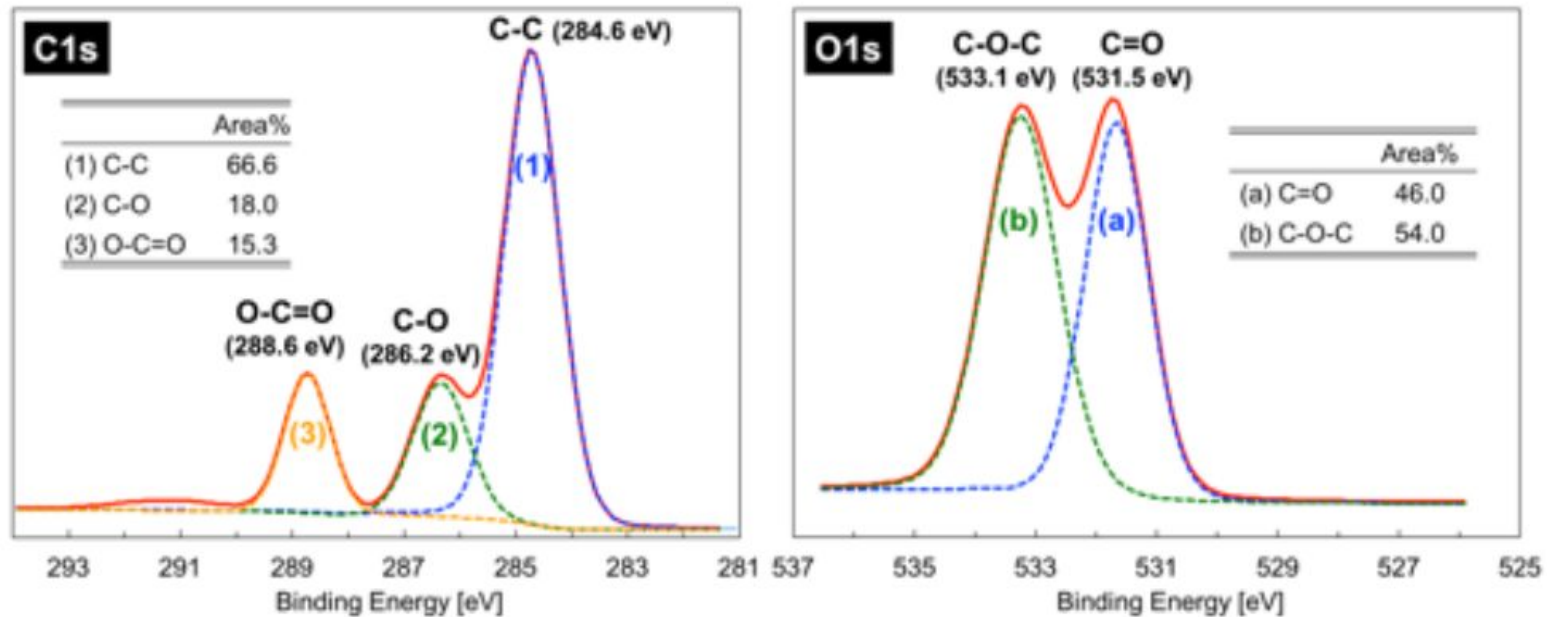
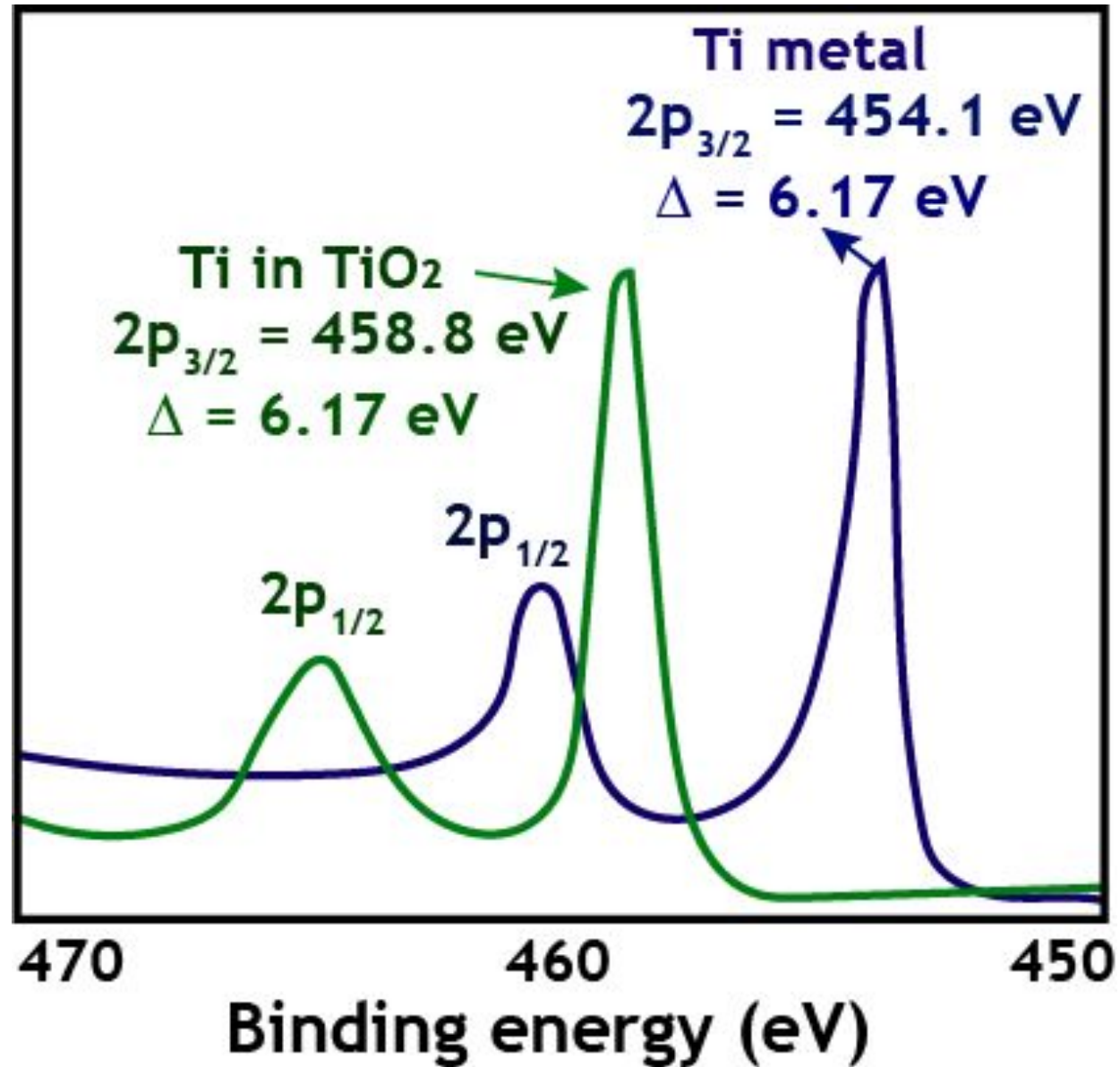


