Module -5
Material Characterization and Instrumentation Techniques

SYLLABUS:

Introduction to nano materials: Nanomaterial and nanocomposites. Principle, construction and working of X-ray Diffractometer, Crystallite size determination by Scherrer equation, Atomic Force Microscopy (AFM): Principle, construction, working and applications, X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Numerical Problems.

Nano materials

Nanomaterials can be defined as materials possessing, at least, one external dimension measuring 1-100 nm. The properties exhibited by nanomaterials strikingly different from those of bulk materials due to the surface effects and size effects. Nanotechnology is the design and fabrication of devices using such nanostructures.

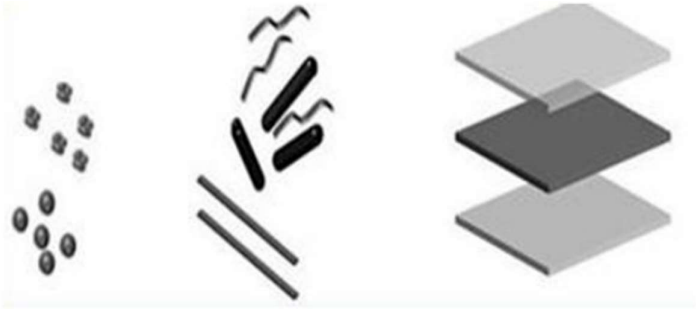
Nanoparticles have a high surface to volume ratio. As a result, they can display physical and chemical properties significantly different from the bulk material. Because at this level quantum effects are significant. At nano level, the mechanical, electrical, optical, electronic, catalytic, magnetic, etc. properties of solids are significantly altered with reduction in particle size.

For example:

- Nano scale copper is five times stronger than ordinary copper.
- Silver foil does not react with dilute HCl but silver nanoparticles rapidly react with dilute HCl.
- Gold and silver both are chemically inert but their nanoparticles show catalytic property.
- Gold nanoparticles are deep red but its bulk material (gold pieces) is gold coloured.

CLASSIFICATION OF NANOMATERIALS:

Nanomaterials are classified based on the number of dimensions at nano-scale as follows.



a. Zero-dimensional (0D) nanomaterials or quantum dots:

Here, all dimensions (x, y, z) are at nanoscale, i.e., no dimensions are greater than 100 nm.

Eg: nanospheres and nano-clusters.

b. One-dimensional nanomaterials (1D) or Quantum wires:

Here, two dimensions (x, y) are at nanoscale and the other is outside the nanoscale. This leads to needle shaped nanomaterials.

Eg: nano-fibres, nano-tubes, nano-rods, and nano-wires.

c. Two-dimensional nanomaterials (2D) or Quantum wells:

Here, one dimension (x) is at nanoscale and the other two are outside the nanoscale. The 2D nanomaterials exhibit plate like shapes.

Eg; nano-films/thin-films nano-layers and nano-coatings.

Properties of nanomaterials:

Due to large fraction of surface atoms, large surface energy, spatial confinement, and reduced imperfections the nanomaterials exhibit

- Enhanced mechanical properties
- Different optical properties
- Higher or lower electrical conductivity
- Altered magnetic properties
- Enhanced chemical reactivity

Applications:

Nanomaterials find wide range of applications in various fields. They are used in

1. targeted, controlled drug delivery in cancer therapy

2. CNTs attached to the tips of the scanning probe, microscopes are used to identify and characterize biological specimens. Lung cancer cells etc.

3. contact lenses, Dental implants and artificial heart valves

4. Integrated memory circuits in electronic gadgets.

5. CNTs act as EM shield for costly electronic materials as they are poor transmitters of Electro-magnetic radiations

6. fuel cells - hydrogen storage is made easy with CNT

7. Transistors with p-n junctions can be made by nano wires.

8. Ag nanomaterials are used as anti-bacterial agent in air-conditions and refrigerators.

9. Nano ATO (Antimony-Tin-Oxide) is used in car windows to reduce solar heat radiation.

10. Nano fibre is used to produce wrinkle free, stain resistance fabrics in textile industry.

NANOCOMPOSITES:

Nano composites are materials that incorporate Nano-sized particles into a matrix of standard material. The idea behind Nano composite is to use building blocks with dimensions in nano-meter range to design and create new materials with improved physical properties. A very small quantity of nano scale materials added to the bulk matter results in drastic improvement in their mechanical strength, toughness and electrical or thermal conductivity. Nanoparticles have an extremely high surface to volume ratio which dramatically changes their properties when compared with their bulk sized equivalents. It also changes the way in which the nanoparticles bond with the bulk material.

