Course Name: NANO MATERIALS AND APPLICATIONS

COURSE CODE: PHY335

Topics:-

Characterization techniques:

(a) Optical Microscopy,

(b) Scanning Electron Microscopy (SEM and ESEM)

(c) Energy Dispersive X ray Spectroscopy

Notes:

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Nanomaterials behave differently as size changes w.r.t bulk. It is necessary to characterize physical, structural and optical properties of a material to qualify as nanomaterial. Various characterizations techniques are used to known characteristics of nanomaterials for different applications of materials information about shape, lattice constants and crystallinity of material structural characterization is done. The techniques are.

(i) X-ray diffraction techniques -

(ii) Electron Microscopy - There are mainly following types of electron microscopes are :-

(a) Scanning Electron Microscopy (SEM)

(b) Transmission Electron Microscopy (TEM)

We shall begins with some basics of Microscopes.

The state of your life is nothing more than a reflection of your state of mind.

Our eye is sensitive to visible radiation. Size of object observed by an eye depends upon the angle substended by object at lens behind the retina of the eye. Smaller the distance from eye, bigger is the image of object in the eye. There are however two limitations. An object kept at a distance smaller than ~ 25 cm (this distance is known as distance of distinct vision) from the eye cannot produce a sharp image of object and other is that human eye cannot detect an object smaller than ~ 100 um as a distinct object if place close to another object. However by placing convex lens close to an eye, a magnified virtual image can be formed at a larger distance. Such a magnifying lens forms simplest kind of microscope.

Magnification is defined as ratio of angle substended by image (θ') to that by object (θ) or it is size of image to size of object.

$$M = \frac{\theta'}{\theta}$$

Magnification is approximately related to focal length of lens as

How you treat your customers determines how long your business stays open.

$$M = \frac{25}{f}$$

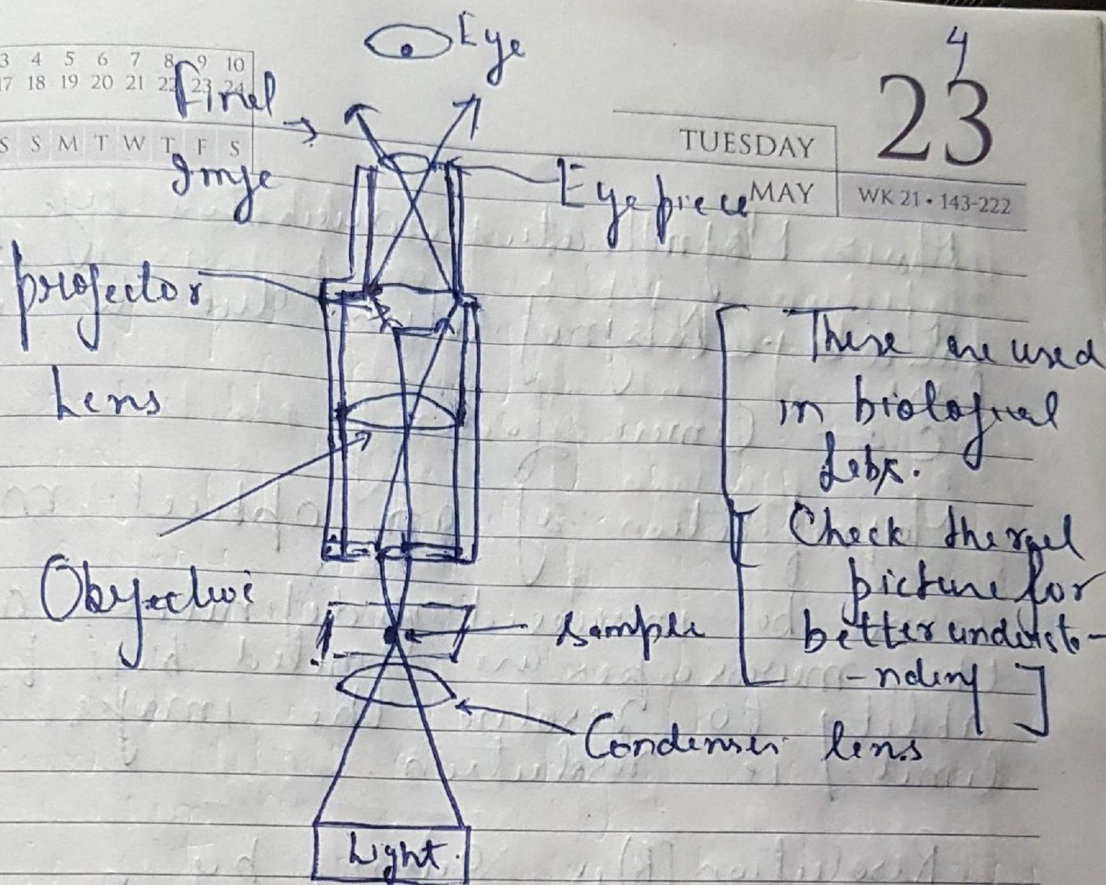
where 25 in numerator is due to distance of distinct vision in cm & f is focal length of magnifying lens in cm.

