Chapter- Chemistry of nano materials

Topic-Characterization of Nanoparticles

❖ CHARACTERIZATION OF NANOPARTICLES

- Characterization refers to study of materials features such as its composition, structure, and various properties like physical, electrical, magnetic, etc.

Important characterization of nanoparticles

- Nanoparticle properties vary significantly with size and shape.
- Accurate measurement of nanoparticles size and shape is, therefore, critical to its applications.

General characterization method

- **Microscopy**

1- **Scanning Electronic Microscopy (SEM)**

2- **Transmission ElectronMicroscopy (TEM)**

3- **Scanning Tunneling Microscopy (STM)**

Spectroscopy

1- **X-ray Diffraction (XRD)**

2- **Small Angle X-ray Scattering (SAXS)**

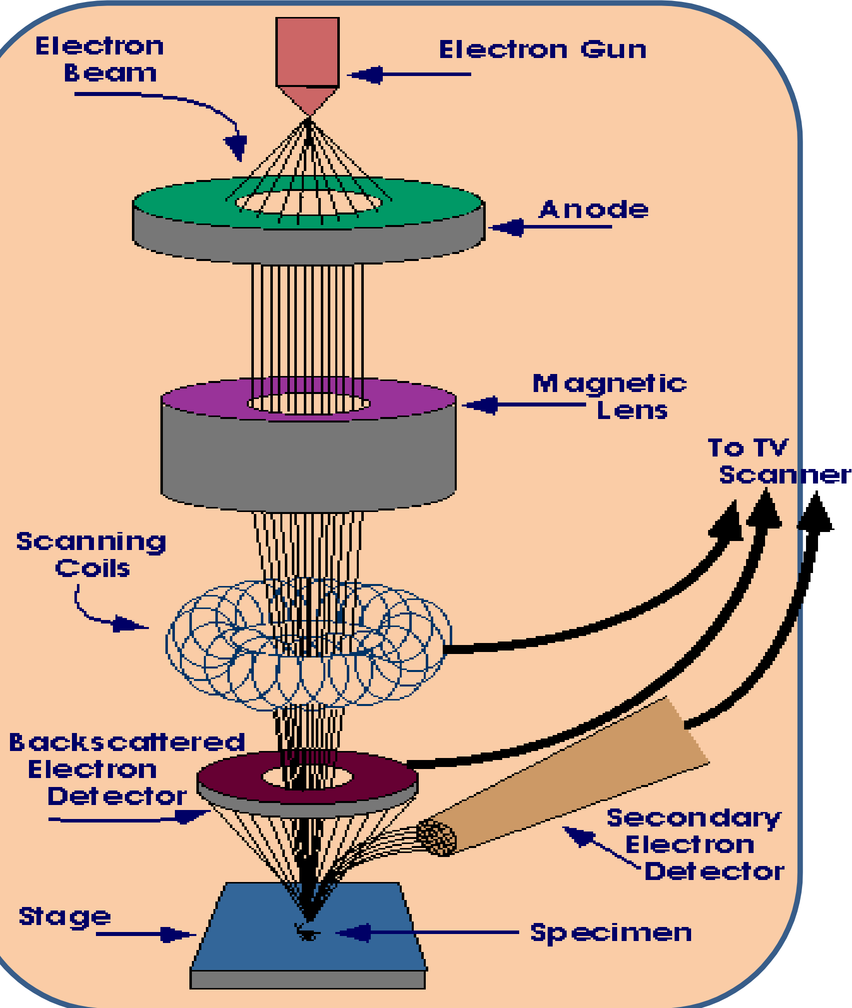
3- **X-ray Photoelectron Spectroscopy (XPS)**

4- **UV-vis spectroscopy**

5- **FT-IR spectroscopy**

Scanning Electron Microscopy

Basic principle



When the beam of electrons strikes the surface of the specimen & interacts with the atoms of the sample, signals in the form of secondary electrons, back scattered electrons & characteristic X-rays are generated that contain information about the samples' surface topography, composition etc.

What can you see with an SEM?

-Topography

Texture/surface of a sample

-Morphology

Size, shape, order of particles

-Composition

Elemental composition of sample

-**Crystalline Structure**

Arrangement present within sample

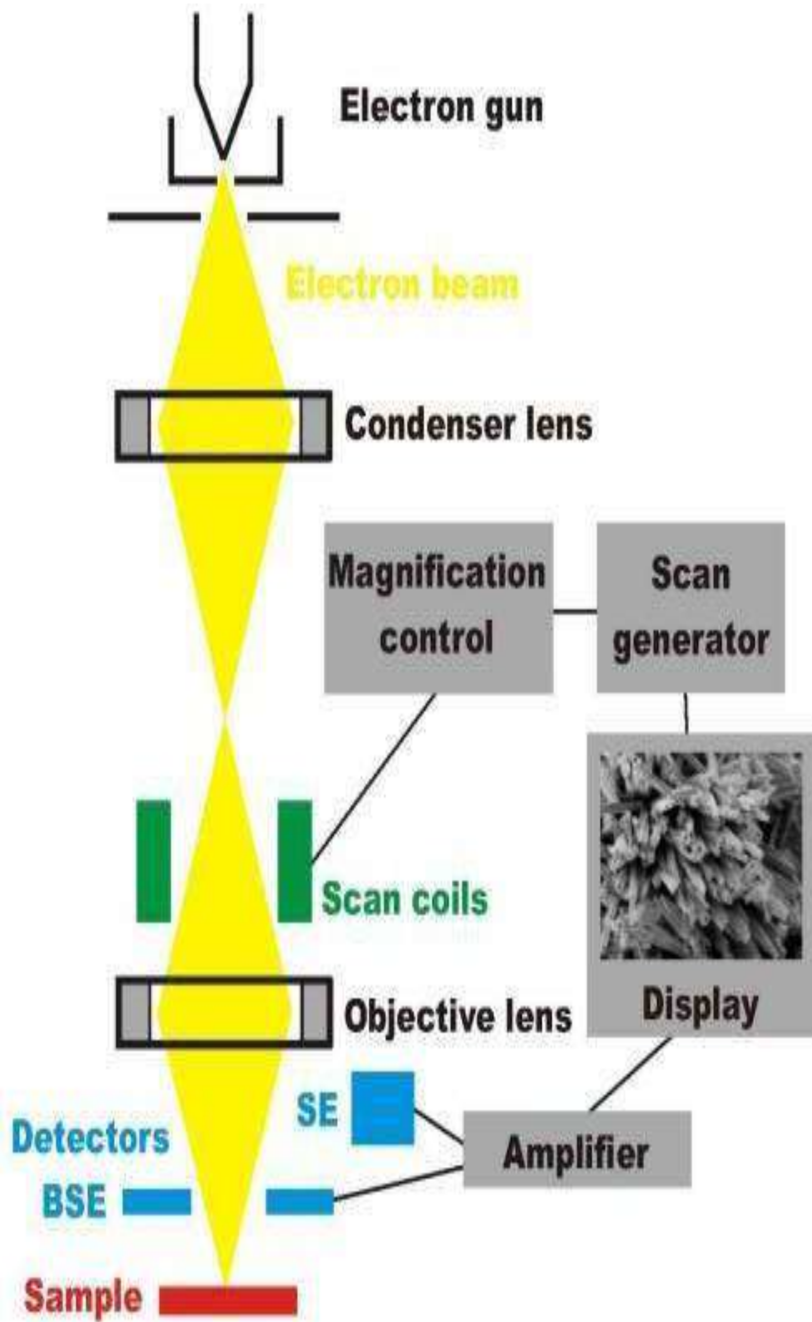
Operation modes

There are 3 modes

-Primary: High resolution (1-5 nm); secondary electron imaging

-Secondary: Characteristic X-rays; identification of elemental composition of sample by EDX technique

-Tertiary: Back-scattered electronic images; clues to the elemental composition of sample

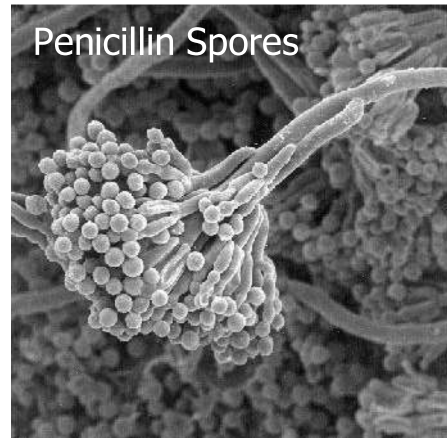


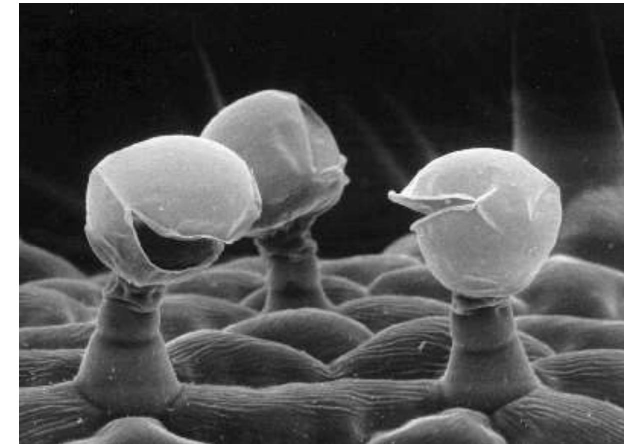
Electronic devices are used to detect & amplify the signals & display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of the microscope.

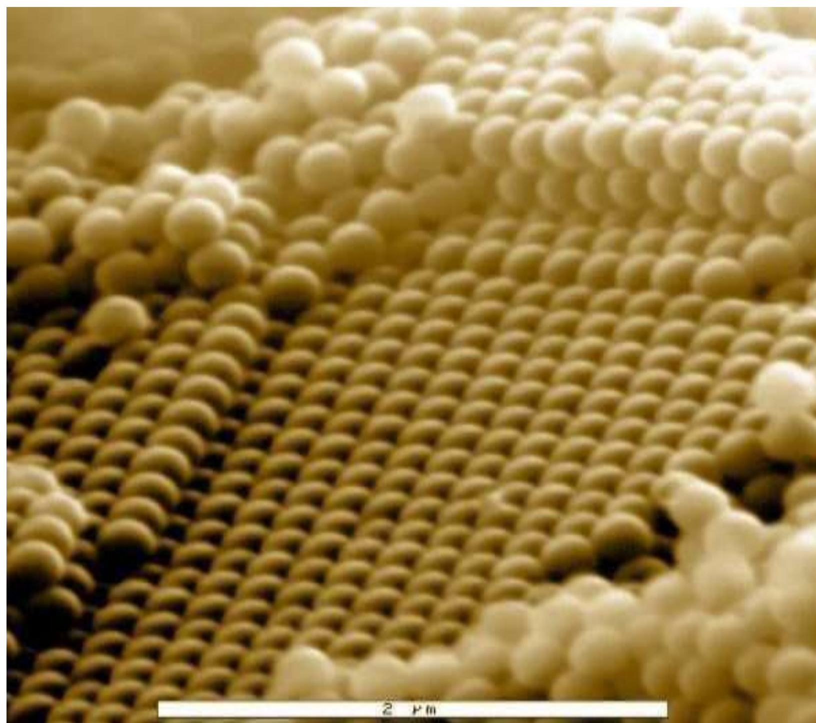
In a typical SEM, the beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally & vertically.

