MODULE – 05

Material Characterization Techniques and Instrumentation

Nano 1materials

Matter arranged by exercising control over lengths of one to hundred nano meter and the formulating structures exhibit characteristics that are specific to their size and dimensions, the resulting materials are called nano materials.

Nanocomposites

- A nanocomposite is as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm. These materials show differing in properties due to dissimilarities in structure and chemistry.
- The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ noticeably from that of the component materials.
- Size limits for these effects is <5 nm for catalytic activity, <20 nm for making a hard and soft magnetic material, <50 nm for refractive index changes, and <100 nm for achieving mechanical strengthening.

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The properties of materials can be different at the Nanoscale for two main reasons:

- Nanomaterials have a relatively larger surface to volume ratio when compared to bulk materials.
- Quantum effects can begin to dominate the behavior of matter at the nanoscale.

Types of nano materials based on dimensions

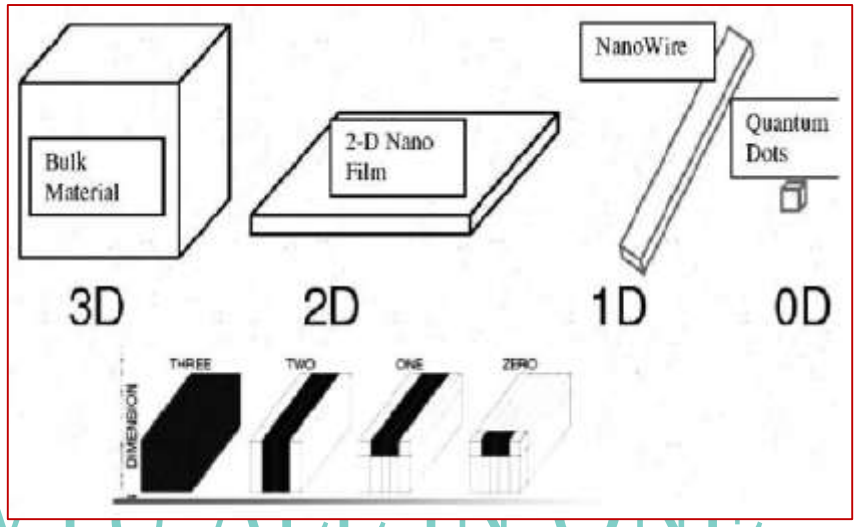
Based on dimensions the nano materials are classified into four types vary in size from 1 nm to 100 nm.

- **3D Bulk materials:** -The charge carriers can move in all the three directions and it has all parameter of length, breadth and height. (for example, Nano Particles).

- **2D films**- The movement of the charge carriers are confined to two directions and it has only length and breadth (for example, nano films and nanotubes)

- **1D quantum wire** –The movement of the charge carriers are restricted to one directions and it has only one parameter either length (or) breadth (or) height. (example: nano wires)

- **0D quantum dot –** The movement of the charge carriers are confined in all the three directions then the resulting structure is called quantum dot or nano particle and its length, breadth and heights are confined at single point. (for example, Quantum dots)



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Charge carriers are able to move in all directions in a 3-D material, confined to a plane in a film in only one direction in a quantum wire but in a 0-D structure they will remain confined to a very small space. The film, wire and dots have certain thickness for the material along the direction where we say the corresponding dimension is absent. The thickness is less than the mean free path for the electron in the material; this thickness will be in nanometer range.

The material along these directions exhibits mesoscopic properties.

