MODULE 5

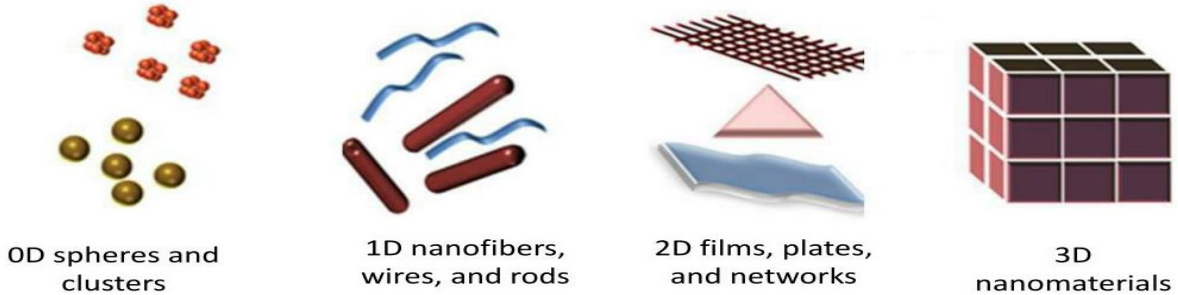
Material Characterization Techniques and Instrumentation

Nanomaterials:
The materials in which the atoms are arranged in the order of 1 to 100nm in any one of the dimensions and these atoms will not move away from each other, is called as nano materials.
Ex: C, ZnO, Cu – Fe alloys, Ni, Pd, Pt etc.

Nanocomposites:
Nanocomposites are materials that incorporate nanosized particles into a matrix of standard material. The result of the addition of nanoparticles is a drastic improvement in properties that can include mechanical strength, toughness and electrical or thermal conductivity.
Nanocomposites are made by embedding materials (called the *reinforcing phase*) into another material (called the *matrix phase*). Either one or both phases can be nanomaterials.

Nanotechnology:
It deals with the design, characterization, production and application of nanostructures, nano-devices and nano-systems.

Classification of Nanomaterials:
This nanomaterial classification is based on the number of dimensions of a material, which are outside the nanoscale (<100 nm) range.
Zero-dimensional nanomaterials:
Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm). The most common representation of zero-dimensional nanomaterials are nanoparticles.
One dimensional nanomaterial: Materials having one dimension outside the nanoscale (two dimensions at the nanoscale) is called as one dimensional nano materials. This leads to needle shaped nanomaterials. Examples: Nanotubes, nanofibers, nanorods and nano wires.
Two dimensional nanomaterials: Materials having two of its dimensions outside the nano scale (one dimension at nanoscale) is called two dimensional nano materials. They exhibit plate like shapes. Examples: Nanofilms, nano plates, nanolayers.
Three dimensional nanomaterials: Materials having none of the dimensions in nano scale is called three-dimensional nano materials.
The bulk (3D) nanomaterials are composed of a multiple arrangement of nanosized crystals in different orientations.



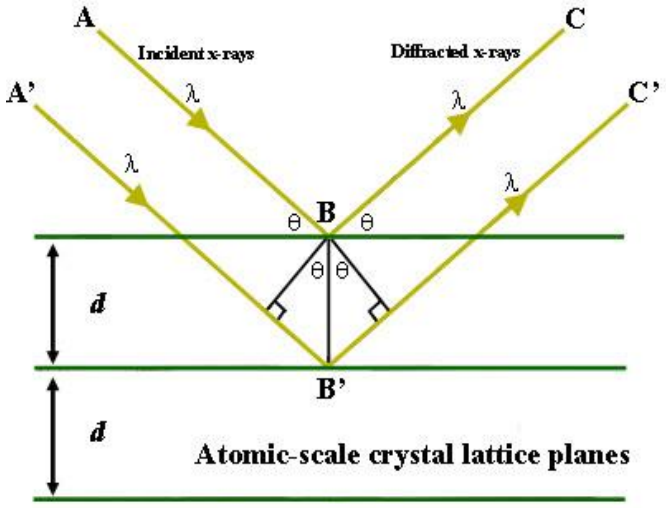
X -ray diffraction

X rays are electromagnetic radiation of short wavelength. X- rays exhibit the phenomenon of diffraction which is one of the basic properties of the waves. But as the wave lengths of the X rays are few angstrom units, ordinary grating cannot be used to study the diffraction of X-rays. In crystals spacing between the atoms is of the order of the wavelength of X-rays. Therefore crystal acts as three dimensional natural grating.