An object would appear ten times larger with lens having f = 2.5 cm ($M = \frac{25}{2.5}$) and is written as 10X. When an image is 100 times bigger than the object, it is written as 100X & so on.

With the magnifying ability of lenses in mind Galileo invented in the year 1610, simplest optical microscope. Current used microscopes make use of at least two lens viz objective and eyepiece. Objective lens is the lens close to the object and eyepiece is close to the eye, as shown in fig.

The objective lens (from a distance larger than its focal distance) forms the real image of an object, which in turn gets magnified as a virtual image due to eyepiece.

Life lets us ask for what we want, but gives us only what we deserve.



[These are used in biological labs. Check the real picture for better understanding]

Compound light Microscope

The overall magnification by is given by product of magnification produced by various components of a microscope & Camera factor.

$$M = M_o \times M_e \times M_c \times C$$

$M_o \rightarrow$ Magnification due to objective lens

However X ray radiations has shorter wavelength than visible light (0.01nm to 10nm), so X rays are useful to characterize materials. UV light can be used in no. of optical microscopes.

[Human eye can see things of 0.1 mm size.
Best light Microscopes can see things 0.2 μm wide i.e. 1000 times smaller than what we can see with our eye]

Electron Microscopes :-

In electron microscopes, electrons are used in place of electromagnetic radiation and electrostatic or magnetic lens are used in place of glass lens.

According to wave particle duality electrons have both particle & wave

nature. Therefore, just like electromagnetic radiation which can be used to image the objects.

The wavelength of electron is described by equation

$$\lambda = \frac{h}{mv}$$

h → planck's con
v → Velocity of electron
m → Mass of electron

$$= \frac{1.227}{\sqrt{V}} \, nm$$

$$\left[\frac{1}{2} m v^2 = eV \right]$$

Velocity of electron depends on voltage used to accelerate it.

Velocity	Electron Wavelength (in nm)	Applied Voltage
1.6×10^8 m/s	0.0039 nm	100kV
2.3×10^8 m/s	0.0027	300 kV
2.8×10^8 m/s	0.0012	1000 kV

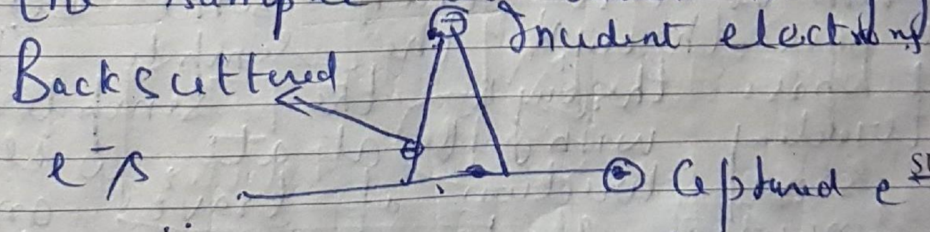
So wavelength of electron is very small.

So high resolution can be obtained by using e^- beam.

So accelerated electron should be able to allow us to image very small things.