The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

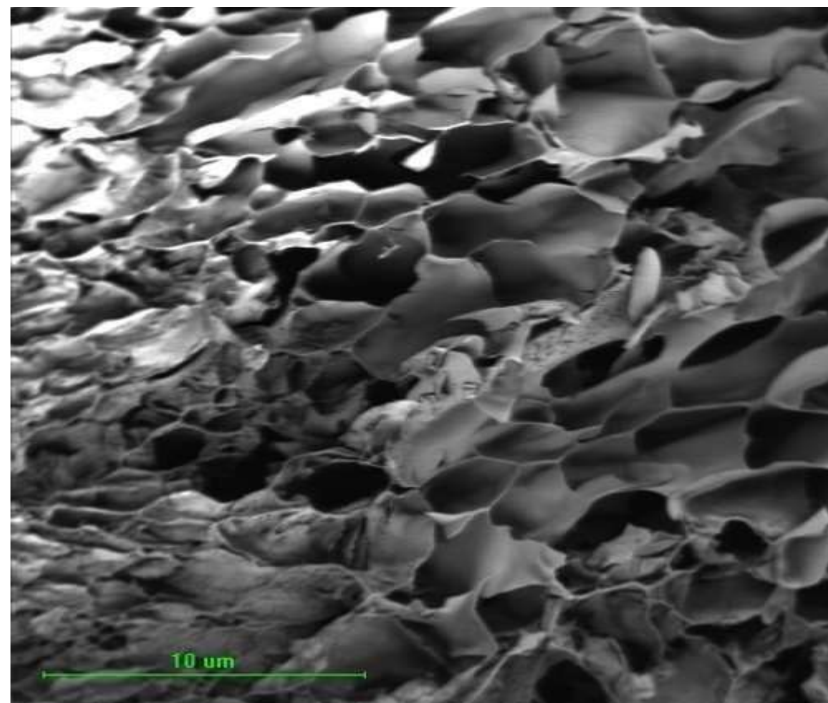
Scanning Electron Microscopy



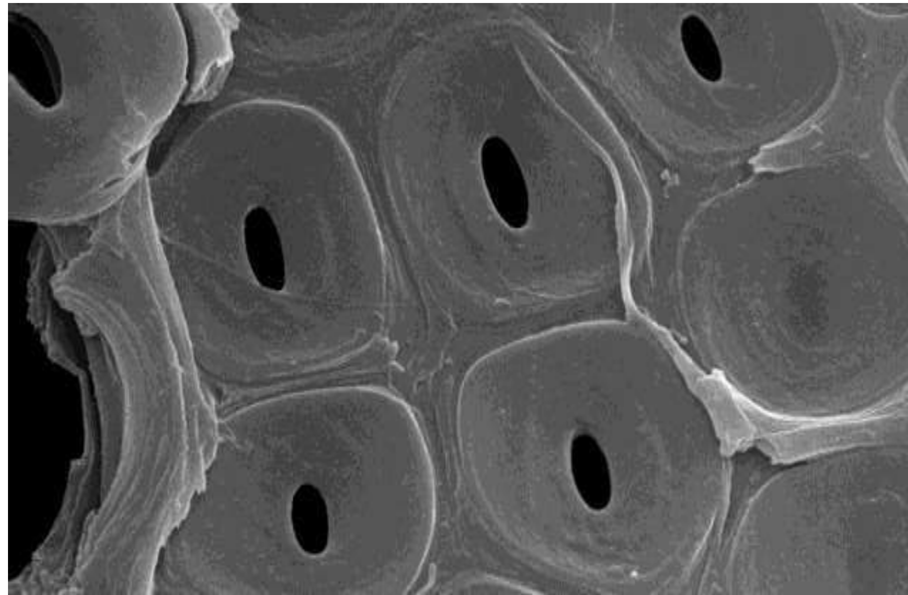




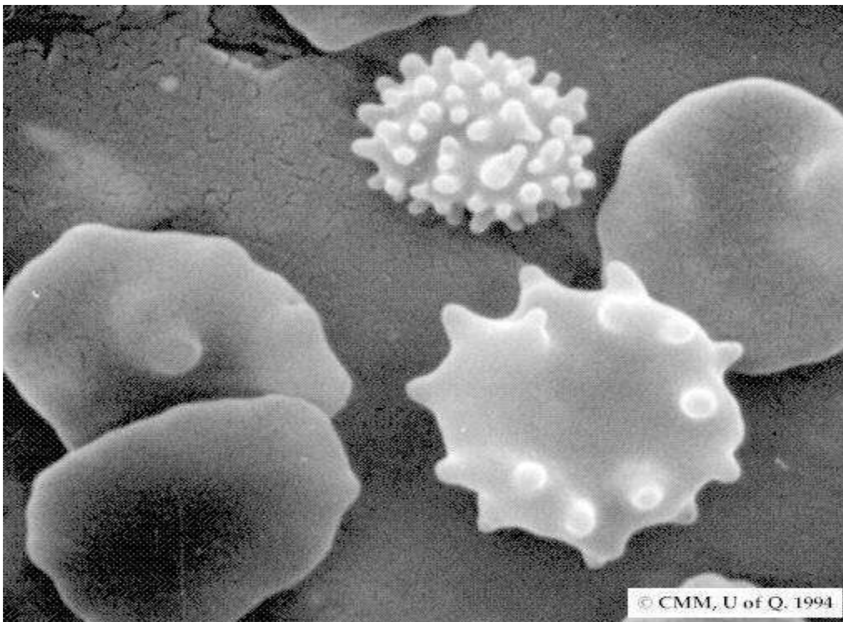
Crystalline Latex Particles

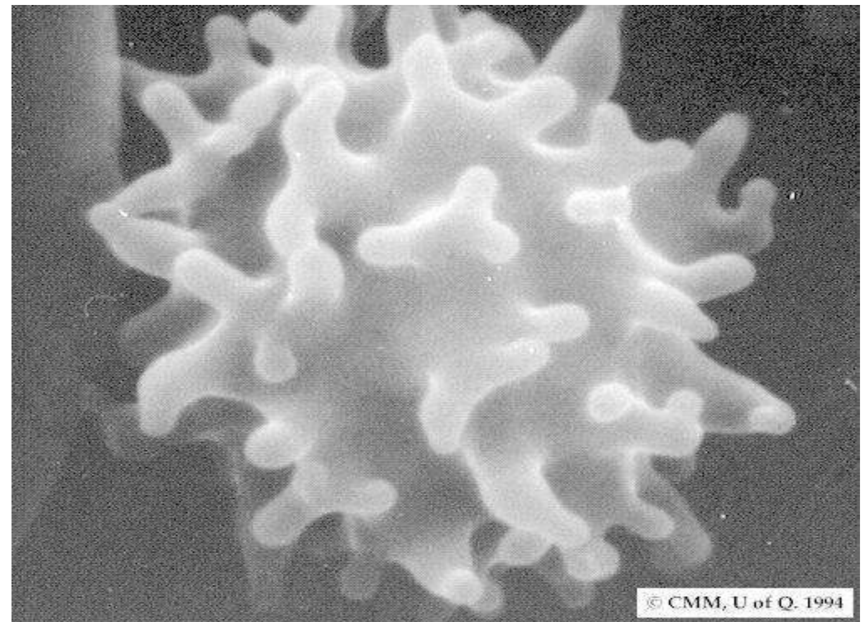


Polymer Hydrogel Surface



Wood Fibers





➢ Advantages:

1- Bulk-samples can be observed and larger sample area can be viewed,

2- generates photo-like images,

3- very high-resolution images are possible

4- SEM can yield valuable information regarding the purity as well as degree of aggregation

➢ Disadvantages:

1- Samples must have surface electrical conductivity

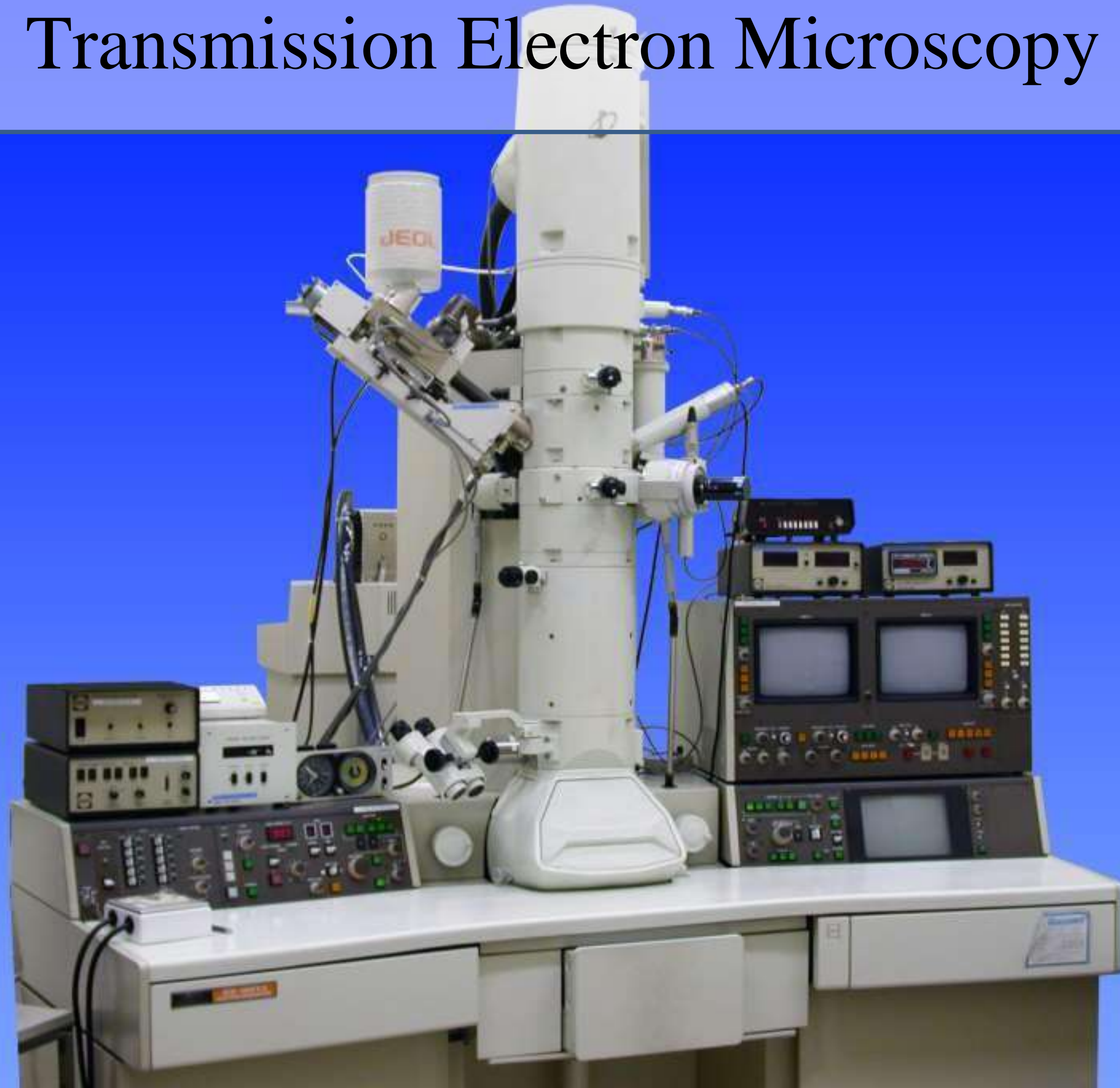
2- non- conductive samples need to be coated with a conductive Layer

3- Time consuming & expensive.

4- Sometimes it is not possible to clearly differentiate nanoparticle from the substrate.

5- SEM can't resolve the internal structure of these domains.

Transmission Electron Microscopy



❖ *What can we see with a TEM?*

-Morphology

- Shape, size, order of particles in sample

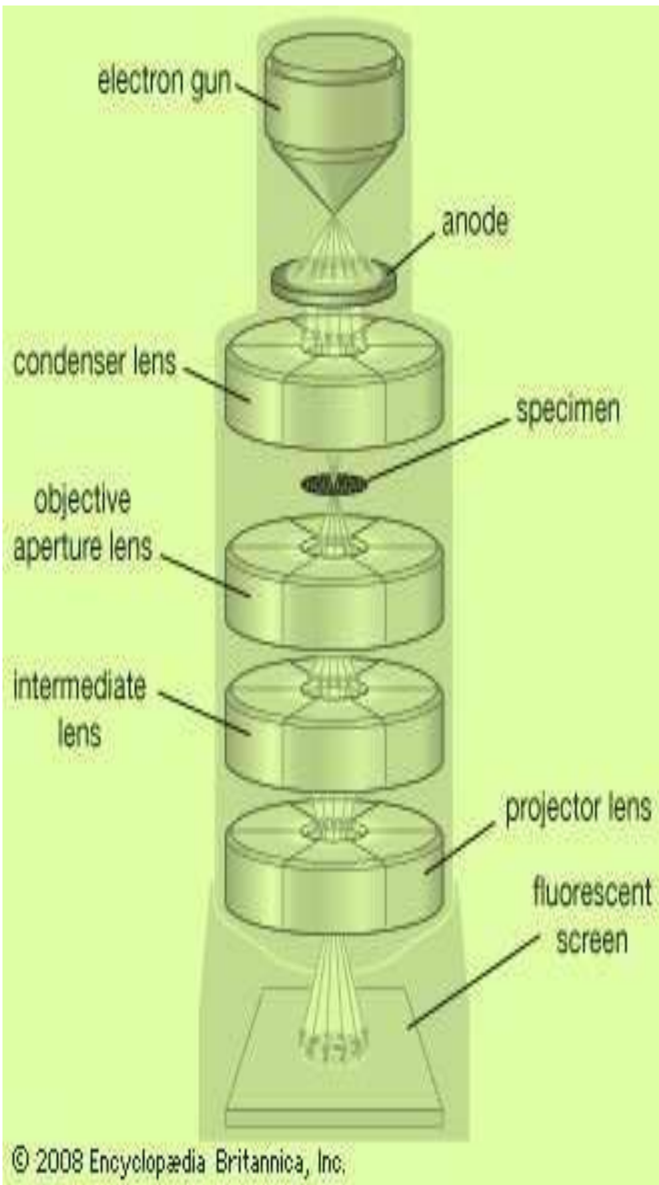
-Crystalline Structure

- Arrangement of atoms in the sample
- Defects in crystalline structure

-Composition

- Elemental composition of the sample

Basic principle



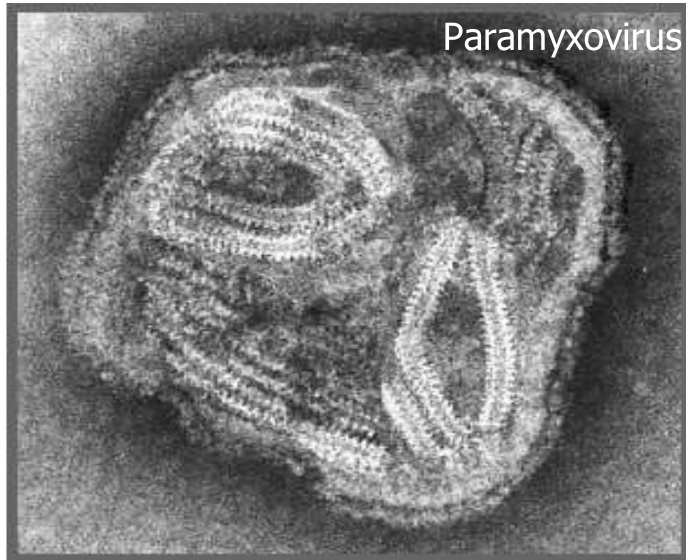
The crystalline sample interacts with the electron beam mostly by diffraction rather than by absorption.

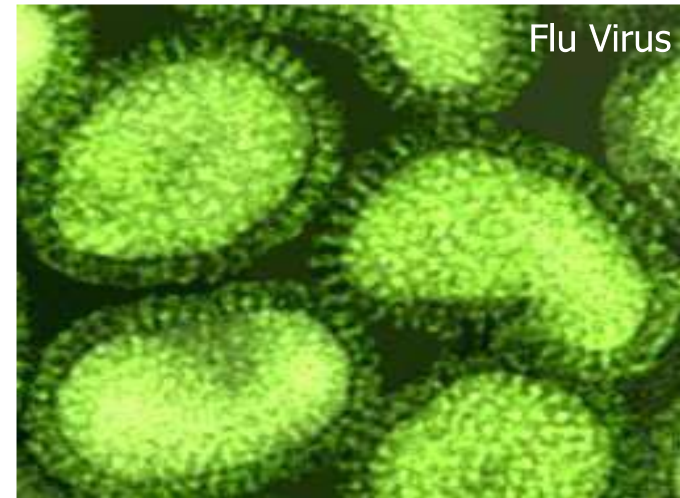
The intensity of the diffraction depends on the orientation of the planes of atoms in a crystal relative to the electron beam.

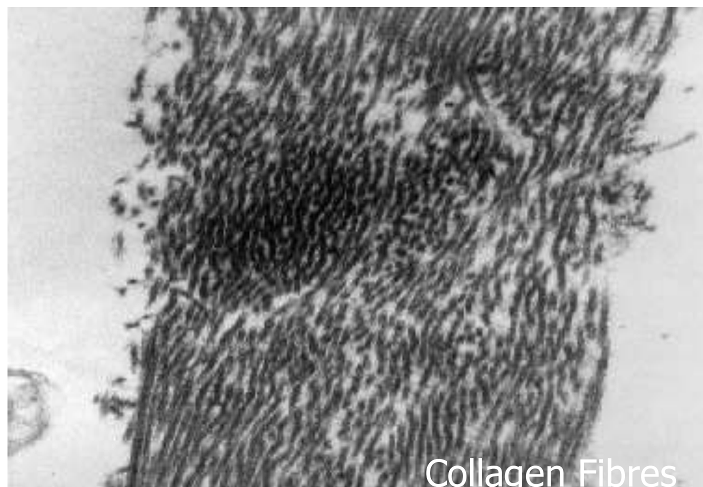
A high contrast image can be formed by blocking deflected electrons which produces a variation in the electron intensity that reveals information on the crystal structure.

