

Module 3

Introduction - Characterization

- Requires sophisticated characterization tools.
- Developed from critical advancements in conventional characterization methods developed for bulk materials.
- Characterization and manipulation of individual nanostructures require not only extreme sensitivity and accuracy, but also atomic-level resolution.
- The physical properties and short-range forces may have significant impact at the nanometric-scale.

Structural & Chemical characterization techniques

- Characterization techniques are classified as:
 - a) Chemical characterization
 - b) Structural characterization
- To know the size, shape, lattice constants and crystallinity of the material, structural characterization is done.
- To study the internal chemical structural details, chemical characterization is done.

Nanomaterials-characterization tools

- X-ray diffraction (XRD) has been widely used for the determination of **crystalline character, crystallite size, crystal structures and lattice constants** of nanoparticles, nanowires and thin films.
- Scanning electron microscopy (SEM) and transmission electron microscopy (TEM), together with electron diffraction, have been commonly used in the characterization of nanoparticles to get an idea of the **size, shape and defects** present in these materials.

Nanomaterials-characterization tools

- Optical spectroscopy is used to determine the **size** of semiconductor quantum dots.
- Scanning probe microscopy (SPM) is a relatively new characterization technique which has two branches - scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). They produce **topographic images** of a surface with atomic resolution in all three dimensions.

Nanomaterials-characterization tools

- In combination with appropriately designed attachments, STM and AFM have found a much broader range of applications, such as **nanoindentation, nano-lithography and patterned self-assembly.**
- Almost all solid surfaces, whether hard or soft, electrically conductive or not, can be studied with STM/AFM.
- Surfaces can be studied in a gaseous medium such as air or vacuum, or in liquid.

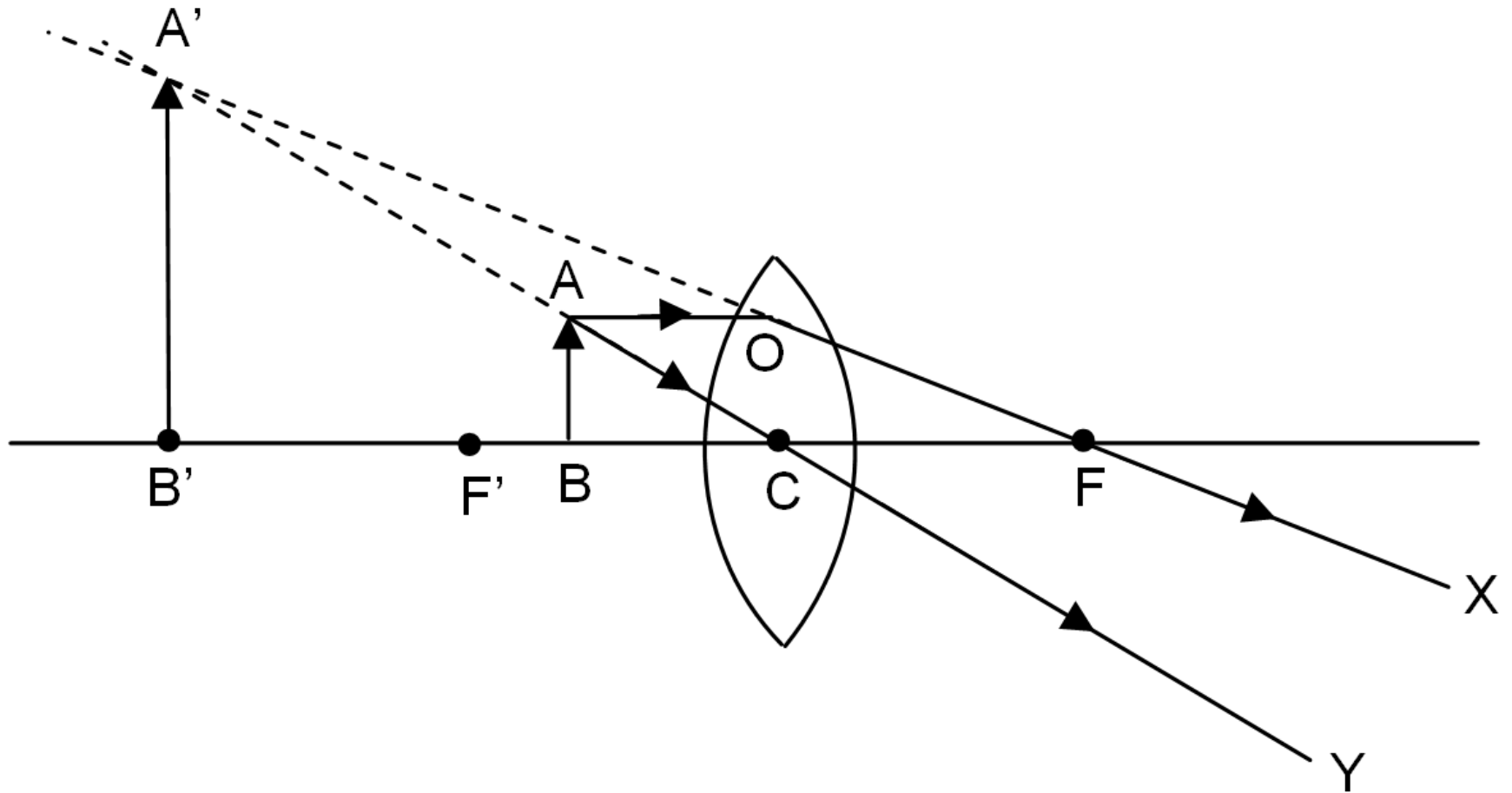
Microscope- Optical & Electron

- Microscopes are of three basic types: optical, electron (or ion), and scanning probe.
- Optical microscopes use transparent lenses and visible light to enable viewing of objects in the micrometer scale, e.g., red blood cells, human hair.
- Electron microscopes use electromagnetic or electrostatic lenses and a beam of charged particles (instead of light) to view particles of size in the nanometer scale, e.g., atoms.
- They have the capability to magnify objects more than 500,000 times, thus allowing visualization of tiny structures such as DNA and microbes at very high resolution.

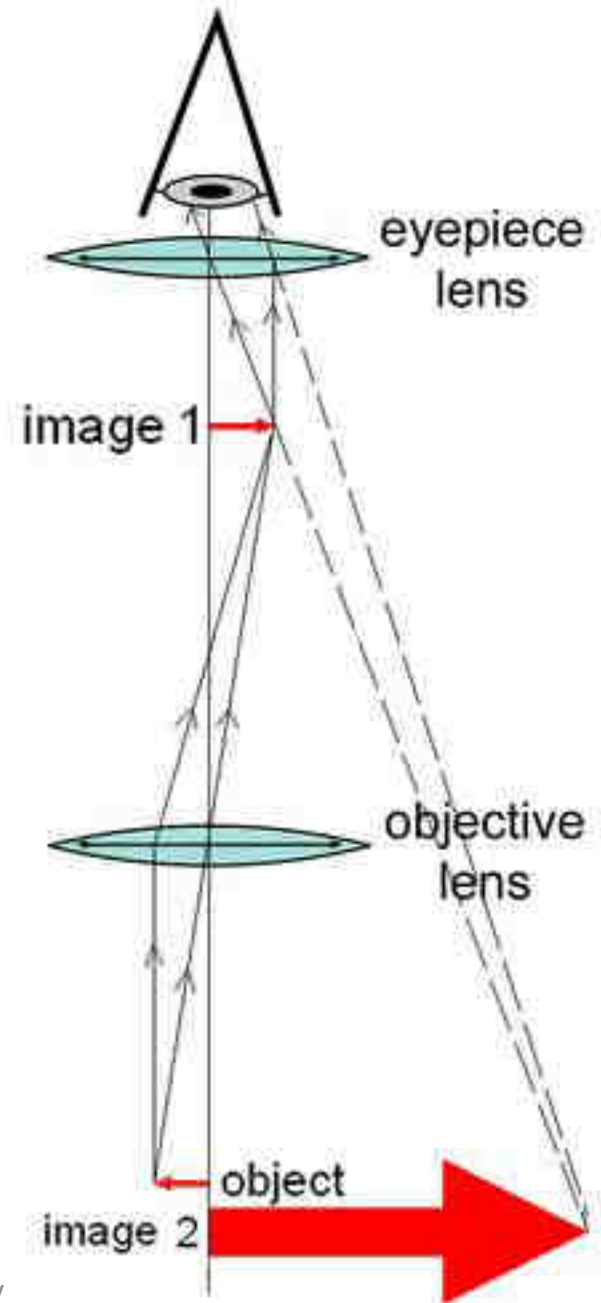
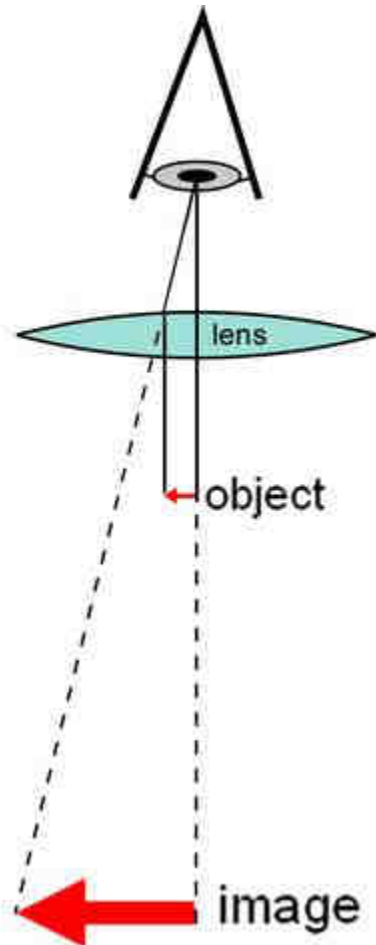
Optical microscope

- It is a type of microscope that commonly uses visible light and a system of lenses to magnify images of small objects.
- There are two basic types of optical microscopes: simple microscopes and compound microscopes.
- A simple microscope is one which uses a single lens for magnification, such as a magnifying glass.
- A simple microscope works on the principle that when a tiny object is placed within its focus, a virtual and magnified image of the object is formed at the least distance of vision from the eye held close to the lens.
- A compound microscope uses several lenses to enhance the magnification of an object.