Braggs X-ray Diffractometer:

Principle:

When a beam of monochromatic X-rays falls on the crystal each atom becomes a source of scattering of X-rays. In crystal there are certain planes which are particularly rich in atoms. Such planes are called Bragg planes. At certain glancing angles, reflections from sets of parallel planes are in phase with each other hence they reinforce each other to produce maximum intensity. For other angles the reflections from different planes are out of phase and hence they reinforce to produce either zero or minimum intensity.



The general relationship between the wavelength of the incident X-rays, glancing angle and spacing between the crystal lattice planes of atoms is known as Bragg's Law, expressed as:

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

where n (an integer) is the "order" of reflection, 'λ' is the wavelength of the incident X-rays 'd' is the interplanar spacing of the crystal and θ is the glancing angle.

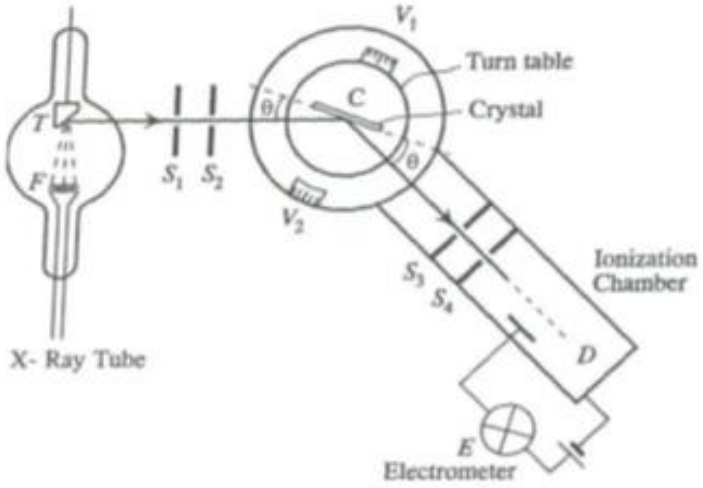
Construction:

The schematic arrangement of Bragg's diffractometer is as shown in the figure. It consists of following three parts namely.

1. A source of x-ray
2. A circular turn table and.
3. A detector (ionization chamber).

X-ray from the x-ray tube is collimated by two slits S_1 and S_2 provided in the lead screens. The beam is then allowed to fall on a crystal mounted on a circular turn table of the diffractometer. The turn table is capable of rotating through any desired position about the vertical axis. The position of the turn table can be determined by means of a vernier scale V_1. The reflected beam is collimated by slits S_3 and S_4 and is collected by an ionization chamber. Using the electrometer, ionisation current in the chamber can be measured. The ionization chamber is mounted on movable mechanical arm about the same axis of the crystal. The turn table and mechanical arm are linked together such that when turn table rotates through an angle θ,

mechanical arm rotates through an angle of 2θ. In this way the beam is always reflected into the ionization chamber whatever may be the glancing angle at the surface of the crystal.

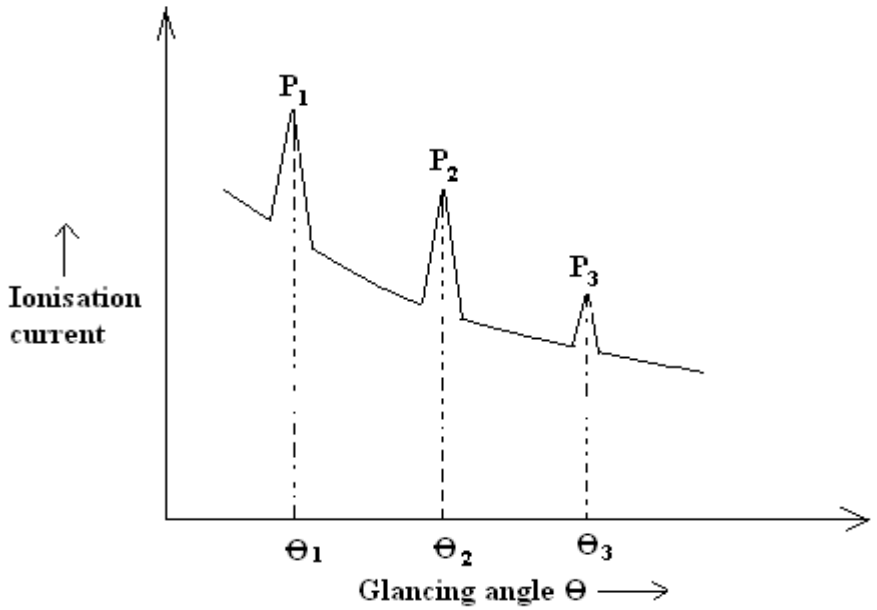


Working:

The collimated beam of x-ray is allowed to fall on the crystal. The glancing angle θ for the incident beam is kept very small while starting the experiment. The ionization chamber is adjusted to receive the maximum intensity of the reflected beam. The glancing angle θ and intensity of the currents are measured. The glancing angle θ is increased in equal steps by rotating the crystal table. The ionization current is noted for different glancing angles. The graph of ionization current against glancing angle is plotted. The graph obtained is as shown in the figure. The peaks P_1,P_2,P_3 are observed for glancing angles θ_1, θ_2, θ_3 etc.