In general, the interaction b/w electrons and solids are quite complicated due to charge on electrons

Electrons that are accelerated towards a sample will enter the sample and interact with electrons already present. Some of incident electrons will scatter or bounce around in sample. At each scattering event, they will lose some energy until they run out of energy and are left stuck in the sample. These electrons are captured by the sample as shown in fig.



Some of electrons from the incident electron beam will scatter in the sample and will eventually make their way out of samples. These are

back scattered electrons. Sometimes an incident electron will strike an electron already present in sample and knock it out of sample. This is called a secondary electron.

Both secondary electrons and back scattered electrons can be used in Scanning electron Microscopy (SEM)

After a secondary electron has been produced, a byproduct of relaxation process is production of X-rays. We can measure the energy of these X rays in a technique called Energy dispersive Spectroscopy (EDS).

If sample is thin enough around 150 nm or less then some electrons will pass through the sample. Electrons that pass through the sample without interacting with it at all, will retain the same direction of travel and energy as incident electrons. These electrons are used in transmission electron microscopy (TEM)

Many business leaders have failed and derailed because of arrogance than any other flaw.

Other electrons will pass through the sample, but will scatter either elastically or inelastically. Elastically scattered electrons will change direction but retain same energy as incident electrons. These electrons can be used in a technique called electron diffraction to understand crystalline nature of sample. Inelastically scattered electrons will change direction and also lose some energy as they interacts with the sample.

They can be used in technique called electron energy loss spectroscopy or EELS to characterize the atomic conc. of sample.

So electrons are very useful for variety of nanocharacterization technique.

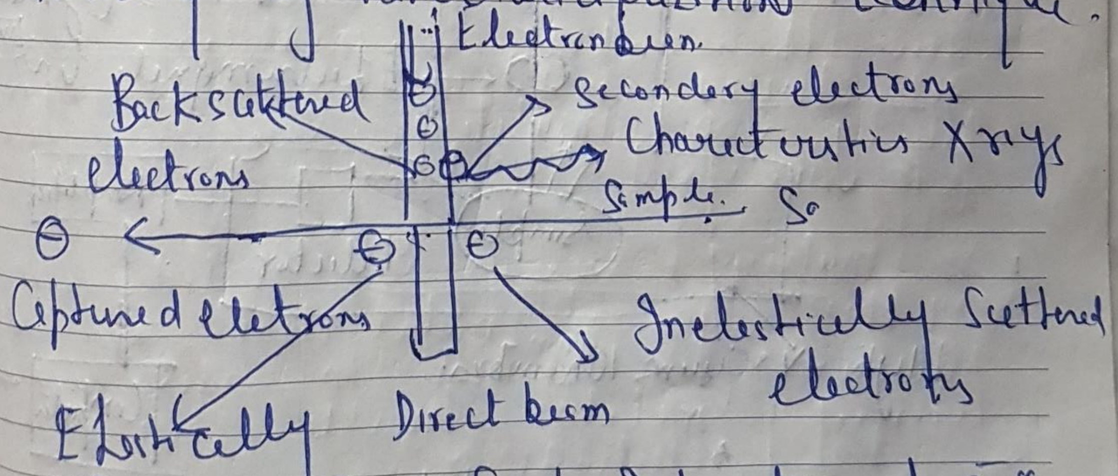
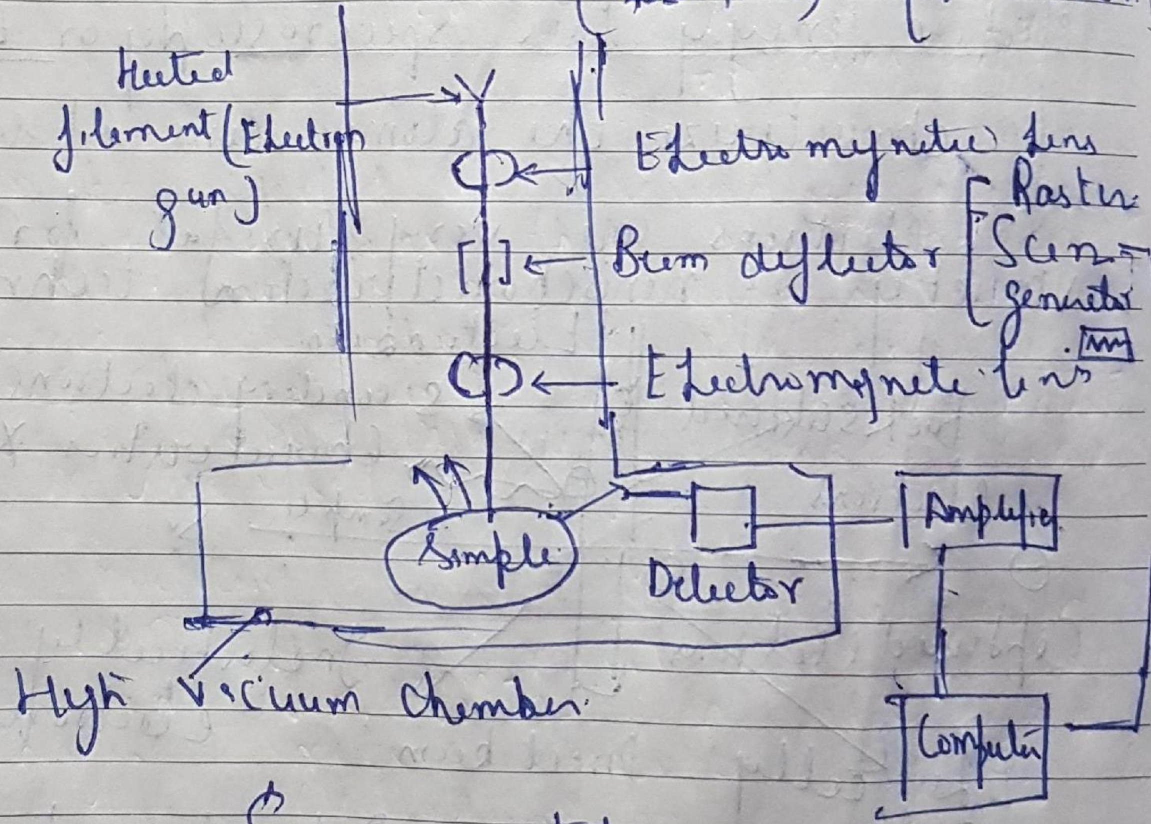


