Membrane Technology
Department of Chemical engineering
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Lecture-09
Porous and non-porous membranes, nominal and absolute rating

Good morning students today is module 3 and lecture 9. So, we are discussing the characterization of various membranes. So, this class will discuss the porous and non porous membrane characterization and what is the meaning of nominal and absolute rating of membranes. Then we will go and discuss the various characterization techniques for microfiltration membranes and today's class will discuss scanning electron microscope transmission electron microscope and atomic force microscopy AFM.

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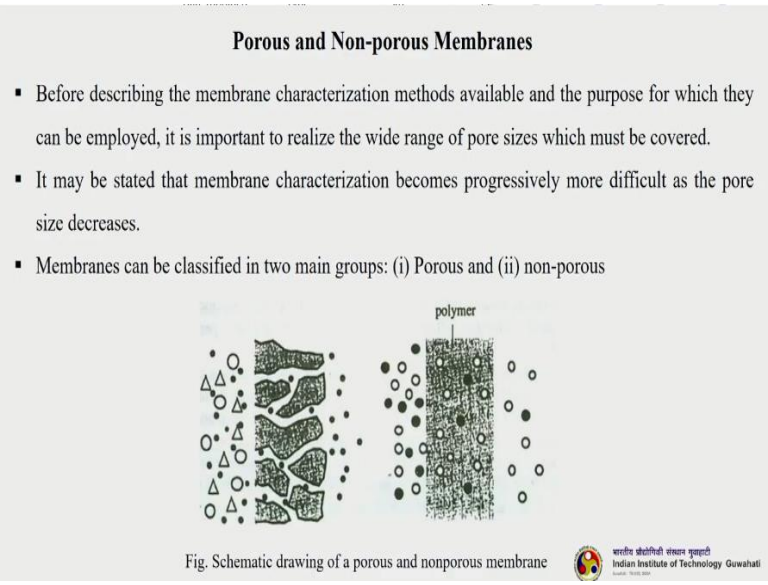

So, before describing the membrane characterization methods available in the purpose for which they can be employed, it is actually important to understand the pore sizes, what pore sizes we are going to cover. So, we have been discussing about pore sizes, the dimensions, the IUPAC classification since so many days in our various lectures, so, you may understand that as the pore size actually decreases the membrane characterization also becomes little difficult.

So, membrane can be classified western 2 2 categories actually, with respect to characterization, so, you can see one is porous and one is non-porous, so, the porous membranes in which the pore suppression and their basically microfiltration all these membranes and non porous membrane

said that dense membranes are usually used for our arrow and as well as your gas suppression applications.

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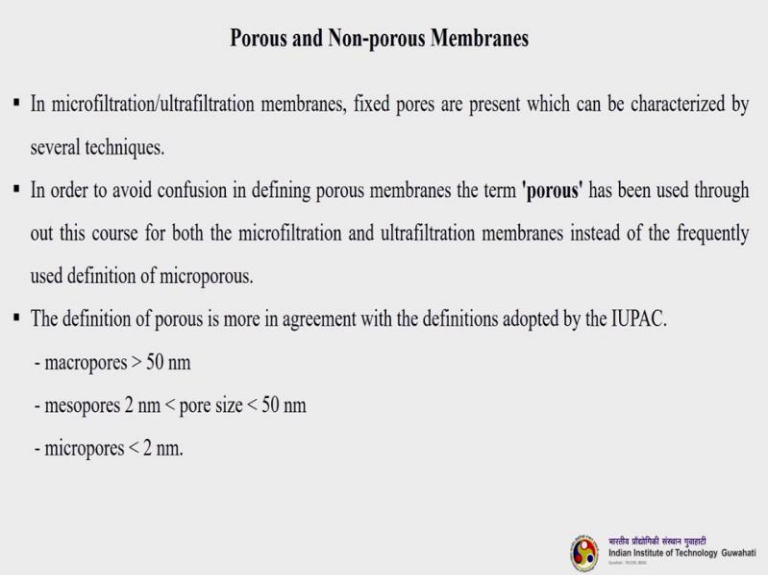

Now, in microfiltration and ultrafiltration membranes, fixed pores are present which can be characterized by several techniques. So, the pores are actually fixed, which are already present. So, we need to characterized them. So, that distinctly visible under different techniques. In order to avoid confusion in defining porous membrane the term porous has been used throughout this course for both microfiltration and ultrafiltration, instead of frequently using the definition of microporous.

So, you can see the definition of porous more in agreement with the definitions adopted by a IUPAC. So, this is the IUPAC classification macropores greater than 50 nanometer and mesopores in between 2 nanometer to 50 nanometer and micropores lesser than 2 nanometer.

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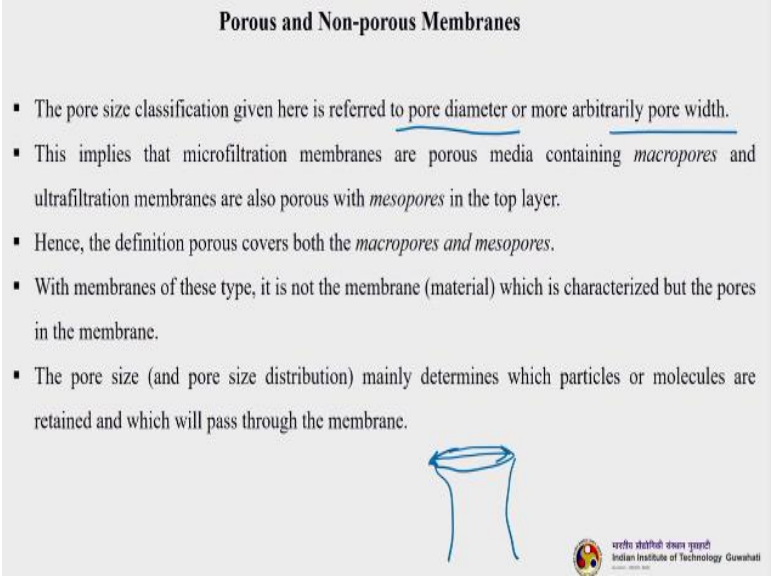

The pore size classification given here is report to pore diameter or pore width. Actually, this also a very important to note that you can see, let us say this is a pore, so, what is being we are discussing here about the pore size. Actually this is what this is the pore diameter or pore width, but how the pore is actually. So, it depends upon the poor shape and its geometry. So, it can be different types of geometries are available.

However here we are discussing only the pore diameter. So, whenever we are characterizing the pore diameter. So, this implies that microfiltration and membranes are porous media containing macropores and ultra filtration membranes containing mesopores in that top layer. So, hence the definition porous covers both macro pores and mesopores. So, with the membrane of this type it is not the membrane material which is characterized but the pores in the membrane.

So, when we are talking about porous membrane characterization and please note that we are characterizing the pores the membrane material is nothing to do with it, the pore size and the pore size distribution mainly determines which particles or molecules are retained and which will pass through that membrane.

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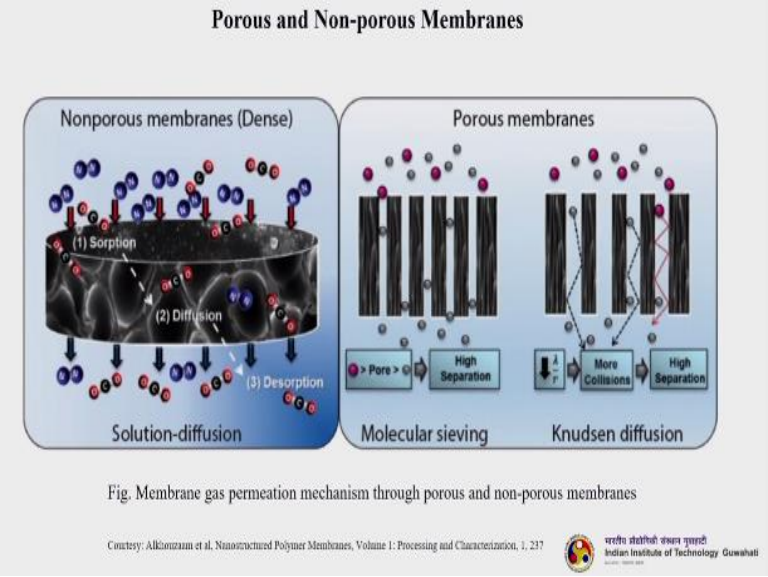

Fig. Membrane gas permeation mechanism through porous and non-porous membranes

So, let us now again discuss a little about the porous and non-porous membrane and how they actually work their mechanism actually. So, you see the first one and non-porous membrane, which is actually also called as dense membrane so they do not have any distinct pores. So, the working mechanism actually solution diffusion. So, we have heard about solution diffusion in few of our classes, and I explained in a notch cell also so today again, I am telling that so, what is the meaning of solution diffusion is essentially the 2 2 factors which play a big role.

One is the solubility and the diffusivity are part of the solutes that we want to transport across the membrane. So, initially, the solutes which are supposed to permeate through the membrane will come and sit on the surface of the membrane and virtue of their solubility, their solubilize inside their membrane metrics. So this is, this is a membrane metrics. So once they solubilize, then by virtue of their diffusivity, they will travelled across the membrane material, and then they deserved out or the permit out.

So here there are no pores of solubility and diffusivity is playing important role. But now let us look into the porous membrane. So porous membrane to distinct features can be a transport mechanism can be identified one is molecular sieving. So, molecular sieving is something in which it is basically size explosion. So, based on size the permission is happening you can see the cylindrical ports which are being shown here and particles which are larger than the pore size are getting written on the surface of the membrane.

And whereas, which are so, smaller than the pore size are permeating through the membrane. So, this is extremely high suppression can be achieved with this so, this is called molecular sieving and then Knudsen diffusion, so Knudsen diffusion actually takes place this is for gas separation. This separation also achieved very high level of separation can be achieved and the particles which are smaller than the pore diameter will be eventually collide inside the pore this one length.

So you can understand you can call this is the length of the pore. So inside it travels so it gets collided many times inside the, this one and then travels across its minimum path length and then comes out in the permeate side. So, this is actually Knudsen diffusion. So, we learn it in detail when you discuss about gas separation.

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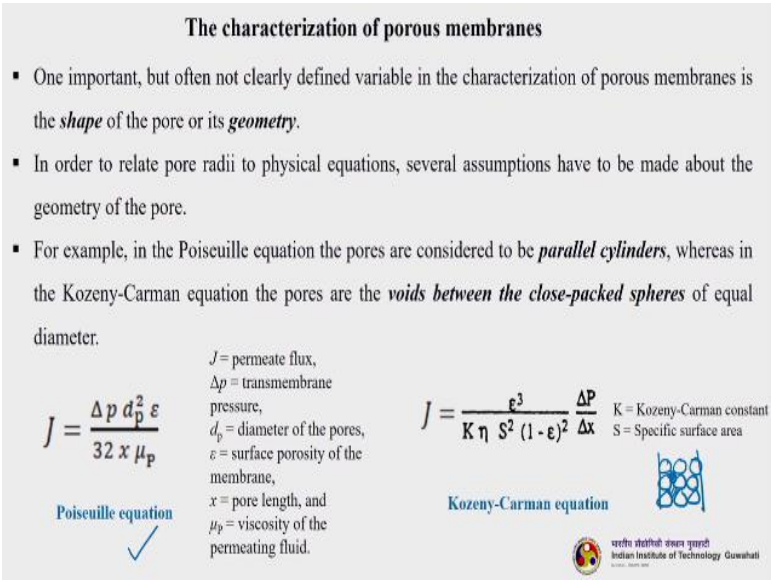

So one important but often not clearly defined variable in the characterization of porous membrane is shape of the pore or its geometry as I told many times during our earlier discussions, then the pore shape or its geometry is of permeate importance, because please do not mistaken that all the pores are cylindrical or parallel in nature it is never so, except few geolytes that are available either synthetic geolytes or natural geolytes.

We do not have any cylindrical parallel pores and existing in any commercial membranes or any membrane which you prepare. So, in order to relate pore radii to physical equation, several

assumption have to be made. So there are various equations that actually were being utilized to predict the flux and other parameters to calculate the port size or diameter. So, 2 classical equations were showing is one is this second poiseuille equation another is Kozeny-Carman equation.

So, here this is the poiseuille equation against poiseuille equation. So, flux equals to delta p dp square epsilon then 32 x mu p. So, J is the permeate flux here delta p is the transmembrane pressure that is applied across dp is the diameter of the pores which we want to actually find out epsilon is the surface porosity of the membrane understand that it is the surface porosity. So, otherwise you do not confuse it is the volume porosity.

And then x is the pore length and mu p is the viscosity of the permeating fluid. Now, another equation is Kozeny Carman equation. Here and the difference between poiseuille and Kozeny Carman equation is that in poiseuille equation is a pores are considered to be parallel cylinders, which is actually an assumption in real life it is not so but in Kozeny-Carman equation. It is assumed that the ports of the voids between the closely packed spheres of equal diameter I just try to show you how it will be. So, let us see this is how.

So in the Kozeny Carman it is telling that. So, the pores are the voids. So, this is the void this is the void this is the space which is the void between the closely packed spheres, but actually in practice it is not so, but to simplify the understanding and to use the physical equations to certain extent. So, these are actually assumed.

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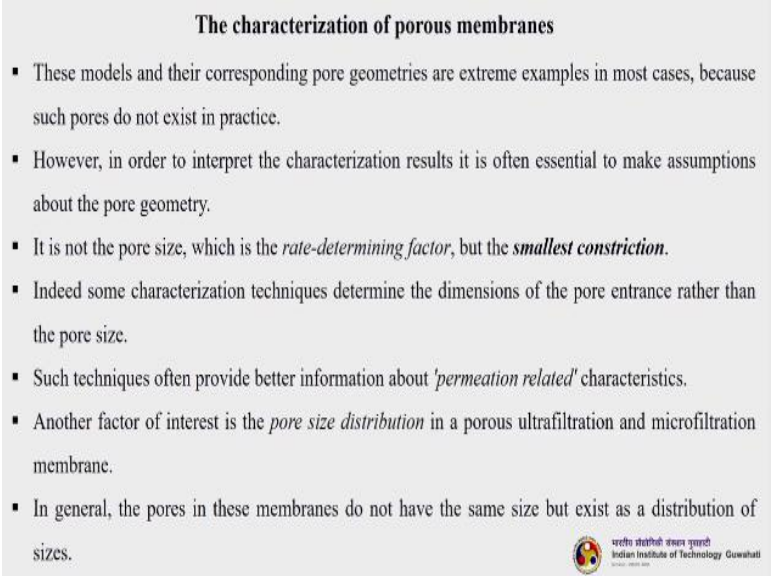

So, these methods, models and their corresponding pore geometries are extreme example, in most cases, because such pores do not exist in practice. However, in order to interpret the characterization results it is often essential to make assumptions about the poor geometry. Now, it is not the pore size, which is the rate determining factor but the smallest construction. So, actually the pore size what we are characterizing is nothing but the diameter of the pore on the surface, but that is not actually contributing or that is not rate determining factor.

And that is not the thing which is deciding whether a particular solute will be permeating through a particular pore or not what will decide is that smallest construction inside the pore. So, indeed some characterization techniques determine the dimension of the pore entrance rather than the pore size such techniques open provide better information about permeation related characteristics.

So, another factor of interest is the pore size distribution or in a porous ultrafiltration and microfiltration membrane in general pores in these membranes do not have the same size but exist as a distribution of sizes let us say a commercial membrane is written 10 kilo delta is the cutoff. So, what is the inherent meaning of that, so, it does not mean that all the ports which are actually presenting that will allow all the particles which are lesser than 10 kilo delta it may not be so.