It is found that $\text{Sin}\theta_1$: $\text{Sin}\theta_2$: $\text{Sin}\theta_3$=1:2:3

This shows that peaks P1, P2, P3 refer to respectively 1st, 2nd and 3rd order reflections of the same wavelength. By substituting θ, n, d and λ, the Braggs law is verified using the relations $2d\ \text{Sin}\theta = n\lambda$,



Determination of wavelength of x-rays:

In sodium chloride crystal 'd' has been calculated using the molecular data. Using sodium chloride crystal glancing angle 'θ' is experimentally determined from the graph for first order maximum. Wavelength '**λ**' of the x-rays can be calculated by substituting the value of 'd' and 'θ' using equation **$\lambda = 2d\ \text{Sin}\theta$.**

Determination of crystal structure.

The crystal inter planar distance 'd' is determined by knowing the glancing angle θ for first order maximum and using the equation $d = \frac{\lambda}{2Sin\theta}$.

One gets different values for 'd' depending upon the particular set of parallel planes that satisfy Bragg's reflection as θ is changed. By taking the ratios of the different values of 'd' obtained, it is possible to decide the particular crystal system to which the experimental crystal would belong.

For example if d_1, d_2, and d_3 be the interplanar spacing for the planes (100) (110) and (111) respectively, it can be shown that

For cubical crystal $d_1:d_2:d_3=1:1/\sqrt{2}:1/\sqrt{3}$.

For fcc $d_1:d_2:d_3=1:1/\sqrt{2}:2/\sqrt{3}$

and for bcc $d_1:d_2:d_3=1:2/\sqrt{2}:1/\sqrt{3}$.

Crystal size determination by Scherrer equation

Ideally a Braggs diffraction peak is a line without width. In reality diffraction from a crystal specimen produces a peak with a certain width. This is known as peak broadening. The peak width depends on the size of the crystals. Peak width is inversely related to crystal size i.e. peak width increases with decreasing crystal particle size.

The Scherrer equation in X-ray diffraction and crystallography is a formula that relates the size of sub-micrometre crystallites in a solid to the broadening of a peak in a diffraction pattern. It is named after Paul Scherrer. It is used in the determination of size of crystals in the form of powder. The Scherrer equation can be written as

$$D = \frac{K\,\lambda}{\beta\,Cos\theta}$$

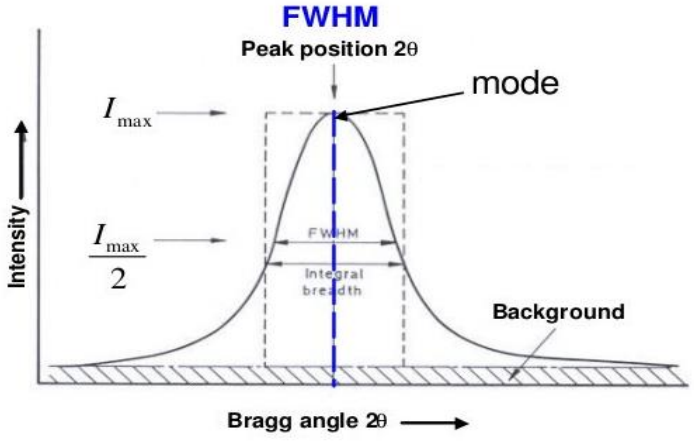
Where D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, which may be smaller or equal to the particle size

K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite.

λ is the X-ray wavelength.

β is the line broadening at half the maximum intensity (full width at half maximum -FWHM value in radians), after subtracting the instrumental line broadening, in radians.

θ is the peak position Bragg angle.



The Scherrer equation is applicable only for small size crystallites, having size below 100nm.

Atomic Force Microscope

The Atomic Force Microscope is a kind of scanning probe microscope in which a topographical image of the sample surface can be achieved. It provides 3D profile of the surface in nanoscale.