ray diagram of simple microscope

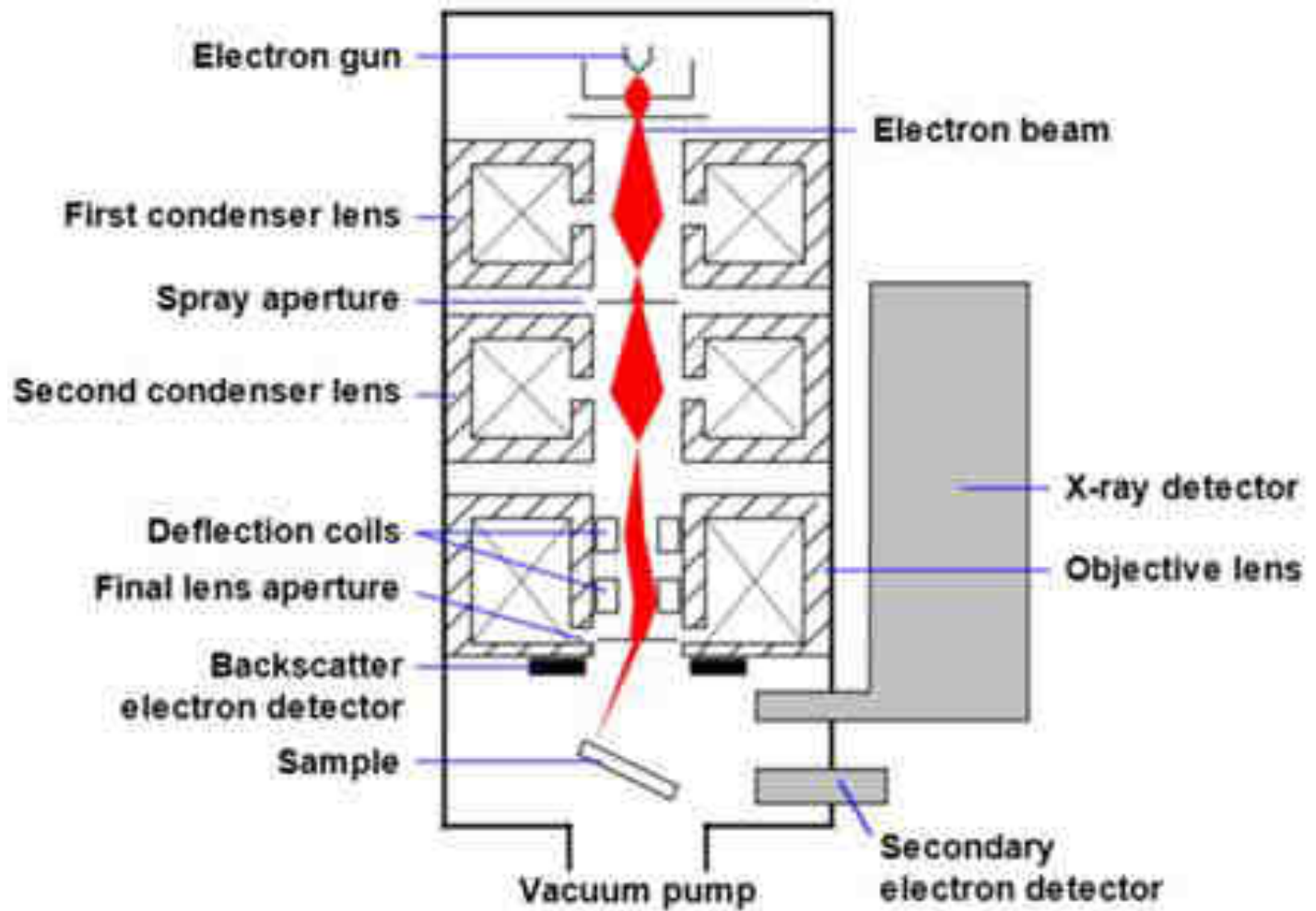


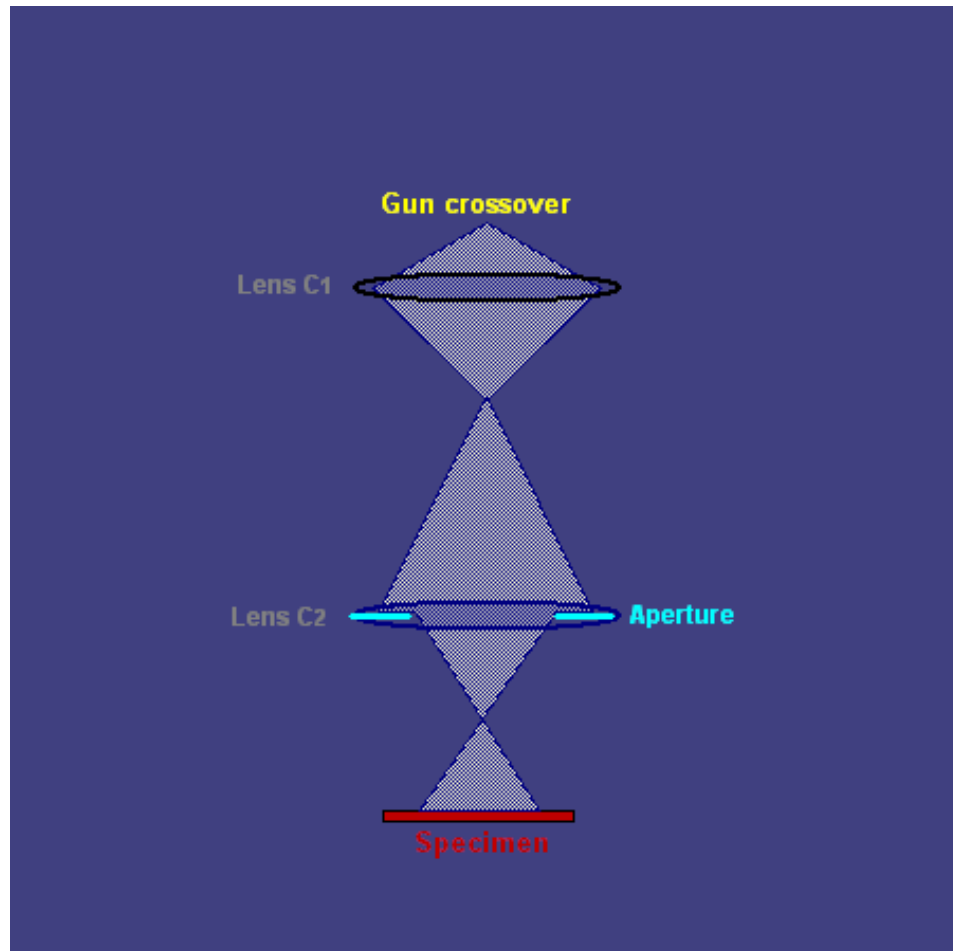
- A small object AB which is to be magnified is placed between the principal focus F' and optical centre C of the convex lens.
- Now, a ray of light AO parallel to principal axis which is coming from the point A of the object passes through the focus F along the straight line OX after getting refracted by the convex lens.
- A second ray of light AC coming from the point A of the object passes through the optical centre C of the convex lens along the straight line CY.
- As is clear from the figure that the two rays i.e. OX and CY are diverging rays so these rays can intersect each other only at point A' when produced backward.
- Now, on drawing $A'B'$ perpendicular from point A' to the principal axis, we get the image $A'B'$ of the object which is virtual and magnified.

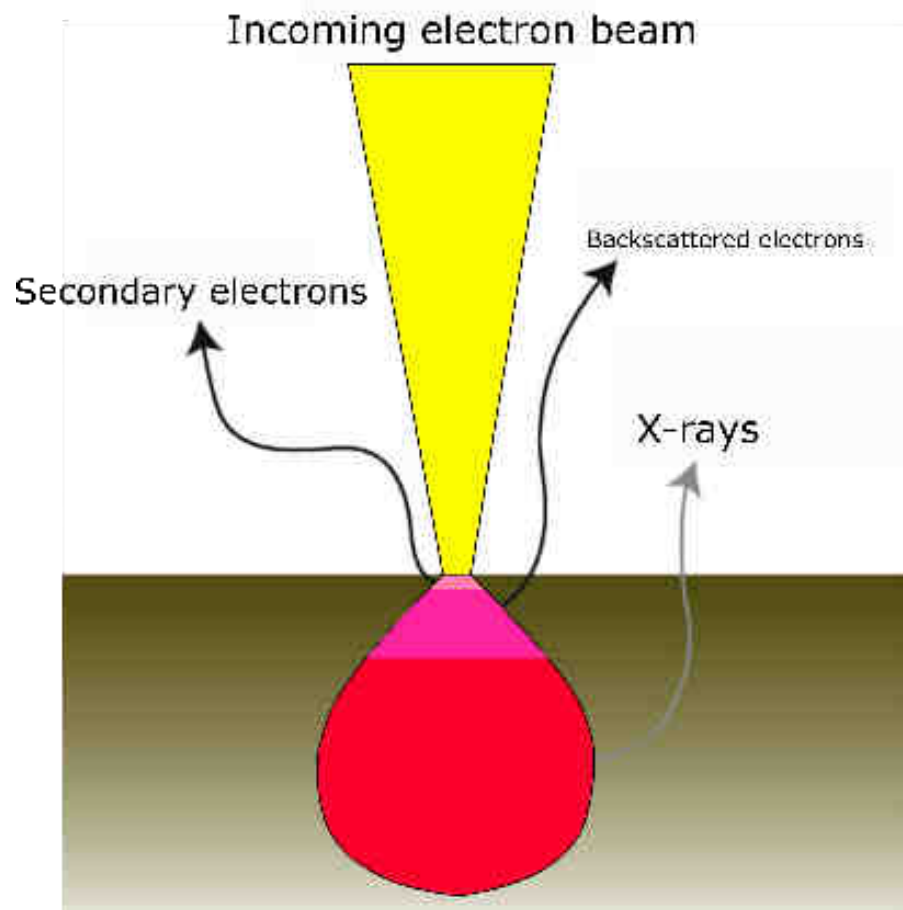


Scanning Electron Microscopy

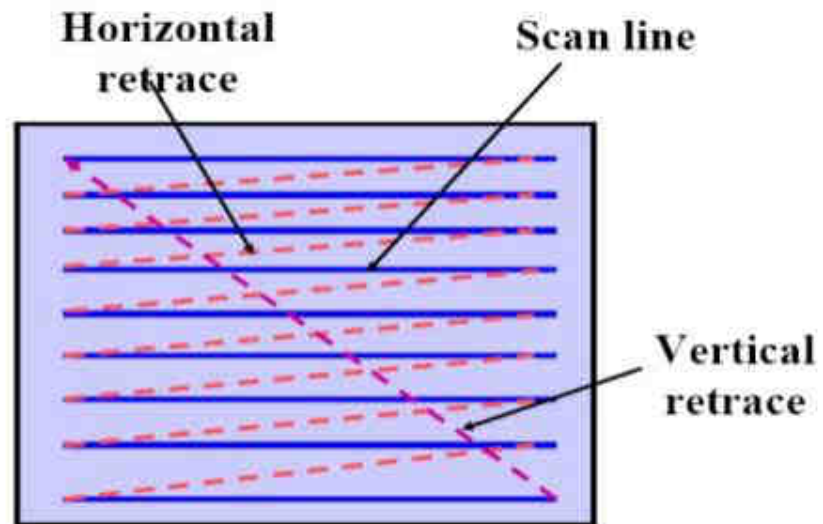
- A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image.
- The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface and composition.