So that is in there is pore size distribution some pores will be more than a particular size and some parts will be less than a particular pore size. Whenever we are characterizing membrane on we are talking about pore size it is the average process rather than the pore size of individual pores.

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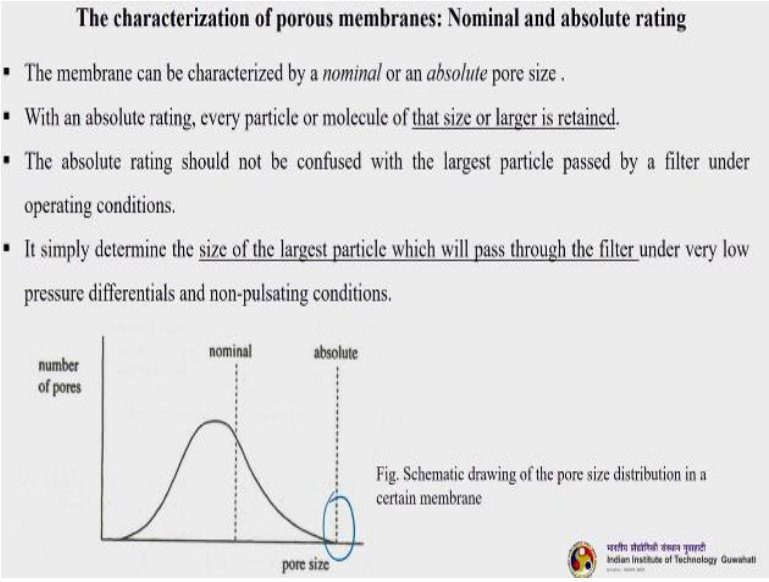

So, the membrane can be characterized by a nominal or absolute pore size. So, with an absolute rating every particle or molecule of that size or larger is retained and this is your absolute rating, you can understand that anything that is more than this particular size will be retained on the surface of the membrane, so that we can say 100% rejection. And in the absolute rating should not be confused with the largest particle passed by filter. So it simply determines the size of the largest particle which will pass through the filter under very low pressure differential and non pulsating conditions.

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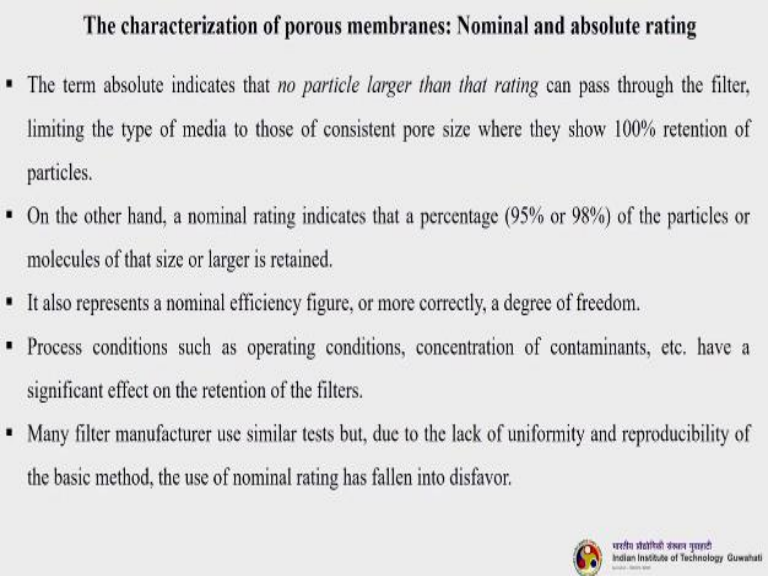

The absolute indicates that no particular larger than rating can pass through the filter, limiting the type of media to those of consistent pore size where they show 100% retention of particles. On the other hand, and nominal rating indicates that a percentage is usually 95 to 98% of the particles or molecules of that size or larger is retained. So whenever I am talking about a nominal size, so you understand that here 95 to 98% of the solutes will be retained with respect to this particular size.

It also represents a nominal efficiency figure or more correctly degree of freedom. So, process conditions, such as the here operating conditions, concentration of here solutes, etcetera. have a significant role on the retention of the filters and many filter manufacturers use similar test but due to lack of uniformity and reproducibility, the use of dominant rating has fallen into disfavor. So, mostly whatever we see nowadays, and the ratings these are all absolute ratings.

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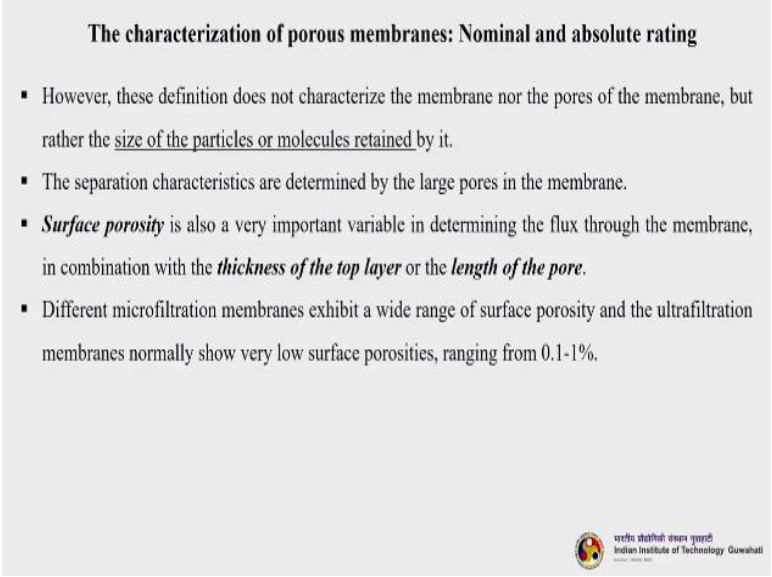

However, this definition does not characterize the membrane or the pores of the membrane but rather the size of the particles are molecules that is written by it. Since the separation characteristics are determined by larger pores in the membrane, so, another important feature is surface porosity. So, surface porosity is also a very important variable in determining the flux through the membrane in combination with the thickness of the top layer as well as the length of the pores surface, porosity means the number of pores actually present in the surface of the membrane or per membrane area.

So different microfiltration membrane exhibit a wide range of surface porosity, and the ultrafiltration membrane normally show very low surface porosities almost 0.1 to 1%.

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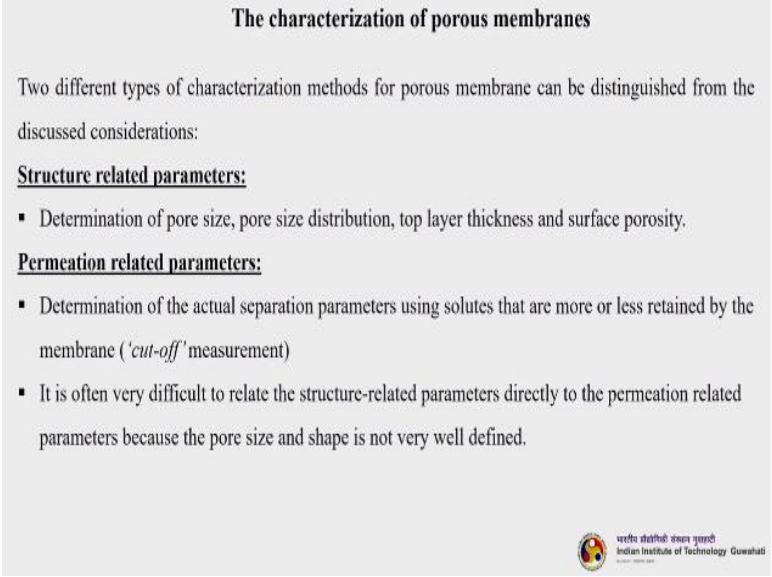

Now, when you talk about characterization of porous membrane, it is actually of 2 2 types. So one is structure related parameters another is permeation related parameters. So that is see under structure related parameters. So we determine basically pore size, pore size distribution top layer thickness and surface porosity and in case of permeation related parameters so we actually determined the separation parameter using some real solutes that are more or less retained by this membrane surface.

So, this is called cut off measurement or cut off experiments. So, it is often very difficult to relate the structure related parameters directly to the permeation related parameters because the pore size and shape are not very well defined, even though we know we are seeing the pores or pores diameter or the surface from the top surface, but we do not exactly know what is the shape and geometry of the pores inside the membrane metrics. So, that is actually going to play a big role in the separation.

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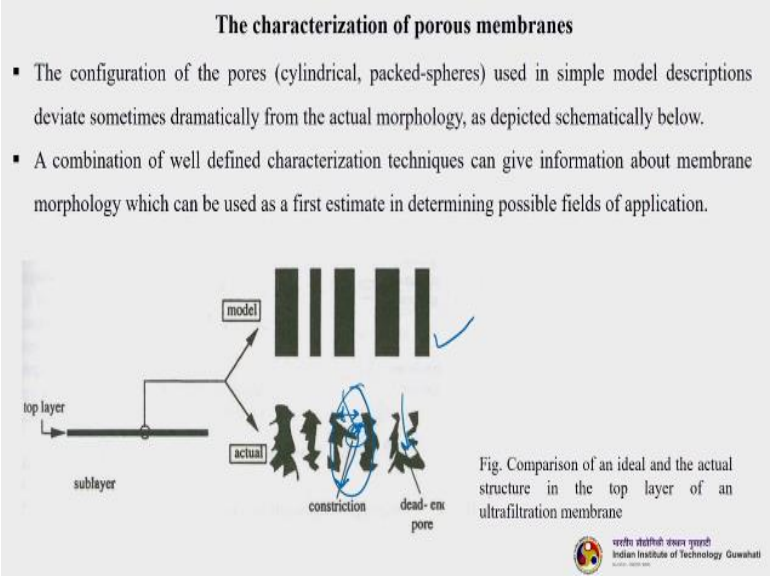

So, let us now understand the different types of pores actually, so the configuration of the pores either cylindrical packed spheres used in simple model description deviate sometimes dramatically from the actual morphology, actually. So those are idealistic situations because they are assumed in real life it is not so. So a combination of a well defined characterization techniques can give information about membrane morphology, which can be used as a fast estimate in determining possible fields of application.

So, you can see this; your model or this one ideal pores looks like this cylindrical parallel pores. However, your actual pores are like this. So, this was I was talking about the smallest constriction you can see this is the pore diameter that actually we are going to characterize for this particular pore, but you see how the flow takes place from here. If the size of the solute is smaller than this pore diameter, the solute will flow inside the pore however.

Then it will come and then it will get retained on this particular constriction, because there is this constriction the solute is not able to permeate through that constriction. So, the after some time what will happen that this particular pore will be of no use. So, this becomes just like a dead end port and it is not contributing to the permeation. So, this is a dead end pore in which the pore is actually sealed at the bottom.

That means anything that is coming are getting deposited inside this particular dead end pore and this is not contributing to your separatism.

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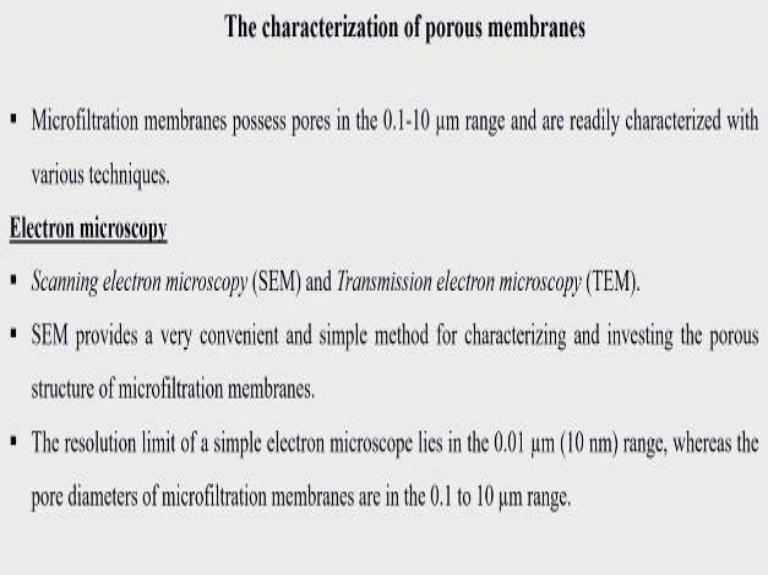

And microfiltration membranes possess pores in 0.1 to 10 micron range and are readily characterized with various techniques. So, let us start discussing techniques today will discuss 3 SEM, TEM and AFM. So, under electron microscopy we have 2 distinct this one techniques one is scanning electron microscopy another transmission electron microscopy SEM and TEM. So, SEM is a very convenient and simple method for characterizing and investigating the porous structure of micro filtration membranes.

So, the resolution limit up a simple electron lies in the range of 0.01 micron that is 10 nanometer range whereas, the pore diameters of micro filters and members are in 0.1 to 10 micron range.

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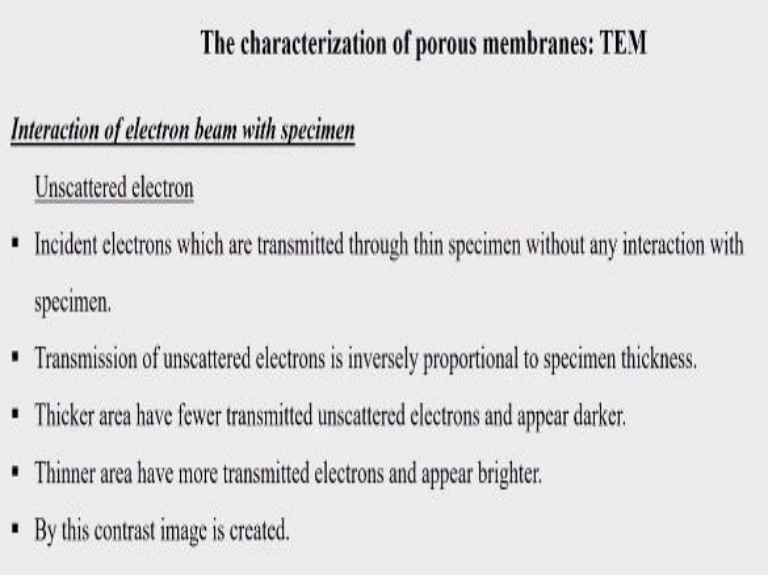

Now, let us start understanding how the SEM works and what is the different parts is so, students in this particular lecture and even our consequent lectures also, when we are discussing characterization, I will be giving the techniques little more in detail. So, because it is very understood once somebody is working with a membrane, so, here see must understood the analytical techniques, their principles, how a particular instrument works, because it will immensely help you to understand what is actually happening inside the instrument when we are going to characterize it.

And it will enhance your knowledge. So, let us understand how this TEM works. So, interaction of electron beam with specimen, so, we have unscattered electron, so incident electrons which are transmitted through thin specimen without any interactions with specimen. So, these are called unscatterd electron transmission of unscattered electrons is inversely proportional to specimen thickness, thicker area fewer transmitted unscattered electrons and they appear darker.

So, a area if it is thick. Let us let us assume the membrane only if it is very thick then what will happen that we have very few transmitted unscattered electrons. So, due to that that particular reason will appear dark in your final microgram or image so thinner area have more transmitted electrons and they will appear brighter. So, you can read actually more easily what is inside. So, by this constant image is actually created. So, here contrast image is actually getting decided by how much unscattered electrons are transmitted.