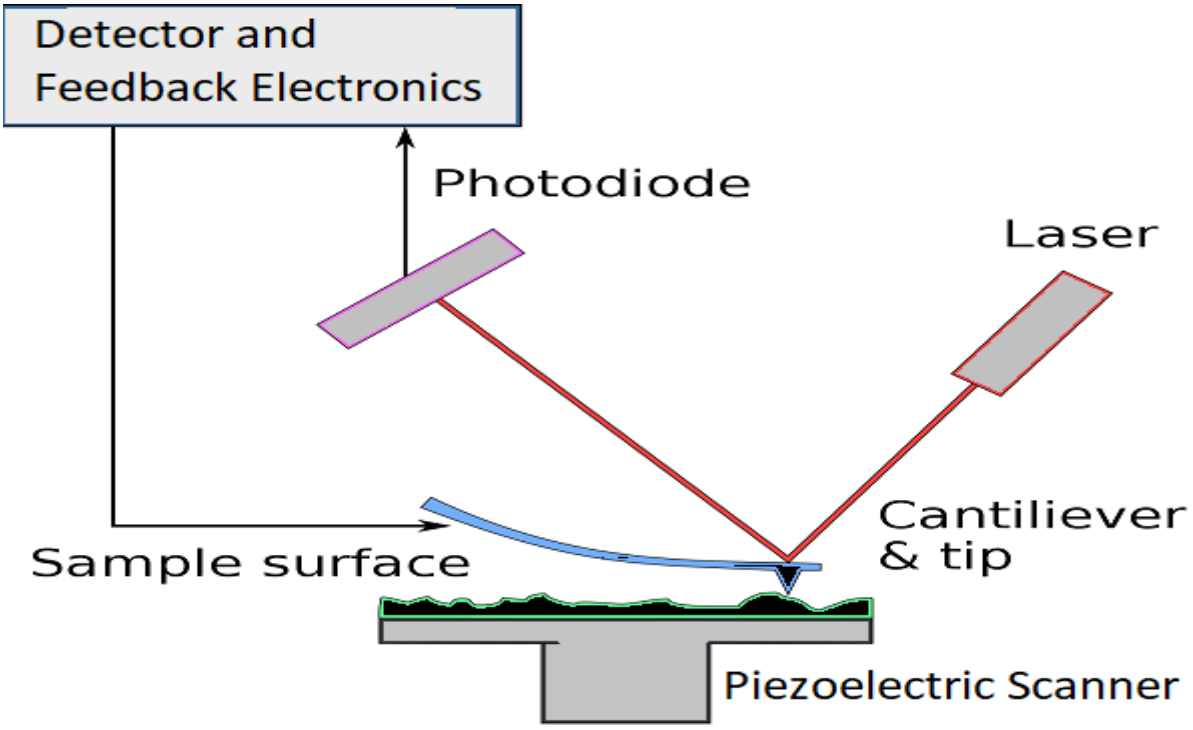
Principle:

The AFM works on the principle of the force between the sample surface and the probe. The probe is placed at the end of the cantilever. The amount of force between the probe and the sample is dependent on the spring constant of the cantilever and the distance between the cantilever and sample surface. From Hooke's law the force is given by F = -kx where x is the distance between the probe and the sample and k is spring constant.

Construction:

The Atomic Force Microscope consists of following components

1. Laser beam
2. Photodiode
3. Cantilever with sharp tip (probe)
4. Detector and feedback circuit
5. Piezoelectric scanner



Working:

AFM consists of microscale cantilever with a sharp tip (probe) at its end used to scan the specimen surface. The cantilever is typically made up of silicon or silicon nitride with the tip radius of curvature of the orders of nm. When the tip, which is attached to the free end of the cantilever, come very close to the surface attractive and repulsive forces due to the interactions between the tip and the sample surface takes place. This causes negative or positive bending of the cantilever according to Hooke's law. As the scanning continues tip

will have the vertical movement depending on the topography of the sample. A laser beam is made to incident on the back of the cantilever and reflected beam is detected by means of 4-quadrant photodiode detector. By the help of this position sensitive photodiode, the bending of the cantilever can be measured precisely. The cantilever deflects according to the atomic force variations between tip and the sample and thereby the detector measures the deflection. A plot of laser deflection verses the tip position on the sample surface provides the resolution of the hills and valleys that constitute the topography of the surface.
AFM can work with three different modes. In **contact mode**, the tip is in a soft physical contact with the surface. **Dynamic (Tapping) mode** eliminates the frictional force by intermittently contacting the surface and oscillating with sufficient amplitude to prevent it from being trapped in by adhesive forces. **Non-contact mode** tip does not touch the sample, however it oscillates above the surface during scan.
Depending upon the situation, AFM measures different types of forces like a Vander Waal's forces, capillary force, mechanical contact force etc.

Advantage:

- Easy to prepare samples for observation.
- It has a 3D imaging.
- It is used in dynamic environments.