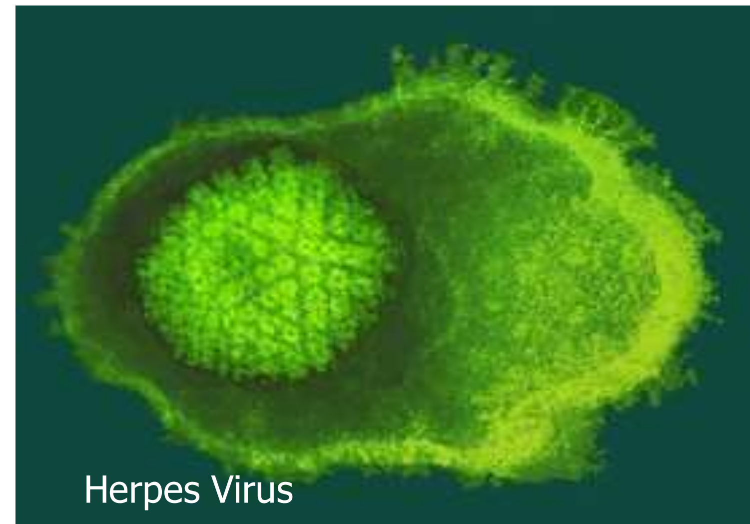
This can generate both 'bright or light field' & 'dark field' images.

Transmission Electron Microscopy

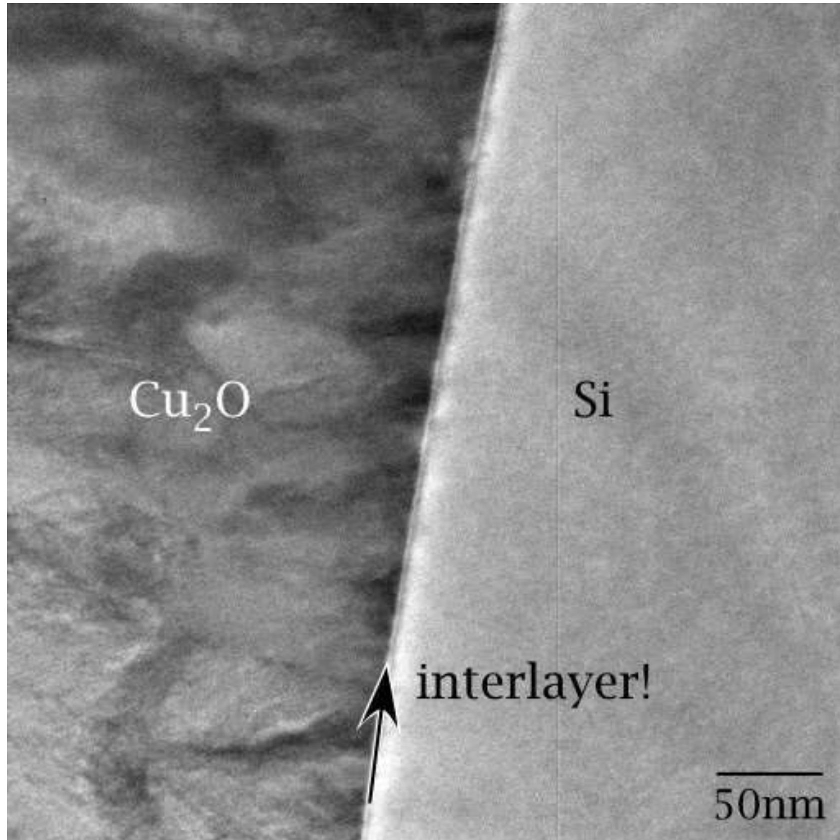




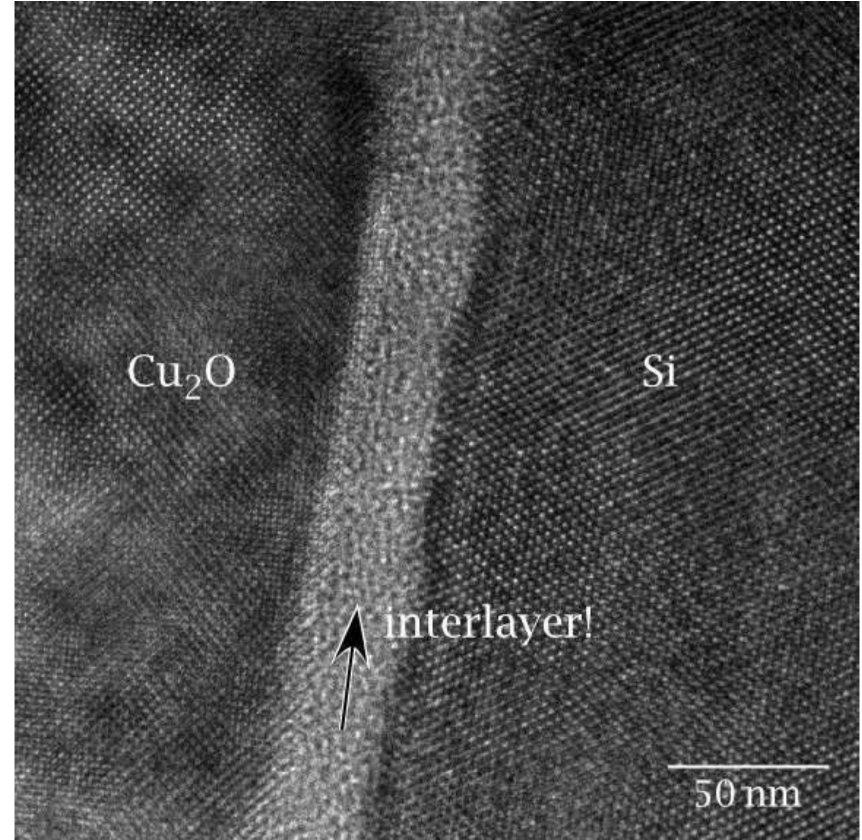




TEM comparison

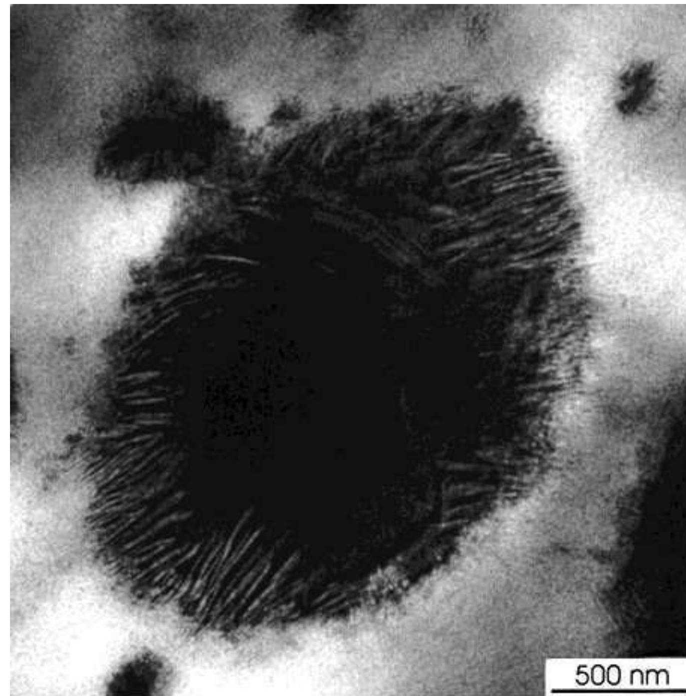


Standard TEM

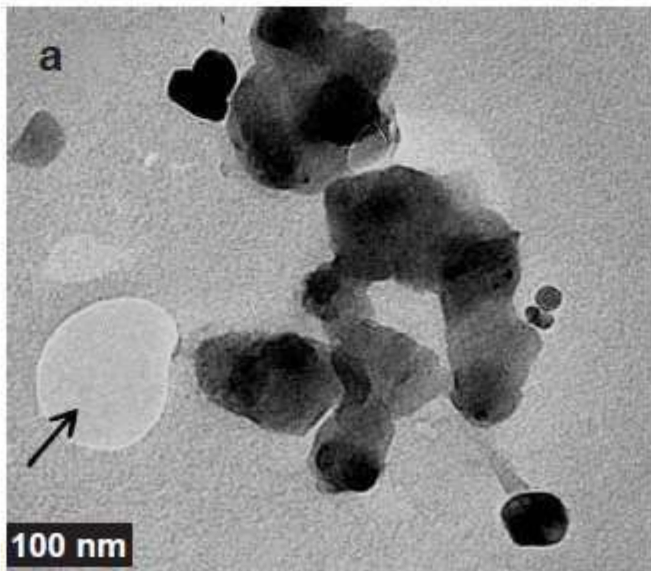


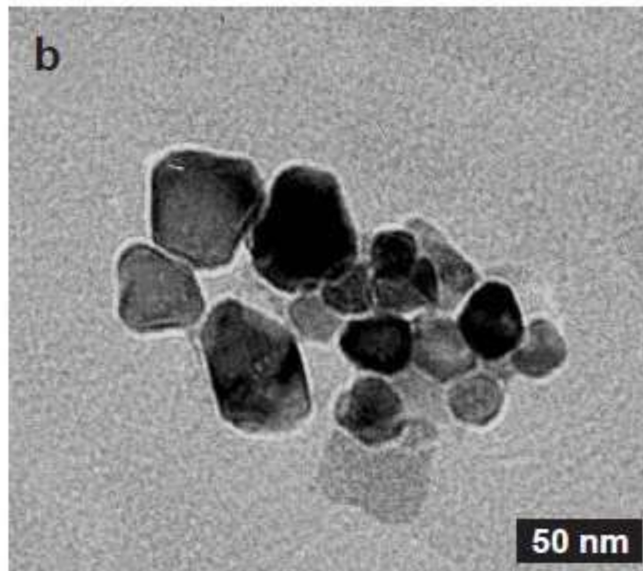
High resolution TEM

TEM Micrographs



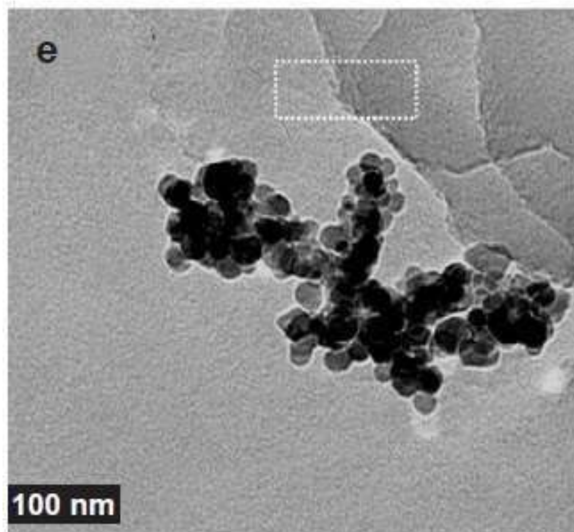
Isotactic Polypropylene Particle

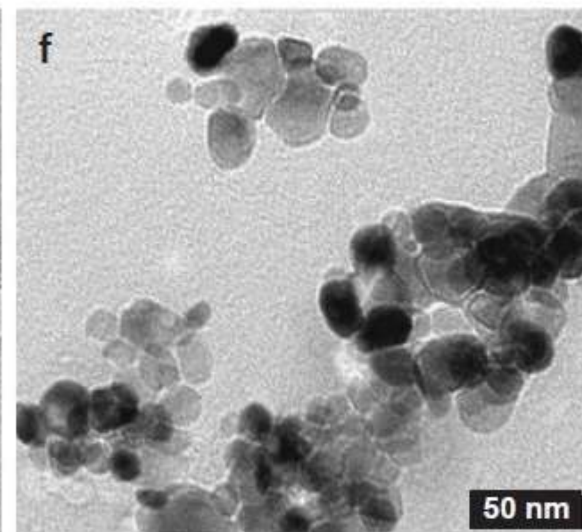




Large Ceria Nanoparticles

Small Ceria Nanoparticles





* Advantages:

1- Additional analysis techniques like X-ray spectrometry are possible with the STEM.

2- high- resolution

3- (3-D) image construction possible but aberrant.

4- Changes in nanoparticle structure as a result of interactions with gas, liquid & solid-phase substrates can also be monitored.

* Disadvantages :

1- Sample must be able to withstand the electron beam & also the high vacuum chamber.

2- sample preparation necessary, mostly used for 2-D images.

3- Time consuming.

SEM vs TEM

SEM	TEM
-High Resolution of bulk specimens (no need to make sample thin)	-High Resolution of thin specimens
-20 - 50 Å: most commercial instruments (less than 10 Å for research instruments)	-1.2 - 1.5 Å: most commercial instruments
-3-D appearance of the specimen image as a result of the large depth of field (depth of focus)	-No 3-D appearance of the specimen image
-Capable of very low magnifications complementing the information available from the optical image	-Technique that provides crystallographic/structural information (lattice arrangement, orientation relationships, dislocations, twins...)

➢ Synthesis and optical characterization of copper oxide nanoparticles:

SEM and TEM study

-**Figure 2** shows the SEM image of as prepared CuO nanoparticles. It shows that the CuO nanoparticles are in rectangular shape.

-Figure 3 (a) shows the TEM image of as prepared nanoparticles. The size of particle observed in TEM image is in the range of 5-6 nm which is in good agreement with calculated by Scherrer formula using XRD. Figure 3 (b) shows the selected area diffraction pattern (SAED) of as prepared CuO nanoparticles. It shows that the particles are well crystallized.

-The diffraction rings on SAED image matches with the peaks in XRD pattern which also proves the monoclinic structure of as prepared CuO nanoparticles [18]

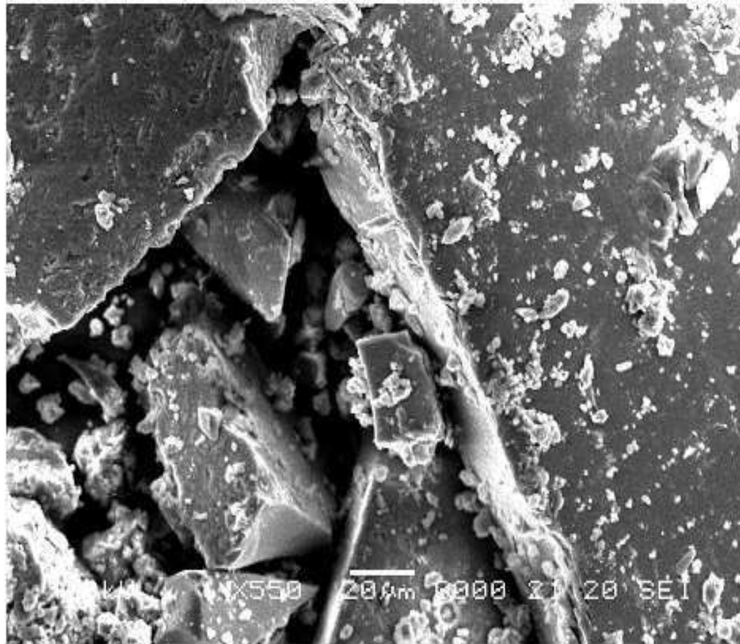


Fig. 2: SEM image of as prepared CuO nanoparticles.