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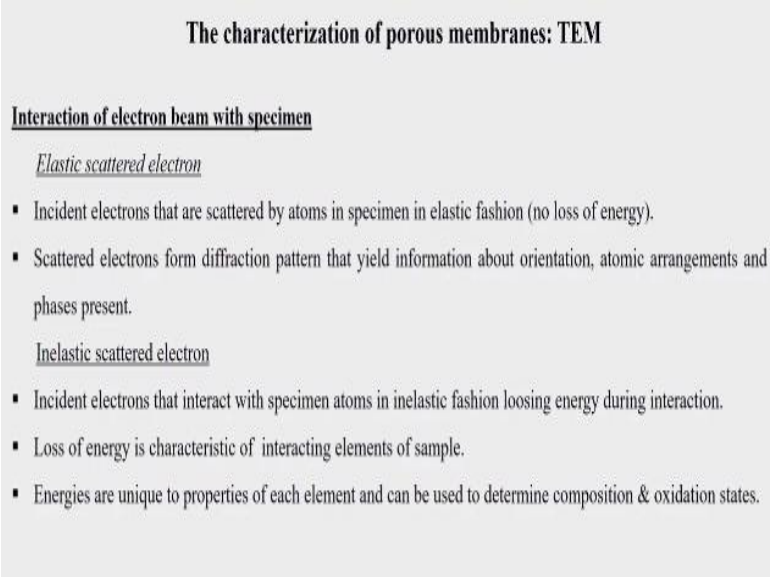

Then elastics scattered electron, so, incident electrons that are scattered by atoms in specimen in elastic fashion. So, that means there is no loss of energy. And scattered electrons form diffraction pattern that yield information about orientation atomic arrangements and phases present. Then another form is inelastic scattered electron. So, incident electrons that interact with specimen atoms in inelastic fashion loosing energy during interaction.

So, the difference between elastic and inelastic is that in elastic, there is no loss of energy whereas in inelastic, there is a subsequent amount of energy that is cost that is getting lost during the interaction. So, loss of energy is the characteristics of interacting elements of the sample. So, energies are unique to properties of each element and can be used to determine composition and oxidation states.

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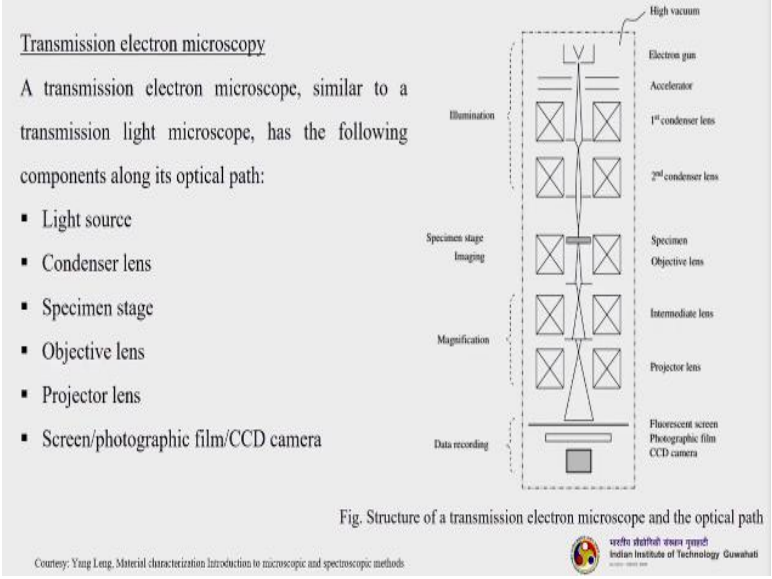

Fig. Structure of a transmission electron microscope and the optical path

Let us understand how TEM works actually what is the different parts. So, you can see the figure on your hand side. So, this is the structure of transmission electron microscope and its optical path, you can see there is something retain high vacuum we call the TEM itself the entire setup works under vacuum. So, we will subsequently learn why it is. So, term similar to a transmission light microscope has the following components.

So, there is a light source, there is a condenser lens, there are specimen stage, there are objective lens there are projector lens then there is screen and photography film and CCD camera. So you can see there is electron gun here then this one then we have accelerator then we have first condenser lens second condenser lens then we have a specimen So, this is the specimen you remember an metal anything any polymer and then it go it passes through the objective lens.

And then there are intermediate lens then there are projected lens which is finally projecting the image to the screen and the intermediate lens and projector lens actually helping in magnifying the rays or image whatever it is getting produced due to the secondary scattered electrons through the specimen. So, in the basic difference between SEM and TEM, we will discuss SEM later on. So, is that in TEM, the electrons are passing through the membrane, whereas in SEM it is just scanning across the top of the surface.

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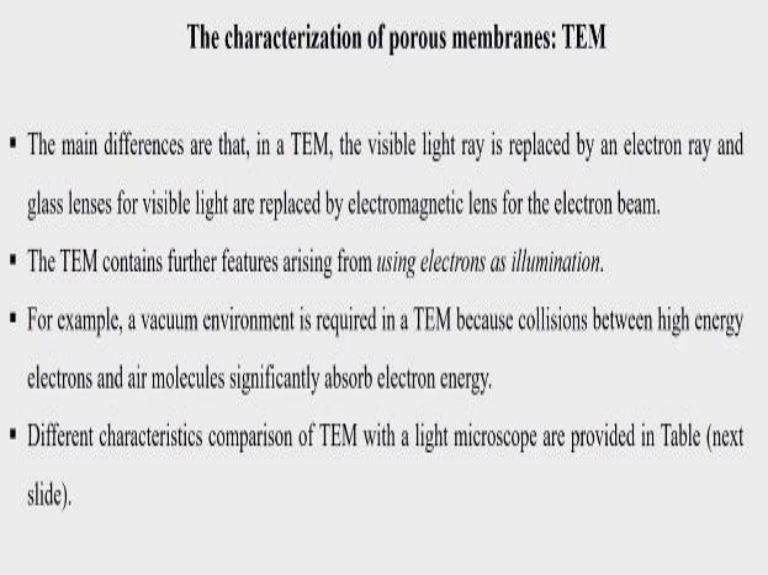

So, the main difference are that in a TEM the visible light ray is replaced by an electron ray and glass lenses for visible light are replaced by electromagnetic lens, the TEM contains further features arising from using electrons as illumination for example, a vacuum environment is required as I was telling the vacuum environment is required for TEM which is not so important or AFM. So, because collisions between high energy electrons and air molecules significantly absorb electron energy.

So, if there is no vacuum when the electrons very highly excited state, they will collide with each other and along with the air molecules and they will try to observe the energy. So, that is not good, so, that a lot of energy will be lost and eventually you will not get any particular image which were actually supposed to. So, different characteristic comparisons of TEM with a light microscope are provided.

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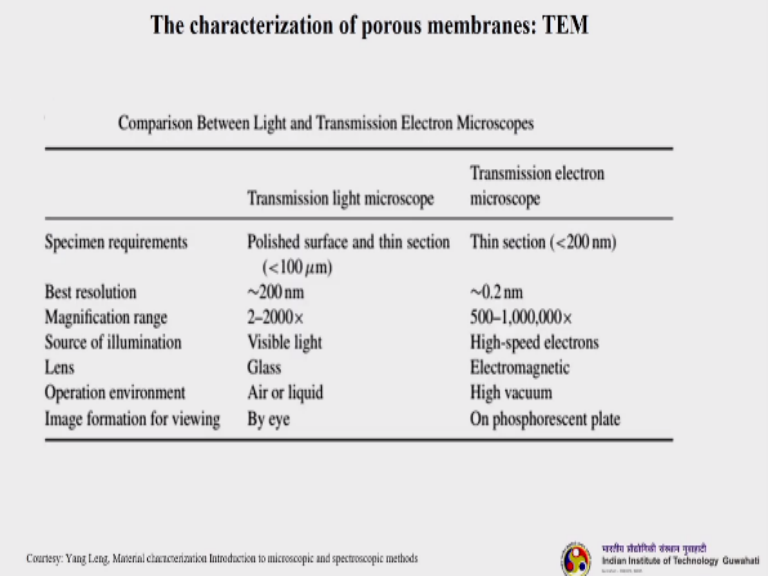

So, let us look at this particular actually table here it is telling us what is the difference between a transmission light microscope and a transmission electron microscope. So, the specimen that is required for both for a TLM is that a poly surface and thin section less than 100 micron is fine but for TEM it should be very thin less than 200 nanometer. So, best resolution is 200 nanometer and pore time it is 0.2 nanometer.

So, similarly magnification range is very high in case of TEM so, source of illumination is high speed electrons that is why time is a very sophisticated instrument and we are using vacuum to do the imaging lenser electromagnetic whereas a TLM only glass lensor are used and operation environment is either air or liquid or here it is high vacuum in TEM. And we can see the image formation by the naked eye just by observing looking at the inside the lens whereas in TEM it is on phosphorous and plate the image is that is getting formed.

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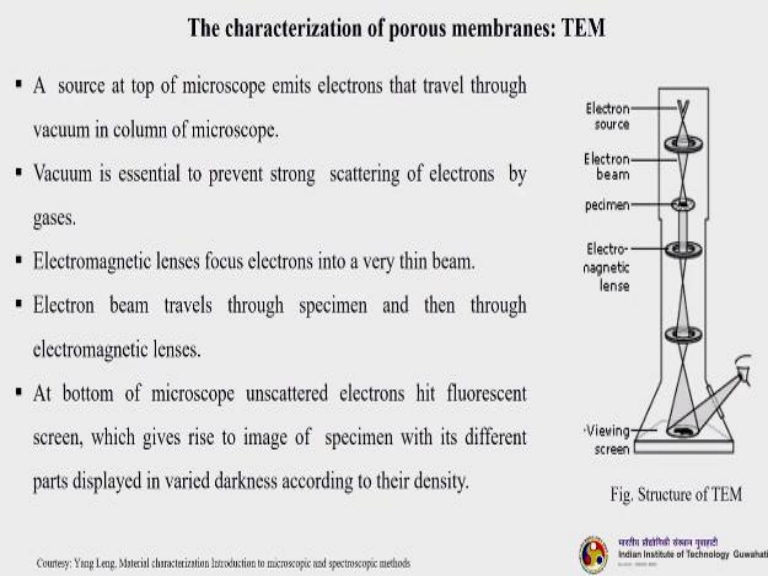

So, this is a structure of the TEM actually you can see the electron sources here then the beam is coming here. So, here it is here the specimen is being hold here So, that means the membrane or polymeric metal whatever it is then whatever the electrons that is transmitted through the specimen or coming to this electromagnetic lens then it is magnifying and it is projecting to this another lens here.

Then whatever it is coming out this particular lens can be viewed in a screen, so a source at top of microscope emits electrons that travel through the vacuum. In column of microscope, there are multiple lens depending upon management of a particular TEM, we can have the various types of lens. So, vacuum is essential to prevent strong scattering of electrons. So, electromagnetic lenses focus electrons into a very thin beam.

So, this is very important in case of TEM electron beam travels through specimen and then through electromagnetic lenses. So, at bottom of microscope unscattered electrons hit fluorescent screen, which gives rise to image of specimen with its different parts displayed in very darkness according to their density.

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The characterization of porous membranes: TEM

Electron Sources

- High energy electron beam used for illumination is generated by electron gun.
- Electrons are emitted from surface of cathode and accelerated toward anode by high voltage (V_o) to form a high energy electron beam with energy $E = eV_o$.
- Additional electrodes are placed between cathode and anode to stabilize electron beam.

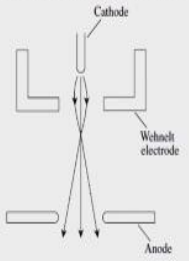

Fig. General structure of a electron gun

Courtesy: Yang Leng, Material characterization: Introduction to microscopic and spectroscopic methods

So, let us understand the different electron sources. So, high energy electron beam used for illumination is generated by electron gun electrons are emitted from the surface of cathode and accelerated toward anode by high voltage to form a high energy electron beam with energy = e V0 so, v 0 is the voltage and additional electrodes are placed between cathode and anode to stablish electron beam. So, this is how actually the electron gun looks like there is a cathode and there is a anode through which actually the electron beam is getting generated.

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The characterization of porous membranes: TEM

- Wavelength of electrons is determined by electron energy.
- Since resolution of microscope depends on wavelength, hence for TEM, acceleration voltage determines the resolution to large extent.
- TEM resolution is calculated for $\alpha = 6.5\times10^{-3}$ radians.

$$\lambda^2 = \frac{h^2}{(2eVm_e + e^2V^2/c^2)}$$

$$\lambda = \left[\frac{1.5}{(V + 10^{-6}V^2)}\right]^{1/2} \text{nm}$$

$$\lambda = \left[\frac{1.5}{V}\right]^{1/2} \text{nm}$$

$c = 2.998\times10^{8}\,\text{ms}^{-1}$

$e = 1.602\times10^{-19}\,\text{C}$

$h = 6.62\times10^{-39}\,\text{Js}$

$m_e = 9.108\times10^{-31}\,\text{kg}$

Acceleration voltage (kV)	Electron wavelength (nm)	TEM resolution (nm)
40	0.00601	0.56
60	0.00487	0.46
80	0.00418	0.39
100	0.00370	0.35
200	0.00251	0.24
500	0.00142	0.13

200 kV is commonly used and meets most resolution requirements

Courtesy: Yang Leng, Material characterization: Introduction to microscopic and spectroscopic methods

So, wavelength of electrons is determined by the electron energy. Since the resolution of microscope depends on wavelength, hence for TEM acceleration voltage determines the resolution to large extent. So, it is the acceleration voltage which is actually determining the

resolution. So, TEM resolution is calculated for alpha equals to 6.5 into 10 power - 3 radians. So, you can use this particular equation said 200 kilo volt is commonly used and meets most resolution requirements. So, you can see in this particular table it tells us the acceleration voltages the electron wavelength and the TEM listen corresponding TEM resolution.

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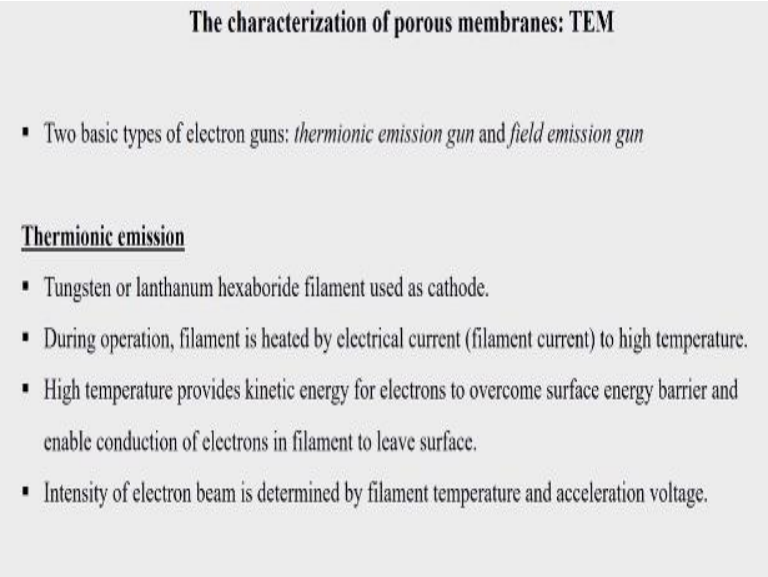

So, 2 basic types of electron guns are use thermionic emission gun and field emission gum. So, thermionic emission we can use either a tungsten or lanthanum hexaboride filament use. So, that is the cathode. The cathode is the source of actually generation of the electrons during operation filament is heated by electric current to a very high temperature, high temperature provides the kinetic energy for the electrons to overcome surface energy barrier and enable conduction of electrons in filament to leave the surface then they will move ahead. So, intensity of electron beam is determined by filament temperature and acceleration voltage.

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The characterization of porous membranes: TEM

- Lanthanum hexaboride gun

✓ Better cathode

✓ More widely used

✓ lower cathode temperature required

✓ generate higher intensity electron beam

✓ longer life than a tungsten filament

✓ higher level of vacuum required

So, this is the characteristic features of lanthanum hexaboride gun which is most widely used actually. So, it is a better cathode than more widely used lower cathode temperature is required. So, we do not need very high temperature actually and to generate the electrons generate higher intensity electron beam compared to other gun type longer life than a tungsten filament tungsten filament needs to frequent the placement actually and high level of vacuum is equal. So, this is actually a little disadvantage that in case of lanthanum hexaboride gun, high vacuum level is actually required.