Raster Scan



- Electrons are produced at the top of the column.
- Electrons are accelerated down and passed through a combination of lenses and apertures to produce a focused beam of electrons which hits the surface of the sample.
- The position of the electron beam on the sample is controlled by scan coils situated above the objective lens

- As the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X-rays.
- These signals are collected by one or more detectors to form images which are then displayed on the computer screen.
- When the electron beam hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample.

SEM- Specimen Interactions

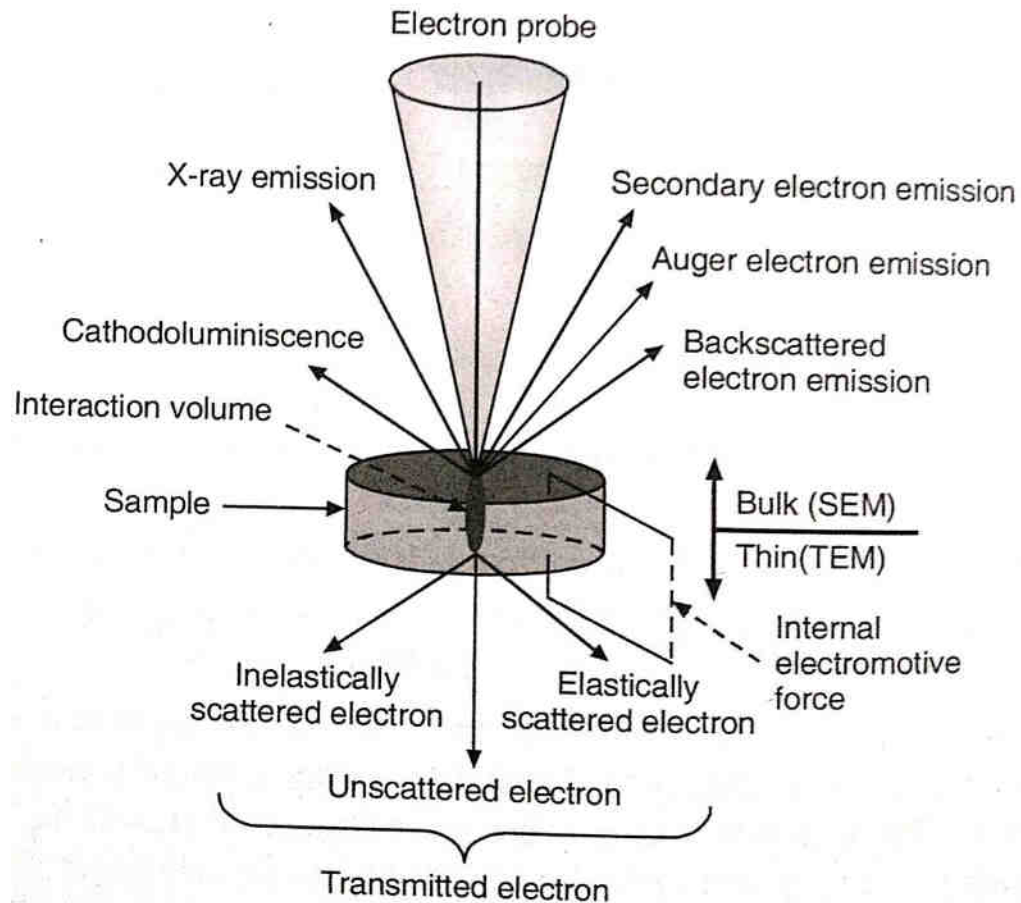


Fig. 7.36 Various interaction processes inside a sample.
ECE Dept., FISAT, Angamaly

Resolving Power

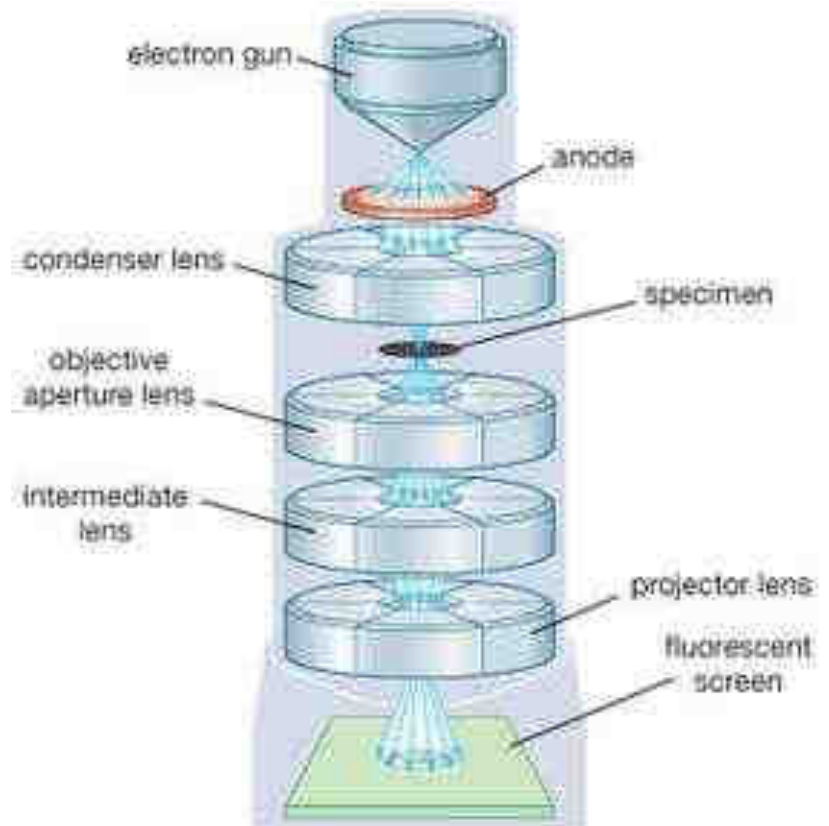
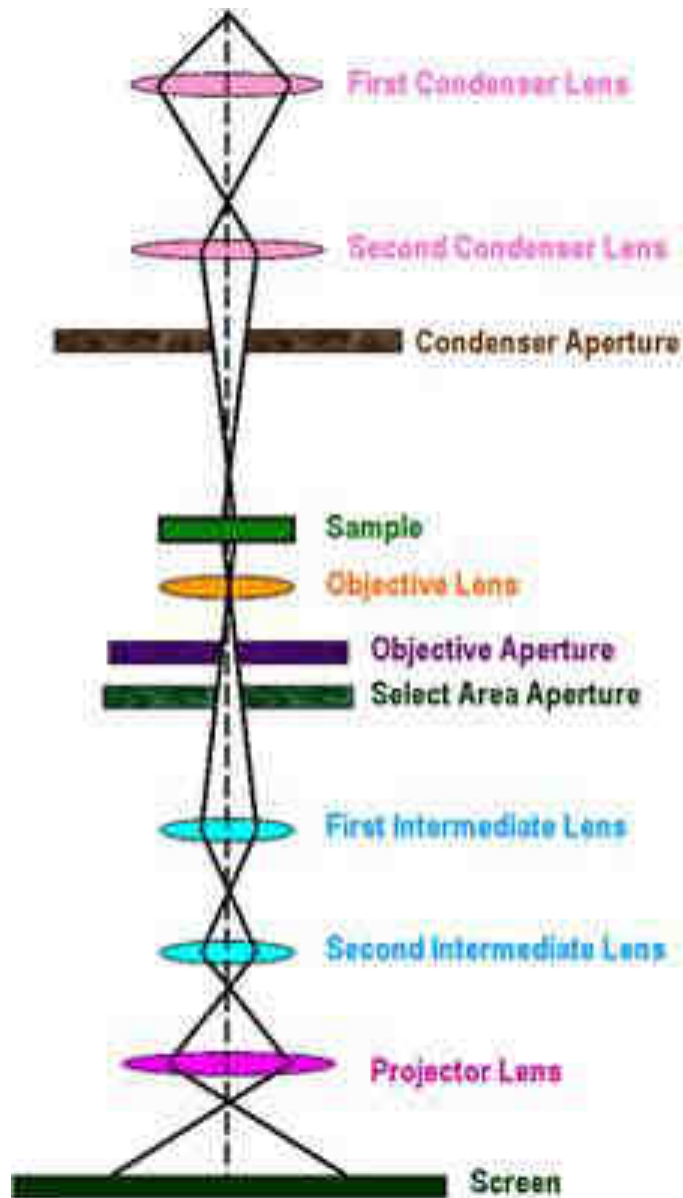
- The resolving power is defined as the ability to differentiate two lines or points in an object.
- The theoretical limit to an instrument's resolving power is determined by the wavelengths of the electron beam used and the numerical aperture about the system.
- The resolving power, R , of an instrument is defined as:
$$R = \lambda / (2NA)$$
- where λ is the wavelength of electrons used and NA is the numerical aperture.
- The greater the resolving power, the smaller the minimum distance between two lines or points that can still be distinguished.

- Information that can be investigated using SEM are:
 - ***Topography***: The surface features of an object or 'how it looks.
 - ***Morphology***: The shape, size and arrangement of the particles making up the object
 - ***Composition***: The elements and compounds the sample is composed.
 - ***Crystallographic information***: The arrangement of atoms in the specimen and their degree of order

TRANSMISSION ELECTRON MICROSCOPY (TEM)

- It is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image.
- The specimen is most often an ultrathin section less than 100 nm thick
- An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen.
- The image is then magnified and focused onto an imaging device, such as a fluorescent screen.

- Transmission electron microscopes are capable of imaging at a significantly higher resolution than light microscopes.
- It has three essential systems:
 - Electron gun: which produces the electron beam
 - Image-producing system: consisting of the objective lens, movable specimen stage, and intermediate and projector lenses
 - image-recording system: consists of a fluorescent screen.



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Working of TEM

- Electron gun, fires a beam of electrons.
- The gun accelerates the electrons to extremely high speeds using electromagnetic coils and voltages of up to several million volts.
- The electron beam is focused into a thin, small beam by a condenser lens, which has a high aperture that eliminates high angle electrons.
- Electrons will zoom through the ultra-thin specimen and parts of the beam are transmitted depending on how transparent the sample is to electrons.
- The objective lens focuses the portion of the beam that is emitted from the sample
- The image produced by the TEM, called a micrograph, is seen through a fluorescent screen.

- When the beams strike the phosphor image screen light is generated, which causes the image to be visible to the operator.
- The area through which very few electrons are transmitted look darker (they are thicker or denser).
- The lighter areas of the image represent those areas of the sample through which more electrons were transmitted (they are thinner or less dense).

Informations that can be investigated using TEM are

- ***Morphology***: The size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other.
- ***Crystallographic information***: The arrangement of atoms in the specimen and their degree of order.
- ***Compositional information***: The elements and compounds the sample is composed

The electron that pass through the sample is classified as

- unscattered electrons:
 - The unscattered electrons pass right through the sample after inciding with the sample without any interaction with the sample atoms.
 - Transmission of these electrons is inversely proportional to the thickness of the sample.
- scattered electrons :
 - The scattered electrons are collated by magnetic lenses and it form a pattern of diffraction spots.
 - These diffraction pattern gives information about orientation and atomic arrangement in the area probed.