Nano composites can dramatically improve properties like:

1. Mechanical properties including strength, modulus and dimensional stability

2. Electrical conductivity

3. Decreased gas, water and hydrocarbon permeability

4. Flame retardancy

5. Thermal stability

6. Chemical resistance

7. Surface appearance

8. Optical clarity

Applications Nano-composites being used in a number of fields and new applications are being continuously developed.

Applications for nanocomposites include:

1. Thin-film capacitors for computer chips

2. Solid polymer electrolytes for batteries.

3. Automotive engine parts and fuel tanks

4. Impellers and blades

5. Oxygen and gas barriers

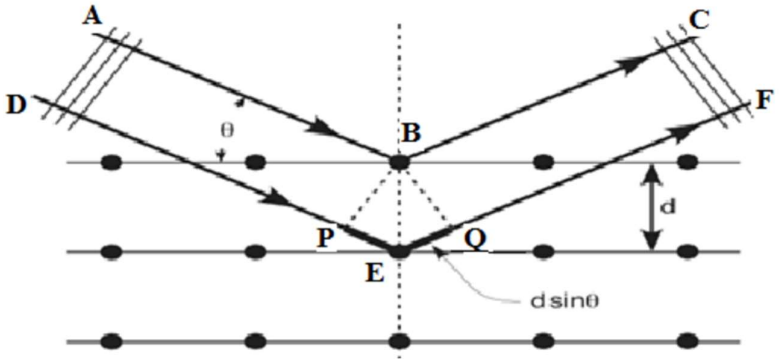
6. Food packaging materials

X-ray Diffraction

The basic principle of an X-ray diffractometer is the Bragg's law which is the fundamental equation relating the wavelength (λ) of X-rays, the inter planar distance (d) in crystalline materials, and the glancing angle (θ) or angle of diffraction.

Consider a set of parallel atomic planes of the Crystal such that the distance between the two successive planes is d. Let a beam of monochromatic X-rays fall on a crystal plane at a glancing angle of $\boldsymbol{\theta}$. Let AB and DE be the two parallel rays of the incident beam get reflected by the atoms B and E. In a crystal, each of the atoms scatters the incident ray in all directions. For constructive interference and hence maximum to observe, the path difference between the rays ABC and DEF must be an integral multiple of wavelength, ($\boldsymbol{n\lambda}$), given by

$$\boldsymbol{n\lambda = 2d\ sin\ \theta}$$



X-ray Diffractometer

Principle:

X-ray diffractometer works on the principle of constructive interference of x-rays diffracted from different atomic planes in crystals satisfying the Bragg's law given by

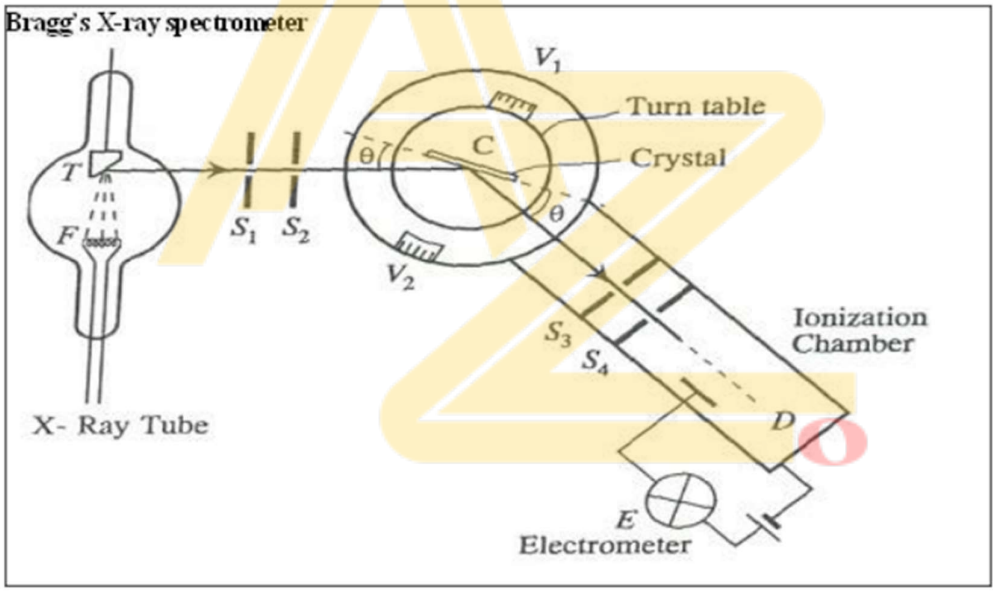
$n\lambda = 2d \sin\theta$; n = 1, 2, 3….