Properties of nanomaterials

Due to the particle size in nano regime it affects many properties when compared to their bulk counterparts such as

- Melting point
- Boiling point
- Band gap
- Optical properties

➢ Electrical properties ➢ Magnetic properties

Applications of nanomaterials

➢ Nanotechnology Applications in Medicine
- Detect disease and the deliver treatment.
- Nano shells as Cancer Therapy
- Nanowires – used as medical sensor

➢ Nano Computing Technology
➢ Sunscreens and Cosmetics
➢ Sunscreens and Cosmetics
➢ Displays
➢ Batteries
➢ Catalysts
➢ Magnetic Nano Materials applications
➢ Medical Implantation
➢ Water purification

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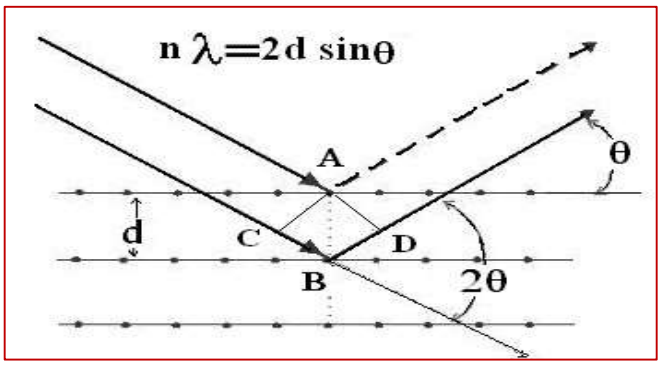
Principle, construction and working of X-ray Diffractometer

PRINCIPLE:

The Bragg's X-ray Diffractometer works on the principle of Bragg's law of diffraction $2d\sin\theta = n\lambda$. where

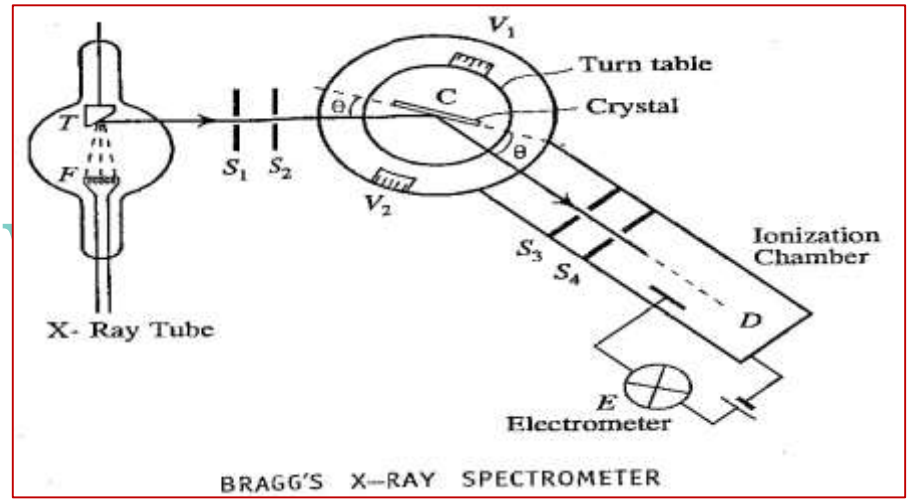
d - interplanar distance θ - glancing angle λ - wavelength of X-ray



X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin\theta$). These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.

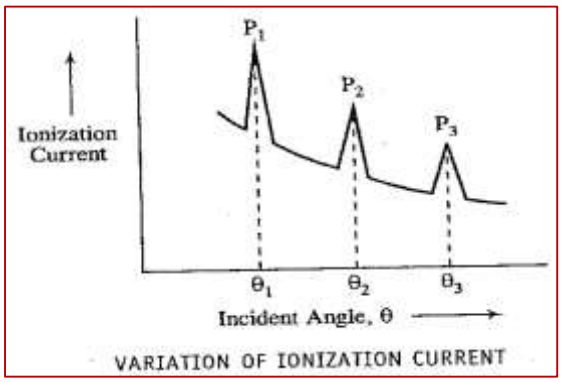
Bragg's X-Ray Diffractometer

The schematic diagram of Bragg's x-ray spectrometer is shown in fig. It has 1) x-ray source 2) A Crystal fixed on a circular table provided with scale and Vernier. 3) Ionization chamber.