Applications

- Can be used in various industries from medical research where it is employed to investigate viruses and bacteria.
- TEM has also been used to determine the melting points of nanocrystals.
- Heating of a nanocrystal by the electron beam can cause melting, which can be identified by the disappearance of crystalline diffraction.

challenge

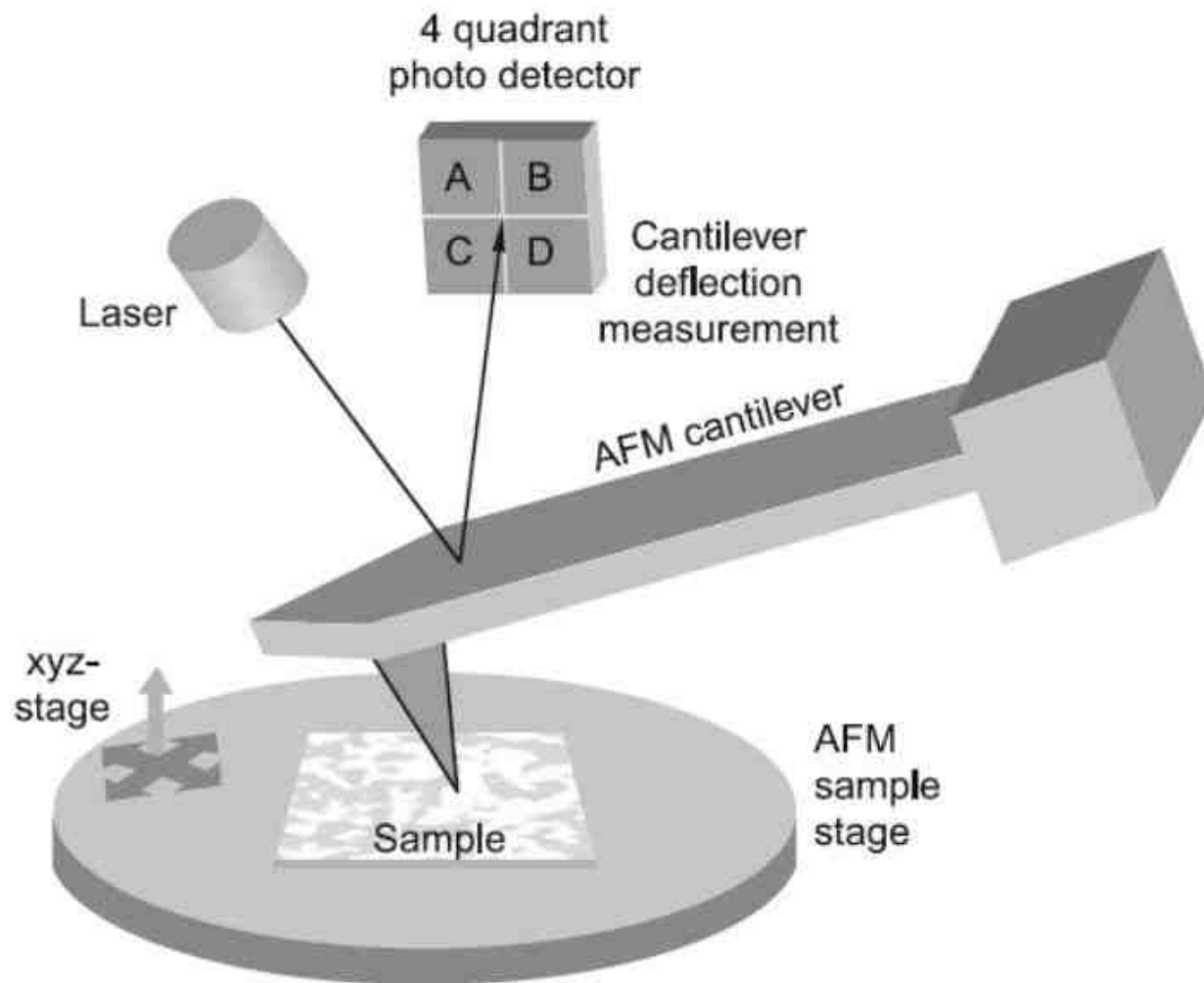
- The main challenge in any TEM investigation is specimen preparation.
- Obtaining specimens thin enough is a big task.
- Electron scattering information in a TEM image originates from a three-dimensional sample, but is projected on a two-dimensional detector.

ATOMIC FORCE MICROSCOPY (AFM)

- AFM is a high-resolution imaging technique.
- It is also commonly referred to as scanning probe microscope (SPM).
- Almost every material ranging from polymers to ceramics to composites are being investigated using AFM.
- AFM involves measurement of surface atomic forces in the range of a few nano-Newtons to image the surface topography.
- In the AFM, an atomically sharp tip is scanned over a surface.
- The AFM offers visualization in three dimensions

General Working

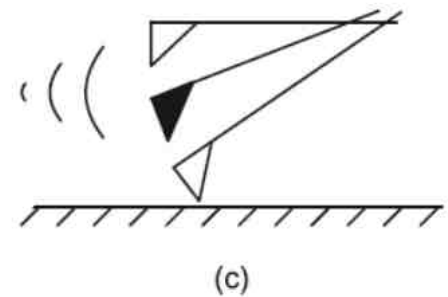
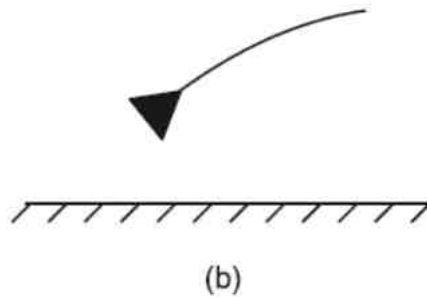
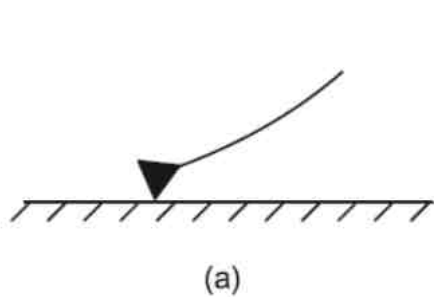
- The AFM works on the principle of a cantilever.
- A small hook is attached to one end of the cantilever.
- The force between the tip and sample is measured by tracking the deflection of the cantilever as the hook is pressed against the sample surface.
- This was done by monitoring the current to a second tip positioned above the cantilever.
- most of the tips are microfabricated from Si or Si₃N₄.



- New AFMs are based on optical principles.
- Small changes in the tilt of the tip can cause changes in optical scattering
- This influences the interference pattern and hence the surface can be studied for force variations.
- light is reflected from the surface of the cantilever onto a position-sensitive detector.
- Thus, even a small deflection of the cantilever will cause a tilt in the reflected light, changing the position of the beam falling on the detector.

- In the AFM, an atomically sharp tip is scanned over a surface.
- The tip is attached below a reflective cantilever.
- Tip can maintain at two positions
 - 1. a constant force (to obtain height information), or
 - 2. at constant height (to obtain force information) above the sample surface.
- A diode laser is focussed on this reflective cantilever.
- The tip moves on the surface of the sample up and down, tracing the contour of the surface and the laser beam is deflected off the cantilever into a photodiode.
- The photodetector measures the difference in light intensity between the upper and lower photodetectors, and then converts to voltage.

- AFM can work in three mode
 - contact mode
 - non-contact mode
 - tapping mode



Contact mode

- Tip is in close contact with the surface being scanned.
- A piezoelectric positioning element pushes the tip against the sample surface.
- The deflection of the tip is sensed and compared with a desired value in contact mode AFM.
- Thus, the voltage applied to the piezo is a measure of the height and depth of features on the surface of the sample.

- When the tip comes in contact with contaminant layer, it is pulled by surface tension towards the sample surface.
- The magnitude of the force depends on the details of the probe geometry.
- there could be problems such as liquid leakage, sample damage, etc
- All these effects can lead to difficulty in imaging or to destruction of the cantilever probe.
- Non-contact mode is a preferred technique for imaging such specimens.

Non-contact mode

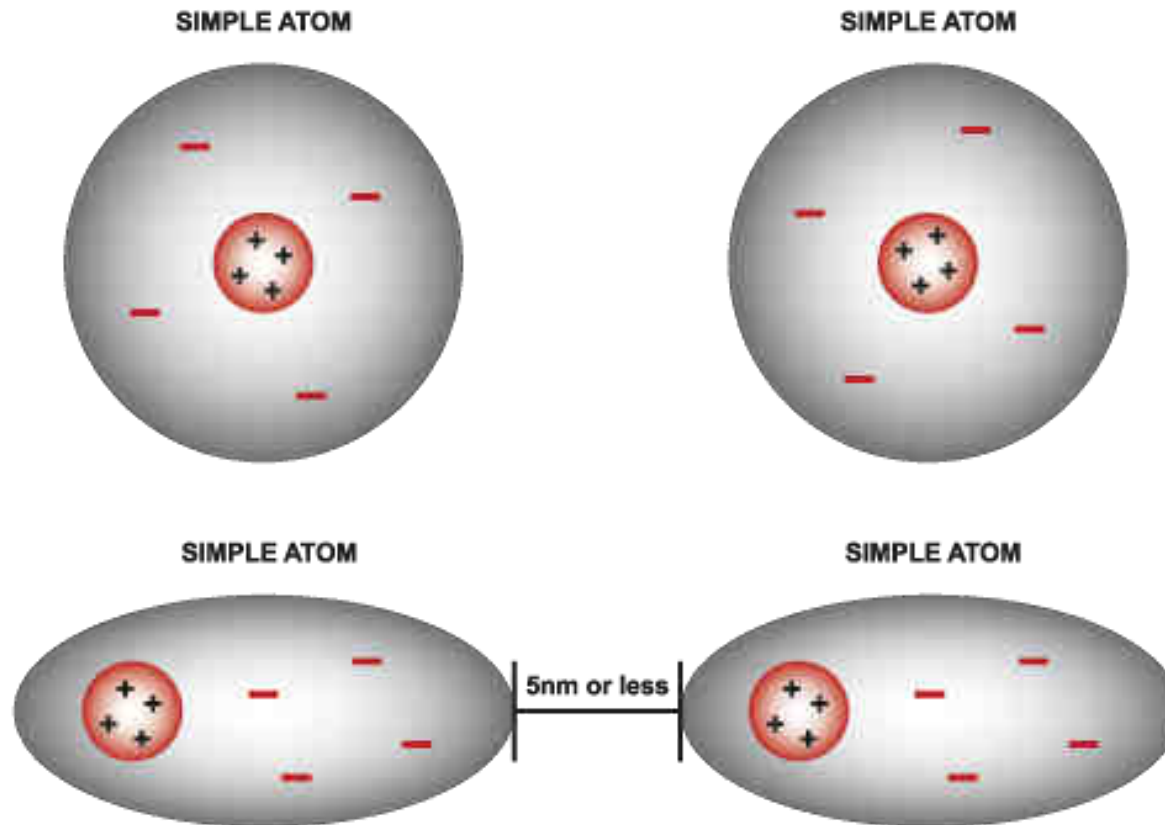
- Imaging surfaces without fear of damage to surface features or the tip.
- The cantilever tip is placed at a height of about 5–15 nm above the sample surface.
- The topographic image of the surface is obtained based on the van der Waals forces acting between the tip and the sample.
- However, the van der Waals forces are weaker.
- In order to overcome this problem, a small oscillation is given to the tip to detect the small forces between the tip and the sample surface by monitoring the change in amplitude, phase and frequency of the oscillating tip.