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The characterization of porous membranes: TEM

Field Emission Gun

- Very high electric field is applied to metal surface for electrons to overcome surface potential barrier.
- During operation, electrons are physically drawn off from a very sharp tip of tungsten crystal (~100 nm tip radius) by an applied voltage field.

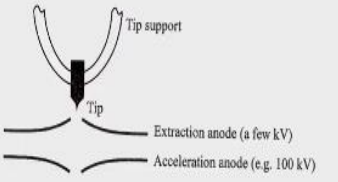

Fig. Field emission gun

- Field emission gun generates the highest intensity electron beam
- 10^4 times greater than that of the tungsten filament gun and 10^2 times greater than that of the LaB_6 gun.

Let us understand what is field emission gun. So very high electric field is applied to metal surface for electrons to overcome surface potential barrier. So, the difference between field

emission gun and the thermionic gun is that in case of field emission gun, you need to supply more energy or you need to supply more temperature to the cathode. So that it will overcome the surface potential barrier.

So that the electrons will get released, however, that is not true in case of the thermionic guns. So, during operation electrons are physically drawn up from a very sharp tip of tungsten crystal. So, you can see this is the tip actually of a tungsten crystal, this is the support of the tip. Almost 100 nanometer that tip radius under an applied voltage feed and field emission gun generates the highest intensity electron beam, it is 10 to the power 4 times greater than that of the tungsten filament gun and 10 to the power 2 times greater than that of the
LaB 6 gun.

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The characterization of porous membranes: TEM

- Two kinds of field emission guns:
  - ✓ Thermal gun
  - ✓ Cold gun
- Thermal field emission gun works at elevated temperature of 1600-1800 K but lower than that of thermionic emission gun.
- Cold field emission gun works at room temperature.

	Tungsten filament	LaB_6	Field emission	
			Thermal	Cold
Operation temperature (K)	~2800	~1800	1600 ~ 1800	~300
Brightness[a] At 200 kV ($A\,cm^{-2}\,sr$)	$\sim 5 \times 10^5$	$\sim 5 \times 10^6$	$\sim 5 \times 10^8$	$\sim 5 \times 10^8$
Requirement to vacuum (Torr[b])	10^{-4}	10^{-6}–10^{-7}	10^{-9}	10^{-9}–10^{-10}

[a] Intensity emitted per unit cathode surface in unit solid angle.

[b] 1 torr = 133 Pa.

sr : steradian, SI unit of solid angle

So, 2 kinds of field emission guns are there thermal and cold gun. So thermal field emission gun works at elevated temperature of around 1600 to 1800 Kelvin, but lower than that of thermionic emission gun and Cold field emission gun works at room temperature. So, that is the beauty of cold field emission gun. So, you can see the table itself is giving us an understanding about the 2 types of guns it comes total comparison it is tungsten is there la b 6 is there then under field thermal

And cold you can see that the operating temperature is the lowest for the cold one. And the brightness comparison is also given requirement to vacuum comparison is also given. So, sr is the steradian that is the unit of the solid angle.

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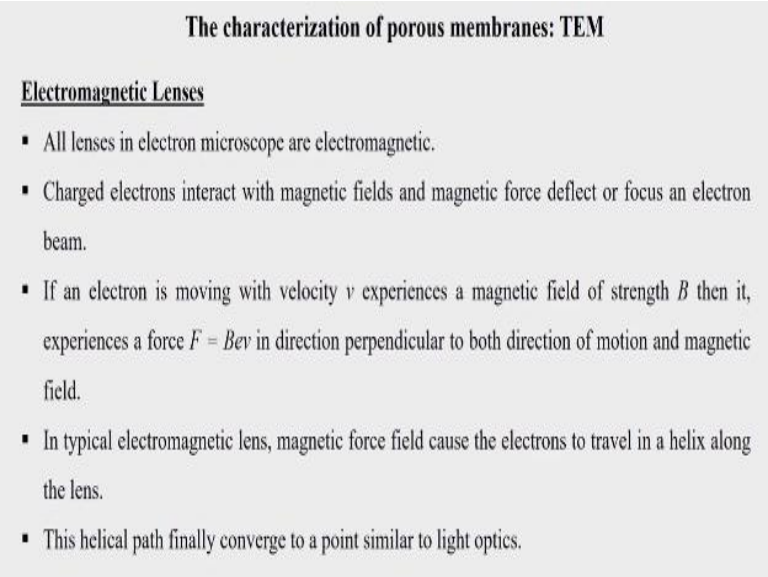

So, then, let us come to the electromagnetic lenses so, what are those, so all lenses in electron microscope are electromagnetic. So charged electrons interact with magnetic fields and magnetic force deflect or focus an electron beam. So if an electron is moving with a velocity v experiences a magnetic field of strength B then it experiences a force F = Bev, in direction that is perpendicular to both the direction of motion and magnetic field. Now in typical electromagnetic lens magnetic force will cause the electron to travel in a helix along the lens. This helical path finally, converts to a point similar to light optics.

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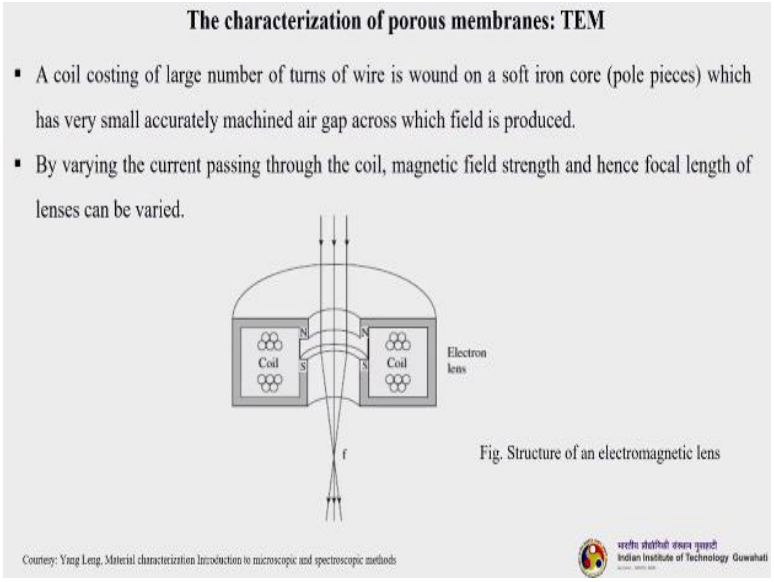

A coil consisting of a large number of turns of wire is wound on a soft iron core which is very small accurately machined air gap across the field across the field is actually produced. So by varying the current passing through the coil, magnetic field strength and hence focal length of the lenses can be varied. Actually, we are controlling the current which is passing through the coil. So, by doing that the magnetic field strength and the focal length of the lenses can be varied. So this is an element of the electromagnetic lens.

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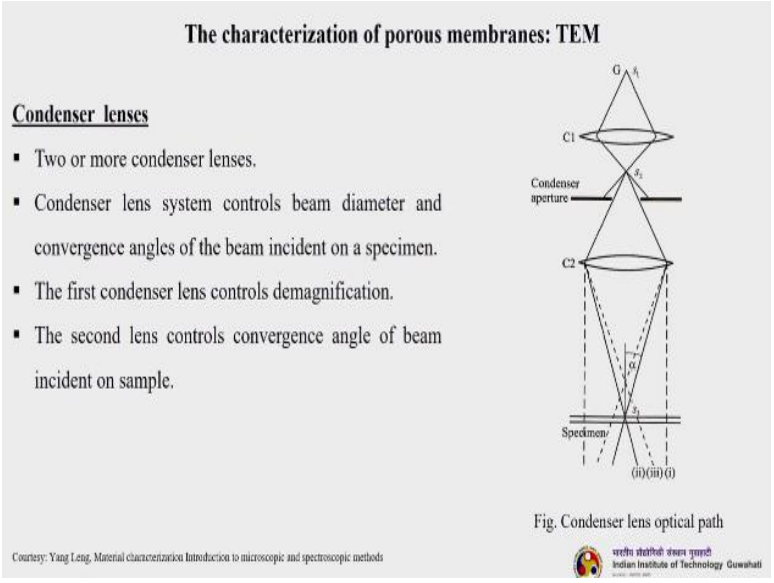

Then condenser lens 2 or more condenser lens at present in actually TEM. So condenser lens system controls beam diameter and convergence angles of the beam incident on a particular specimen and the first condenser lens controls the demagnification there are 2 condenser lens

actually 2 or more usually 2 to his minimum basically. So, the second lens control the convergence of angle of beam incident on the sample.

So, this is a condenser lens optical path which is on in this particular image here you can see the first condenser lens this is the first condenser lens. So, this is what it is doing it is doing the demagnification, demagnification of the incident rate which is passing through it and then the second one is actually converging, then angle of incidents, and then it is falling on the surface of the beam. So here it is converging you can see like this and this is the sample or the specimen on which it is falling.

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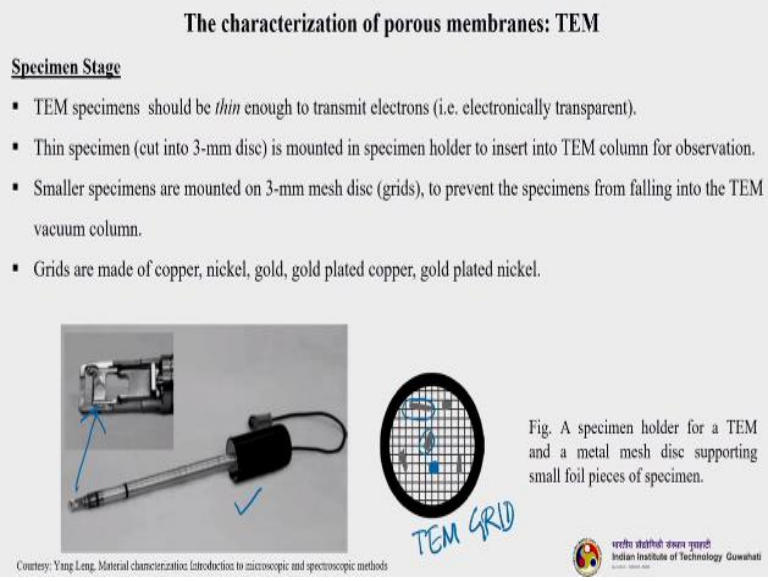

Then let us understand the specimen attempt specimens should be thin as thin as possible because here the electrons are getting transmitted through the specimen. So, if it is thick then transmission will be very less and thin specimen cut into usually 3 mm disc is mounted in a specimen holder to insert into the TEM column. So, this is the specimen holder this image and this is the magnification here you can see.

So, you can take it like this it is a slip type of system arrangement in which you are going to spicier grid. So, there is something called TEM grids so, you call it a TEM grid. So, smaller specimens are mounted in 3 mm disc. It is called grid, usually made up of copper. So to prevent specimens from falling into the TEM vacuum column because it is under vacuum this specimens

would not follow. So, you have to be very careful. So, here this one cares would be taken in such a direction you are seeing now please see these are specimens.

So, you should be in such a way that it is the size is more than this particular size up this the grid here, this is one grid, this particular grid, so, the specimen size should be more than that it size a single grid size also otherwise the vacuum will try to pull it inside the TEM so, grid are made up of various materials. So, copper is usually used we can have nickel, gold, gold plated, copper and gold plated nickel also. So, those are very costly that is why usually copper plates are used.

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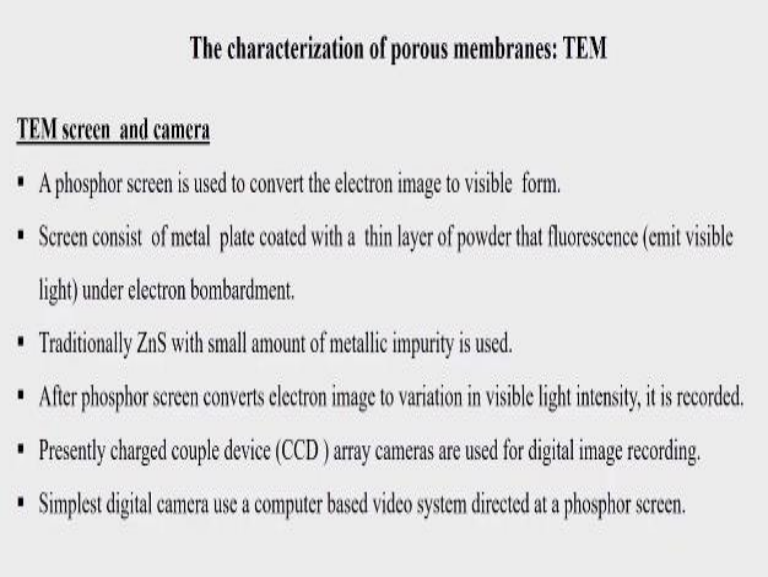

So, a phosphor screen is used to convert the electron image to visible form in case of TEM. The screen consists of a metal plate coated with a thin layer of powder that fluorescence under electron bombardment. Additionally zinc sulphide with small amount of metallic impurity is used after phosphor screen converts electron image to various an invisible light intensity, it is record. Presently charged coupled device, CCD which is very famously known as a charge coupled device cameras are used for digital image recording simplest digital camera use a computer based video system directed at phosphor screen.

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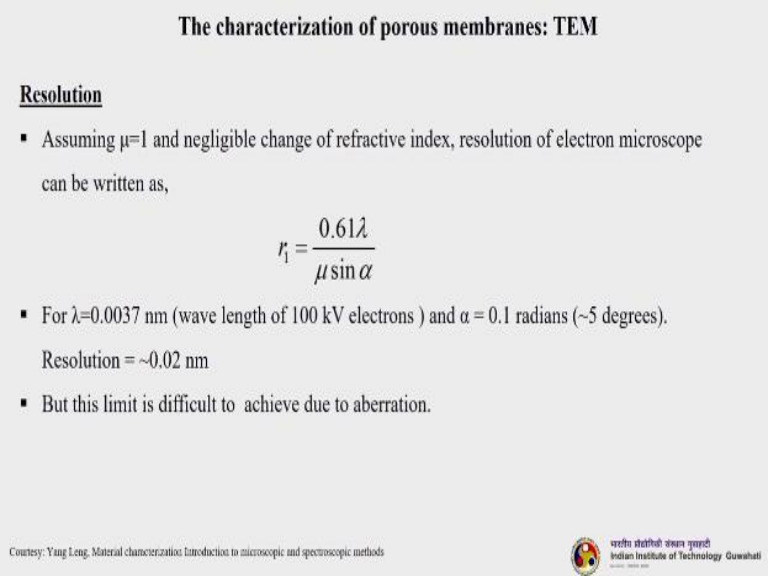

So, resolution is something that is a very important for TEM because it is this feature which is actually distinguishes itself from other scanning other electron microscopy techniques. So, assuming mu =1 and negligible change of refractive index resolution of electron microscope can be written as r 1 = 0.61 lambda divided by mu sin alpha. So, here, lambda is 0.0037 that is the wavelength of 100 kilovolt electrons and alpha equals 0.1 radians, is well to more or less approximately to 5 degrees. So, here resolution that you will get will be 0.02 nanometer, but this limit is difficult to achieve due to aberration.