Where λ - wavelength of X-rays; θ - glancing angle; d - the inter planar distance,

Construction:

Three (3) basic components of an x-ray diffractometer are:

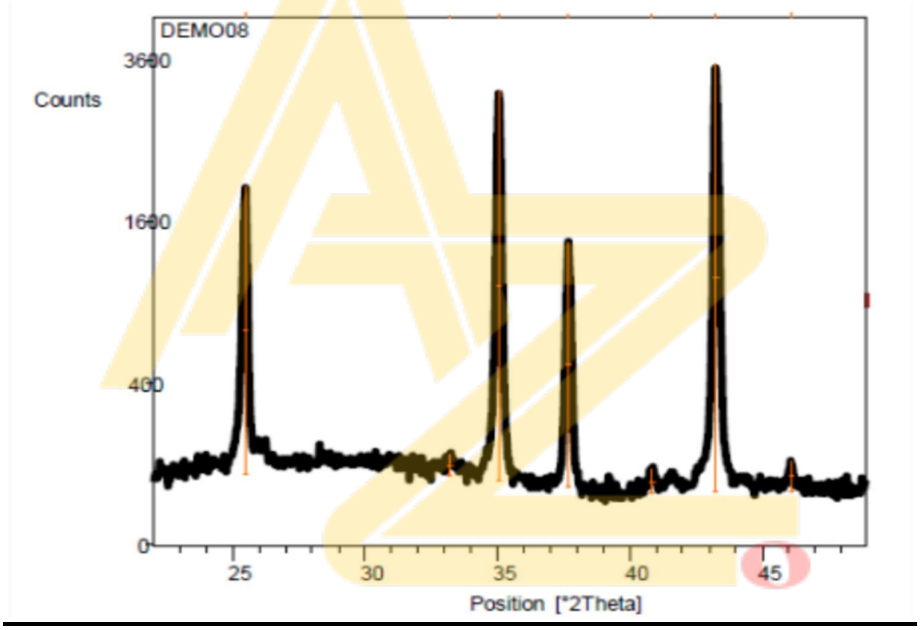
- X-ray source
- Specimen/sample
- X-ray detector



Schematic of an X-ray diffractometer

X rays produced from X ray tube are passed through two slits S_1 and S_2 to obtain a fine collimated X-ray beam. This beam is made to fall on the crystal/sample C fixed on the top of a thin wire mounted exactly at the centre of a turn table. The position of the turn table can be read by means of a vernier V_1. The reflected X ray beam is made to enter an ionization chamber D filled with a gas. The ionization chamber is mounted on a mechanical arm which can rotate coaxially with the turn table. When the turn table rotates by an angle θ, the mechanical arm rotates by 2θ. The position of the arm can be read by means of vernier V_2. The X rays in the

arm are made to pass through the slits S_3 and S_4. The ionization current is measured by the electrometer E. Working: The X -ray beam is made to fall on the sample mounted on the turn table. The sample and the detector are rotated and the intensity of the diffracted/reflected X-rays is recorded in the form of ionization current. When the geometry of the reflected X-rays satisfies the Bragg's equation, the constructive interference occurs and the intensity of the X-rays will become maximum. The detector detects these X-rays and converts into pulses of electric current. The number of current pulses per unit of time is counted which is directly proportional to the intensity of the X-ray beam entering the detector. A typical x-ray diffraction pattern is a plot of peak intensity against the measured diffraction angle 2θ as shown. The positions of the peaks in an x-ray diffraction pattern depend on the crystal structure (shape and size of the unit cell) of the materials.