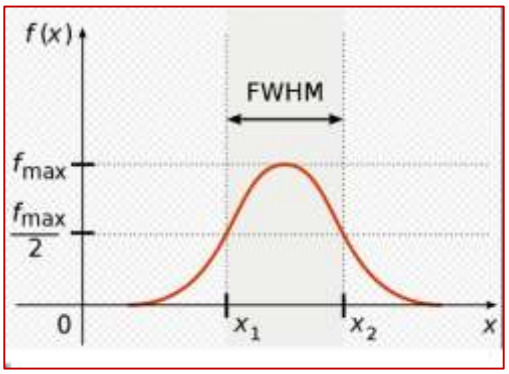


- X-rays from the X-ray tube are allowed to pass through the slits S_1 and S_2, then it is made to fall on a crystal C mounted at the center of rotating turn table provided with a graduated scaleV_1 to measure the angular displacement of crystal.
- X-ray after reflection enters into ionization chamber fixed to the turn table and the position can be noted on the scale V_2.
- The X- ray enters into ionization chamber ionizes the gas and produces ionization current which is measured by electrometer connected to it.
- For every rotation of turn table by an angle 'θ' on the crystal, the ionization chamber must rotate by an angle 2θ to satisfy Brags law.
- While the experiment is carrying out by rotating the turn table at different reflected rays the sudden rise in current is observed.

- A plot of ionization current for different incident angles to study the x-ray diffraction spectrum is shown in fig.
- Let Peaks are observed at angles θ_1, θ_2, θ_3 etc. for n=1,2,3, etc. for a set of parallel planes in the crystal, when the x-ray beams satisfy Braggs law of diffraction
- By knowing, wavelength of X-ray, interplanar spacing (d) and order of diffraction (n), the diffraction angle θ can be calculated using Braggs Law **2dsinθ = n λ.**



VARIATION OF IONIZATION CURRENT



Crystallite size determination using Debye Scherrer equation

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Scherrer equation is the oldest form of X-ray diffraction method used to determine the size of the crystals in the form of powder. The Scherrer equation relates the crystallite size in a solid with the broadening of the peak in a diffraction pattern. By knowing the values of θ, λ, β and K the mean crystallite size D can be determined by using equation.

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad \text{m}$$

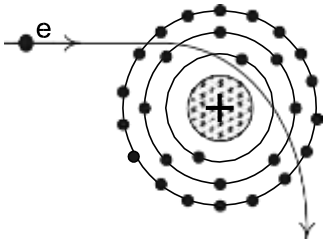
Where
D - the mean crystallite size β - Full width at half maxima (FWHM)
θ - Bragg's angle
K- Scherer's Constant → 0.9 for Cu –Kα target

Prerequisites to understand the electron microscopes

Scattering of electrons

Scattering usually implies that the electron changed the path after 'hitting' some other small particle like the nucleus of an atom, or another electron. As the electrons come very close to other particles, their masses and all of their related fields, interact on a quantum level. Due to this the deviation occurs in the path of the electron.

For example, when high speed electrons penetrate into the atom, they are attracted by a positively charged nucleus. Due to this, they deviate from their original path. This is equivalent to collision with nucleus. Electrons slow down and lose their energy in this process.



Tunneling Effect

Consider a thin layer of insulator sandwiched between two metal layers as shown below-

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Metal Insulator Metal

10-20 A^0

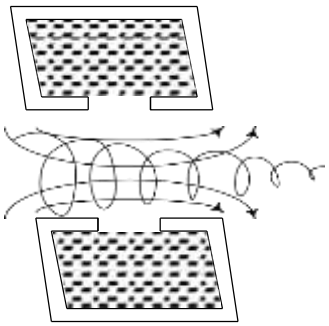
Insulator layer sandwiched between two metals

The insulator works as a barrier to the flow of conduction electrons travelling from one metal to the other. However, when the size of the barrier is extremely small of the order of 10-20 A^0.

Magnetostatic Focusing (Magnetic lenses)

Magnetic fields, which are axially symmetric, can be used for focusing an electron beam passing through them. The axially symmetric magnetic fields are produced by short solenoids. The electron traveling in such field describes a helical path and can be focused to a particular point. Such

solenoids are called as thin magnetic lenses. These magnetic lenses are used in electron microscopes.