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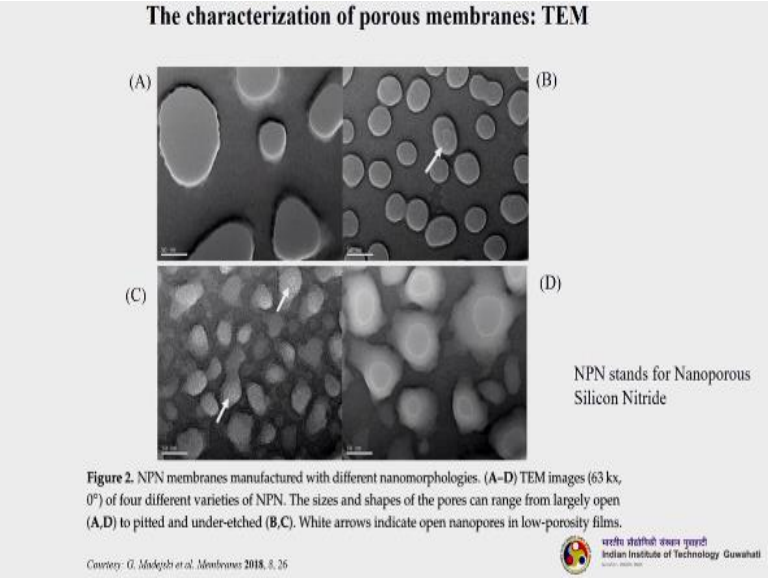

So, this is the TEM image of a porous membrane. So, you can see there are 4 distinct images micrographs we call it TEM micrographs. So, you say NPN membrane NPN and actually nano

porous silicon nitride NPN stands for manufacturers different nano morphologies. So, the sizes and shapes can be range from largely open to pitted and under etched. So, A and D you can see that this one this and this they are largely open structure and B and C. So, this one, this one and this one. So they are pitted or under etched.

So, this is you can see there are some white arrows, this is the white arrows. So that indicates open nanopores in low porosity films. You can see very small, open nanopore here, here also you can see this one. So they are in indicative of the small open nanopores in low porosity films.

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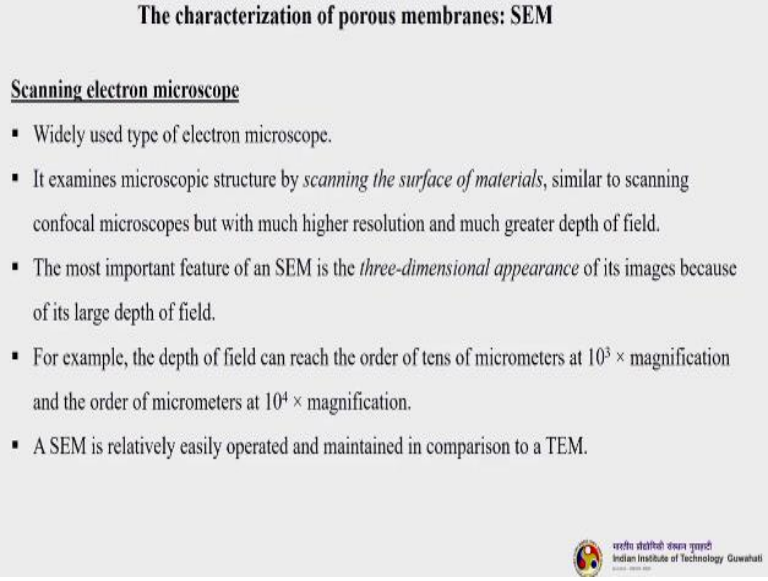

Now students let us understand how the same works and what is it principle of operation and what is it different parts. So, scanning electron microscope is widely used type of electron microscope, It examines microscopic structure by scanning the surface of the metals published again I am repeating that the difference between SEM and TEM is that in TEM the electrons are getting transmitted across the surface of the polymer membrane.

Whereas, or any sample whereas in SEM, the electrons are not getting transmitted, rather they are scanning the surface of the material. So, it is the surface that is getting characterized. So, similar to scanning confocal microscope but with much higher resolution and much greater depth of the same, the most important feature of the same is 3 dimensional appearance of its image because the depth is actually depth of the field is high.

So for example, the depth of the field can reach the order of 10s of micrometers or 10 Power of 3 magnifications and the order of micrometers 10 power of 4 magnifications. SEM is a relatively easily operated and maintained in comparison to TEM.

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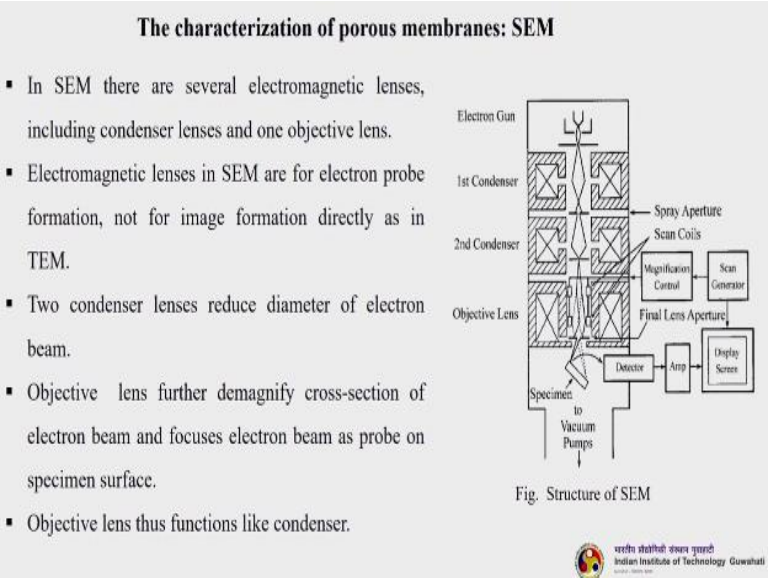

Please look at this particular image which is showing the structure of SEM. So, there are several electromagnetic lenses including condenser lenses and one objective lenses. So, here also minimum 2 condenser lesson lenses are you used please understand that whatever we have discussed under TEM So, most of them also holds good for SEM also like the number of consultants would be minimum 2 it can be more also, but minimum 2.

So, and then electromagnetic lenses are used for electron probe formation not for image formation as in the case of TEM. So, this is another distinctive feature. So, in TEM the electromagnetic lenses are doing the image formation whereas in SEM, they are not doing an image formation they are helping you electron probe formation. So, here the 2 condenser lenses are used, so they reduce the diameter of electron beam.

Look at the condensing that is why the name condenser lens. So, objective lens for the demagnify the cross section of electron beam and focuses electron beam as probe specimen surface you can see this is a specimen, this is actually holding a tilted position. So, objective lens

functions like a condenser. So, here we are first condenser lens here we have a second condenser lens, this is the electron gun which is providing your electrons.

Then there are different types of aperture there are different scan culture there which is used for magnification purposes. Then we have final lens aperture through which final electrons with high energy passing and getting and bombarding on the surface of the specimen. And then whatever the secondary electrons coming out of this specimen, they are being detected by the help of the detector. And then there is the amplifier which is helping in amplifying the images and then we see whatever the image in a display screen.

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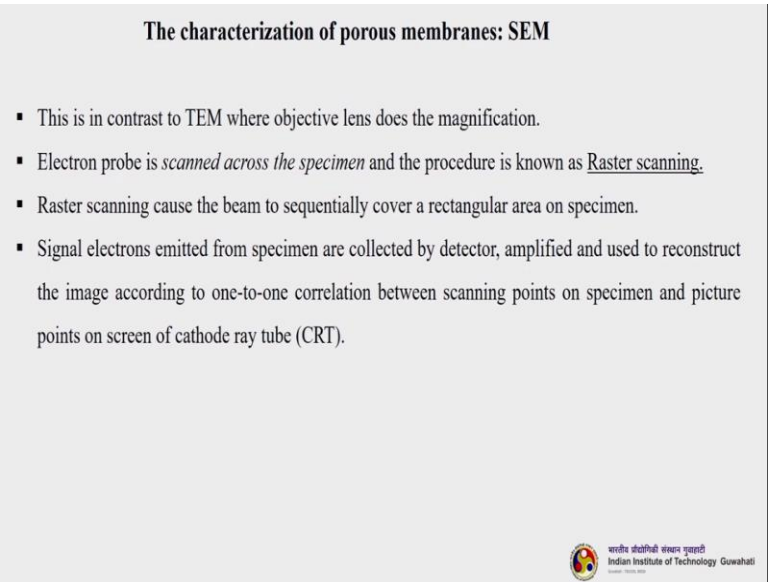

This is in contrast to TEM objective lens does the magnification. So, electron probe is scanned across the specimen and the procedure is known as raster scanning. So, rest of scanning cause the beam to sequencing recovery rectangular area on specimen signal electrons emitted from specimen are collected by detector and amplified and used to reconstruct the image according to one to one correlation between scanning points on specimen and picture points on the screen of cathode ray tube so CRT.

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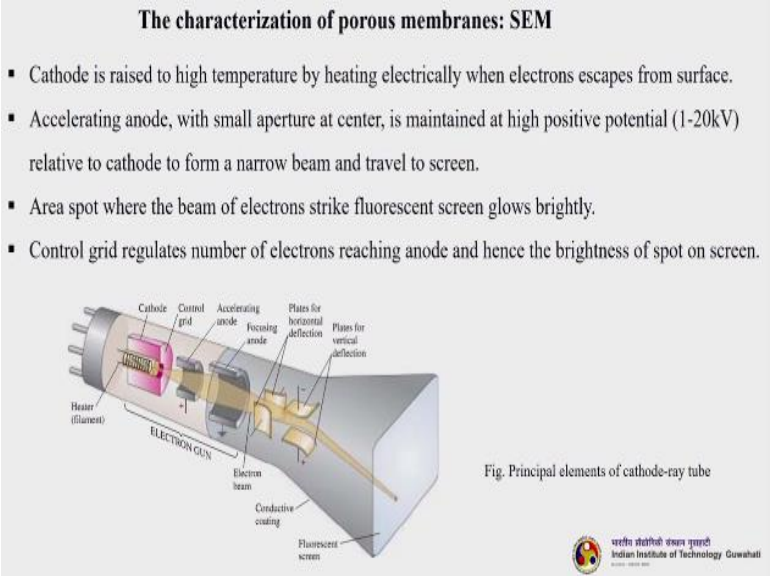

Let us understand what is that actually how CRT looks like the cathode ray tube so, cathode is raised to high temperature by hitting electrically when electrons escaped from the surface. So, there must over the resistances and then after that only so sufficient amount of minimum temperature amount of energy to be supplied so that it will cross the barrier. And so that electrons will come out from the cathode.

So, accelerating and not with small aperture at center is maintained at high positive potential relative to the cathode to form an narrow beam travel to screen. So, you see this is the cathode actually and this is the filament. So, then we have the accelerating anode here. So, there is a smaller aperture inside the accelerating and not. So, then there is a focusing anode here this one then there are plates for horizontal deflection and then there are plates for vertical deflection.

So, there is a area spot where the beam of electron strike fluorescent screen glows very brightly control grid regulates number of electrons reaching anode and hence the brightness of sport on the screen. So, this horizontal plates and vertical deflection plates that helping to actually neutralize the different types of electrons that are passing out of the anode.

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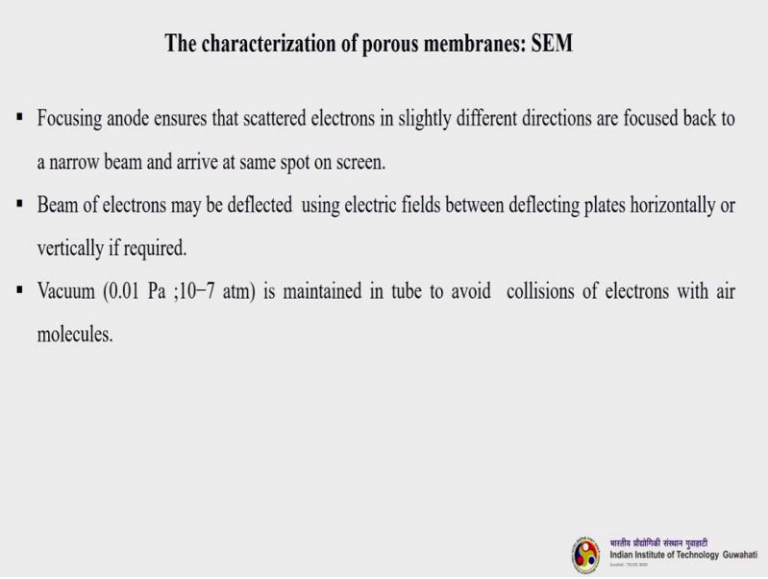

So, focusing anode ensure that scattered electrons in slightly different directions are focused back to a narrow beam and arrive at same spot on screen, beam of electrons may be deflected using electric fields between deflecting plates horizontally or vertically if required so, it is actually what is the requirement depending upon you can use either one of these are both also so vacuum is maintained in tube to avoid collisions of electron with air molecules.

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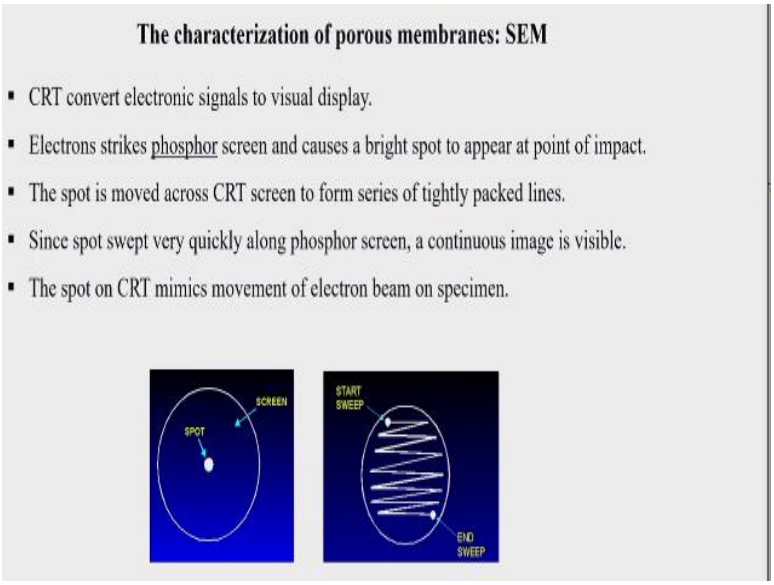

So, CRT converts your electronic signals to visual display cathode ray tube. So electrons strikes a phosphor screen, the screen here actually is phosphor screen and causes a bright spot to appear at the point of impact, so any and there is a when their impacting it will create a bright spot. Now this spot actually moves rapidly the spot move across the CRT screen to form a series of tightly

packed lines. This is how it looks like. So since spots swept very quickly along the screen phosphor screen, so continuous images visible. So, they are very fast. So, the spot on CRT mimics the movement of electron beam on specimen.

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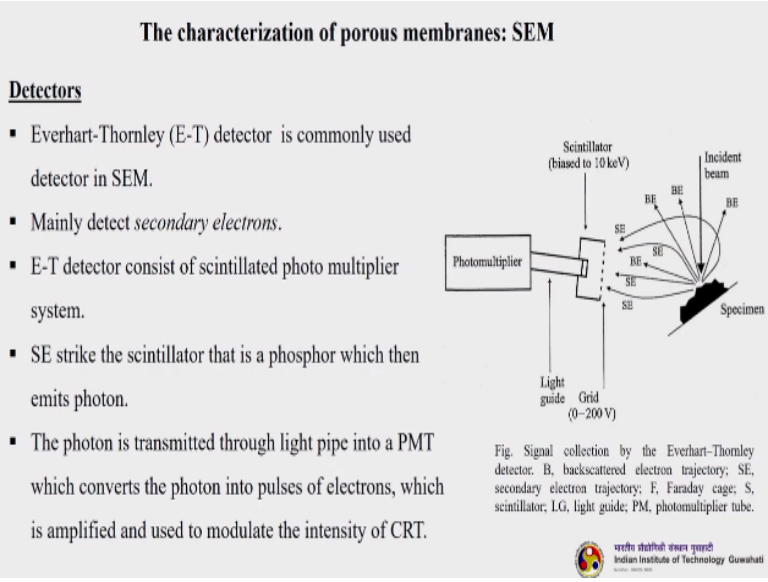

Let us understand the different types of detectors. So, detectors plays a very important role in electron microscope because ultimately this is the instrument which is detecting whatever the incident rays coming out from the microscope and then converting it into the final image. So, E-T detector which is called Everhart Thornely detector is commonly used in SEM. So, it mainly this detect the secondary electrons.