Application:

XRD is used in

1. Phase identification
2. Identification unknown crystalline materials
3. Determination of crystal size
4. Identifying crystal quality
5. Determination of crystal structure, unit cell dimensions.

Crystal size determination by Scherer equation

The Scherer equation, in X-ray diffraction and crystallography, is an equation that relates the size of tiny crystallites (Particle size) in a solid to the broadening of a peak in a diffraction pattern.

It is given by

$$D = \frac{k\lambda}{\beta cos\theta}$$

Where D – particle size,

K is a constant, called shape factor with a value close to unity depending on the

crystallite shape

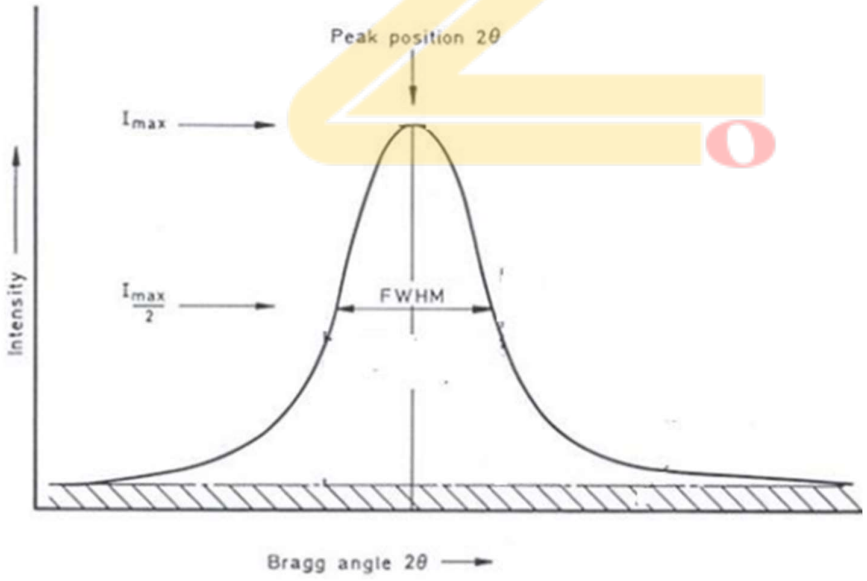
λ − Wavelength of the X-ray used for the diffraction

β − Full width at half maximum (FWHM). It is the width of a line shape at half of its

maximum amplitude.

θ − Peak position Bragg angle.

FWHM can be determined as the distance between the curve points at the peak half maximum level. On a data graph, draw a vertical line from the peak maximum to the baseline. Measure the length of this line and divide it by 2 to find the center of the line. Draw a line passing through the line center and parallel to the baseline, the length of this line is the FWHM.



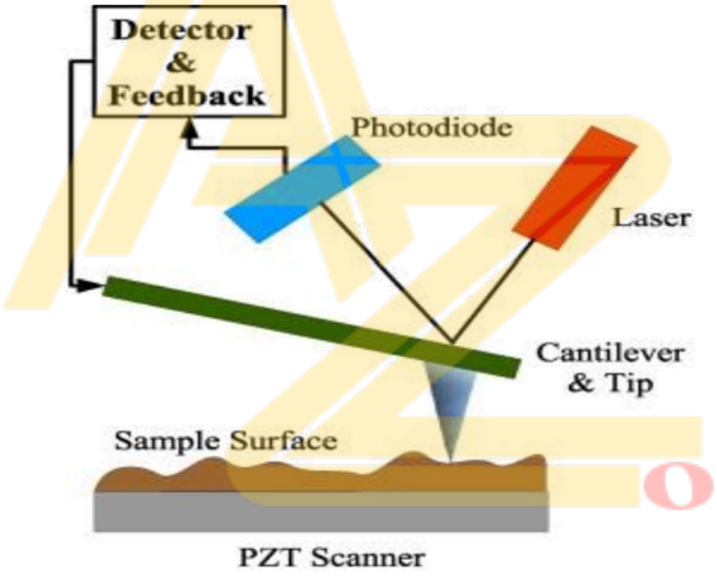
Atomic Force Microscope (AFM)

Atomic Force Microscope or AFM is a high-resolution form of scanning probe microscope that employs a sharp tip in a raster motion to measure and visualize materials at the atomic and nano scales

Principle:

The basic principle of AFM is measuring the intermolecular forces. It is based on the cantilever/tip assembly known as probe that interacts with the sample. A laser beam is focused on the back of the cantilever that moves up and down as it scans the surface of a sample and the deflections are captured by photo detector.