Fig 1 – Interactions of e's with Sample

In electron microscopes electrons need to reach the simple without getting scattered by air. Therefore, the electron microscopes need vacuum for their operations.

Scanning Electron Microscope (SEM) [$< 10^{-5}$ torr]

and Environmental Scanning electron Microscope (ESEM) [1-5-20 torr]



Scanning Electron Microscope

The jealous person knows nothing, suspects a great deal and fears everything.

SEM & FESEM are microscopes that produce images using electrons instead of visible light. As wavelength of light limits the resolution in an optical microscope. Electron have much shorter wavelength then visible light for imaging purpose. The basic compomponents of electron microscopes are same as light microscope. Instead of light source electron microscope

→ uses an electron gun to produce electrons. Electron gun ~~consist~~ extracts electrons from hot filament [using thermoionic emission] or cold cathode [using high electric field called field emitter]. SEM which uses, field emitters are called FE-SEM and can give better image than hot-filament SEM.

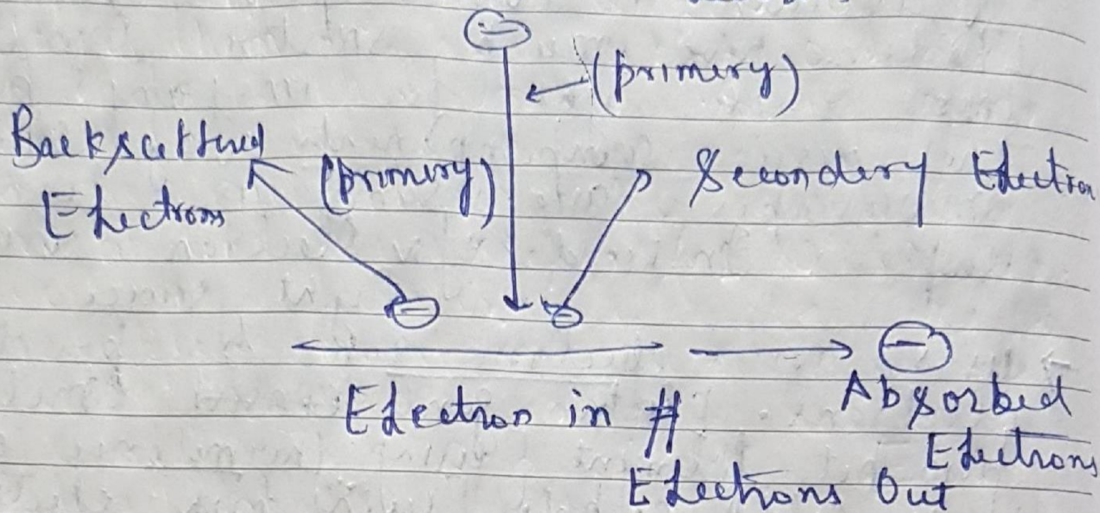
→ Electromagnetic lens are used to focus the electrons and detector is sensitive to electrons instead of visible light.

- The fine beam is scanned or rastered on sample surface using a scan generator

- Electron can interact with sample in no of ways as discussed earlier. SEM using backscattered and secondary electrons for imaging.

If hard work is the key to success, most people would rather pick the lock.

- When electrons strike on sample some of electrons are absorbed and other are backscattered and some electrons



Can be ejected as secondary electrons. If no of electrons that strike the sample is not equal to no of electrons that leave the sample, so insulating samples get charged and images becomes blurred/faulty. So insulating samples can not be analysed directly.

So insulating samples are coated with a very thin layer of metal like gold or platinum (< 100 nm) in order to avoid charging [metals provide easy path to electrons]

Signal from Scan generator along with amplified signal from electron collector generates the image of sample surface. In order to avoid oxidation and contamination of filaments as well as reduce the collisions b/w air molecules and electrons, filament and sample have to be housed in vacuum chamber. Usually vacuum ~ 10^{-5} Torr or better is required for normal operation of SEM.

Most SEMs used secondary electrons. Backscatter SEM images shows fewer surface features than secondary electron images. Often, backscatter images look very flat. The contrast changes that we can see in a backscatter image is due to difference in average atomic number. Regions of samples with high atomic no (larger no of electrons) will produce more backscattered electrons and appear bright.

Many electron microscopes have both secondary and backscattered electron detectors and can acquire two types of images. The secondary electron image clearly shows the surface topology, while backscattered image shows the atomic number contrast.

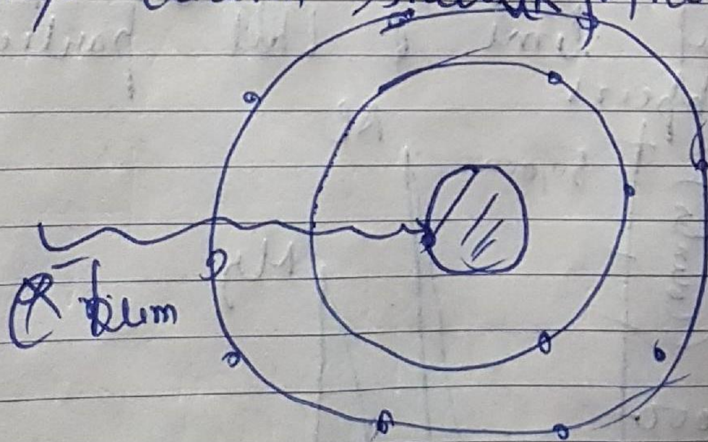
— As SEM operates at < 10^{-5} torr vacuum, so only dry samples can be imaged in SEM i.e. if we want to image the wet samples, we need to dry them first, which often distort their shape. This makes SEM inconveni-ent. So

Some manufacturers are supplying environmental microscopes (ESEM), which allows the operator to introduce a controllable amount of water vapour into SEM vacuum chamber. So even wet samples can be imaged. ESEM has disadvantages that electron that are travelling towards the sample will hit these water molecules and scatter. The result is that electron beam is not tightly focused as in traditional low pressure SEM. So resolution of image is not good. The main advantage of an ESEM is that it can image 'wet' samples without having to dry them out. These include many types of biological samples such as cells, bacteria & plant. Also water vapours prevent charging. This allows us to image on non-conductive samples without the need for conductive coating.