Spiralling and focusing of electrons in a magnetic field

Magnetic lens

SCANNING ELECTRON MICROSCOPE (SEM)

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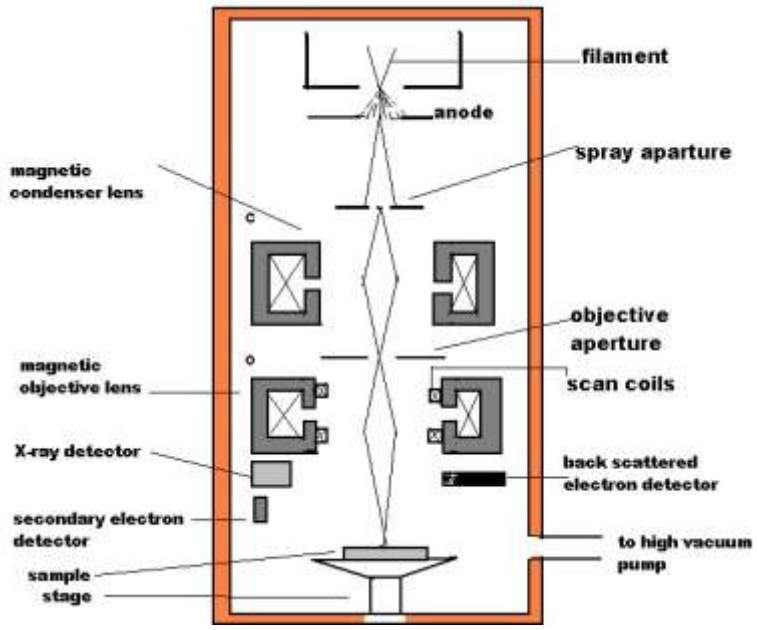
PRINCIPLE:

The basic principle involved in the working of all kinds of electron microscope is the wave nature of electrons. An electron accelerated under a potential difference of V volts behave like a wave of wavelength.

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

CONSTRUCTION:



The apparatus consists of a highly evacuated chamber inside which there is an electron gun. There are 2 magnetic lenses one is the condensing lens C and the other one is the objective lens O. A scan coil accompanies the lens O. there is a spray aperture using which, spherical aberration during focusing will be minimized. A flat surface called stage is provided at the bottom portion of the apparatus to place the sample under study.

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There are 3 types of detectors – back scattered electron detector, secondary electron detector, and an X-ray detector

WORKING:

- The sample to be investigated is placed on the specimen stage after which, inside of the chamber is evacuated by connecting it to a high vacuum pump.
- Electrons are emitted by the filament by thermionic emission. A suitable positive potential is applied to the anode with respect to the filament.
- The accelerated electrons from the electron gun pass through the spray aperture from where the electron beam emerges.
- The condensing lens C converges the beam & eliminates some high angle electrons.
- The beam then passes through the objective aperture where the size of the beam can be controlled. A thinner beam then enters into the field of objective lens O. the objective lens focuses the beam onto the desired part of the specimen.

- A set of coils called scan coils placed along with the objective lens enable the beam to scan the specimen in the particular way called raster. The scan coils are connected to the raster scan generator which directs the beam onto the spot on the specimen & dwells on it momentarily.
- The electrons incident on the sample are called primary electrons. Upon incidence some of the electrons are knocked out from the atoms in the specimen due to the impact of the beam which are called secondary electrons. Some of them will be scattered by the specimen called back scattered electrons. X- Rays are emitted when electrons from a higher shell in the atom transit to a vacant position created in its lower shell from where an electron has been knocked off.
- Back scattered electrons, secondary electrons & the X-rays emitted are detected by the respective detectors & a corresponding signal is produced. This signal is converted into a micro spot of corresponding brightness on a screen. The beam focus is then shifted to the next adjacent spot in order, where it again dwells momentarily. This way the image is built on the screen point by point.
- Image produced on the screen will be in grey scale. For aesthetic purposes, these are colorized by using feature-detection software.