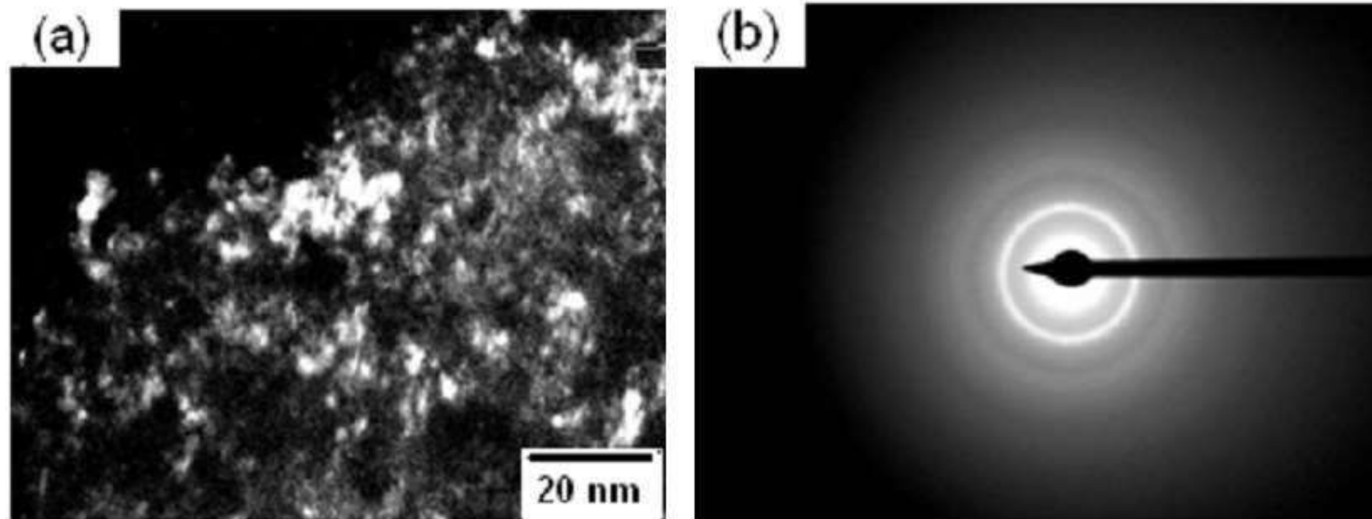


Fig.3: (a) TEM image, (b) SAED pattern of as prepared CuO Nanoparticles.

Scanning Tunneling Microscopy

Basic principle

It is based on the concept of quantum tunneling. When a conducting tip is brought very near to a metallic or semi-conducting surface, a bias between the two can allow electrons to tunnel through the vacuum between them

Variations in tunneling current as the probe passes over the surface are translated into an image.

They normally generate image by holding the current between the tip of the electrode & the specimen at some constant value by using a piezoelectric crystal to adjust the distance between the tip & the specimen surface

Control voltages for piezotube

Piezoelectric tube with electrodes

Tunneling current amplifier

Distance control and scanning unit

Tip

Sample

Tunneling voltage

Data processing and display

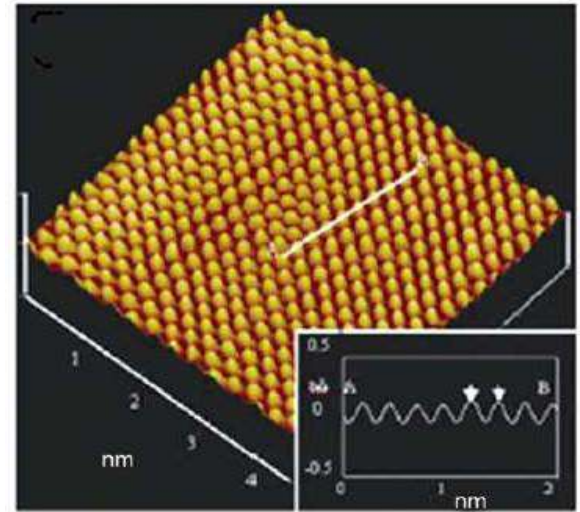
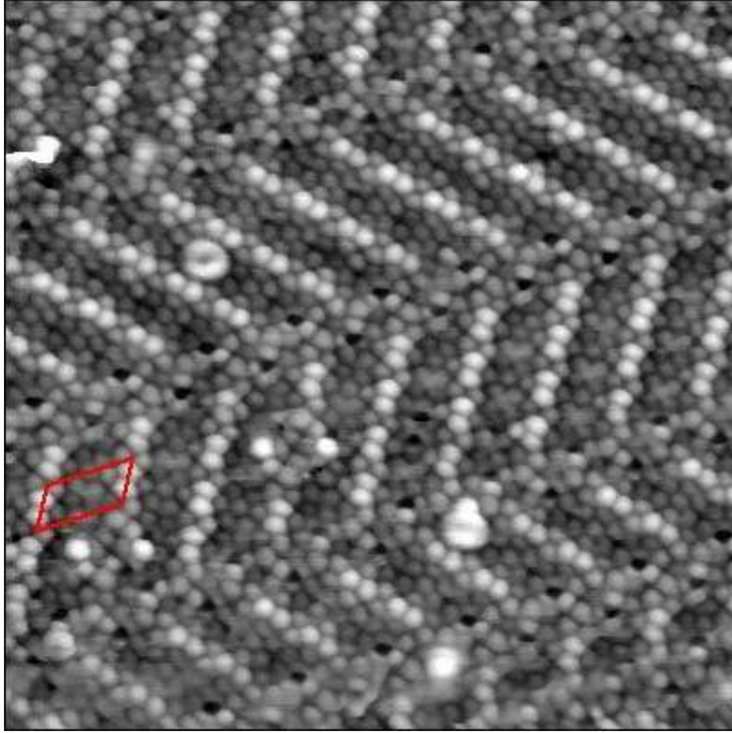
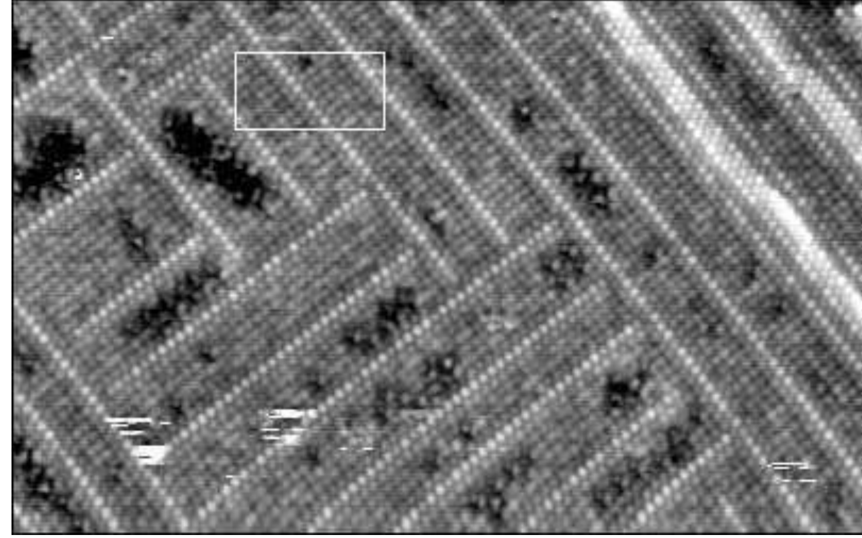


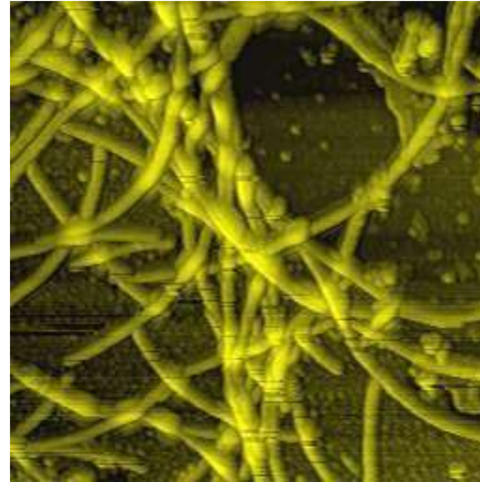
Fig. Highly oriented pyrolytic graphite sheet under STM

Lateral resolution ~ 0.1 nm **Depth resolution ~ 0.01 nm**

STM Images







➢ Advantages:

1- Very high image resolution (capable of „seeing‟ and manipulating atoms).

2- STM can be used not only in ultra high vacuum but also in air & various other liquid or gas, at ambient & wide range of temperature.

➢ *Disadvantages* :

1- Again

2- radius of curvature of tip

3- extremely sensitive to ambient vibrations

4- STM can be a challenging technique, as it requires extremely clean surfaces & sharp tips.

❖ Spectroscopy

1- X-ray Diffraction (XRD)
2- Small Angle X-ray Scattering (SAXS)
3- X-ray Photoelectron Spectroscopy (XPS)
4- UV-vis spectroscopy
5- FT-IR spectroscopy

Optical Spectroscopy

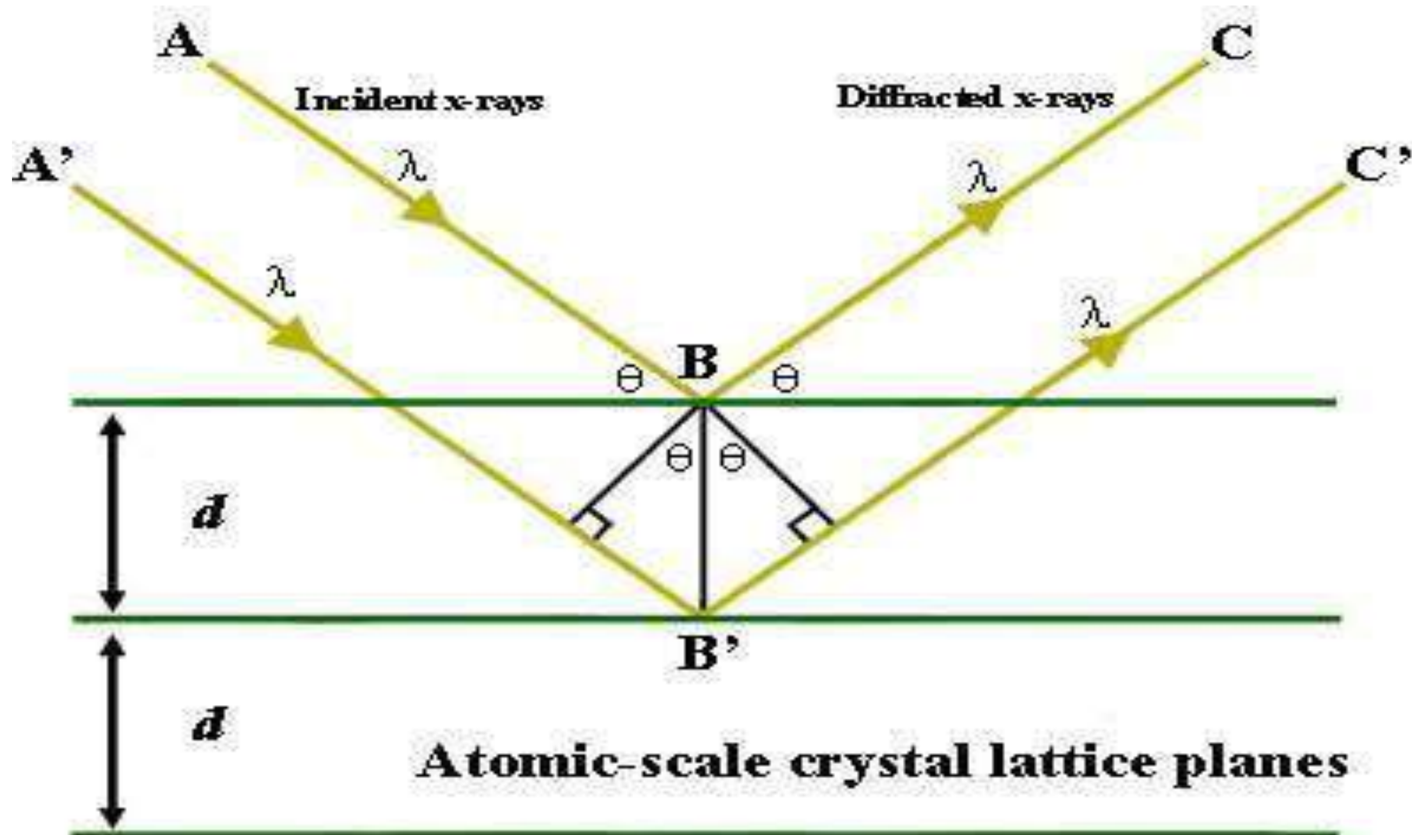
Optical spectroscopy uses the interaction of light with matter as a function of wavelength or energy in order to obtain information about the material.

Typical penetration depth is of the order of 50 nm. Optical spectroscopy is attractive for materials characterization because it is fast, nondestructive and of high resolution.

X-ray Diffraction

XRD can be used to look at various characteristics of the single crystal or polycrystalline materials using Bragg's Law ,

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



X-ray Diffraction XRD

Characterizations

1. Lattice constant
2. d-spacing
3. crystal structure
4. Thickness (films)
5. sample orientation
6. Particle Size (grains)

XRD is time consuming and requires a large volume of sample.