So, E-T detector consist of a scintillated photo multiplier system. So, if photo multiplier is a unit which actually amplified the this one electrons and secondary electron strike the scintillator that is a phosphor, which then emits photon, so, this is a scintillator you can see, this is photo multiplier. So there are grids here you can see there are grids here you 0 to 200 ball then once the secondary electrons strike the scintillator then it will emit the photons.

So, this photons transmitted through light pipe into a PMT which converts the photon into pulses of electron which is amplified and used to model as the intensity of the CRT you can see this is the specimen how incident beam is falling here then secondary electrons are getting generated and these are secondary electrons these are back electrons.

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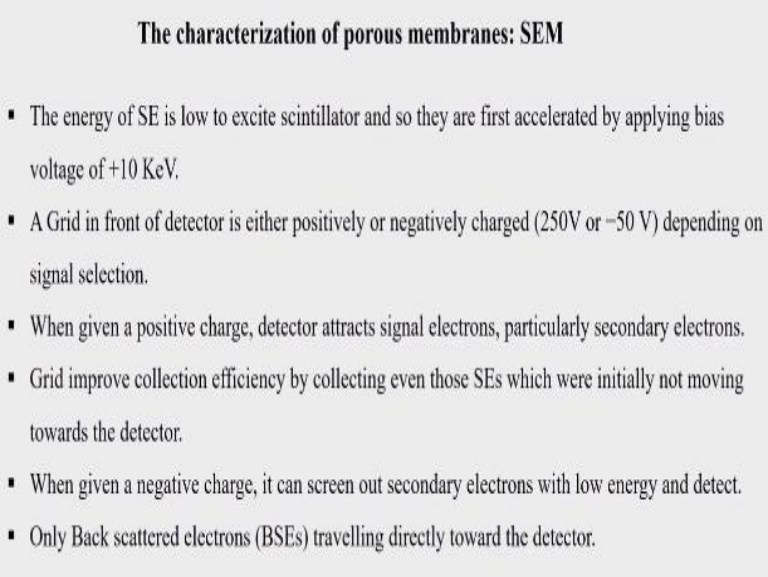

So, the energy of secondary electron is low to excite scintillator and so, their first accelerator by applying bias voltage plus 10 kilo eV. A grid in front of detector is either positively or negatively charged depending upon the signal detection. When given a positive charge detected a track signal protons, electrons, particularly secondary electrons, the grid improved collection efficiency by collecting even those secondary electrons which are initially not moving towards the detector.

So, when given a negative charge is screen out, secondary electrons with low energy and then detect and only backscattered electrons which have knowledge bases travelling directly towards the detectors.

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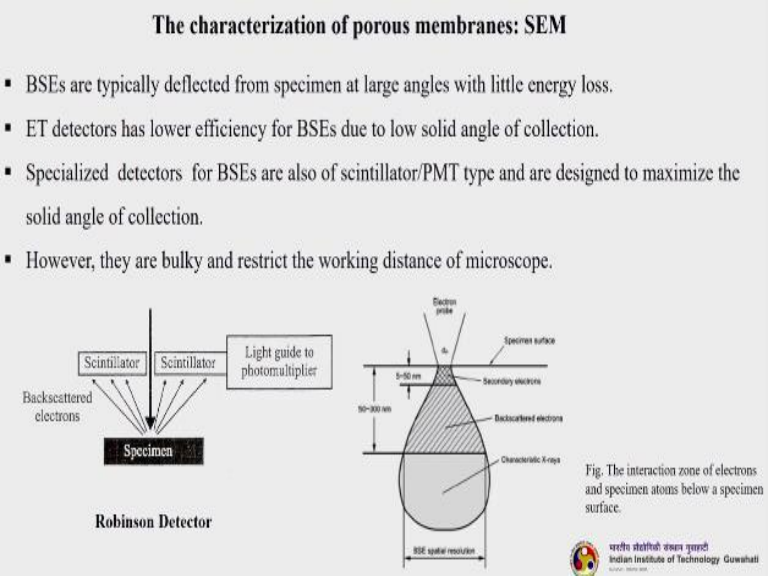

So BSEs are typically deflected from specimen at large angles with little energy loss. So ET detectors has lower efficiency for backscattered electrons due to low solid angle of collection and there are specialized detectors for BSEs you can see this particular structure actually, it is again showing how the center the light actually the backscattered electrons are going back to the scintillator. And here also you can see what is the see this is the specimen surface.

So, electrons are getting bombarded on the surface of the specimen, then secondary electrons are coming here. You can see that this is the area which the backscattered electrons is actually occupying, so if the backscattered electrons will be more it is not good for the imaging purposes. So you need to minimize them.

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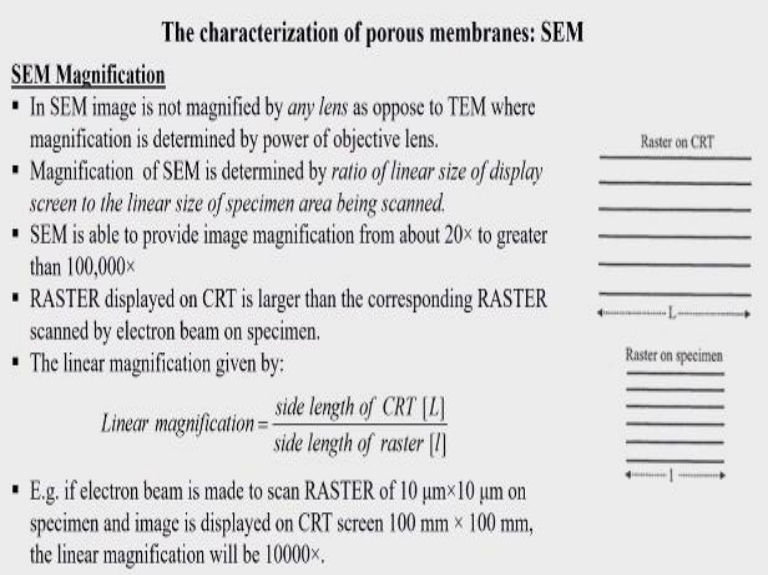

The same image is not magnified by any lens as opposed to TEM, magnification is determined by the objective lens. So, magnification of SEM is determined by the ratio of linear size of display screen to the linear size of the specimen that is being scanned. Since; it is a scanning process actually. So, that is why the magnification is defined or determined in a different way other than of the TEM.

So, SEM is able to provide image magnification from about 10x to greater than 100000x, raster display on CRT is larger than corresponding to raster scan by electron beam. So, you can see so, this is the raster that is getting displayed on the CRT. So, this is actually larger than that of the raster on specimen. So, your linear magnification it is nothing but the side length of the CRT divided by the side length of the L. So, this this L divided by this l. So, as for example, if electron beam is made to scan raster of 10 micron to 10 micron specimen and images displayed on a CRT of 100 mm to 100 mm then the linear magnification will be 10,000 x.

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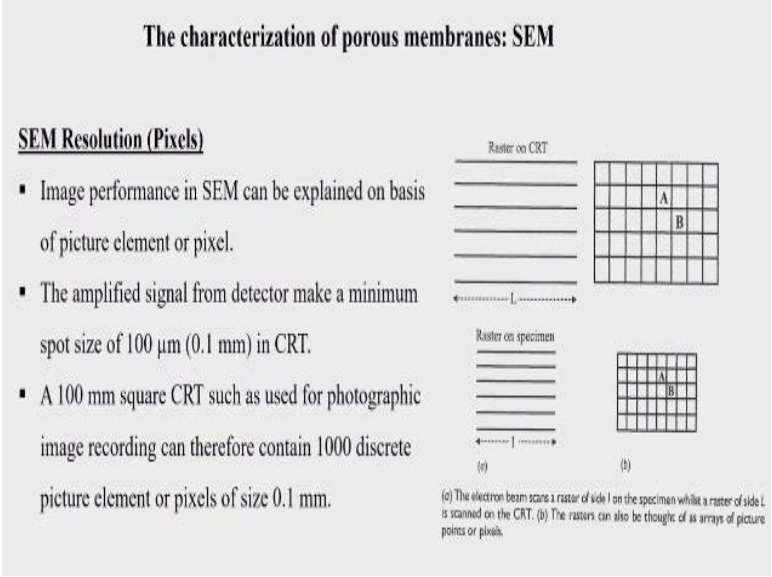

So, same resolution, so, pixels, so, image performance in SEM can be explained on the basis of picture element or pixel. So, please see this particular figure the amplified signal from the detector making minimum spots size up 100 micron in CRT and 100 mm square CRT such as used in photographic image recording can therefore content 1000 discrete picture element of pixels of size 0.1 mm.

So, the electron beam scans raster of side L. So, this is the raster scanning of the specimen and this is the lengthy scanning of that is getting reflected on the surface of the CRT. And the raster also can be brought to thought of as arrays or pictures point or pixels. You can see that these are pixels.

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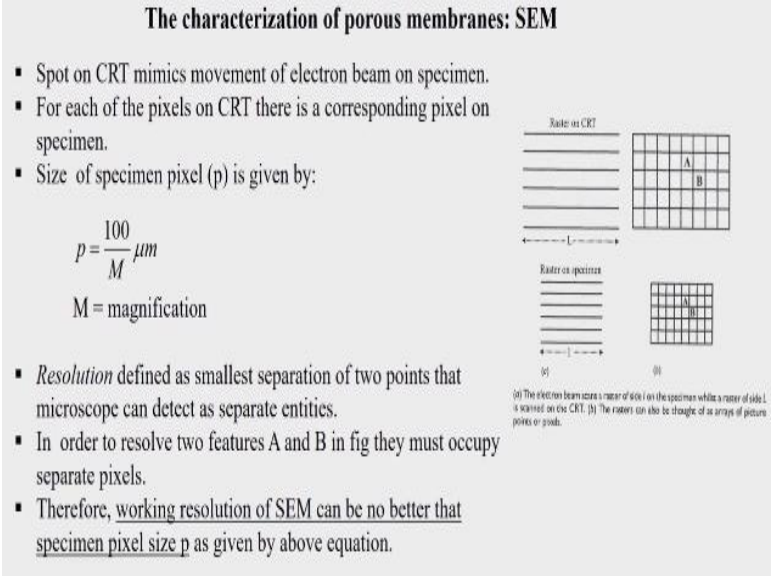

Spot on CRT mimics movement of electron beam on specimen for each of the pixel on CRT there is a corresponding pixel on specimen size of specimen a pixel is given by p equals 100 by M micron, where M is actually magnification. So, resolution is defined as smallest separation of 2 points that microscope can detect as separate entities. So, here you can look at. So, these are the 2 pixels that contents been marked as A and B. So these 2 pixels should be distinctly visible separately.

That is how much they are distinctly visible is actually the resolution. So, in order to deserve to creatures and being triggered, they must occupy separate split pixels. So if the occupied let us see the same pixel here both A and B are occupied in the same pixel, then the problem will be that the resolution will be very low. We cannot see A and B completely and differently. So, that is why they should occupy different pixels. So, therefore, working the resolution of SEM cannot be can be no better than specimen pixel size p as given by the above equation.

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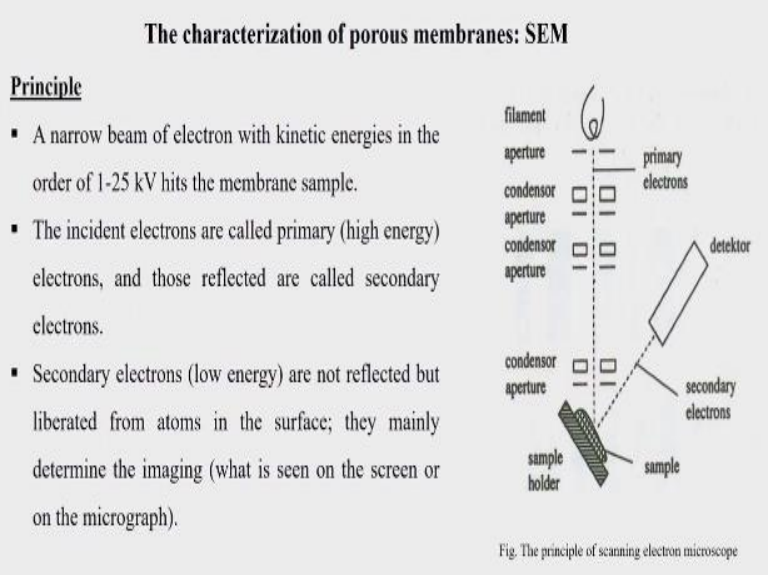

So, in a in a quick nutshell let us understand the principle of SEM again So, a narrow beam of electron with kinetic energy in the order of 1 to 25 kilo volt hits the membrane sample. So, there are primary this is a filament source then the which is actually generating the primary electrons then it passes through the condenser aperture 1 or 2 we have to condenser lens then it goes through another condenser aperture and finally membrane the sample then what it is doing it is generating secondary electrons as well as some BSEs.

Now, these secondary electrons are getting detected by that detector. So, the incidental electrons which are called primary electrons, there having high energy electrons are deflected are called secondary and those are the political secondary electrons. Now, this secondary having low energy are not reflected, but liberated from the atoms in the surfaces, this we need to understand that the secondary electrons are not reflected. So, they are liberated from atoms in the surface. So, they mainly determine the imaging what is seen on the screen on the micrograph.