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APPLICATIONS:

SEM is used to study

1. External morphology of biological organisms.
2. Chemical composition.
3. Crystalline structure. 4. Forensic investigations.

TRANSMISSION ELECTRON MICROSCOPE (TEM)

Principle: Transmission Electron Microscope (TEM) works on the principle of wave nature and tunneling effect of electrons.

Construction:

Transmission Electron Microscope (TEM) is an electron microscope that has four main systems -

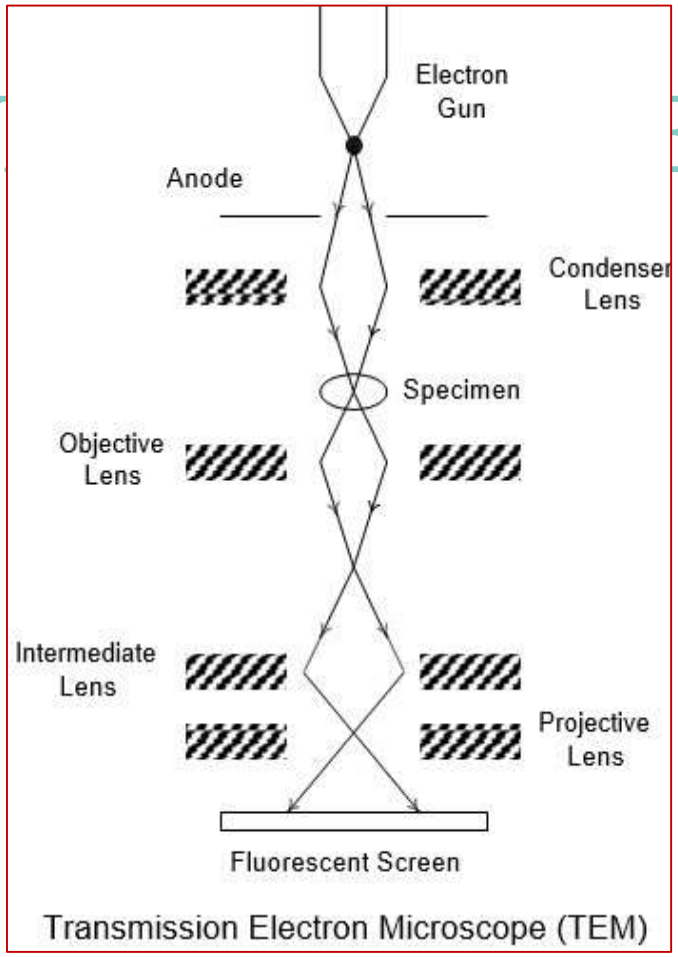
(1) **An electron gun:** It produces the electron beam
(2) **The condenser system:** It focuses the electron beam on the sample.

(3) **The image-producing system:** It consists of the objective lens, movable specimen stage and intermediate and projector lenses to form a real and highly magnified image

(4) **The image-recording system:** This converts the electron image into the format that can be seen by the human eye.

Working:

- The electron beams from electron gun are produced from the heated tungsten filament. Anode with an aperture is kept at positive potential. Electrons accelerate toward the anode and pass through the central aperture.
- These electron beam focused on the specimen by the condenser system. The intensity and angular aperture of the electron beam are also controlled by these lens system, between the electron gun and the specimen.



Transmission Electron Microscope (TEM)

- The electron beams then pass through the specimen mounted on the specimen stage which can be adjustable. Then the beam passes through the objective lens, it is usually of short focal length (1–5 mm) and produces a real intermediate image that is further magnified by the projector lenses.
- Modern instruments employ two projector lenses (one of which is called the intermediate lens) to permit a greater range of magnification without increase in the physical length of the microscope.
- The intermediate electron image that is formed at the projector lenses are converted into the format that can be seen by the human eye by the imagerecording system: This consists of a fluorescent screen for viewing and focusing the image, the higher magnification may be obtained by photographic or digital enlargement. Computerized images are stored in a format such as TIFF or JPEG and can be analysed and processed to get the final image.