"Smaller crystals produce broader XRD peaks"

Scherrer's Formula

$$t = \frac{K\lambda}{B\cos\theta}$$

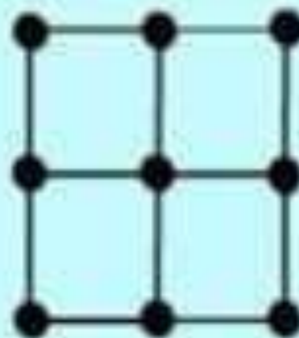
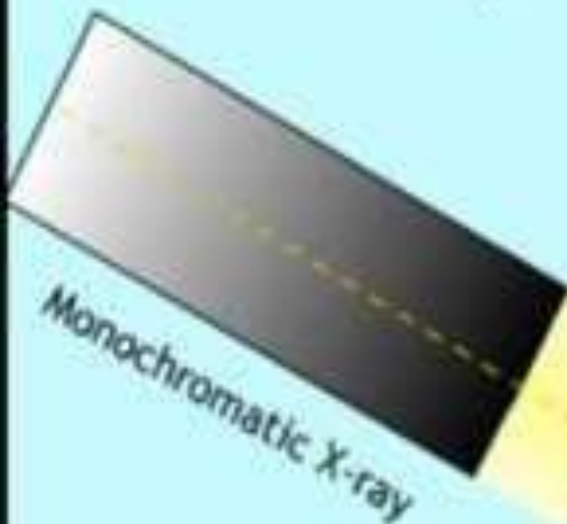
t- thickness of crystallite

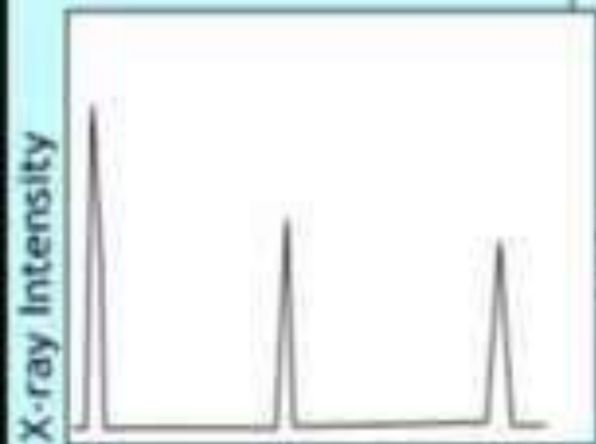
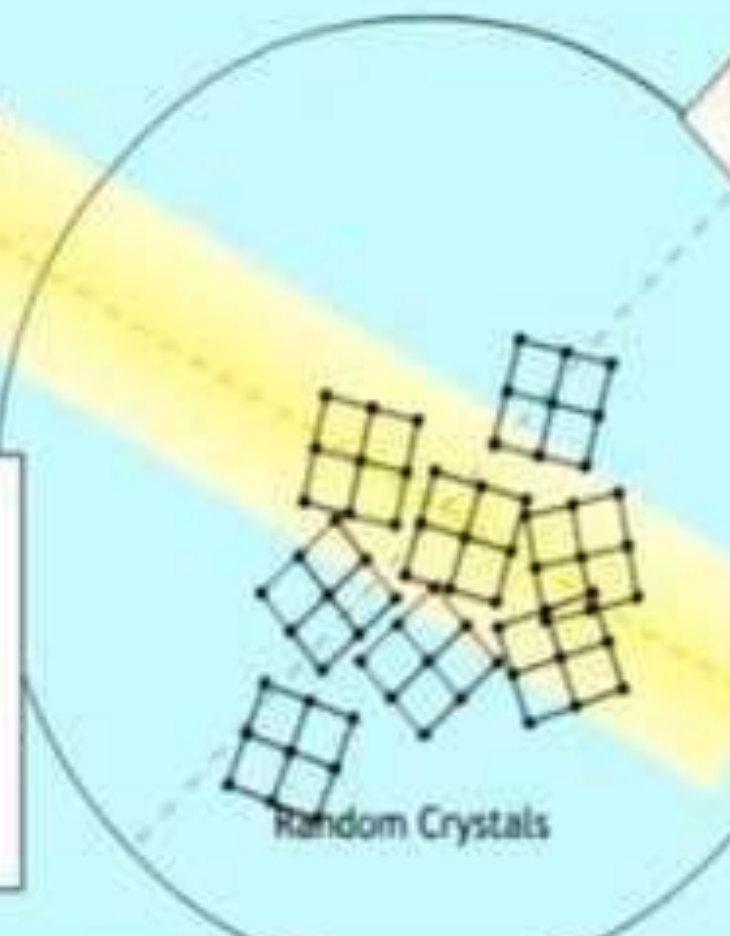
K- shape constant

λ- wavelength

B- FWHM

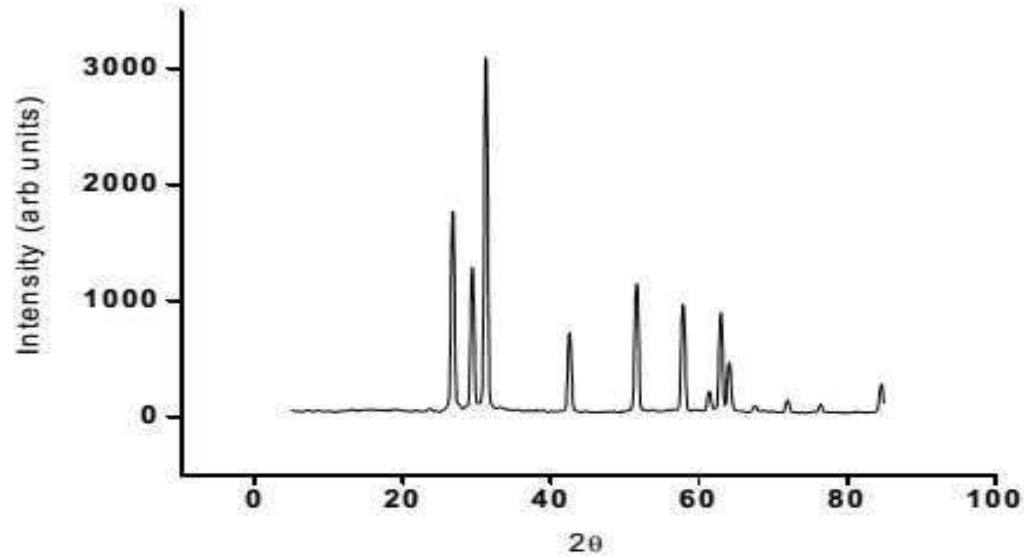
θ- Bragg Angle

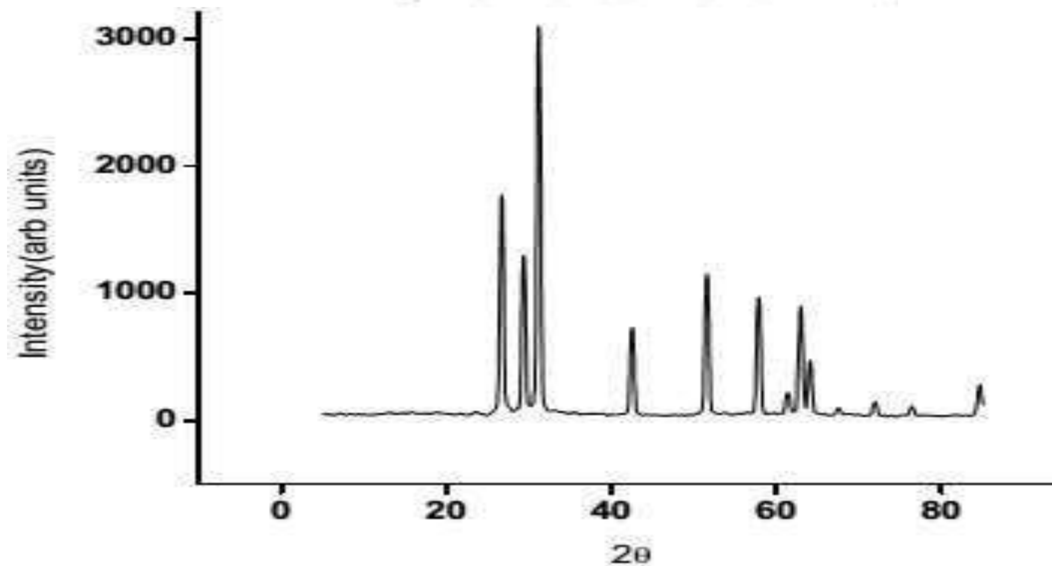



- X-ray interactions depends on the number of atom on a plane. This is why only specific planes would cause diffraction.

Example of ZnO :

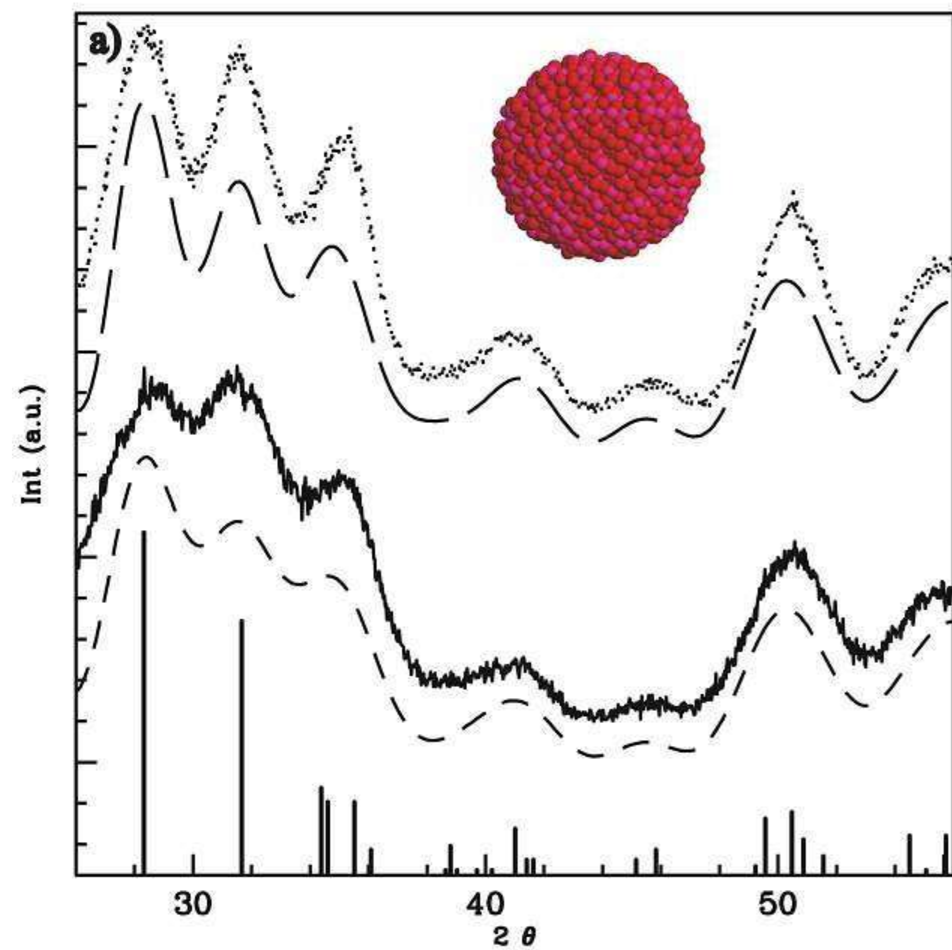


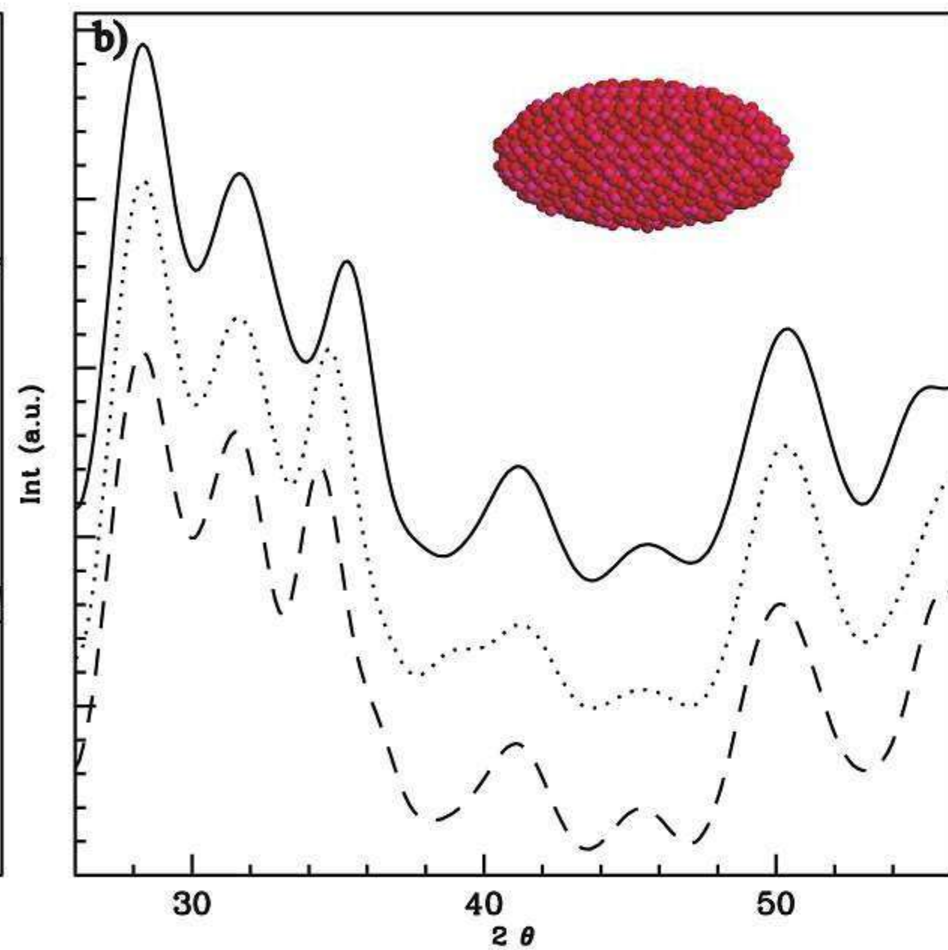
XRD pattern of commercial ZnO



XRD pattern of ZnO prepared in polyvinyl alcohol medium

Example : HfO2





Small Angle X-ray Scattering SAXS

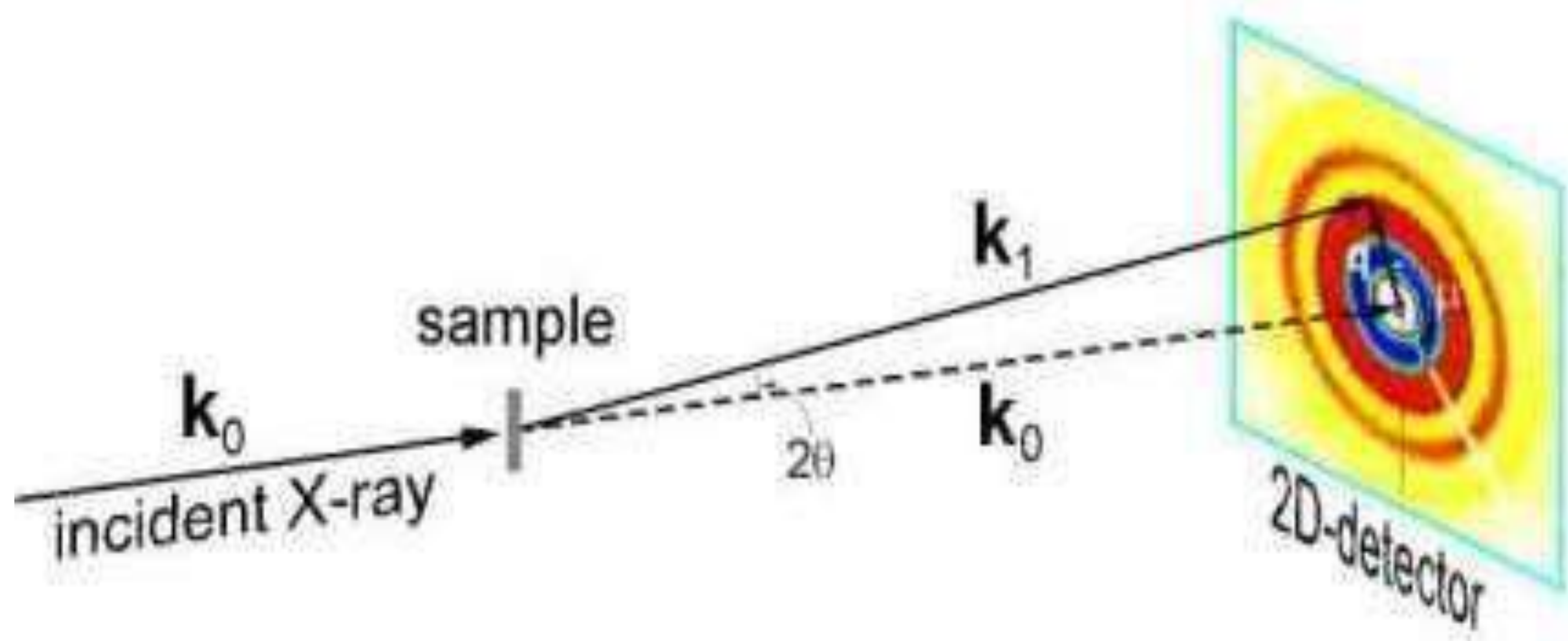
"SAXS is the scattering due to the existence of inhomogeneity regions of sizes of several nanometers to several tens nanometers."