Energy - Dispersive X-Ray Spectroscopy (EDS) Basic func!-

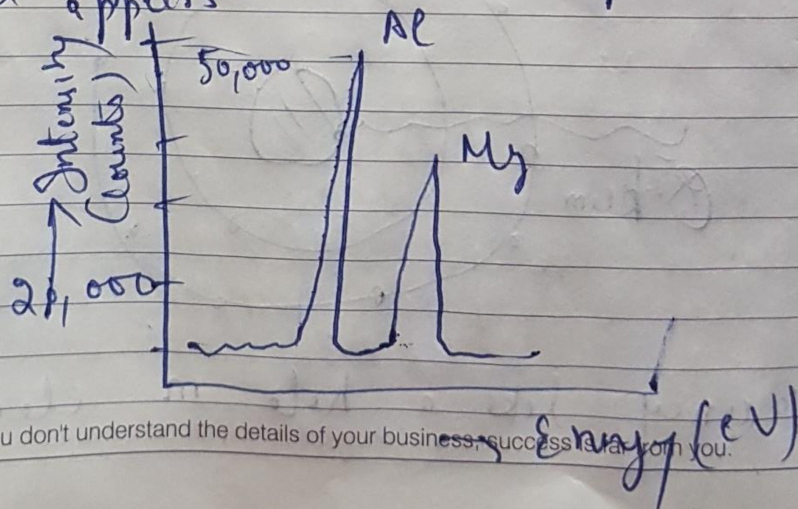
- It is non destructive analytical Technique
- It provide information on elemental & chemical composition of sample. Same microscope that was used in SEM is used here. But It has special detector known as EDS detector and software to analyse the data. The primary electrons when interact with samples also produce X rays to be emitted from sample.

When an electron from incident beam imparts enough energy to sample an electron can be ejected from one of atom's electron shell (K). This leaves a



vacancy like a hole in electron shell

where electron originally was. For atom to return to a stable state an electron must replace the one that was emitted from higher shell (L or M). So an electron from higher energy shell will drop down into this lower energy shell vacancy. During this process, it must lose some of its original energy in form of X ray. These X rays are detected by EDS detector and analyzed by Software to identify the element from where it comes. X rays can have energies measured in KeV. Energy of each generated X ray is dictated by the elements present in sample. i.e. each element has unique X-ray signal. Analyzing the signal from EDS experiment involves measuring the energy of each characteristic X ray signal & counting the no of time that particular signal appears



Beam Analysis software counts energy & plots them on a graph called spectrum.

Limitations :- ① Some elements have overlapping peaks, but careful analysis and experience may avoid misidentification.

② EDS uses high voltage of e beam (15 to 30 K.V.) to excite X rays to produce plenty of signals that can be used to identify elements present in the sample.

③ Some elements like H, He donot have characteristic X-rays. Similarly Li and Beryllium produce X-rays that are too low energy to be detected. So not all elements can be detected by EDS

Reference Books:

1. C.P. Poole Jr. and F.J. Owens, Introduction to Nanotechnology. New Jersey: John Wiley & Sons, 2006.
2. K.K. Chattopadhyay and A. N. Banerjee, Introduction to Nanoscience and Technology, New Delhi: PHI Learning Private Limited, 2009.

Note: Dear Students, For More Clarity, You may go through following video lectures

(i) https://www.youtube.com/watch?v=icRQE73AUII

(ii) https://www.youtube.com/watch?v=gyOIFWhvUn0&t=240s

(iii) https://www.youtube.com/watch?v=6GqhmDdkGGc&t=264s

(iv) https://www.youtube.com/watch?v=2_uN5qj2U2g&t=265s

(v) https://www.youtube.com/watch?v=hCzwKH0QbgU