Advantages:

a) Three dimensional image obtained gives more information about the specimen.

b) Very small amount of specimen is required for analysis.

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Disadvantage:

a) High vacuum is required to maintain.

ATOMIC FORCE MICROSCOPE (AFM)

Atomic Force Microscope is a high resolution scanning probe type microscope. It is a tool for imaging, measuring and manipulating matter at the Nano scale. It can image all type of surfaces including polymers, ceramics, composites, glass and biological samples.

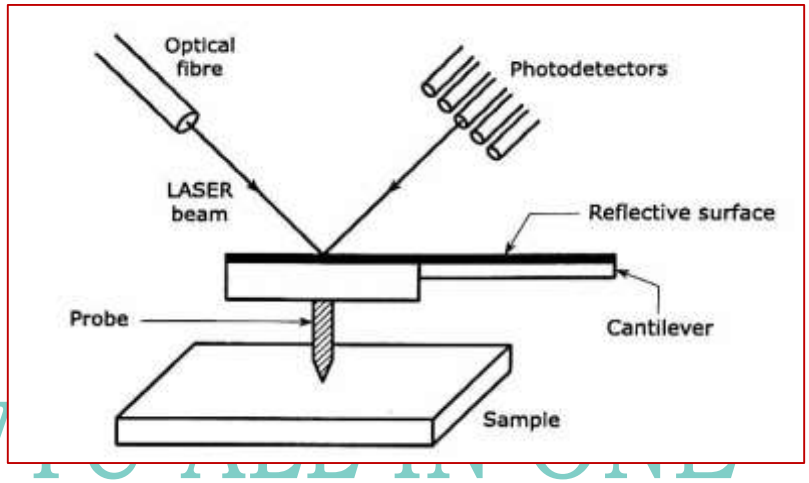
The atomic force microscope was invented by Gerd Binning et al. in 1986 at IBM Zurich based on the STM (Scanning Tunneling Microscope) already presented in 1981. In 1987, the inventors were awarded the Nobel Prize in Physics for the achievements.

PRINCIPLE:

AFM produces image by physically pushing a cantilever probe against the sample. The probe movement is analyzed and converted into a three dimensional image of the sample surface.

CONSTRUCTION:

- A typical AFM consists of a cantilever around 100-500 microns in length with a small tip/probe of radius of 3-15 microns at the free end.
- A laser source, 4-quadrant photodetectors and deflection sensor.
- Sample stage attached to piezo electric sensor.
- Analyzer: The light collected by photo detectors is analyzed with computer controlled devices and a 3D image of the sample surface is constructed.



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WORKING

- When a cantilever probe is brought into proximity of the sample surface, the forces such as Vander Waal's forces, electrostatic forces, magnetic forces and the other forces which arise due to the physical interaction between the surface atoms, cause the cantilever tip to deflect.
- The cantilever can be thought of as a spring. The quantity of the generated force between the probe and the surface depends on the spring constant (stiffness) of the cantilever and the distance between the probe and the surface.
- This force can be characterized with Hooke's Law. F = -k.x
- The deflection of the cantilever is detected by the help of a laser beam and deflection sensor.
- The displacement of the probe is measured and a topographical image is obtained.
- In AFM both conducting and non-conductive samples can be analyzed.

Operation Modes of AFM

Contact mode- In contact mode, the tip is in a soft physical contact with the surface. The tip is able to move above the surface with a specific height or under a constant force. the force between the probe and the sample remains constant and an image of the surface is obtained.
The movement is strongly influenced by frictional and adhesive forces that can cause damage to the sample.