Construction & working:



An AFM consists of a cantilever with a sharp tip at one end, a laser source, a photo detector (photodiode), detection and feedback system and piezoelectric sensor. The working of the AFM involves surface sensing, detection and imaging. The cantilever is typically silicon or silicon nitride with a tip radius of curvature of the order of nanometers. The surface of a sample is scanned in raster motion with a very sharp tip attached to the cantilever. As the tip approaches the surface, the forces such as Vander Waal's forces, electrostatic forces, magnetic forces cause the cantilever to deflect depending on the topography of the sample. A laser beam is focused to the back of the cantilever to detect its deflections. The cantilever deflections will cause slight changes in the direction of the reflected beam. A position sensitive photo diode (PSPD) is used

to track these changes. This information is processed and converted in to a 3D image of the sample surface using the electronic processing unit.

Applications of AFM:

AFM is used in wide range of disciplines which include

1. Identifying atoms from samples
2. Evaluating force of interactions between atoms
3. Studying the physically changing properties of atoms
4. Thin film and coatings
5. Tribology (surface and friction interactions)
6. Cell biology-to differentiate normal cells and cancer cells.
7. Energy storage (batteries) and energy generation (photovoltaic) materials
8. Piezoelectric and ferroelectric materials

Scanning Electron Microscope

Microscope is an instrument which provides a magnified image of an object. Scanning Electron Microscope is the kind of microscope that creates a magnified image of the specimen by scanning it with a high-energy beam of electrons.

Principle:

The principle used in the working of an SEM is the wave nature of electrons. Electrons accelerated under a potential difference of V volts behave like a wave of wavelength.

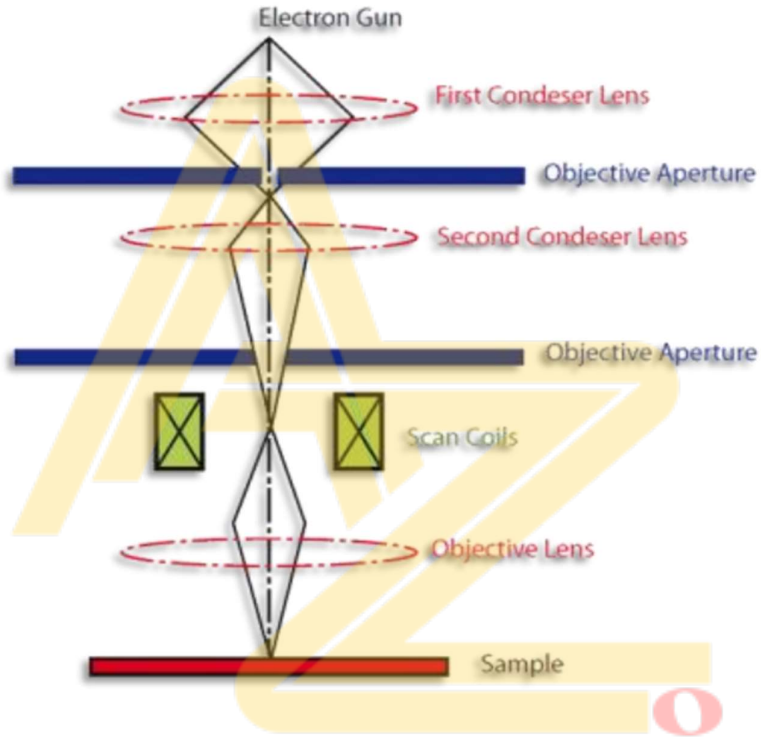
$$\lambda = \frac{h}{\sqrt{2meV}} = \frac{1.226}{\sqrt{V}} nm$$

When an object is illuminated by this electron wave, it results in an increase in the resolving power by a factor of $10^{5.}$

Construction:

• The apparatus consists of a highly evacuated chamber inside which there is an electron gun at the top which comprises of the filament and anode.