Disadvantage:

- Scanning speed is low
- As the tip is in contact with sample, it is likely to distort the sample

Application:

- Identifying atoms from samples.
- Evaluating force of interactions between atoms.
- Studying the physical hanging properties of atoms.
- Used to differentiate cancer cells and normal cells.

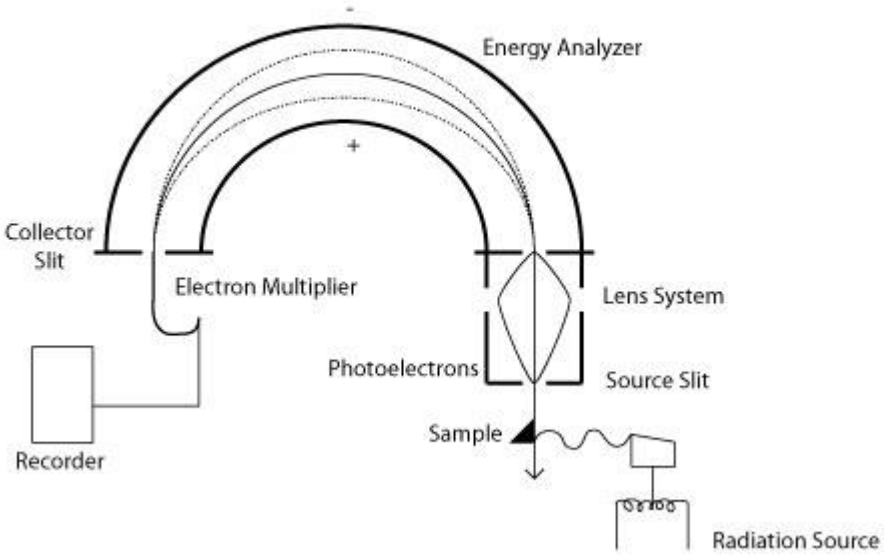
X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a method used to determine the elemental composition of a materials surface. It can be further applied to determine the chemical or electronic state of these elements.

Principle of XPS:
The XPS is based on the photoelectric effect. The X-ray radiations are made to incident on the surface of the sample under study. The incident X-ray photon penetrates through the sample and it ejects photoelectrons from the core level. The kinetic energy of the ejected photoelectron is given by $E_k = h\nu - E_b - \phi$
Where, E_k is kinetic energy of the ejected electron
$h\nu$- energy associated with incident Photon
E_b binding energy ejected electron
ϕ -Work function of the instrument
The kinetic energy of the ejected photoelectrons are plotted against the number of ejected photoelectrons. The spectrum is called **X-ray photoelectron spectrum**. It is used to study

about the quantitative analysis of the surface composition, chemical shifts, oxidation states of the compound etc.

Instrumentation:



The X-ray photoelectron spectrometer consists of following components

- **x-ray Source:** X-rays are typically used to excite the sample so that it emits Photoelectrons.
- **Sample Holder**: solid samples are mounted in a fixed position close to x-ray source and the entrance slit.
- **Electron Analyser:** An electron energy analyzer is used to discriminate among the energies of the photoelectrons that are produced. Electrostatic field analysers are most commonly used.
- **Detector:** The electron multiplier tube is used as detector. When single electron pass through the electron multiplier tube it is converted into number of electrons or pulses of electrons.
- **Ultra-high vacuum (UHV) system:** Ultra high vacuum system is needed to avoid collision between photoelectrons and gas molecules in the spectrometer and also to avoid surface contamination from the residual gases.
- **Processor And Read-Out:** The function of signal processor is to amplify the signal and read out device converts signal into spectrum.

Working

The X-ray beam produced by X-ray source is made to incident on the specimen.
The photoelectrons ejected from the specimen are accelerated by a retarding field lens. These accelerated electrons are passed into the spherical sector electron energy analyser through the entrance slit. An electric field is applied on the spherical sector analyser. The electrons with different energies get separated while passing through this electric field. The electrons with the same energies pass through the exit slit and other electrons are stopped by the exit slit. A detector detects these electrons and computer provides a spectrum drawn between the kinetic energy and the number of photoelectrons emerging from the exit slit. The spectrum is analysed and then the peaks are assigned. This spectrum used for the composition analysis.

Application of XPS.

- To measure the elemental composition of the surface.
- Chemical and electronic state of each element in the surface.
- Determination of surface contamination on semiconductors.
- Study of oxide layers on metals, Analysis of dust on the sample

Advantages:

- It is nondestructive technique.
- It is surface sensitive technique.
- Wide range of solid surface sample can be identified

Disadvantages:

- It is very expensive
- Slow and poor resolution power
- Required high vacuum.