Characterization

1. **Particle Size**
2. **Specific Surface Area**
3. **Morphology**
4. **Porosity**

- **Fluctuations in electron density over lengths on the order of 10nm or larger can be sufficient to produce an appreciable scattered X-ray densities at angles $2\theta < 5^0$**

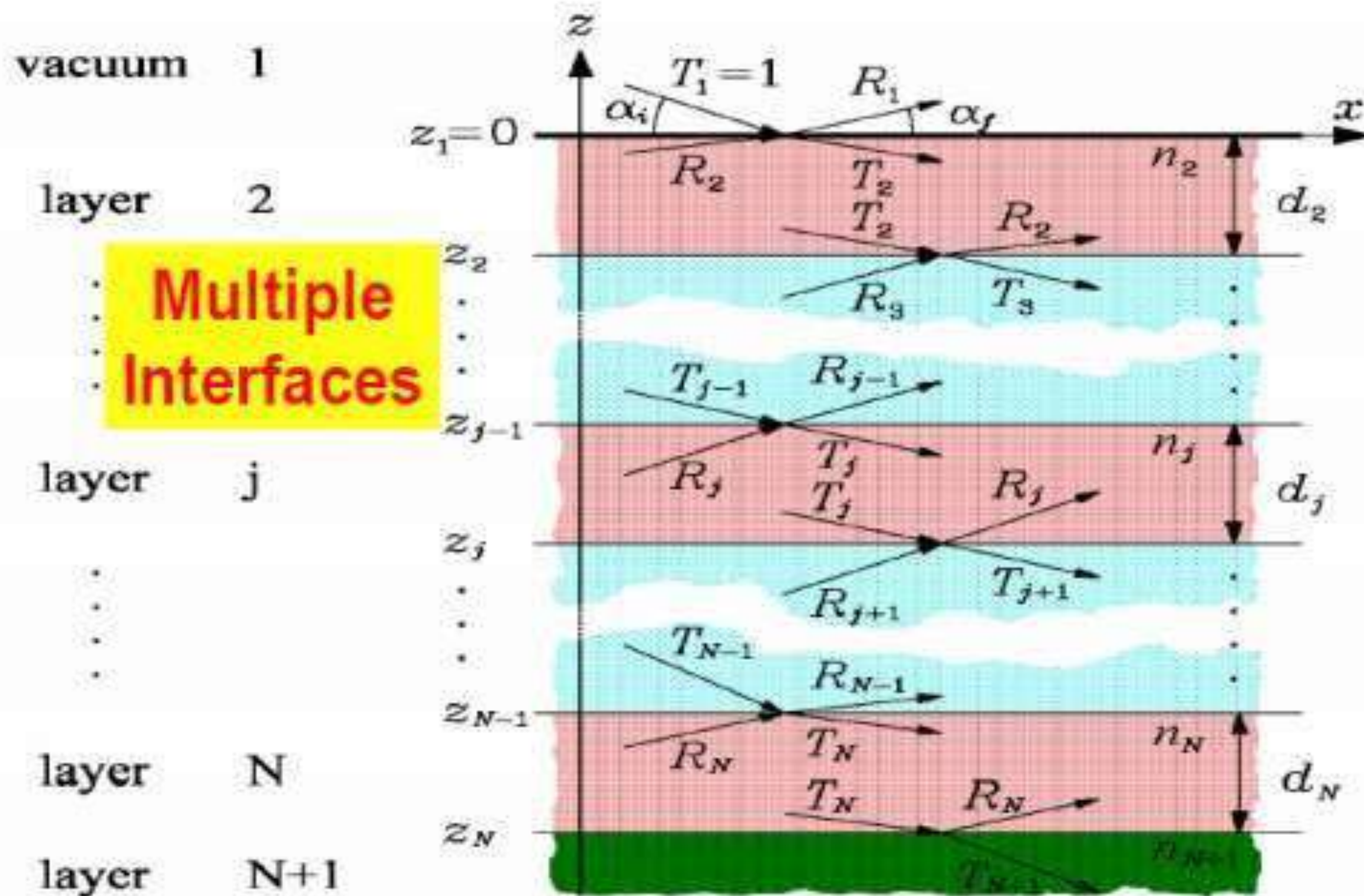
- It is capable of delivering structural information of molecules between 5 and 25 nm. Of repeated distances in partially ordered systems of up to 150 nm.



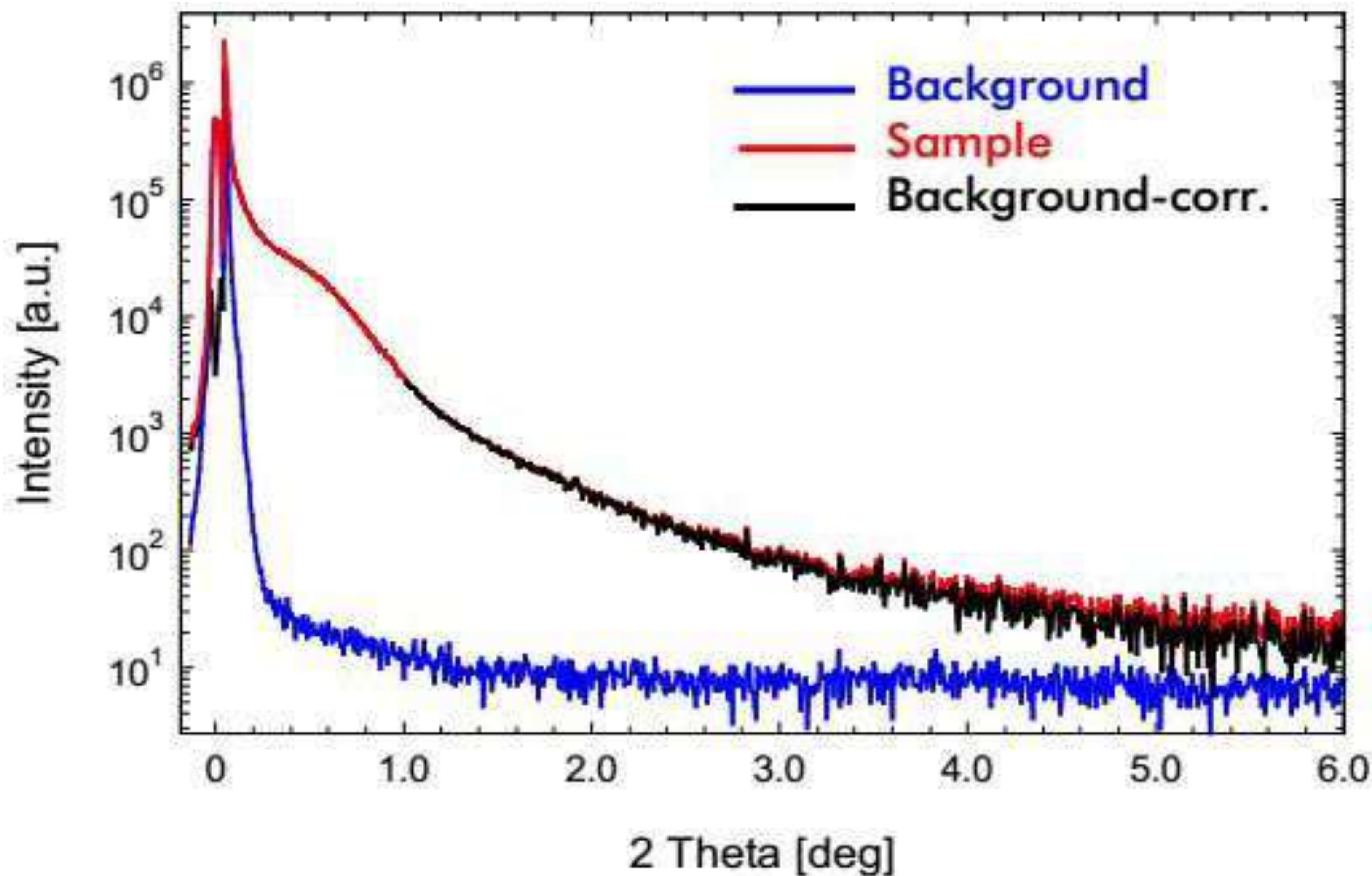
sample
$\mathbf{k}_0$
incident X-ray
$\mathbf{k}_1$
$\mathbf{k}_0$
2θ
2D-detector

Reflectivity from multilayers

Multiple scattering



Example : **SAXS data from a titania nanopowder, before and after background correction, together with the background measurement. In this comparison, the data are already corrected for absorption by the sample .**