- There are two magnetic condenser lenses, used to obtain a fine beam of electron by controlling the beam diameter.
- The number of electrons reaching the sample can be controlled by the objective apertures.
- A flat surface called stage is provided to place the specimen.
- The apparatus has 3 types of detectors namely back scattered electron detector, secondary emission electron detector and X-ray detector.



Working:

- The sample is placed on the specimen stage.
- Electrons are emitted by the filament by thermionic emission and are accelerated by a suitable positive potential.
- The electron beam falling on the condensing lens is converged. The high angle electrons are eliminated.
- The objective lens focuses the thin electron beam on to the desired part of the specimen.
- The scan coils enable the beam to scan the specimen in a particular way called raster (in rectangular fashion).

- Upon incidence, three signals are obtained in the form of Backscattered electrons, secondary electrons and X-rays.
- The emitted signals are detected by the detector and signals are produced. These signals are processed to get the desired information about the sample/specimen.

Applications:

SEM is used in

- Forensic investigations
- Visualizing the virus, bacteria, DNA and other microorganisms.
- Filament bulb investigations at traffic accidents
- High resolution surface imaging
- To study Crystalline structure
- Chemical composition studies
- Study of colloids

Transmission electron microscope (TEM)

A Transmission Electron Microscope (TEM) utilizes energetic electrons to provide morphologic, compositional and crystallographic information of samples. At a maximum potential magnification of 1 nanometer, TEMs produce high-resolution, two-dimensional images, allowing for a wide range of educational, science and industry applications.

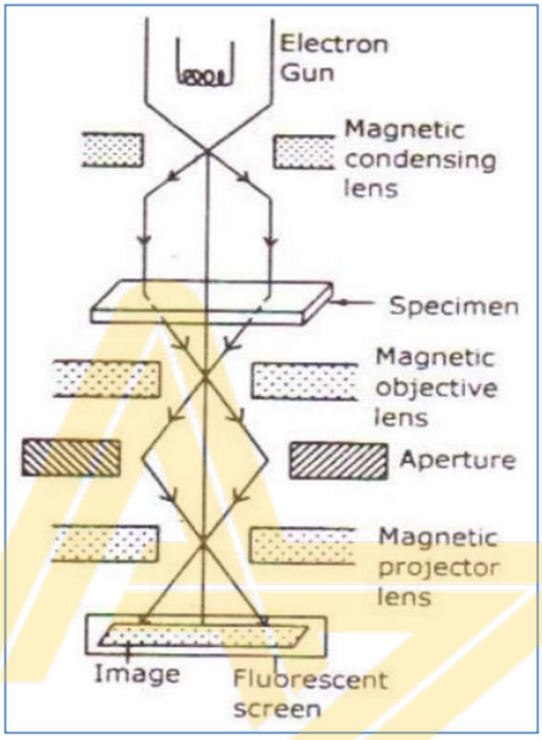
Principle:

In this microscope, an accelerated beam of electrons is made to pass through the specimen and the image is formed on the fluorescent screen, either by using the transmitted beam or by using the diffracted beam.

Construction:

It consists of an electron gun to produce electrons. Magnetic condensing lens is used to condense the electrons and is also used to adjust the size of the electron beam that falls on to the specimen. The specimen is placed in between the condensing lens and the objective lens as shown.

The magnetic objective lens is used to block the high angle diffracted beam and the aperture is used to eliminate the diffracted beam (if any) and in turn increases the contrast of the image. The magnetic projector lens is placed above the fluorescent screen in order to achieve higher magnification. The image can be recorded by using a fluorescent (Phosphor) screen



Working:

Stream of electrons is produced by the electron gun and is made to fall over the specimen using the magnetic condensing lens.

Based on the angle of incidence the beam is partially transmitted and partially diffracted. The high intensity and high contrast image can be obtained only by using the transmitting beam and thus the diffracted beam need to be eliminated.

To eliminate the diffracted beam, the resultant beam is passed through the magnetic objective lens and the aperture. The aperture is adjusted to eliminate diffracted beam. Thus, the final image obtained due to transmitted beam alone is passed through the projector lens for further magnification.