Electron microscope:

It is an instrument by using we can study & analysis of small particles & crystal structures. It's magnification is high i.e. 10^6 times greater than the size of given particle (or) object. In electron microscopes, current carrying coils produce magnetic fields that act as lenses to focus an electron beam on a specimen.

Two types of electron microscope are

- Scanning electron microscope (SEM)
- Transmission electron microscope (TEM)

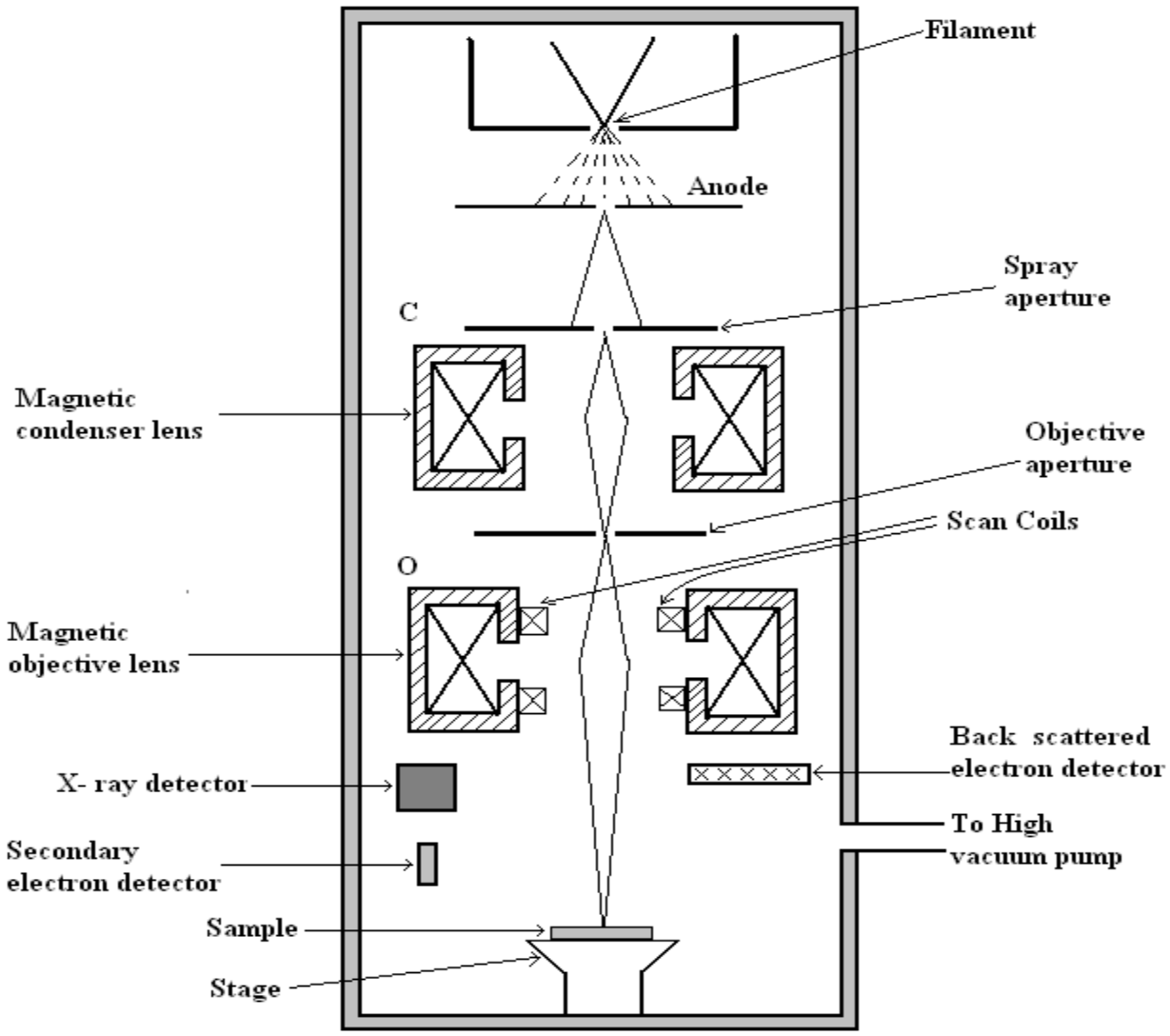
Scanning Electron Microscope (SEM):

Principle:

The surface of sample is scanned using high energy beam of electrons. This gives rise to secondary electrons, back scattered electrons and X-rays. The secondary electrons are collected by positively charged electron detector which gives the three-dimensional image of the sample.