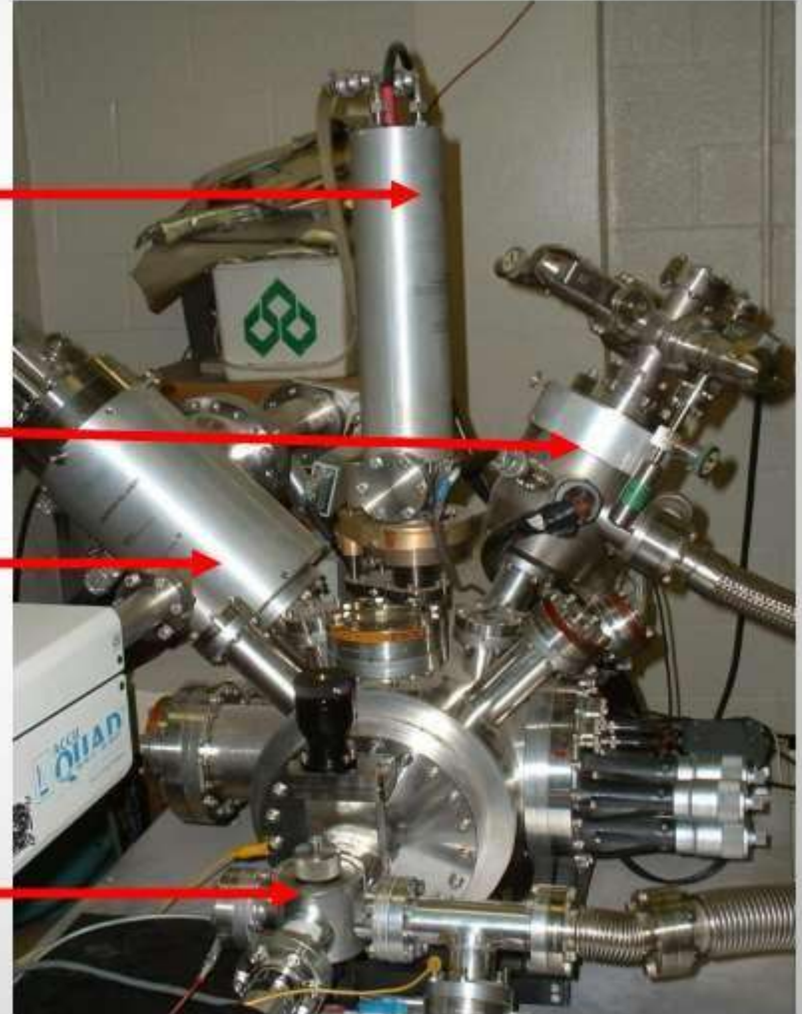
X-ray Photoelectron Spectroscopy XPS

X-Ray Source

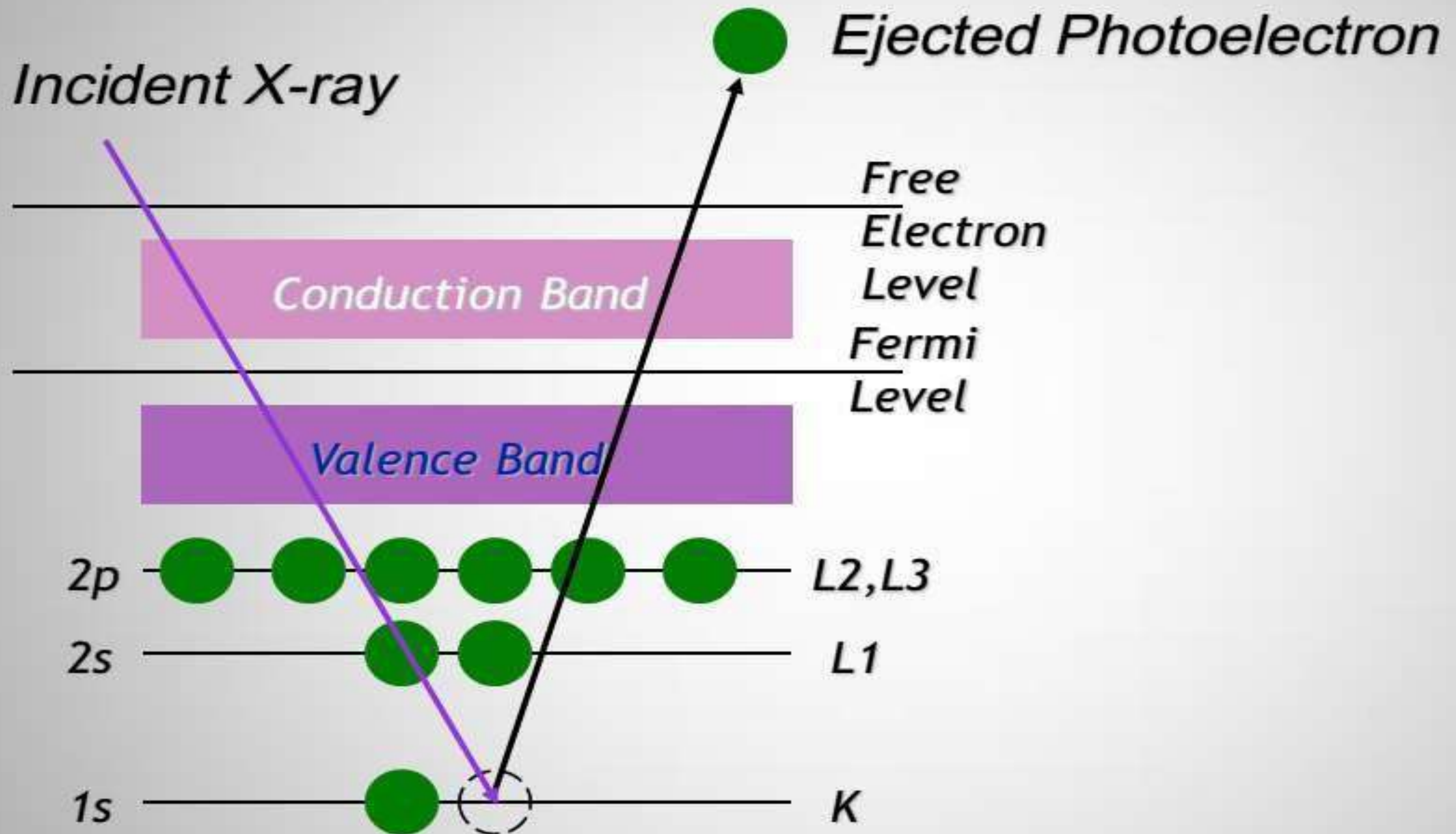
Ion Source

SIMS Analyzer

Sample introduction Chamber

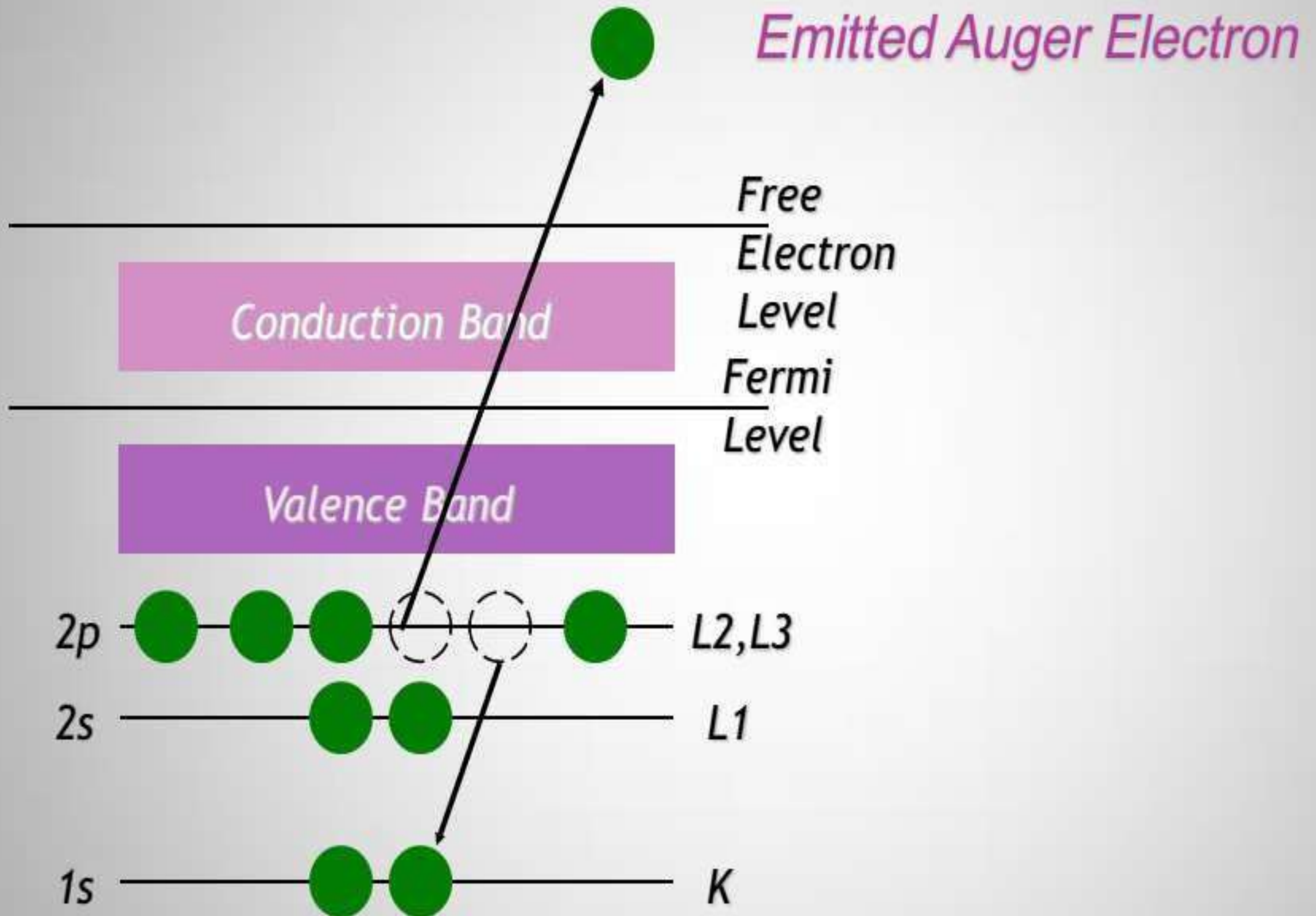


THE PHOTOELECTRIC PROCESS



- *Following this process, the atom will release energy by the emission of an Auger Electron.*

AUGER RELATION OF CORE HOLE



XPS 1S USED FOR :

- What elements and the quantity elements of the sample surface(1-12nm)
- What contamination in the surface or the bulk of the sample
- Empirical formula of a material
- The chemical state identification of the elements in the sample
- The binding energy of electronic states
- The thickness of different materials
- The density of electronic state

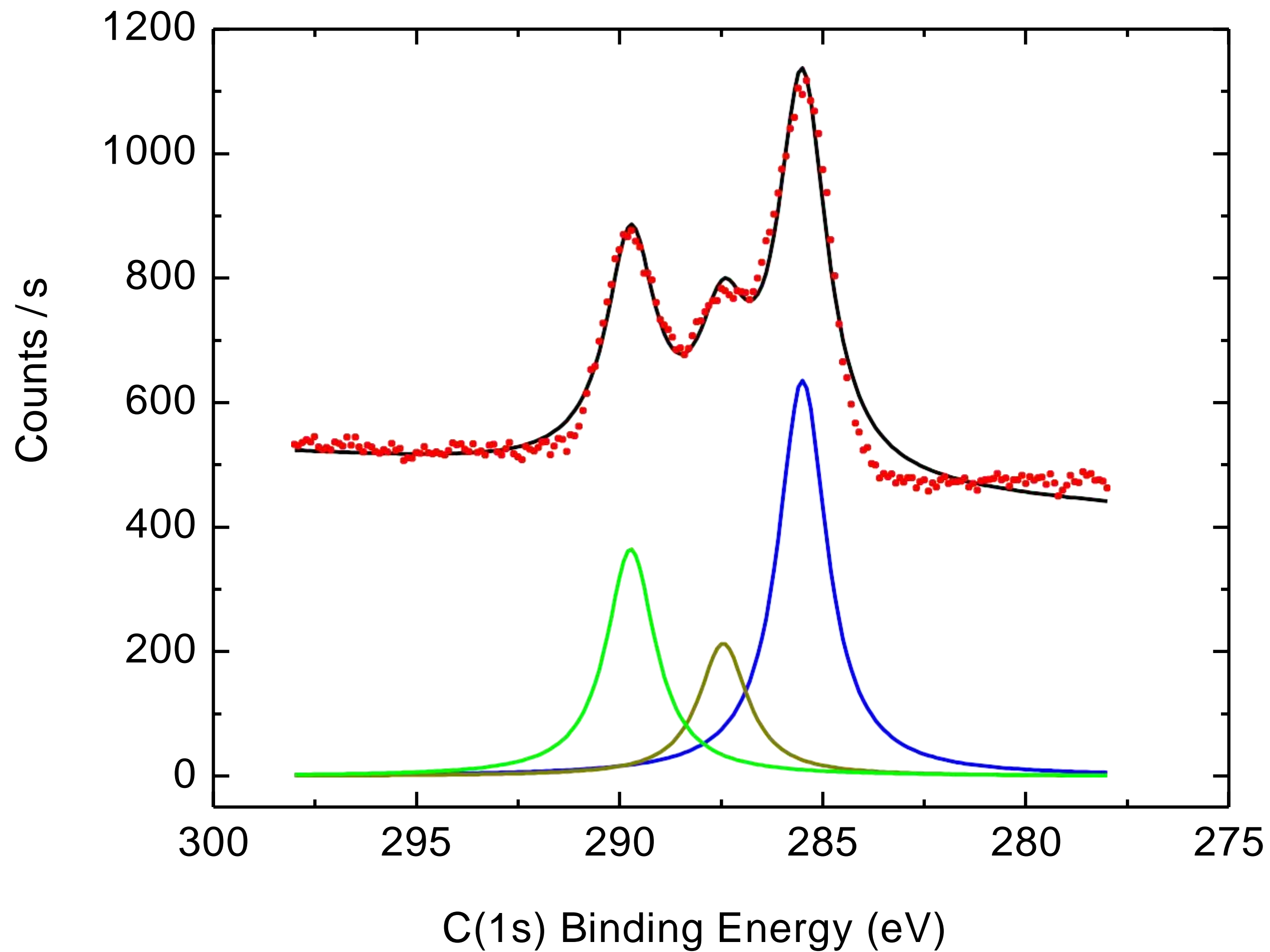
WHICH MATERIALS ARE ANALAZiED?

- XPS is routinely used to analyze inorganic compounds,metals,semiconductors,polymers, ceramics,etc.

- Organic chemicals are not routinely analyzed by XPS because they are readily degraded by either the energy of the X-rays or the heat from non-monochromatic X-ray sources

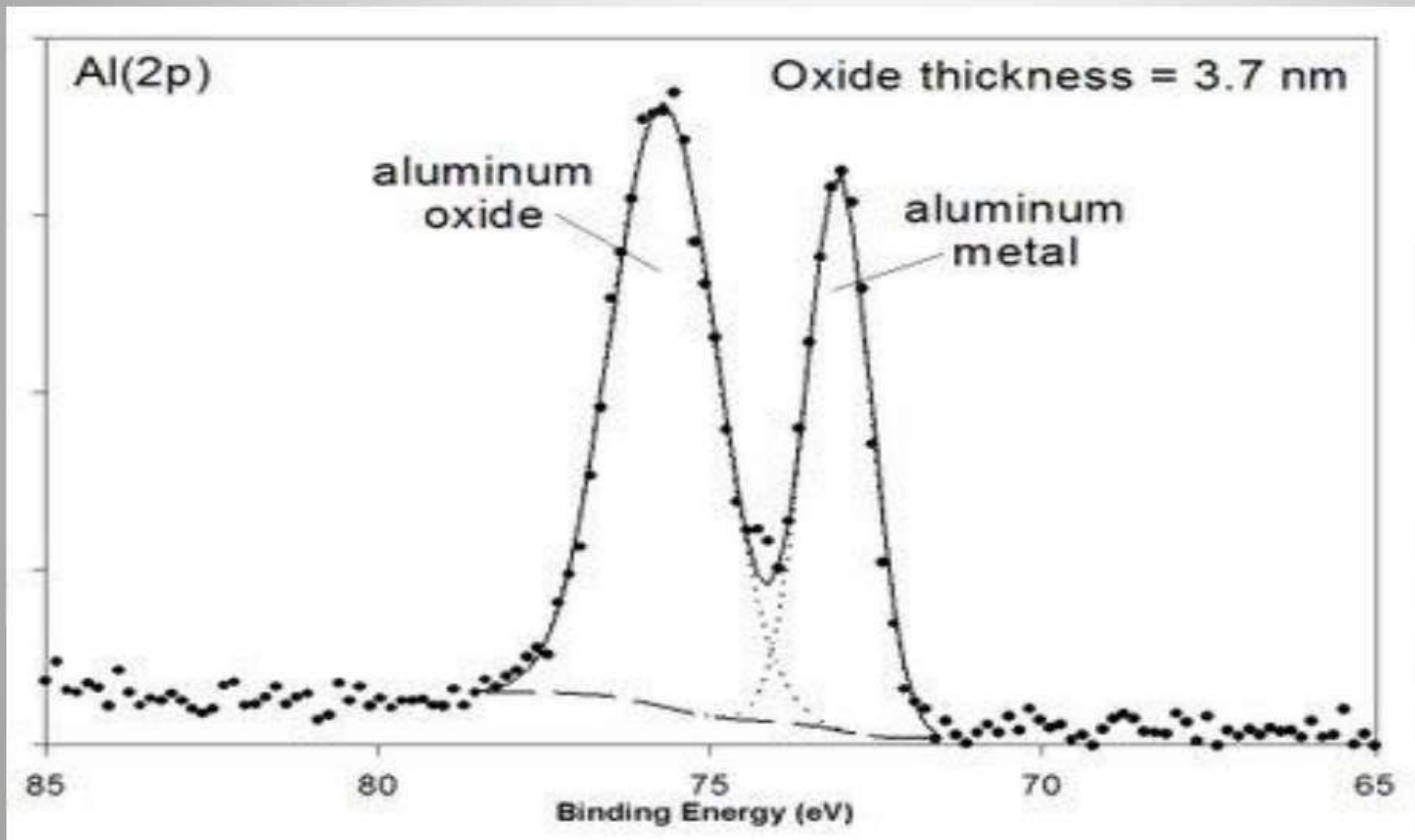
ANALYSIS OF XPS

- XPS detects all elements with (Z) >3. It cannot detect H (Z = 1) or He (Z = 2) because the diameter of these orbitals is so small, reducing the catch probability to almost zero