The magnified image is recorded in fluorescent screen. This high contrast image is called Bright Field Image and is purely due to the elastic scattering (no energy change) or due to transmitted beam.

TEM is used

- to study topographical, morphological composition
- in studying structure of complex materials and atomic structure defects.
- nanotechnology.
- Medical field.
- in determining the phase transformations
- Forensic analysis.
- gemology and metallurgy.
- Industry and education.
-

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface characterization technique based on the photo electric effect that can analyse a sample to a depth of 2 to 10 nanometers (nm). XPS reveals which chemical elements are present at the surface and the nature of the chemical bond that exists between these elements. It can detect all of the elements except hydrogen and helium.

Principle:

The working principle of XPS is the study of kinetic energy of the photoelectrons ejected from the surface of a sample when it is exposed to x-rays (photoelectric effect). When X-ray photon of energy $'\boldsymbol{h\nu}'$ is incident on surface, the ejected electron has the kinetic energy (E_K) given by

$$\boldsymbol{E_K = h\nu - E_B - \varphi s}$$

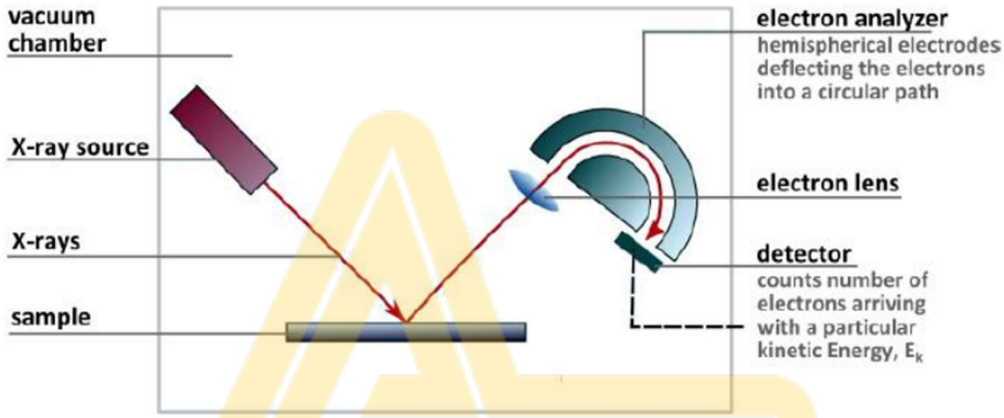
Where $E_B = binding\ enegy\ of\ the\ electron$

φs = work function [The work function is a correction factor for the instrument and correlates to the minimum energy required to eject an electron from an atom] The XPS spectrum

displayed as a plot of the binding energy as function of electron counting rate. Binding energy is a unique character of each element.

Construction:

An XPS instrument contains an x-ray source, sample holder, electron lenses, electron energy analyzer, and detector housed in an ultra-high vacuum environment. A schematic diagram of an XPS system is shown below.



The x-ray source is designed to provide a high intensity x-ray beam, as the number of electrons emitted is proportional to the x-ray source intensity. A common source is an X-ray tube with both Al or Mg target and a suitable filter. Samples are placed in ultra-high vacuum (10^{-9} torr) to avoid any contamination by Air (Oxygen) and water vapours.

Extraction lenses placed between the sample and the analyzer forms the electron optics which defines the acceptance angle for collecting electrons emitted from the sample. Electrons of different energies are identified by hemispheric analyzer. Voltages are applied to the hemispheres, with the outer hemisphere being more negative than the inner hemisphere. As a result, only electrons with a specified energy will be able to travel through the analyzer.

A solid-state detector is used to detect the electrons escaping from the sample and a signal processor is used to determine the electron count and the energy.

Working:

When X-rays shot on the sample, the electrons absorb the incident photon energy and get ejected with certain kinetic energy given by

$$E_K = h\nu - E_B - \varphi_s$$

The work function and photon energy are known and the kinetic energy is measured by the detector. Thus, binding energy of the electrons can be determined. The binding energy of the ejected electrons is analyzed by a detector and a plot of these energies and relative numbers of electrons is produced.