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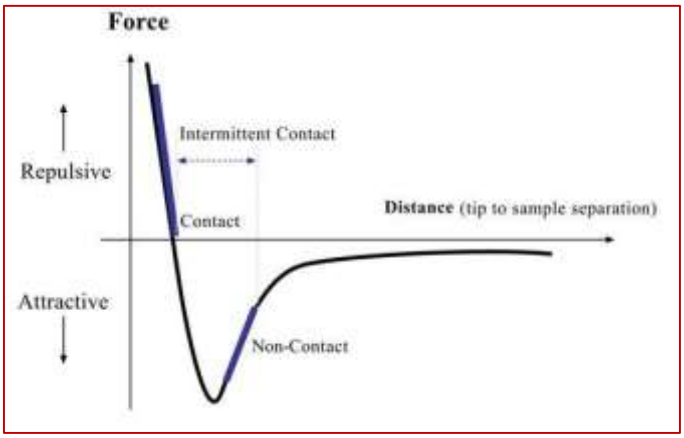

The relationship between force and distance is shown in Figure

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Dynamic (Tapping) Mode-This 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. This mode of operation is less destructive than contact mode. The cantilever oscillates nearby its resonance frequency.

Non-contact mode- In this mode tip does not touch the sample, however it oscillates above the surface during scan. It uses feedback loop to monitor changes in the amplitude due to attractive Vander Waals forces so the surface topography can be monitored. It is better for soft samples and biological samples.

Advantages

1. Easy to prepare samples for observation
2. It can be used in vacuums, air, and liquids.
3. Measurement of sample sizes is accurate
4. It has a 3D imaging
5. It can be used to study living and non-living elements 6. It can be used to quantify the roughness of surfaces

7. It is used in dynamic environments.

Disadvantages

1. It can only scan a single nano sized image at a time of about 150x150nm.
2. They have a low scanning time which might cause thermal drift on the sample.
3. The tip and the sample can be damaged during detection.
4. It has a limited magnification and vertical range.

X-ray Photoelectron Spectroscopy (XPS)

PRINCIPLE:

X-ray photoelectron spectroscopy (XPS) involves irradiating the sample with low energy (1.5 Kev) X-rays such that photoelectric effect is induced. The kinetic energy of emitted electrons is given by

$$K.E. = h\nu - BE - \Phi$$

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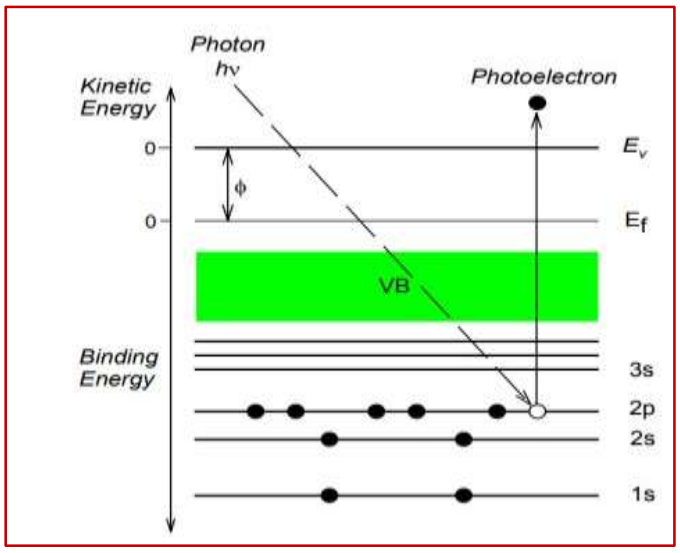
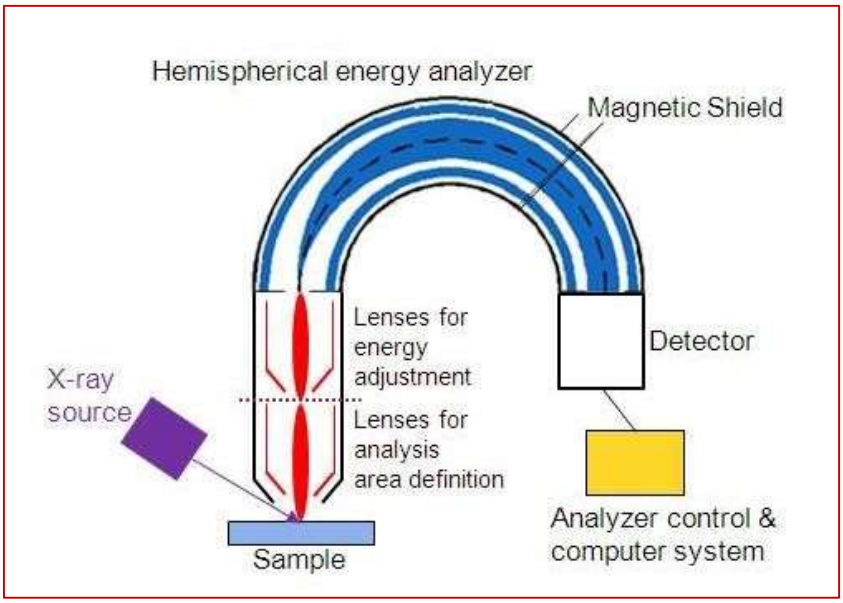
where