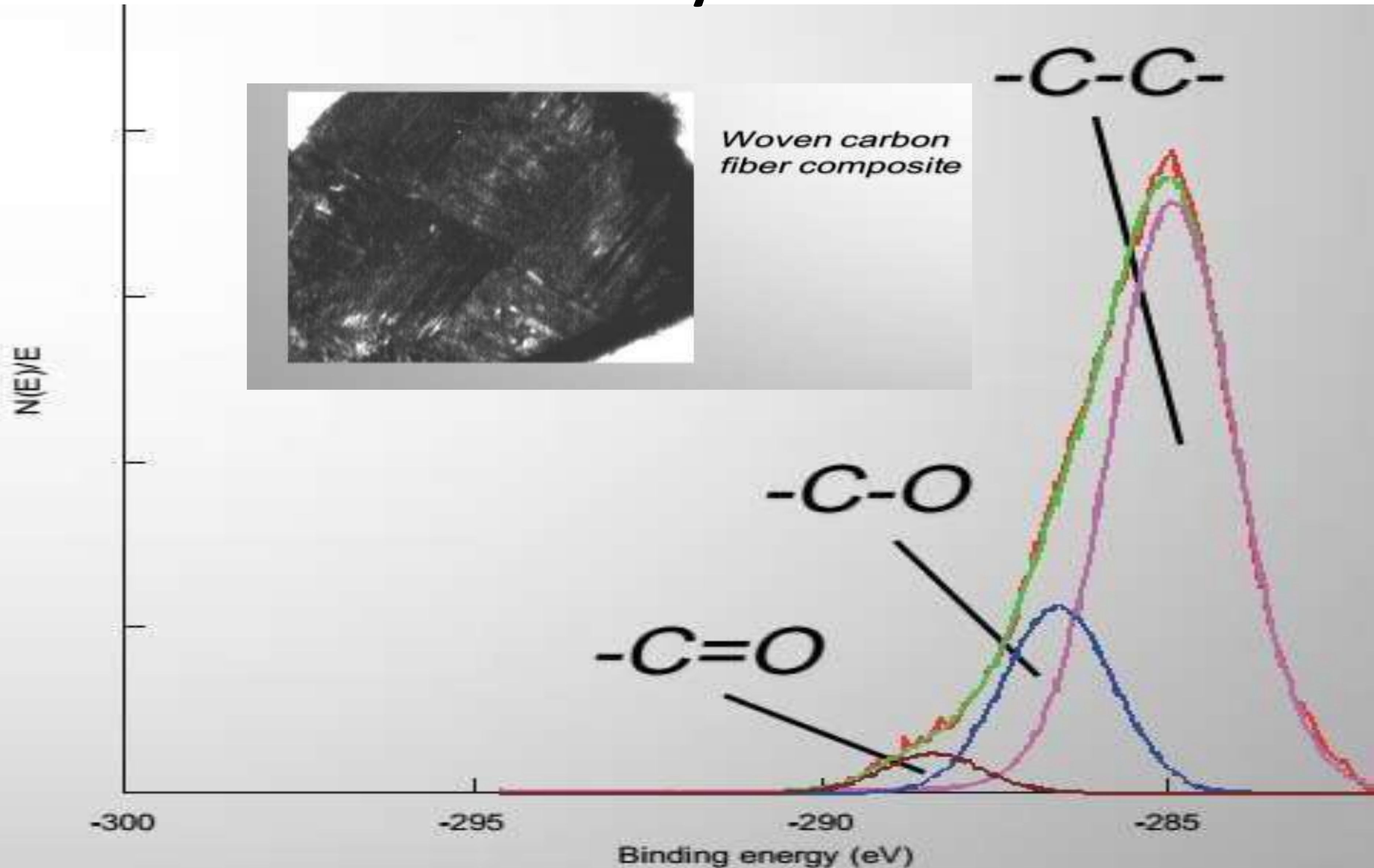


Peak	Position	Area	% C1s	Carbon- ID
1	285.50	1457.1	52%	*Pristine C_{60}*
2	287.45	489.75	18%	Mono-oxidized C
3	289.73	836.67	30%	Di-oxidized C

For example:determination of aluminum oxide thickness with xps



Analysis of carbon fiber – polymer composite material by XPS



UV-vis spectroscopy

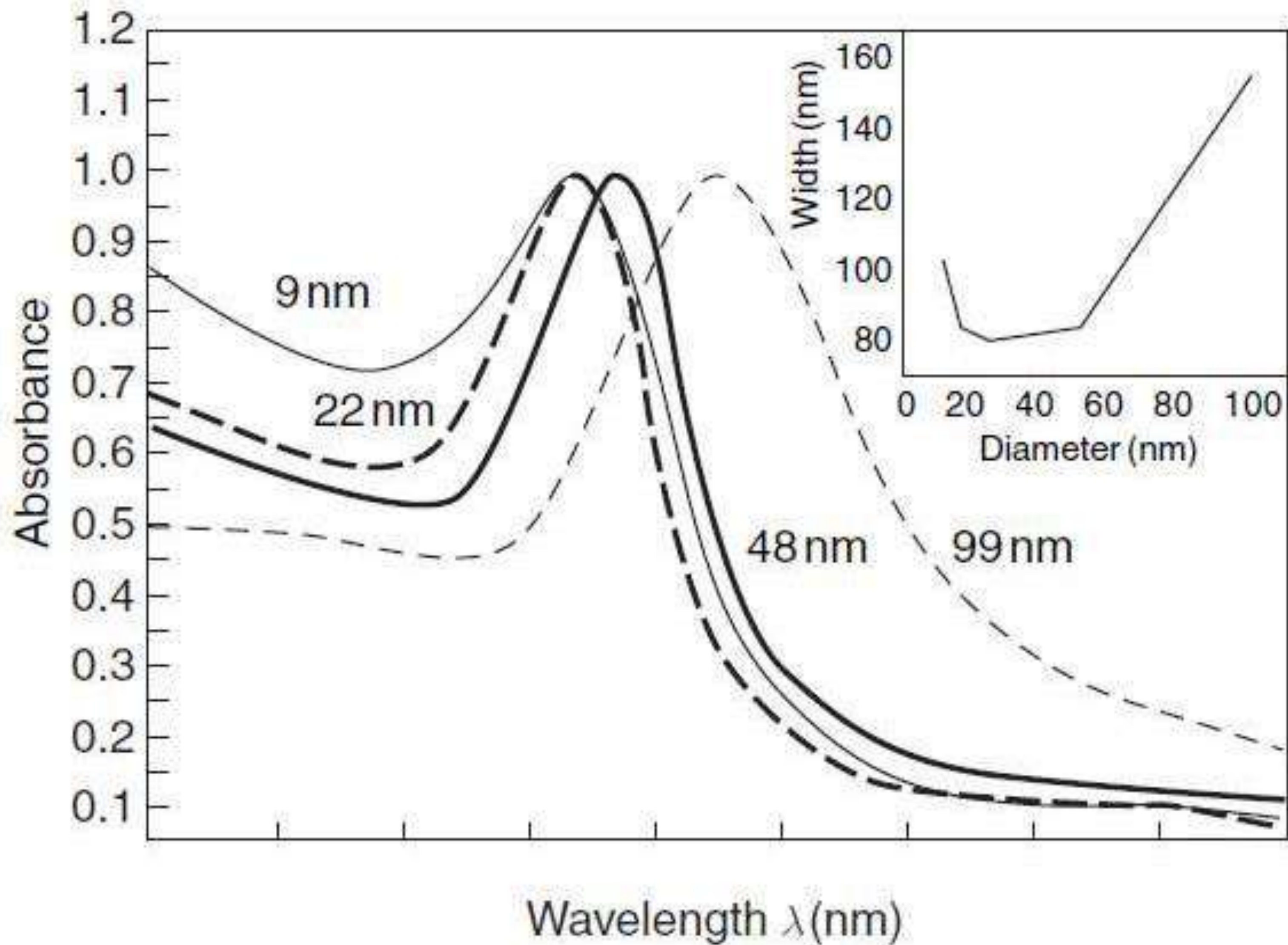
This technique involves the absorption of near-UV or visible light. One measures both intensity and wavelength. It is usually applied to molecules and inorganic ions in solution.

Broad features makes it not ideal for sample identification. However, one can determine the analyte concentration from absorbance at one wavelength and using the Beer-Lambert law:

$$A = -\log(\frac{I}{I_0}) = a \times b \times c,$$

.where a = absorbance, b = path length, and c = concentration

EXAMPLE GOLD :



Infrared Spectroscopy FT-IR

What is the principle behind IR spectroscopy?

Firstly, molecules and crystals can be thought of as systems of balls (atoms or ions) connected by springs (chemical bonds).

These systems can be set into vibration, and vibrate with frequencies determined by the mass of the balls (atomic weight) and by the stiffness of the springs (bond strength).

With these oscillations of the system, a impinging beam of infrared EMR could couple with it and be absorbed.

These absorption frequencies represent excitations of vibrations of the chemical bonds and, thus, are specific to the type of bond and the group of atoms involved in the vibration.

In an infrared experiment, the intensity of a beam of IR is measured before and after it interacts with the sample as a function of light frequency.

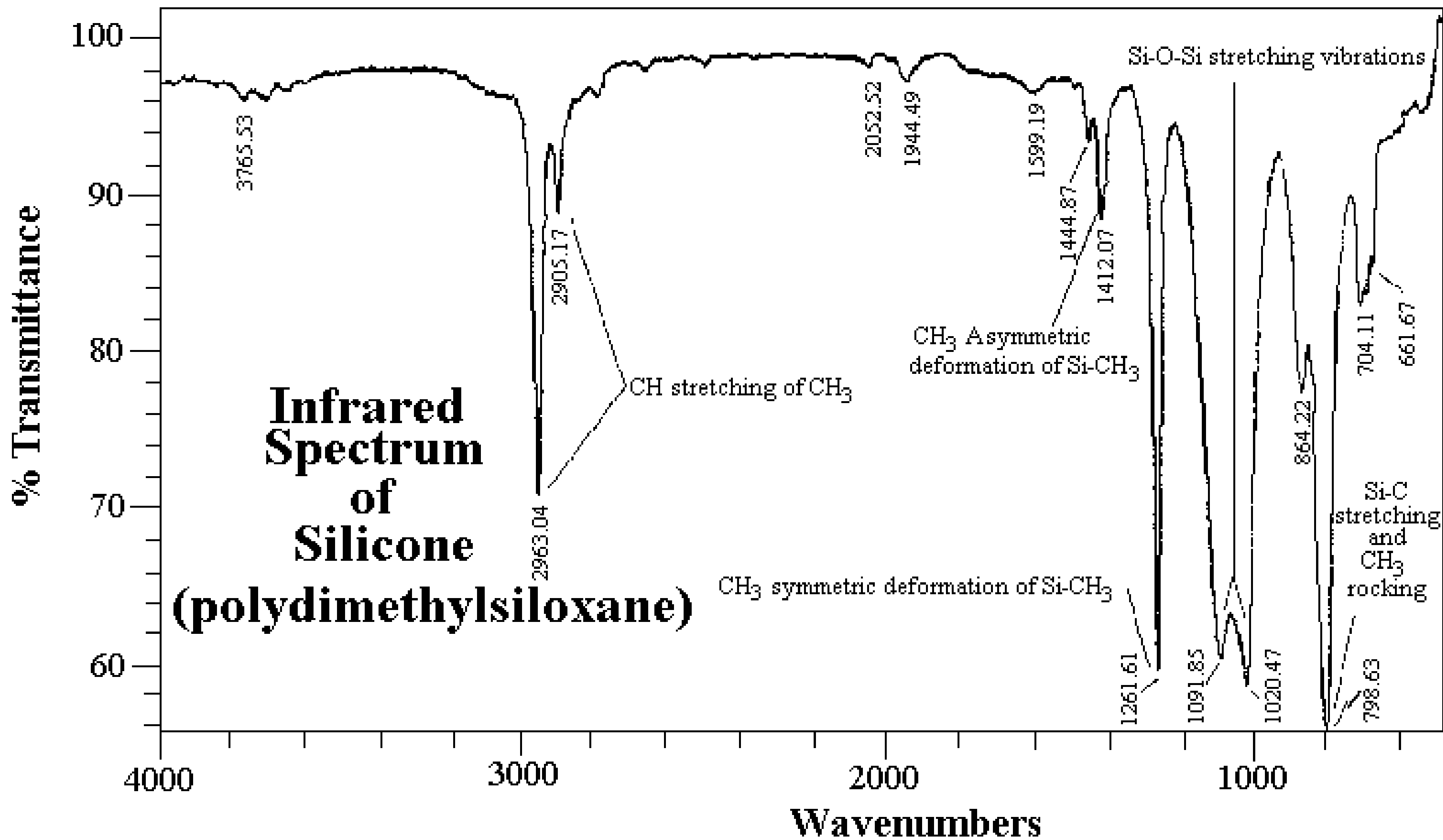
Infrared Spectroscopy FT-IR

Characterization:

1. Compositional
2. Concentration
3. Atomic Structure
4. surrounding environmentsor atomic arrangement

- The mechanical molecular and crystal vibrations are at very high frequencies ranging from 10^{12} to 10^{14} Hz (3-300µm wavelength), which is in the infrared (IR) regions of the electromagnetic spectrum.

- The oscillations induced by certain vibrational frequencies provide a means for matter to couple with an impinging beam of infrared electromagnetic radiation and to exchange energy with it when frequencies are in resonance.


Infrared Spectrum of Silicone (polydimethylsiloxane)
% Transmittance
Wavenumbers
100
90
80
70
60
4000
3000
2000
1000
3765.53
2963.04
2905.17
CH stretching of CH3
2052.52
1944.49
1599.19
1444.87
1412.07
CH3 Asymmetric deformation of Si-CH3
Si-O-Si stretching vibrations
CH3 symmetric deformation of Si-CH3
1261.61
1091.85
1020.47
864.22
798.63
704.11
661.67
Si-C stretching and CH3 rocking

Characterization techniques

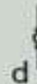
Types of Characterization Techniques

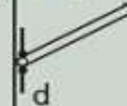
Near Field and Confocal Light Microscopy

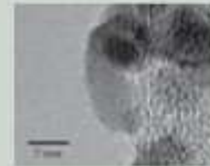
Size
Shape
Topography
3D image reconstruction (confocal)

Transmission Electron Microscope (TEM)

Size
Composition
Crystal structure (inferred)





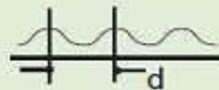


Scanning Electron Microscope (SEM)

Size and shape
Microstructure
Composition
Topography
Grain orientation

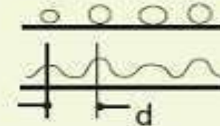
Xray

Size
Crystal
Strain



Atomic Force Microscopy (AFM)

Topography/surface profile
Surface mapping
Mechanical properties



Spectroscopy

Chemical composition
Chemical bonding

Thank you