As electrons are in orbitals farther from the nucleus, less energy is required to eject them, so the binding energy is lower for higher orbitals. Electrons contained in different sub shells (s,p,d, etc.) have different energies as well. Electrons of different energies follow different paths through the detector which allows the computer to differentiate the electrons. By showing the energy of electrons emitted from a material, the composition of a material can be determined.

Applications of XPS:

It can be used to

- Determine elemental composition of the surface (top 2 – 10 nm usually)
- determine elements that contaminate a surface
- determine thickness of thin films
- identify the type of chemical bonds (Si-O or Si-C)
- determine Oxidation states of elements ($Ti3+$)
- determine Chemical or electronic state of each element on the surface
- determine uniformity of elemental composition across the top surface

Important Questions:

1. Define nano-material and classify the nano-materials based on the dimensional constraints.

2. With neat diagram, explain the principle, construction and working of Atomic Force Microscope

3. Explain in brief how crystal size is determined by Scherrer's equation

4. Explain the construction and working of X-Ray diffractometer

5. With neat diagram, explain the principle, construction and working of X-ray photoelectron spectroscope

6. Describe the construction and working of Scanning Electron Microscope with the help of a neat diagram.

7. Mention the principle and applications of X-ray photoelectron spectroscope.

8. Illustrate the working of Transmission Electron Microscope

Numerical:

1. Determine the wave length of X-rays for crystal size of 1.188×10^{-6} m, peak width is 0.5^O and peak position 30^O, for a cubic crystal. Given Scherrer's constant k= 0.92.

Solution: D = 1.188×10^{-6} m, β = 0.5^O(peak width should be in radians), β = 8.276×10^{-3} rad

2Θ = 30^O, Θ = 15^O k = 0.92.

$$D = \frac{k\lambda}{\beta cos\theta}$$

$$1.188\times10^{-6} = \frac{0.92\times\lambda}{8.276\ x\ 10^{-3}\cos 15}$$

λ = 10.87 n m

2. Determine the crystallite size given the Wavelength of X-Rays 10 nm, the Peak Width 0.5° and peak position 25 ° for a cubic crystal given K = 0.94.

Solution: λ = 10 nm = 10 x 10^{-9} m, β = 0.5° (peak width should be in radians),

β = 8.276 x 10^{-3} rad,

2Θ = 25 °, K = 0.94

$$D = \frac{k\lambda}{\beta cos\theta}$$

D = 1.103 x 10^{-6} m

3. The first order Bragg reflection occurs when a monochromatic beam of X-rays of wavelength 0.675A° is incident on a crystal at a glancing angle of 4°. What is the glancing angle for third order Bragg's reflection to occur?

Solution: n =1, λ = 0.675A° = 0.675 x 10^{-10}m

Glancing angle Θ = 4°

d =?

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

d = 3.6 x10 $^{-10}$ m.

4. X-rays are diffracted in the first order from a crystal with d spacing 2.8×10^{-10} m at a glancing angle 60°. Calculate the wavelength of X-rays.

Solution: n =1, d = 2.8×10^{-10} m , Glancing angle $\Theta = 60°$

$\lambda = ?$

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

$$\lambda = 4.84 \times 10^{-10} \text{ m}$$

5. In a x-ray diffraction experiment, the glancing angle for the first order spectrum was found to be 6°. Find the wavelength of the x-rays if inter planar distance is 28.2 nm.

Hint: n = 1, $\Theta = 6°$, $\lambda = ?$, d= 28.2 nm

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

6. First order spectrum is formed when the x-rays of wavelength 1.5 A° is incident on a crystal at 12°. Calculate the inter planar spacing in the crystal. (3.6 A°)

Hint: n =1, λ = 1.5 A°, Θ = 12°, d = ?

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

7. In a calcite crystal, second order Bragg's reflection occur from the planes with d-spacing 3A°, at a glancing angle of 24°. Calculate the path difference between X-rays reflected from the two planes. Also calculate the wavelength of the X-rays.

Hint : n= 2, d= 3A° = 3 x 10^{-10} m, $\Theta = 24^0$,

Path difference $2d \sin\theta = ?$

wavelength of the X-rays $\lambda = ?$ $2d \sin\theta = n\lambda$