VAN DER WAALS' FORCES (VDW) DIAGRAM

KEY

+ POSITIVE NUCLEUS

— NEGATIVE CHARGED ELECTRON CLOUD



When two atoms come within 5 nanometers of each other, there will be a slight interaction between them, thus causing polarity and a slight attraction.

Tapping mode

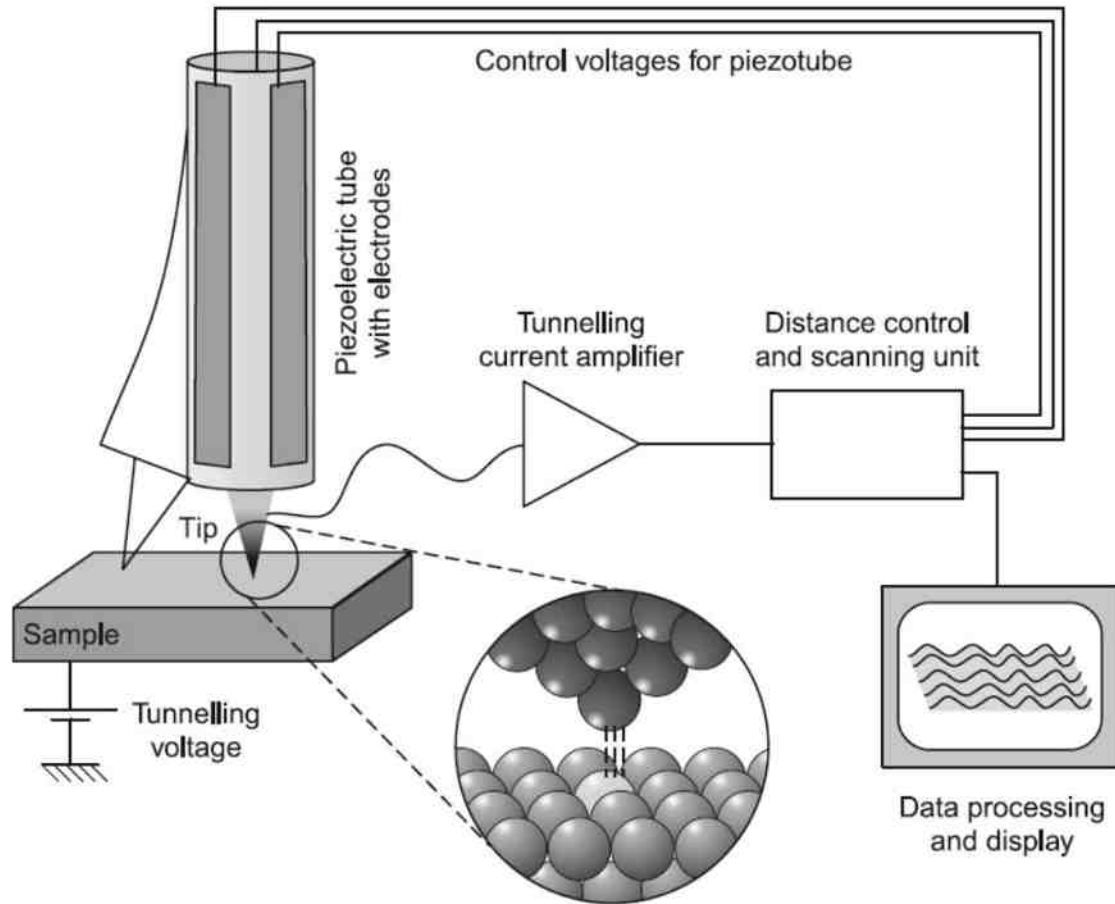
- Allows high-resolution topographic imaging of sample surfaces.
- The tip is oscillated at or near its resonant frequency using a piezoelectric crystal.
- The piezo makes the tip oscillate with a high amplitude (>20 nm) when the latter is not in contact with the surface.
- The tip is carefully lowered to bring it in contact with the surface such that it touches it lightly.
- the oscillating nature of the tip causes the tip to be in contact with the surface and then lift off.

- The cantilever usually taps the surface at a frequency of about 50,000 to 500,000 cycles per second.
- Whenever the oscillating tip comes in contact with the surface, its oscillation is reduced.
- The change in oscillation amplitude is used to identify surface features.
- When the tip passes over a surface projection or depression, the amplitude of oscillation decreases or increases, respectively.

	SEM/TEM	AFM
Samples	Must be conductive	Insulating/Conductive
Magnification	Two-dimensional	Three-dimensional
Environment	Vacuum	Vacuum/Air/Liquid
Time for image	0.1–1 minute	1–5 minute
Horizontal resolution	0.2 nm (TEM) 5 nm (FE-SEM)	0.2 nm
Vertical resolution	n/a	.05 nm
Field of view	100 nm (TEM) 1 mm (SEM)	100 μ m
Depth of field	Good	Poor
Contrast on flat samples	Poor	Good

SCANNING TUNNELLING MICROSCOPE (STM)

- Capable of obtaining three-dimensional (3D) images of solid surfaces.
- STM can be used in any environment such as ambient air, various gases, liquids, vacuum, at low temperatures and high temperatures.



- If a potential difference is applied to two metals separated by a thin insulating film, a current will flow because of the ability of electrons to penetrate a potential barrier.
- Although small, there is a finite current flow.
- The tunnelling current is highly sensitive to the separation distance between tip and sample.
- It decreases exponentially with increase in tip– sample separation distance.
- Tunnelling current decreases by a factor of 2 as the separation is increased by 0.2 nm.

- A sharp metal tip (first electrode) is brought close enough (0.3–1 nm) to the surface to be investigated (the second electrode), such that, at a convenient operating voltage (10 mV–1 V), the tunnelling current varies from 0.2 to 10 nA, which is measurable.
- The tip is scanned over a surface at a distance of 0.3–1 nm, while the tunnelling current between it and the surface is measured.
- The tip movement above the sample surface in three dimensions is controlled by piezoelectric arrays.
- The piezo tube has separate electrodes for x , y and z , movement which are driven by separate drive circuits.

STM is commonly operated in two modes

- constant tip position(Constant height mode)
- constant current imaging

Constant tip position(Constant height mode)

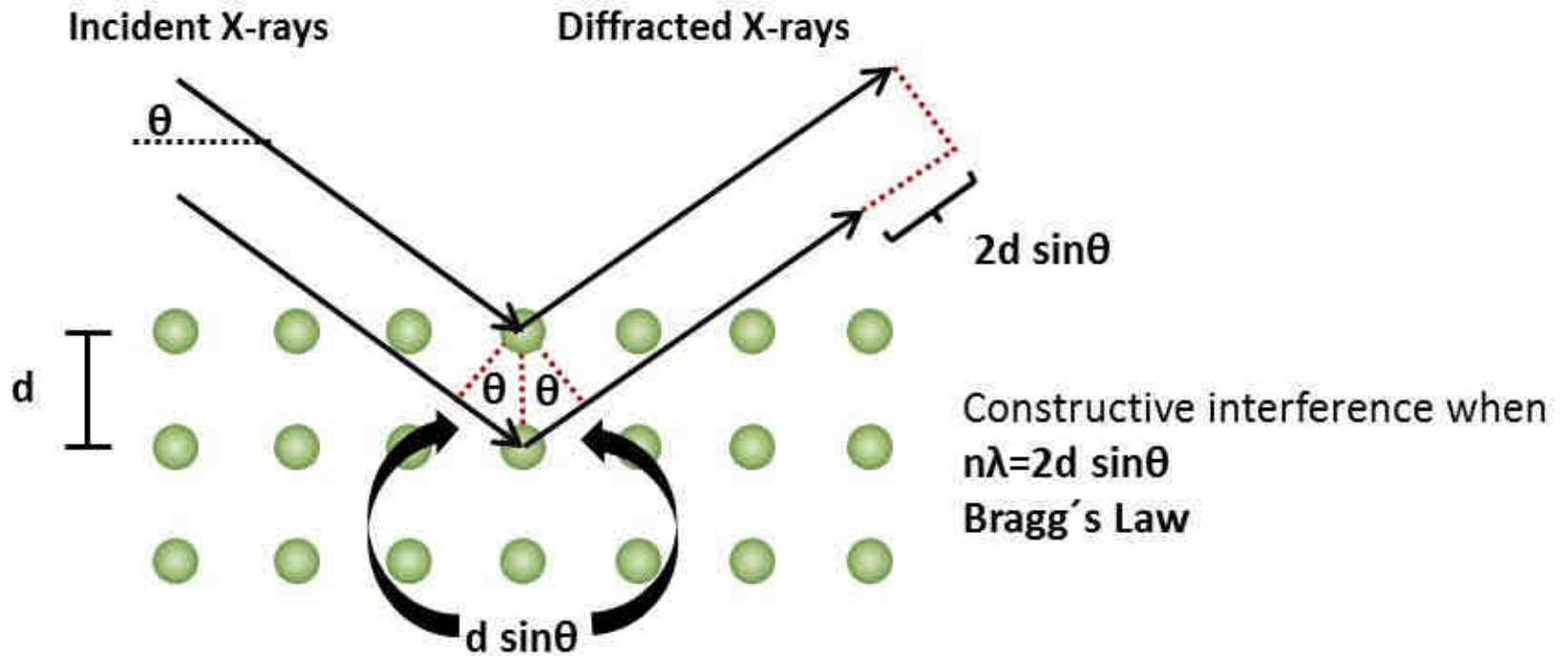
- Variations in tunneling current due to changes in tip separation distance is found out.
- The tip remains at a nearly constant height as it sweeps over the sample surface, variations in current is measured.
- Faster scan rates are possible in the constant height mode