Figure 2. XPS spectra of PET

# Application of XPS



## Pros and cons

Advantages	Limitations
<input type="checkbox"/> Small sample quantity needed, no special preparation, non-destructive	<input type="checkbox"/> Expensive and sophisticated instrumentation required
<input type="checkbox"/> Surface sensitive with depth profiling	<input type="checkbox"/> High vacuum needed
<input type="checkbox"/> High detection level, ppm to ppt unit	<input type="checkbox"/> Lateral resolution is a bit poor
<input type="checkbox"/> Quantitative measurements possible	<input type="checkbox"/> Large area analysis is required
<input type="checkbox"/> Vital chemical bonding information can be obtained easily	<input type="checkbox"/> Slow Data collection and processing
<input type="checkbox"/> Elemental mapping is possible	<input type="checkbox"/> H and He cannot be detected

# Scope of usage and application area of XPS

## **XPS is used to measure:**

- ❖ Elemental composition of the surface (top 1–12 nm usually).
- ❖ Empirical formula of pure materials.
- ❖ Chemical or electronic state of each element in the surface.
- ❖ Uniformity of composition across the top surface (line profiling).
- ❖ Uniformity of elemental composition as a function of ion beam etching (depth profiling).

## **Applications in the industry:**

- ❖ Failure analysis
- ❖ Polymer surface
- ❖ Corrosion
- ❖ Adhesion
- ❖ Semiconductors
- ❖ Dielectric materials
- ❖ Thin film coatings

**XPSPEAK 4.1, FitXPS, CasaXPS and Spectral Data Processor (SDP) V3.0** are the softwares use for XPS analysis