Construction:

The apparatus consists of a highly evacuated chamber inside which there is an electron gun at the top, which comprises of filament and the anode. There are two magnetic lenses, one is condenser lens C and the other one is objective lens O. A scan coil accompanies the objective lens O. The magnetic lens consists of a pair of current carrying coils which produce magnetic fields between them. The magnetic field produced by the coil is such that when the electron enters into the region it resembles the path of light passing through the lens. A flat surface called stage is provided at the bottom portion of the apparatus to place the specimen under study. There are 3 types of detectors-back scattered electron detector, secondary electron detector, and an x-ray detector.



Working:

The sample is placed on the specimen stage. Inside of the chamber is evacuated connecting it to high vacuum pump.

Electrons are emitted from the filament by thermionic emission. Electrons are accelerated by applying suitable potential to the anode. The accelerated electrons are passed through the spray aperture. The condensing lens converges the beam by eliminating some high angled electrons. The beam then enters the objective aperture where the size of the beam can be controlled. A thinner beam then enters into the objective lens. The objective lens focuses the beam on to the desired part.

A set of coils called scan coils placed along with the objective lens enable the beam to scan the specimen.

The electrons incident on the sample are called primary electrons. Out of which some of them will be scattered from the sample and some of them knockout the electrons from the atoms of the specimen. Those electrons which are scattered from the sample are called back scattered electrons and one which is knocked off from the atom is called secondary electrons. X-rays are emitted when electrons from the higher shell in the atom transit to vacant positions in the lower shell from where an electron has been knocked off.

Back scattered electrons, secondary electrons and the x-rays emitted are detected by the respective detectors and corresponding signal is produced.

The collected electrons produce scintillations in the detector and are converted into the electrical signals. These electrical signals are suitably amplified and are fed to the CRT screen.

In order to get three-dimensional image of the surface of the sample, the electron beam scans the surface many times. The image is also recorded using infrared camara.

Applications of SEM:

- SEM gives the information about the surface features of the sample with resolution of the order of few nanometer.
- SEM images give information about the elements and compound in the sample and their relative abundance.
- The SEM is used to study biological specimens like pollen grains
- The SEM is used to study the corroded layers on metal surface.
- In medicine, SEM images are used o compare healthy and unhealthy blood and tissue samples.

Advantages:

- It can be used to examine the specimen of large thickness.
- It can be used to get a three dimensional image of the object.
- Since the image can be viewed in the screen, structural details can be resolved in a precise manner.
- Modern SEM generate data in digital format which is highly portable.

Limitations of SEM:

- SEMs cannot detect the samples of very low atomic number.
- The resolution of the image is limited to about 10-20 nm hence it is very poor.

Transmission Electron Microscope (TEM):

TEM is a powerful tool to investigate the lattice structure and defects on materials directly.

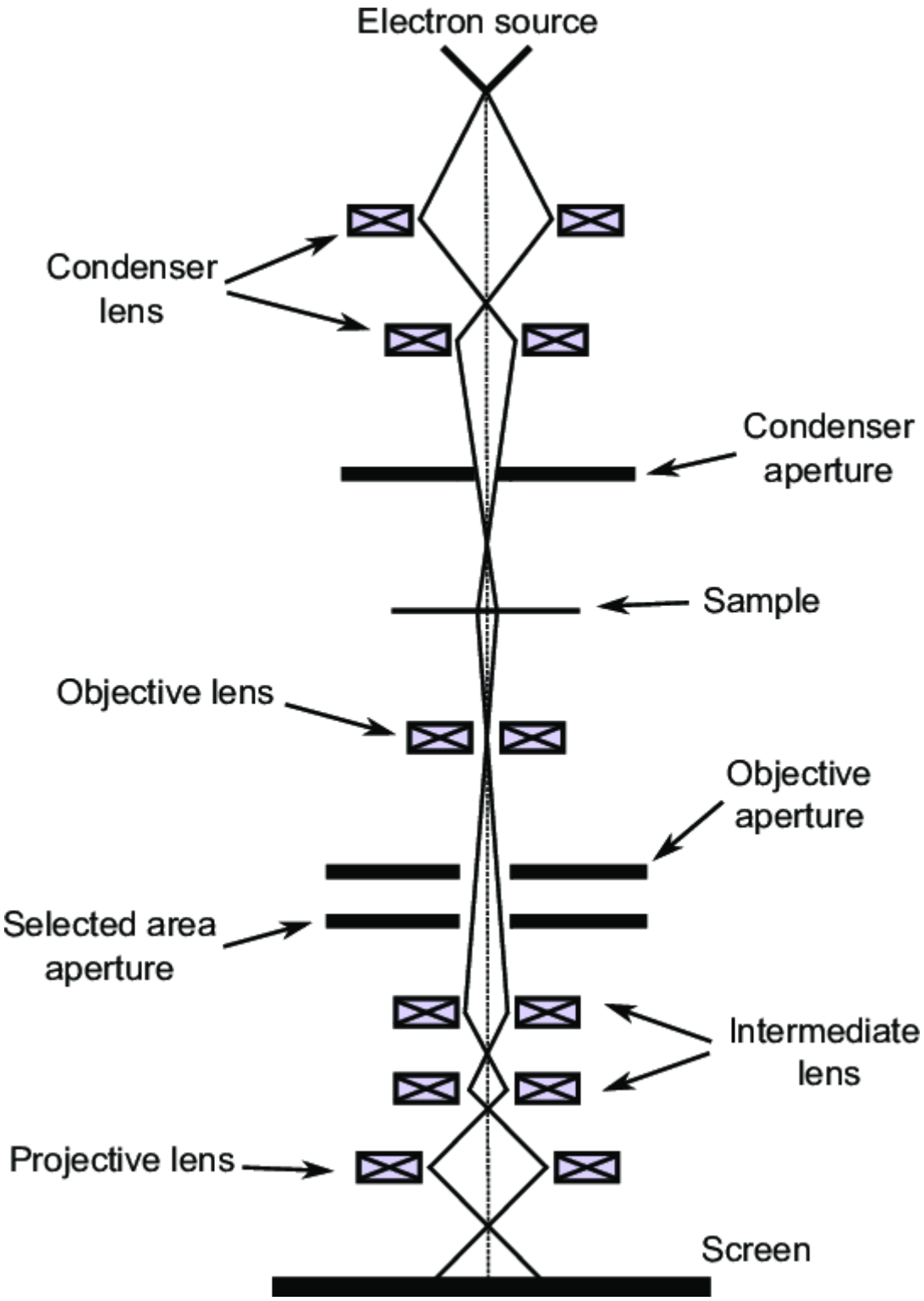
Principle:

Accelerated beam of electrons of high resolving power is transmitted through a very thin specimen under study and then the electrons transmitted is focused and magnified to form an image which is displayed on imaging screen.

Construction:

The apparatus consists of a highly evacuated chamber inside which there is an electron gun at the top, which comprises of filament and the anode. Then electron beam is allowed to pass through the condenser lens systems in order to control the spot size and beam is converged by applying magnetic field. Usually, condenser system consists of two or more lenses. All the lenses in TEM are controlled by the application of magnetic field.

Then the fine beam of electron is made to fall on the specimen and the transmitted electrons are initially focused and magnified by the objective lens system. The purpose of the intermediate lens is to further magnify the image obtained from the objective lens. The intermediate lens is focused on the image plane of the objective lens and an intermediate image is formed in the image plane of the intermediate lens. This image is object for the projector lens which forms the final image on the fluorescent screen.



Working:

The stream of electrons produced by the electron gun is condensed into thin coherent beam by a system of condenser lenses and condenser aperture. The beam is incident on the sample and some part is transmitted. Tis transmitted beam is focused and the contrast is increased by blocking out high angle diffracted electrons by the objective lens system. The image is thus obtained and is magnified with the help of intermediate and projector lenses.

The magnified electron image from the projector lens is projected on to a fluorescent viewing screen which is usually coated with a phosphor material. A TEM micro graph is a black and white image of the diffracted electrons. The darker region of the image represents that fewer electron were transmitted through the specimen and the brighter region represents that more electrons were transmitted through the specimen. The image can also be displayed on a monitor by charge coupled device(CCD) and can be recorded on to photographic film.

Application of TEM

- TEM provides topographical, morphological, compositional and crystalline information.
- The image allows researchers to view samples on a molecular level, making it possible to analyse structure and texture.
- The nature of defects and faults in the crystals can be identified using TEM images.
- The technique is also used to analyse archaeological samples.

Advantages of TEM:

- TEM offer the most powerful magnification, potentially over one million times or more than the most optical microscope.
- TEMs provide information on element and compound structure.
- TEM images are high quality and detailed.
- TEMs are able to yield information of surface features, shape, size and structure.

Limitations of TEM:

- In TEM the material used require extensive sample preparation and must be thin enough to allow the electrons to pass through it.
- Three dimensional image can not be obtained.
- The region of analysis in TEM is too small and sometimes the region analysed may not be the characteristic of the sample.

Engineering Physics

Question Bank

(CBCS Scheme-2021-22)

Module-5

1. Define nano-material and classify the nano-materials based on the dimensional constraints
2. Explain the construction and working of X-Ray diffractometer.
3. Explain in brief how crystal size is determined by Scherrer's equation.
4. With neat diagram, explain the principle, construction and working of Atomic Force Microscope
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. Illustrate the working of Transmission Electron Microscope