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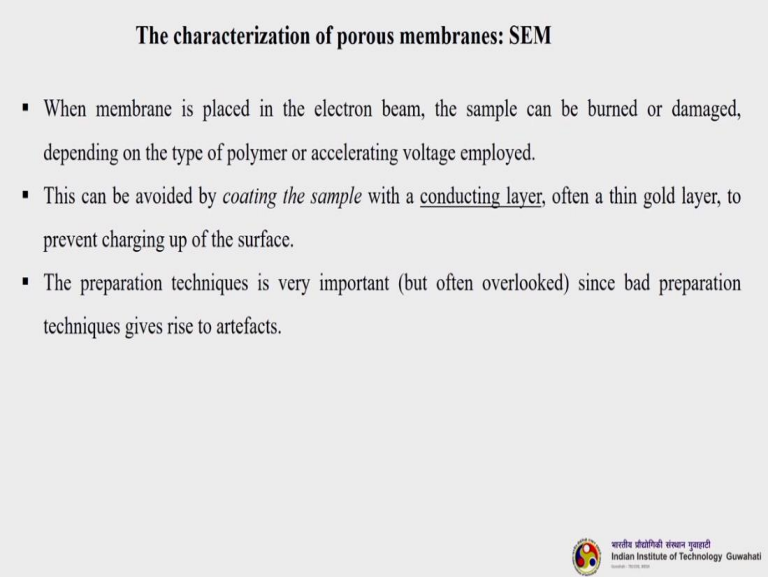

And membrane is placed in the electron beam the sample can be burned or damaged depending on the type of polymer or accelerating voltage employed. This can be avoided by coating the sample with a conducting layer upon a thin gold layer to prevent charging of the surface, the preparation technique is very important, but many times it is overlooked. Because what will happen that if the preparation is not good, then you will get a bad image

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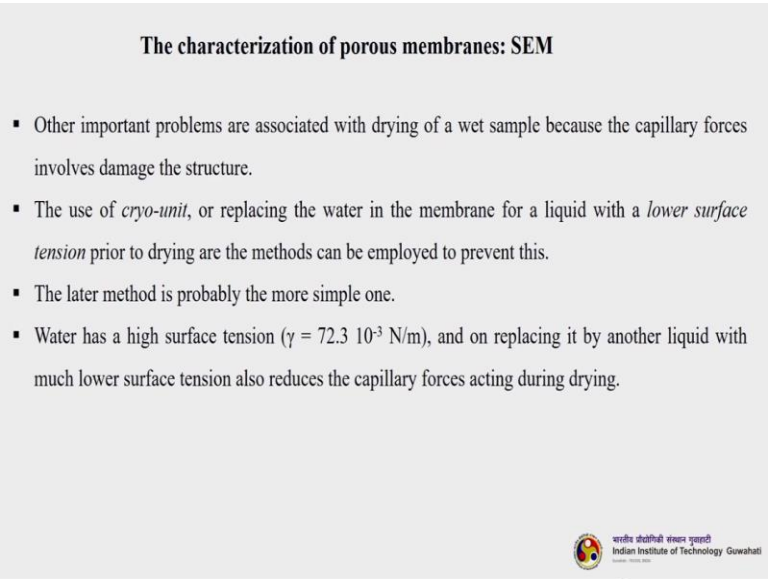

Other important problems associated with drying of a wet simple because the capillary forces involves damage of the structure. So, you cannot go for a sample which is where. So you can use either cryo unit or you can use a liquid with a lower surface tension. So, usually water is used because of water surface tension is one of the lowest.

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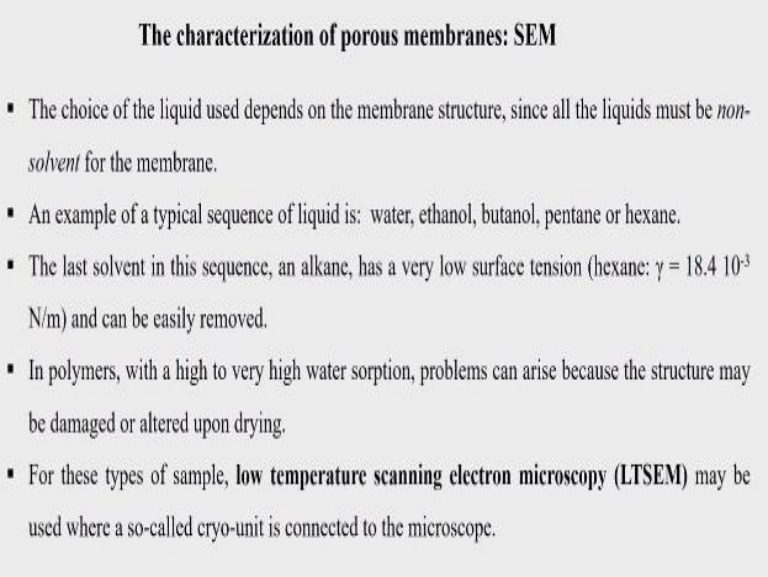

And then the choice of the liquid also depends on the membrane structure because since all the liquids must be non solvent for the membrane and otherwise if you are going to use a solvent which is organic in nature maybe alcohol or something like that, then it will heat may happen that it will swell the pores of the membranes are disuse well the membrane the poresity increase, which you may not understood, but it will eventually happen. So, example of typical sequence of live liquid actually is water.

The water is always prepared by ethanol, butanol, pentane or hexane. So, the last solvent is an alkanes, which is a very low surface tension and can be easily removed in polymers with the height of very high waters of sorption problems can arise because the structure may be damaged or altered during drying if the content liquid support this type of samples, usually low temperature scanning electron microscope which is also known as LTSEM may be used. There is a cryo unit committed to that term this microscope

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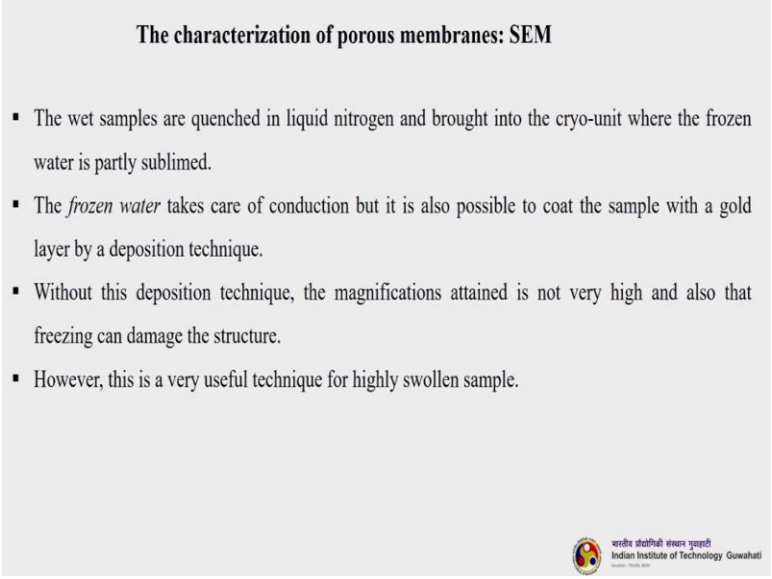

Wet samples are quenched in liquid nitrogen and brought into the cryo unit, but the frozen water is partially sublimed, the frozen water takes care of conduction, but it is also possible to cut the simple with gold layer by a deposition technique, but that the you know cutting by gold layer, it is time consuming a geology it is so costly process. So, however it is done in pure specimen if your one to a particular remains without any hindrance no anticipates nothing then you it is better to court with a gold layer.

So, without this deposition technique, the magnifications attained is not very high and also that freezing can damage the structure also. How about this is very useful technique for highly swollen sample the samples which are actually highly swollen, highly porous and if you are using liquid inside that and that gets freezed then it is fine in a cryo unit, but those who are not swollen and not very micro porous for them actually, if you caught it with gold then it is better.

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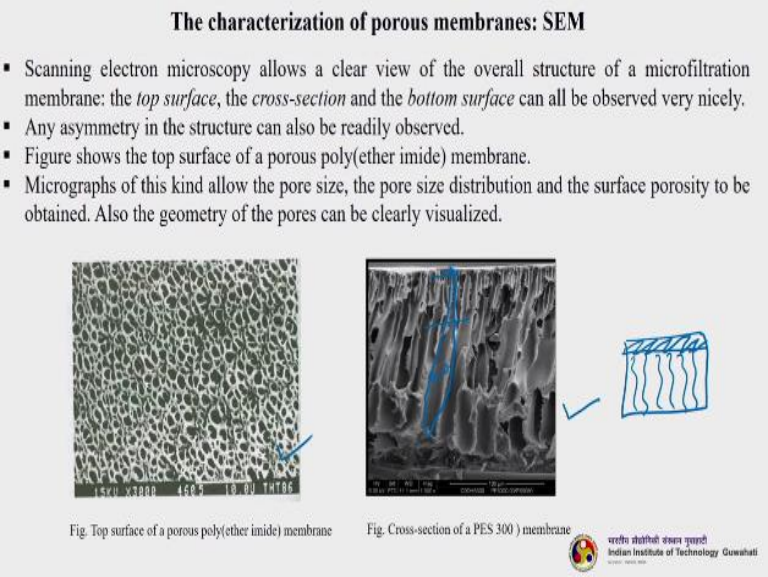

So this is the scanning electron microscope of a particular membrane Same is the technique which will actually give us the view of the top surface as well as the cross section and as well as the bottom surface. So, any asymmetric structure also can be identified if you look at the cross section figures of the top surface of this is the top surface of a porous poly ether imide membrane. So, micrograph of this kind allow pore size, pore size distribution and surface porosity to be often also the pore geometry can be visualized.

So, you can see this is the cross section, this is a cross section of a PES 300 membrane you can see little the structure of the pores, you can see this particular pore more or less it is a cylindrical pore. However the constriction here in this particular area is little lesser and then it become white. So, it is very easily if you use this cross section then you can easily Identify here a symmetric structure we can see this is a dense layer or any layer so we can then see the porous layer here. So easily if you look at the cross section, it will tell us easily whether the membrane is a symmetric membrane or not.

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Field Emission SEM (FESEM)

- FESEM produce a cleaner image, less electrostatic distortions and spatial resolution < 2 nm (3 or 6 times better than SEM).
- FESEM is a high vacuum system.

Electron source	Final spot diameter
thermionic	1nm-1mm
Field emission source	1 nm

- Low final spot diameter makes FESEM, the higher resolution instrument
- FESEM which achieves a small probe diameter and high probe currents at low beam energies resulting in higher resolution
- Reduced penetration of low kinetic energy electrons probes gives information closer to the immediate material surface.
- High quality, low voltage images obtained with negligible electrical charging of samples. Need for placing conducting coatings on insulating materials is virtually eliminated.

So, there is something called a FESEM or it is called field emission SEM, so FESEM produce cleaner image less electrostatic distortion and special distortions then almost 3 to 6 times better than the of the same. So, it is a high vacuum system, so low final spot diameter makes FESEM the higher resolution instrument, FESEM which achieves a small probe diameter and high probe current. Let us understand quickly that FESEM is a technique in which the field emission is being used, and each resolution is 3 to 6 times higher than the resolution of the usual same so you can understand and see this image which will be very clear.

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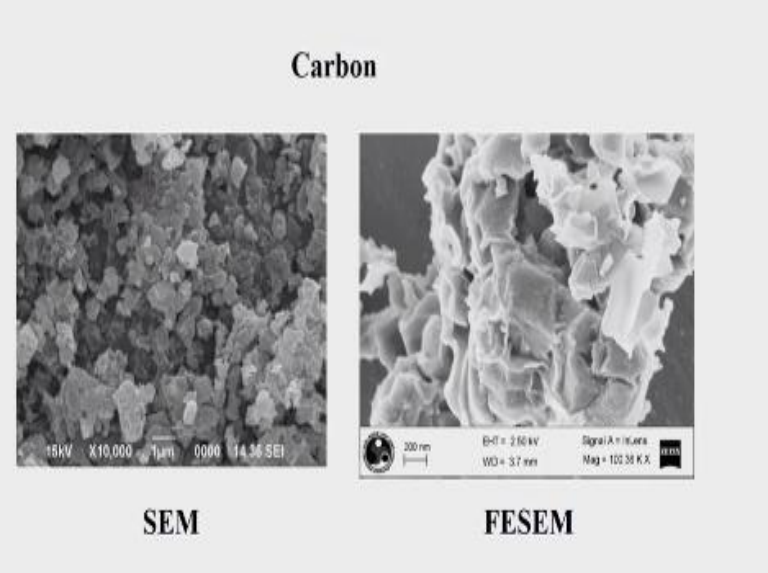

So, you can see this is SEM image of a carbon particles, you can see that particular will so clearly visible However, if you use the FESEM same material, it will give a distinct features more clear more high resolution and brighter image.

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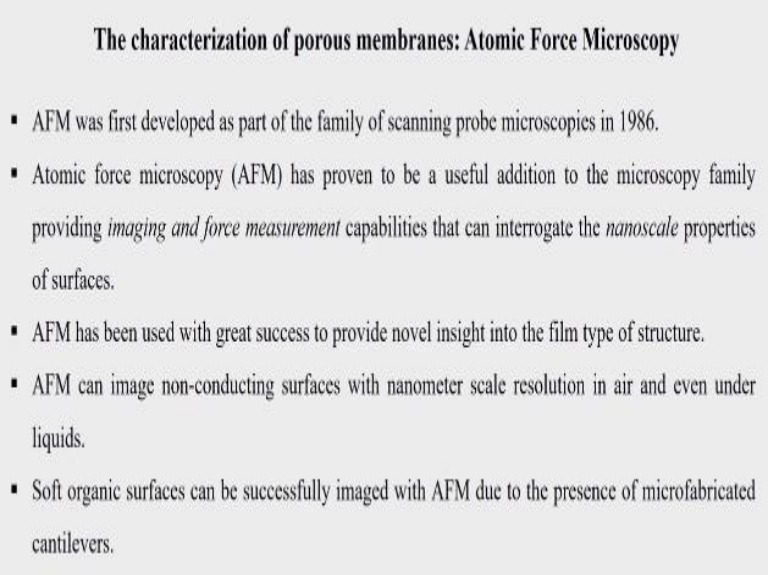

So, now students let us understand quickly what is AFM, at AFM is atomic force microscopy it was invented almost back in 1986. If I correctly remember, scientists at IBM have actually discovered this AFM technique. So AFM has proven to be a useful addition to the microscopy family it providing imaging and post measurement, that can interrogate the nanoscale properties. So basically useful to study the nano properties. AFM has been used with great success to provide noble insight into the film type of structure.

AFM can image not conducting surfaces with nanometer scale dissolution in air and even under liquids. So, soft organic surfaces can be successfully imaged with AFM due to the presence of microfabricated cantilevers.

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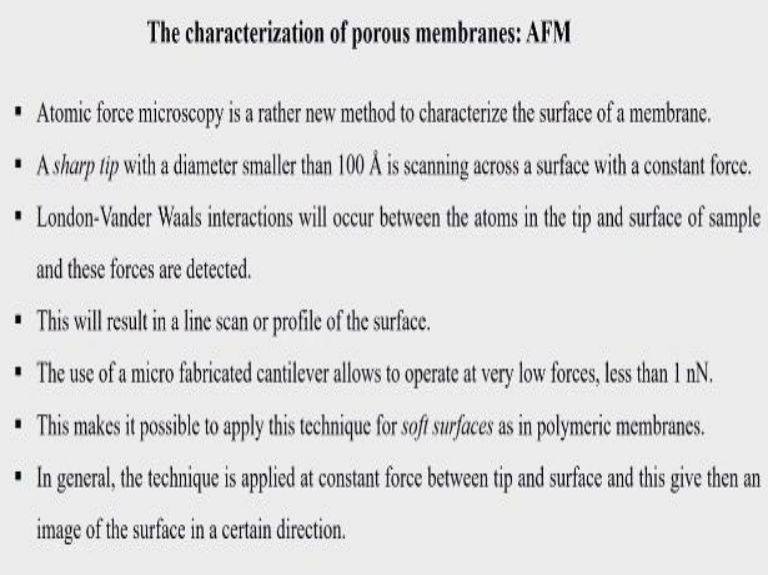

Let us see, actually we will see in an image how it actually works. So, AFM is a rather new method to correct the surface of a membrane there is a sharp tip with a diameter of almost 100 angstrom very small, very thin which is scanning across the surface. So, here in the same the electrons are scanning on the surface of the sample, but here in AFM there is a tip the cantilever is holding a tip that tip is actually scanning like this with the constant form.

So, you have London Vander Waals interaction will occur between the atoms in the tip as well as surface of the sample and those forces are detected, they will eventually result in the micrographs. So this will result in a line scan or profile the use of micro fabricated cantilever allows to operate at a very low forces less than 1 nano Newton This makes it possible to apply this technique to soft surfaces agent polymeric membranes in general these technique is applied at constant pores between tip and surface and this gives them an image of the surface in certain direction.