K.E- Kinetic energy
BE - Binding energy of the electrons
□ - work function of the sample.



CONSTRUCTION:



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- X-ray source; Al Kα of Mgα X-rays are typically used to excite the sample; Sample holder is present between the X-ray source and the entrance slit
- XPS mainly has lens system to collect the photo electrons.
- An electron energy analyzer is used to analyzer to filter the electron energy of the photoelectrons that are produced. This is typically a Concentric Hemispherical Analyzer (CHA).
- The detector is provided to detector to count the electrons. It has electron channel multiplier tube where in single electron pass through this channel plates and emerge as pulse of electrons.
- Analyzer control and computer system contains computer and data reduction software. XPS data are compared to inventories or archives of experimentally determined XPS data of standard reference material.
- Ultrahigh vacuum system; typically operating conditions are at $<10^{-9}$ Torr. This is required because the emitted photoelectrons have a relatively low energy and are readily absorbed by ambient atmosphere or the gas molecules in the chamber.

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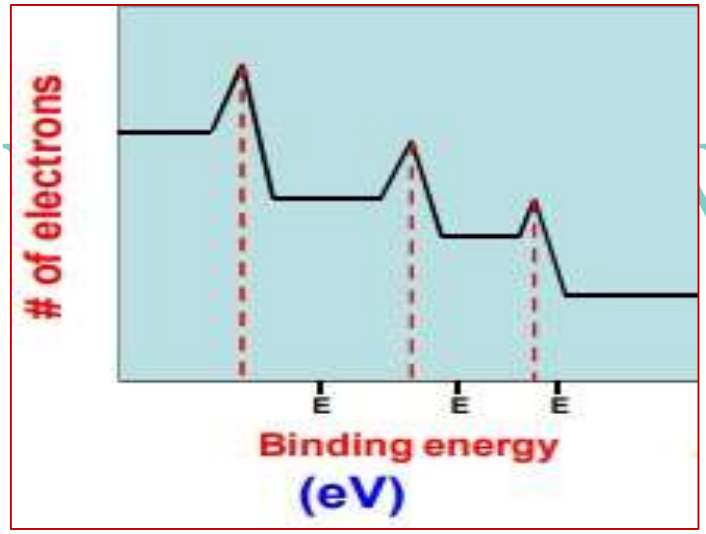
Working:

- The sample is kept in ultra-high vacuum is illuminated by the photons with energy hν; low energy X-rays,
- A bound electron absorbs a photon, resulting in the emission of Photo electrons and converts part of the energy to kinetic energy
- XPS spectra is the plot of number of photo electrons emitted versus the

  KE/ BE. Each element has unique XPS spectra
- The identification of the elements in sample is made directly from the K.E of these ejected photo electrons. Each peak represents the number of electrons at a certain energy that is characteristic of some element. (Binding energy increases from left to right and kinetic energy increase from right to left)
- The relative concentration is made on the photo electron intensities
- XPS is used to determine the elemental composition, stoichiometry and examine surface contamination.



*********ALL THE BEST **********