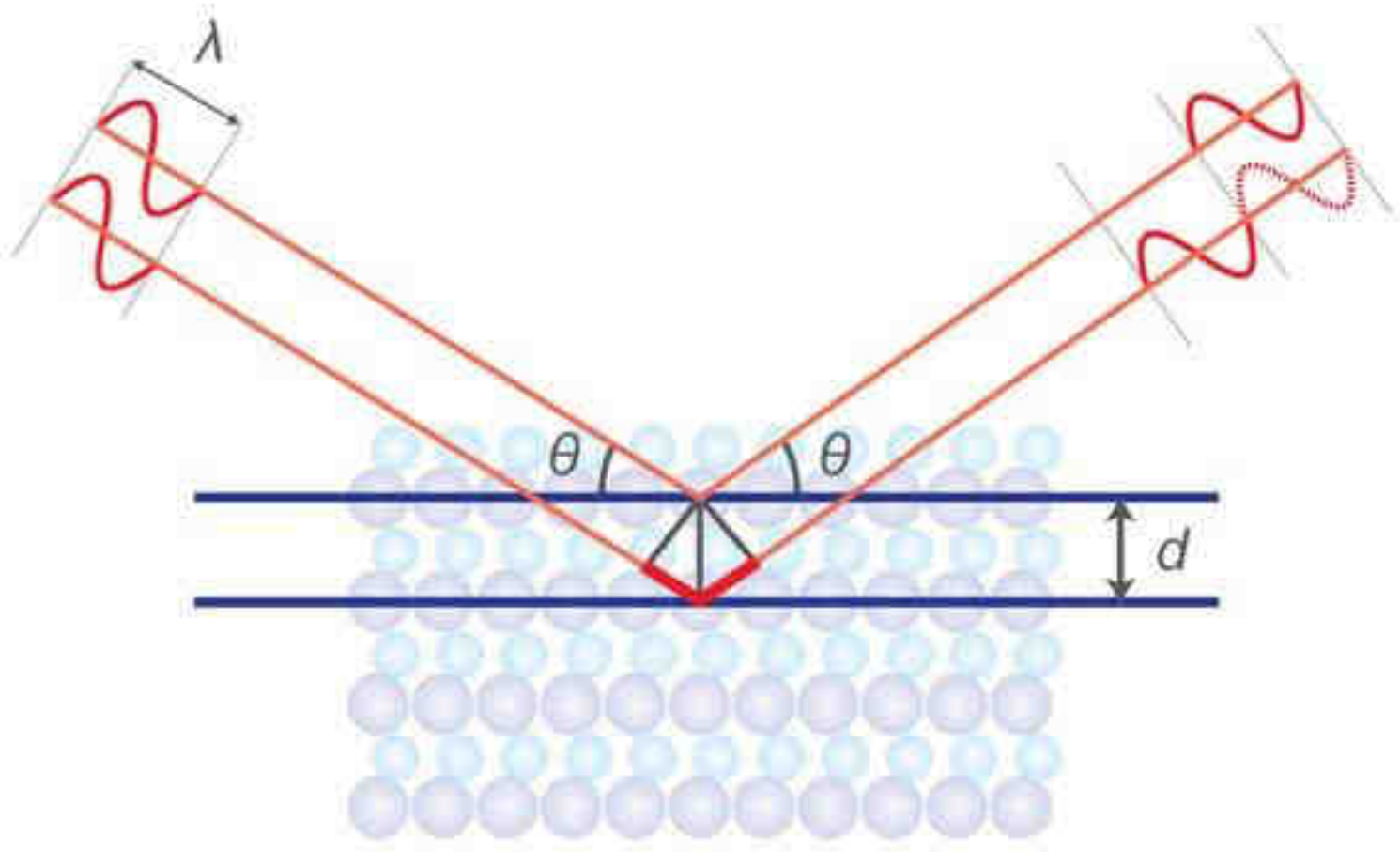
constant current imaging

- A constant current is maintained between the sample and tip.
- During the movement of the tip over the sample surface, the vertical position of the tip is changed to maintain a constant current between the two.
- Since the tunneling current is sensitive to distance.
- Constant current imaging will provide excellent surface topographic information's.

X-RAY DIFFRACTION (XRD)

- XRD is extensively used to study the crystal structure of solids, defects and stresses.
- In XRD, a beam of X-rays, with wavelength ranging from 0.07 to 0.2 nm, is diffracted by the crystalline specimen.
- The scattered X-rays from the sample interfere with each other either constructively or destructively.
- The intensity of the diffracted beam is measured.
- Calculated intensity of diffracted beam is plotted as a function of the diffraction angle (2θ)





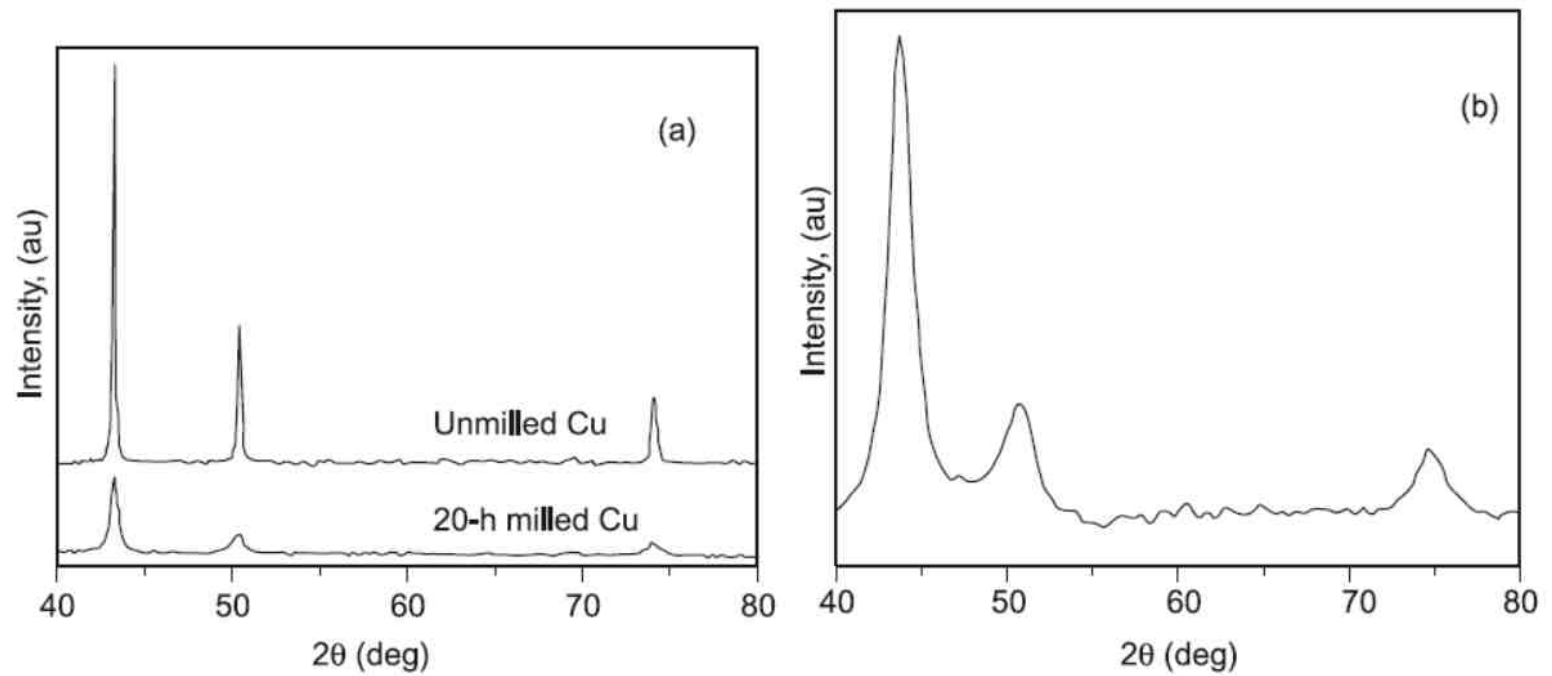
Why XRD

- Measure the average spacing's between layers or rows of atoms
- Determine the orientation of a single crystal
- Find the crystal structure of an unknown material
- Measure the size, shape and internal stress of small crystalline regions

- The dots in the graph correspond to the building blocks of a crystalline material.
- Due to the crystalline nature, the atoms are arranged periodically.
- The incident X-ray beam is scattered at different planes of the material.
- The resulting diffracted X-rays therefore have a different optical path length to travel.
- The magnitude of this path length only depends on the distance between the crystal planes and the incident angle of the X-ray beam.
- The scattered X-rays from the sample interfere with each other either constructively or destructively.
- This is summarized in the famous Bragg – Equation:

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

- In words this equation can be described as follows:
- Constructive interference occurs only if the path difference (given by $2d \sin\theta$) is a multiple ($n=1,2,..$) of the used wavelength of the X-ray beam.
- As the wavelength in XRD experiments is known and the angles at which constructive interference occurs are measured, the use of the Bragg equation allows determining the distance between the lattice planes of the material.
- The result of the measurement is a so called diffractogramm.
- This is a plot of X-ray intensity on the y-axis versus the angle 2θ (2θ is defined as the angle between the incident and the diffracted beam) on the x-axis.



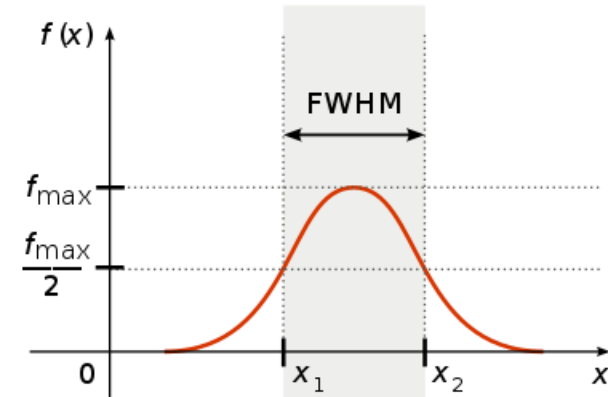
XRD patterns of nanocrystalline (a) copper and (b) NiCoCrFe equiatomic alloy

- This diffraction pattern can be thought of as a chemical fingerprint, and chemical identification can be performed by comparing this diffraction pattern to a database of known patterns.

- XRD is non-destructive and does not require detailed sample preparation.
- Strains in materials can be measured as X-ray intensity.
- Elastic strain shifts the diffraction peak positions, without change in peak profile.
- A shift in the X-ray peak positions indicates a change in d -spacing caused by a change in lattice constants.