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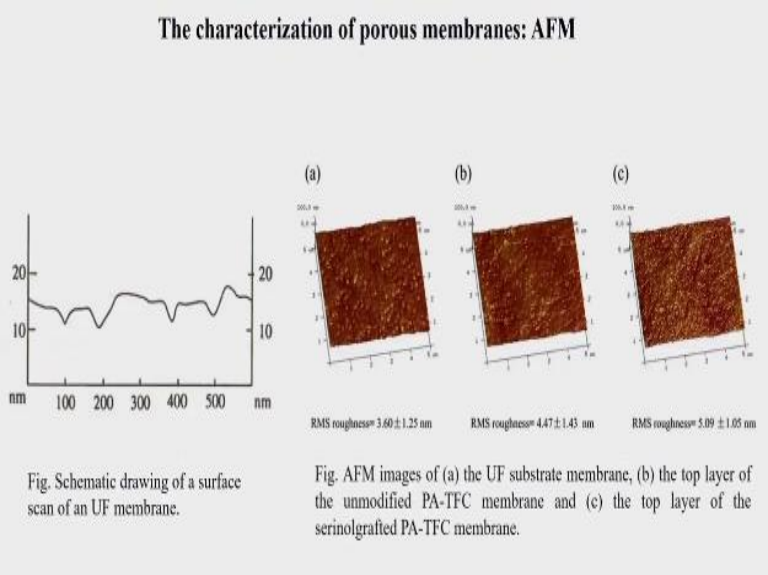

So, let us look at the AFM images you can see seen this side, this is a schematic drawing of a surface scan of an ultra filtration membrane here this particular image there are 3 images it is showing the AFM images of it or ultra filtration substrate membrane this one a one then this is the b the top layer of the unmodified membrane and c the top layer of the serinolgrafted membrane. So, what we if we actually make it a little bigger size then we can understand it a little better. However, we can understand from the image that there is distinct pictures which can be noticed for different types of materials.

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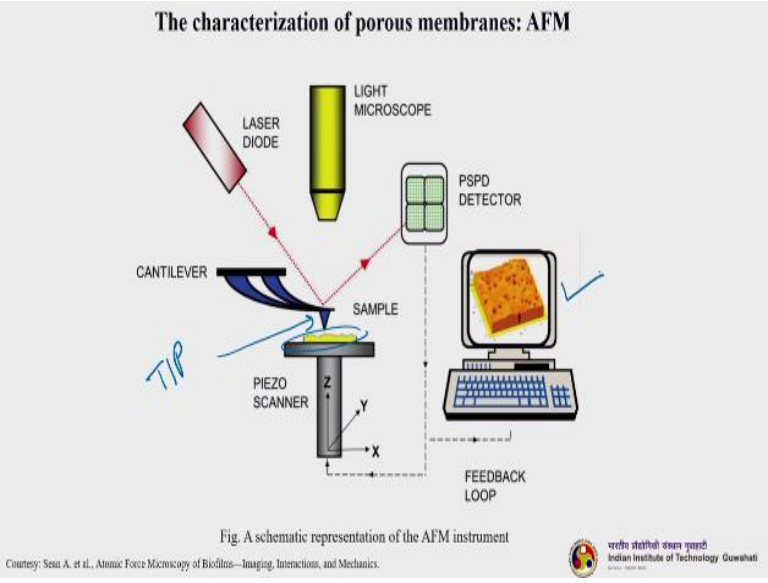

So, this is the AFM instrument actually works. So there is a laser diode and this is the cantilever which is holding this is your sample this is the tip which I was talking about. So the tip actually

doing the scanning that is scanning the surface of the sample then whatever the amount of forces what is that not amount but the types of forces that is actually getting generated by virtue of this Kenny, they are getting detected using a PSPD detector there can be different types of detectors and finally, this detector is amplifying and doing so many other processing intermittently and then getting resulted in an image which will lose something like this.

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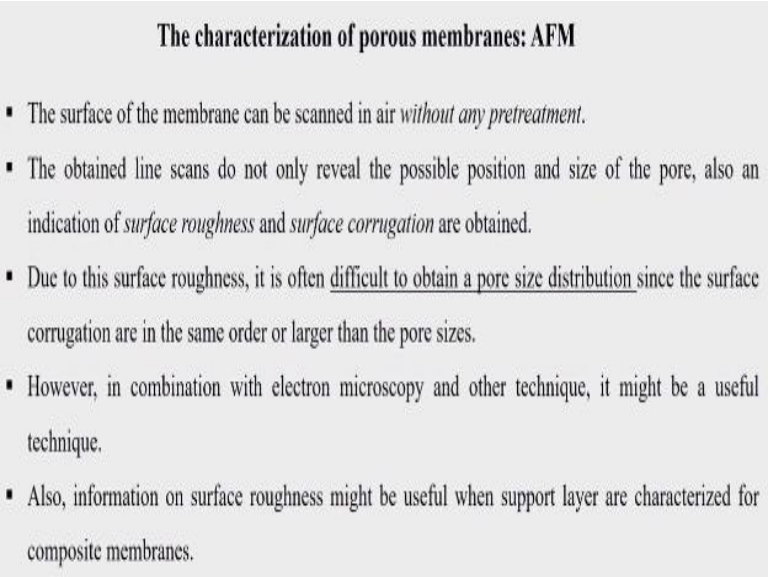

So, the surface of the membrane can be scanned in air without any pretreatment this is another advantage of the AFM so the obtained lines scans do not reveal the possible position and size of the pore also an indication of surface roughness and surface corrugation so AFM is the only one technique which will give us the indication of surface roughness, due to the surface roughness it is often difficult to obtain a pore size distribution. So, PSD or pore size distribution is bit difficult to get in case of AFM which is very easy to do it in case of here SEM.

So, however in combination with electron microscopy and other techniques, it might be useful technique. So, also information or surface roughness might be useful and support layer are characterized for composite membranes.

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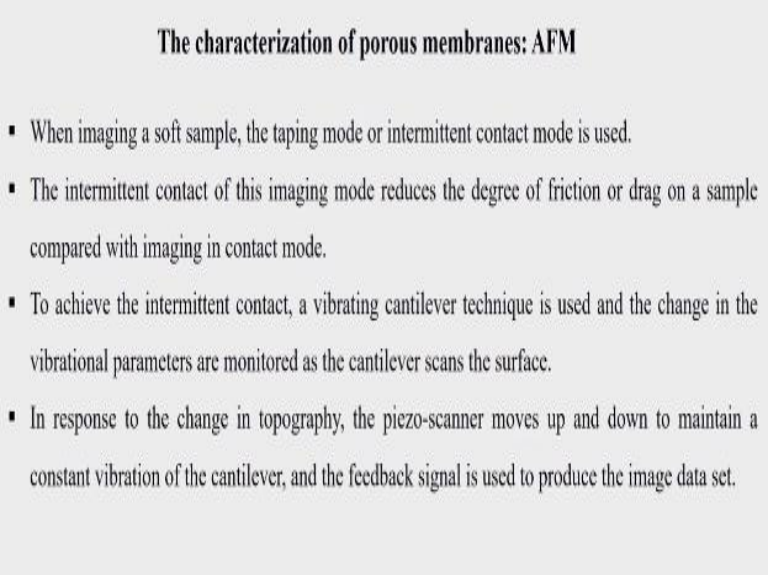

When imaging a soft sample that tapping mode intermitted contact mode is used the intermitted contact of this imaging mode reduces the degree of friction or drag to achieve the intermitted contact a vibrating cantilever is used actually. So, techniques so that cantilever is actually vibrating and changing their vibrational parameters are monitored as the cantilever scans the surface. So, in response to change in topography that piezo-scanner moves up and down to maintain a constant vibration of the cantilever and the feedback signal is used to produce the image.

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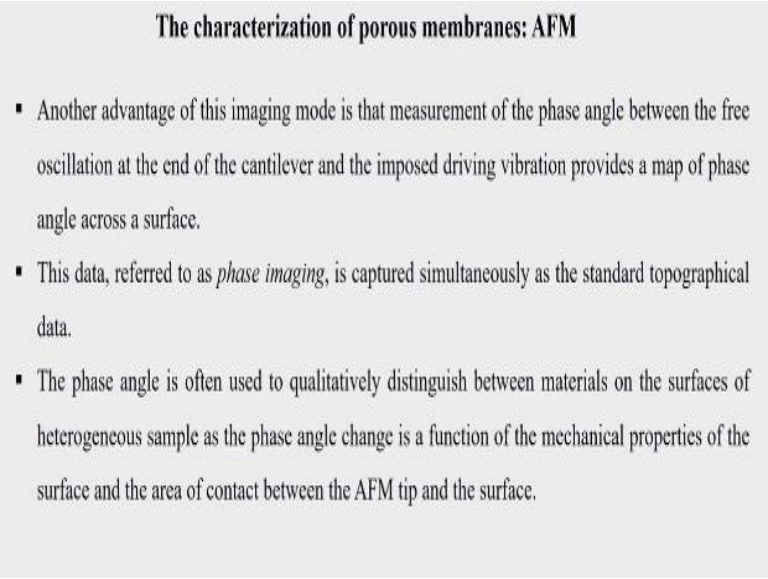

So at the advantage of this imaging mode is that measurement of the phase angle between the free oscillation at the end of the cantilever and the imposed driving vibration, provide some map

has angle across the surface. So, actually this is refered to as phase imaging, this is captured simultaneously is the standard topographical data.

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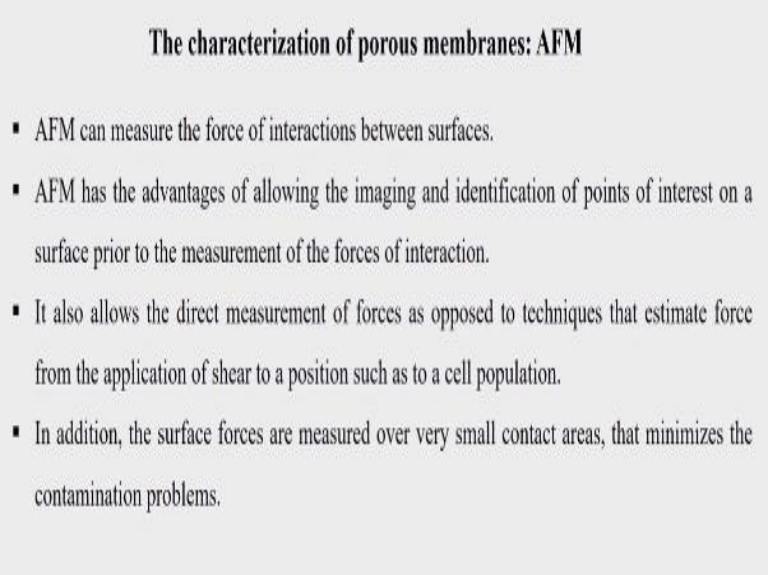

AFM can measure the force of interaction between surfaces. So, AFM has the advantage of allowing the imaging and identification of points of interest on a surface prior to measurement of the forces of interaction. So it also allows the direct measurement of forces that opposed to techniques that estimate force from the application of a shear to a position such as to cell population, in addition surface forces are measured very small contact areas. So that actually minimizes the contamination problem.

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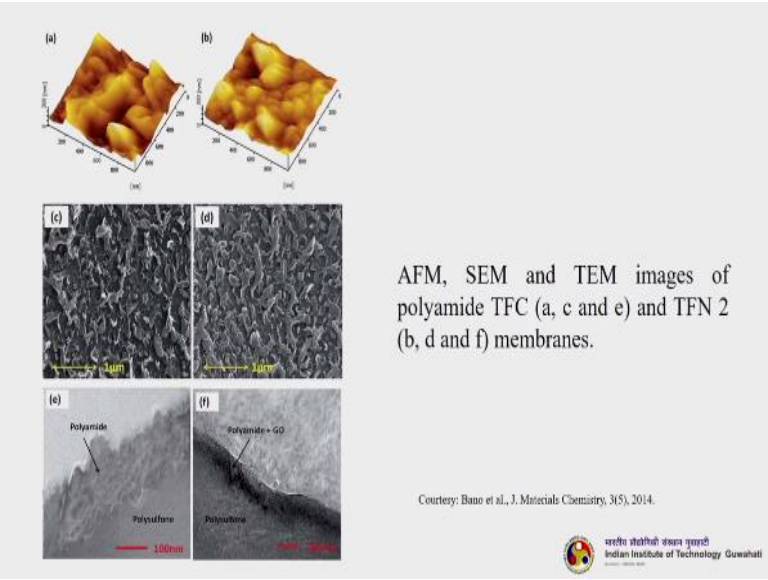

So students please have a look in this interesting figure, images. So in a single this one figure, you can see there are 6 different distinct images. So 3 each. So, the first 3 here A B and sorry A C and E. So, these are corresponding to the AFM The first one is this is AFM, this is scanning electron microscope and this is TEM. So, AFM, TEM and SEM and TEM images of a TFC so thin film composite membrane and similarly here, this is the AFM this is the SEM and this is the TEM image of TFN.

So, thin film nano composite membrane. So, you can see how the images are distinct actually, in case particular subset in case of AFM in case of a SEM and in case of a TEM.

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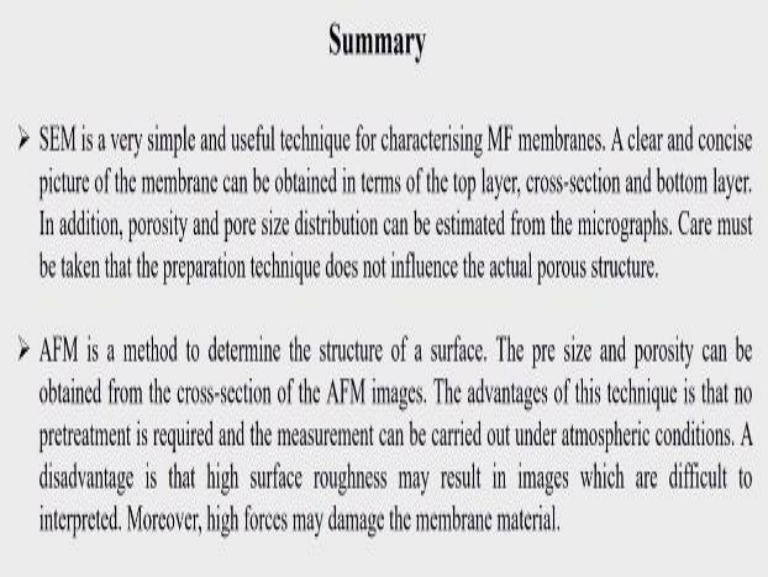

So, let us wind up in today's class. So, in summary, we will just try to tell you that SEM is a very simple and useful technique for characterizing micro filtraizing membrane and clear and concise picture of the membrane can be obtained in terms of top layer cross section and bottom layer. In addition, we can find out porosity and pore size distribution. So, care must be taken for the preparation of the simple.

So, whereas AFM is a method to determine the structure of the surface, the pore size and porosity can be obtained from the cross section of the AFM images, but easily we do not referred to do so, we can do it however, we used to do it from our SEM if you have SEM if you do not have the SEM than AFM or cell from AFM micrographs also you can find out so, the advantages

of this technique is that no pretreatment is required This is one of the beauty of this particular technique

And it can be the measurements can be carried out in under the atmospheric conditions or ambience. So, a disadvantage is that high surface roughness may sometimes result in images which are difficult to interpret because the tip is getting is doing the scanning now. So, there is a forces which are higher getting generated and they may damage the surface actually. So, high forces may damage the membrane material.

But not all for few polymeric material are susceptible to such damage actually. So, students today we understand the micro porous this one membrane characterization techniques, 3 important characterization techniques SEM, TEM and AFM

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And next class you can referred these books and the next class we will understand some other beautiful techniques which is called a Bubble point method, Bubble point with gas permeation method, mercury intrusion method and permeability method. So, some of these methods like here Bubble point method as well as permeability methods this can be done in the lab in anybody's life it can be done with the very small setups, and you get accurate results also. So, thank you very much. So, if you have any query please feel free to write to me at kmohantyatiitg.ac.in. And I will definitely answer your queries. So thank you very much