- Crystallite size, D , can be estimated using Scherrer's formula:

$$D = \frac{K\lambda}{B \cos \theta_B}$$



- where λ is the X-ray wavelength, B is the full width at half maximum (FWHM) height of a diffraction peak, ϑ_B is the diffraction angle, and K is Scherrer's constant,

SMALL ANGLE X-RAY SCATTERING (SAXS)

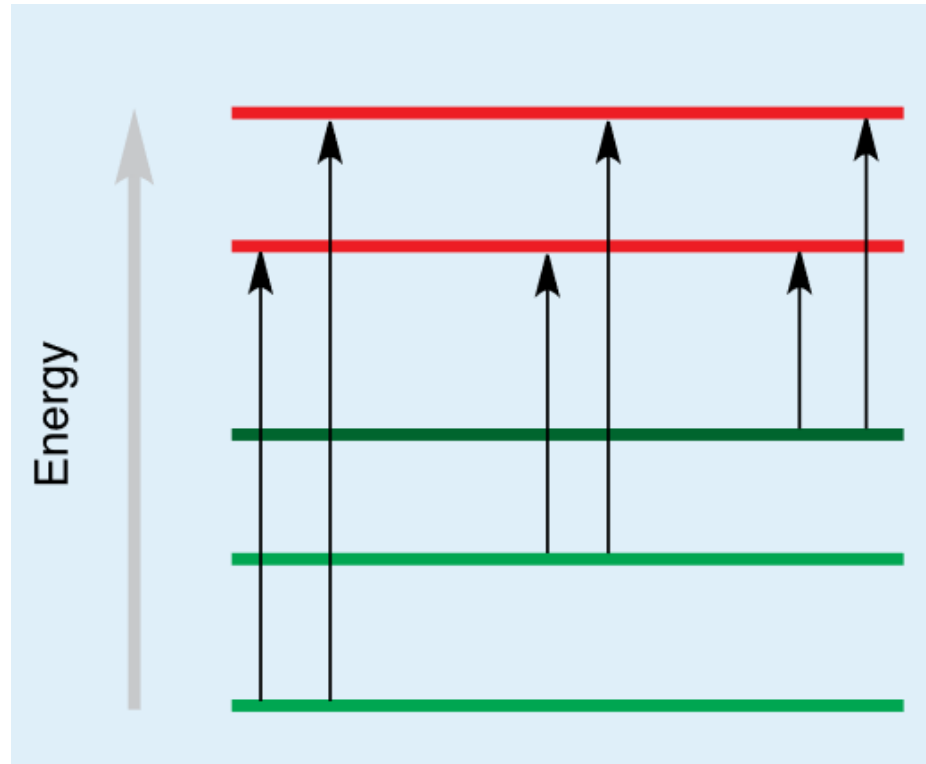
- Strong diffraction peaks result from constructive interference of X-rays scattered from ordered arrays of atoms and molecules.
- A variety of information can be obtained from the angular distribution of scattered intensity at low angles.
- Measurements are made at very small angles, typically in the range of 0.1 deg to 5 deg.
- SAXS is the scattering due to the existence of regions of inhomogeneous, whereas XRD is used to determine atomic structures of the crystallite phases.
- For amorphous and semicrystalline materials better to use SAXS.
- wide angle X-ray diffraction (WAXD) that deals mainly with the atomic structure of crystals.

Optical Spectroscopy:

- Optical spectroscopy uses the interaction of light with matter as a function of wavelength or energy in order to obtain information about the material.
- it is fast, nondestructive and of high resolution.

UV-visible spectroscopy

- This technique involves the absorption of near-UV or visible light.
- Used to determine the presence of a particular substance in a sample and, in many cases, to quantify the amount of the substance present.
- Energy from the light is used to promote an electron from lower orbital into one of the empty higher orbitals.
- Each jump takes energy from the light, and a big jump needs more energy than a small one.



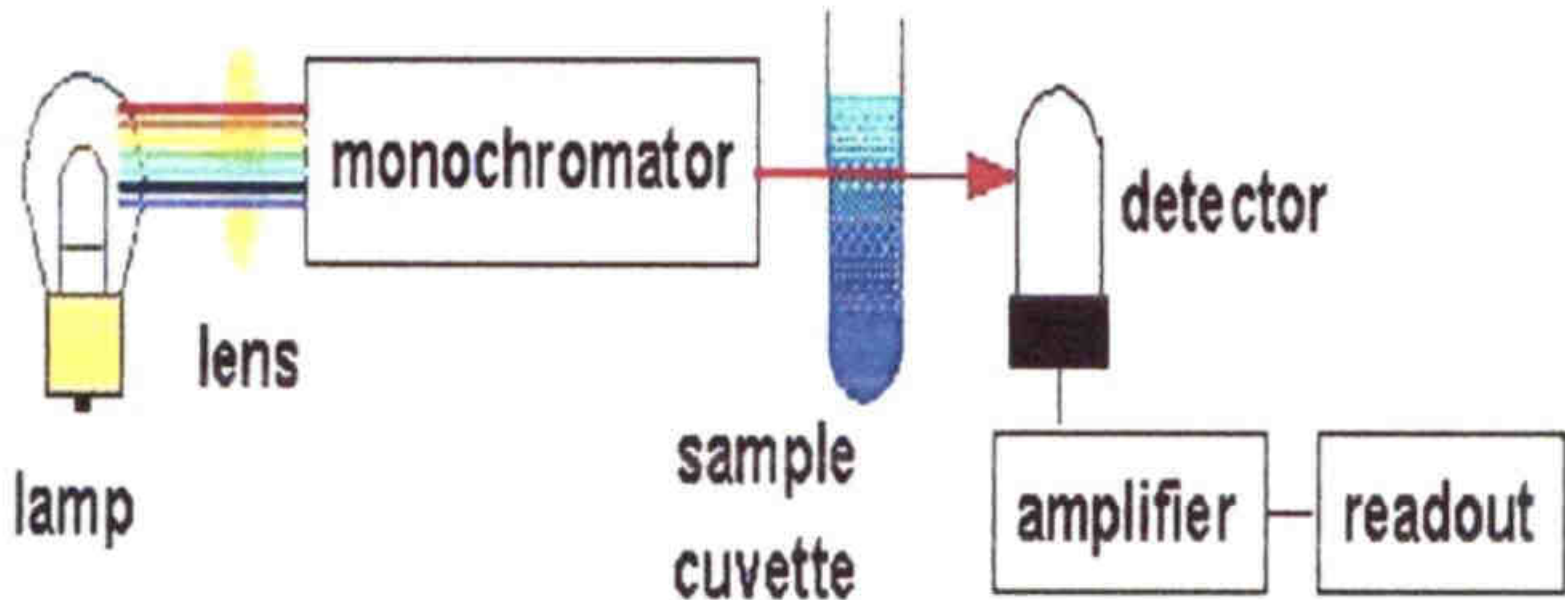
- Each wavelength of light has a particular energy associated with it.
- If that particular amount of energy is just right for making one of these electronic transitions, then that wavelength will be absorbed.
- The larger the gap between the energy levels, the greater the energy required to promote the electron to the higher energy level;
- The relationship between the frequency of light absorbed and its energy is
$$E=h\nu$$
- Where, E is the energy of each quanta of light, h is the Planck's constant and ν is the frequency of light

- For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured.
- This is usually referred to as I_0 .
- The intensity of the light, I passing through the sample cell is also measured for that wavelength.
- If I is less than I_0 then obviously the sample has absorbed some of the light.
- The Beer-Lambert Law gives, the relationship between A (the absorbance) and the two intensities is given by:

$$A = \log_{10} \frac{I_0}{I}$$

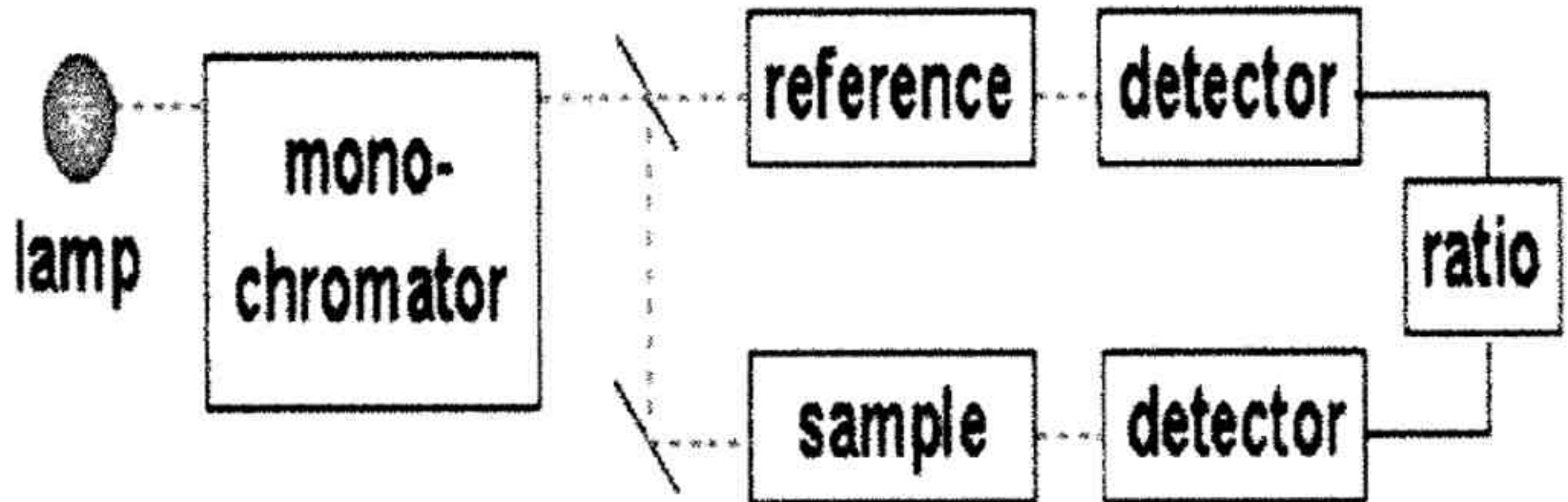
- An absorbance of 0 at some wavelength means that no light of that particular wavelength has been absorbed.
- An absorbance of 1 happens when 90% of the light at that wavelength has been absorbed.
- A spectrophotometer can be either single beam or double beam.

single beam UV spectrometer



- The basic parts of a spectrometer are a light source, a holder for the sample, monochromator to separate the different wavelengths of light, and a detector.
- The radiation source emits visible or UV light.
- Monochromator will filter the light so that only light of a single wavelength passes at one time.
- Light passes through the sample cell and reaches the detector.
- Intensity of each wavelength will be measured using detectors [photodiode array] and represented as I .
- Reference current I_0 is also measured by removing the sample.
- Using Beer-Lambert law absorbance will be calculated.

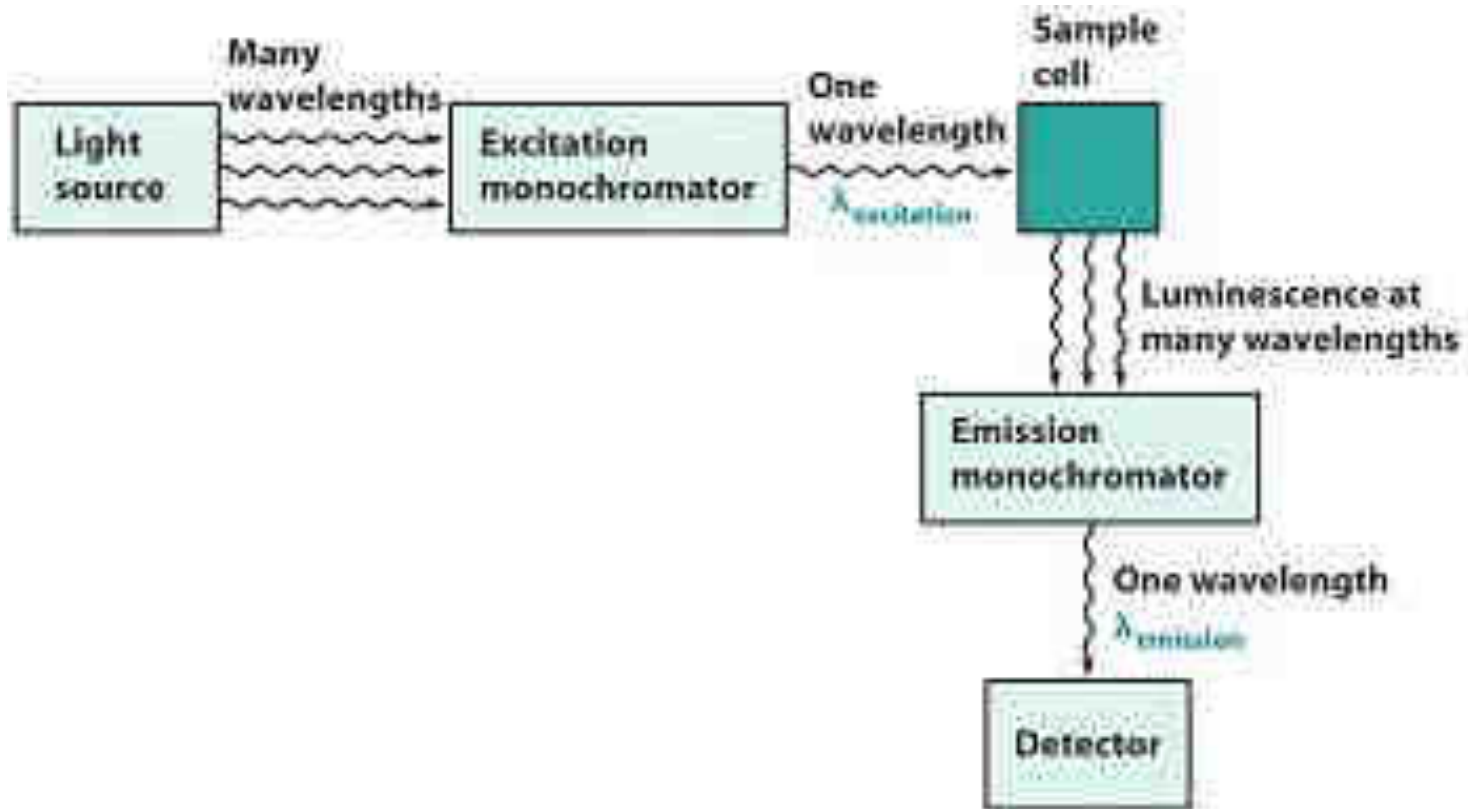
Double-beam UV spectrometer



- Light is split into two beams before it reaches the sample.
- One beam is used as the reference; the other beam passes through the sample.
- The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities.

Photoluminescence Spectroscopy:

- Photoluminescence (PL) is a process in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons.
- This can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of a photon.
- The energy it loses is converted back into a luminescent photon which is emitted from the material.
- Thus the energy of the emitted photon is a direct measure of the band gap energy, E_g .
- The process of photon excitation followed by photon emission is called photoluminescence.



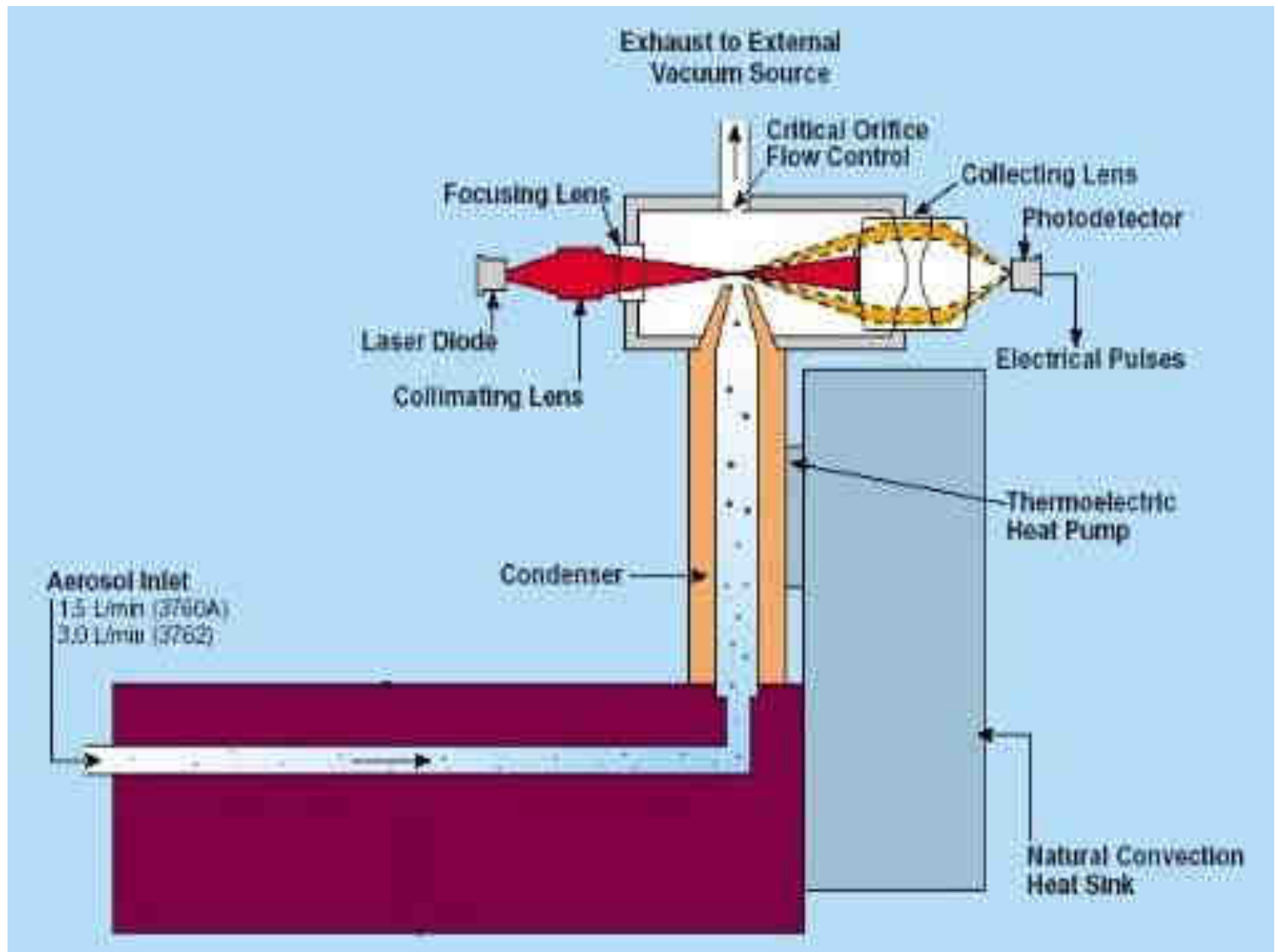
- There are many types of photoluminescent process:
- *a) Resonant radiation:*
 - *When* a photon of a particular wavelength is absorbed and equivalent photon is immediately emitted.
- *b) Fluorescence:*
 - *When* the chemical substrate undergoes internal energy transitions before re-emitting the energy from the absorption.
 - Here some of the original energy is dissipated so that the emitted light photons are of lower energy than those absorbed.

- photoluminescence spectroscopy can also use for the following applications.
 - a) Band gap determination*
 - b) Impurity levels and defect detection*
 - c) Surface structure*
 - d) Recombination mechanisms*

- Laser diffraction particle size analyzers calculate particle size from the angle of light scattered by a stream of particles passing through a laser beam.
- It works on the principle that when a beam of light (a laser) is scattered by a group of particles, the angle of light scattering is inversely proportional to particle size.
- Smaller the particle size, the larger the angle of light scattering
- This technique allows for continuous measurement of bulk material across a wide size range (10 nm to 3 mm).
- The size limits and sensitivity of a laser diffraction particle analyzer depend on the number and placement of detectors in the instrument.

Particle analyzer

- Particle analyzers are used to determine the size and distribution of particles making up a material.
- It is used to characterize the size distribution of particles in a given sample.
- Particle size analysis can be applied to solid materials, suspensions, emulsions and even aerosols
- Particle size analyzers are used in numerous fields for research and development, manufacturing and for quality control and product testing.



- Converting particle into aerosol.
- An **aerosol** is a suspension of fine solid particles or liquid droplets, in air or another gas.
- Examples of natural **aerosols** are fog, dust etc..
- Laser beam is focused by collecting lens to the photo detector.
- Laser will be diffracted with the presence of aerosol and amount of diffraction is measured by the photo detector.
- Beam will cut for longtime if the particle size is large (large width pulse) and takes less time for small particle (small width pulse)

Equivalent sphere theory in Particle analyzer

- One basic problem in particle size analysis is characterizing particles using just one number.
- The shape of a sphere can be described by a single unique number.
- A sphere measures the same across every dimension. If we say we have a 100 micron sphere, this describes it exactly.
- For this reason, all particle sizing techniques measure a one dimensional property of a particle and relate this to the size of an “equivalent sphere”.
- One example is to measure the surface area of a particle and then report the size of sphere which has the same surface area.
- Probably the most common method is to measure the “volume” of each particle in a sample and report the size of a sphere which has the same volume as the particles being measured

AFM vs STM

- In some cases, the resolution of STM is better than AFM because of the exponential dependence of the tunnelling current on distance.
- Only conducting samples can be studied by STM, while AFM can be applied to both conducting and non-conducting samples.
- AFM is more versatile than STM.
- In AFM, the voltage and tip-to-substrate spacing can be controlled independently, while in STM these two parameters are connected.

AFM v/s SEM

- Compared with the scanning electron microscope, AFM provides extraordinary topographic contrast, direct height measurements and unobscured views of surface features (no coating is necessary).
- Both these techniques measure surface topography.
- However, both types of microscopes can also measure other surface physical properties.
- SEM is preferred for measuring chemical composition and AFM for measuring mechanical properties of surfaces.

AFM vs TEM & Optical microscope

- Compared with the transmission electron microscope, three-dimensional AFM images are obtained without expensive sample preparation and yield far more complete information than the two-dimensional profiles available from cross-sectioned samples.
- Compared with the optical interferometric microscope (optical profiles), AFM provides unambiguous measurement of step heights, independent of reflectivity differences between materials.