Materials Chemistry
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Module - 3
Lecture - 6
Applications of Electron Microscopy SEM and TEM

In this module we are looking at different characterisation techniques and so far we have looked at diffraction technique, thermal analysis technique, spectroscopic techniques. And in the previous lecture we have also looked at the tunnelling microscopic technique and atomic force microscopy, but the most important and inevitable characterization tool for all branch of science is microscopy specially with reference to scanning electron and transmission electron microscopy.

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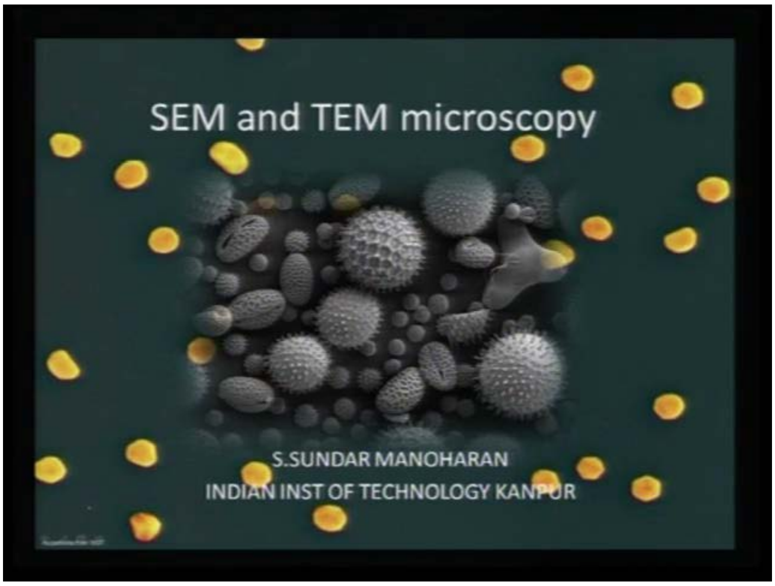

SEM and TEM microscopy

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This particular microscopic tool is used by a range of researchers, biologists rely on SEM as much as the physicists and a chemistry researchers do. The main reason is this is one of the most commonly available instrument, and also it is fairly simple for anyone to access. And the requirements for studying the material using SEM and TEM is comparatively much, much more simpler than the sample preparation requirements needed for STM and AFM techniques.

Therefore, this is one microscopic tool which is very, very popular and I am going to just run through some of the examples or principles behind using SEM microscopy. And then drive home some point as to how carefully we need to look at this microscopy or what are the information's that we can get out of it. And I will also show some of the recent results, which can give idea about the importance of this SEM and TEM tool in materials characterization.

As you see here in the first slide we can use it for a range of materials and the picture that you see in the middle of this cartoon are the pollen, that is present in air. And they are mostly micron range, and one can get an idea about the pollen that is present in air, and how much they contribute even to pollution. So, this gives an idea about the range of a particle suspended in air, which are of micron size and also you would see some of the other images mingled with this those, which are appearing as yellow particles or golden particles are indeed gold particles, the colour is actually camouflage just to drive home the point.

So, we can study a range of material one, which are synthesized in a laboratory scale or in nano scale and those which are already existing in nature, so a range of materials can be studied using SEM and TEM microscopic techniques.

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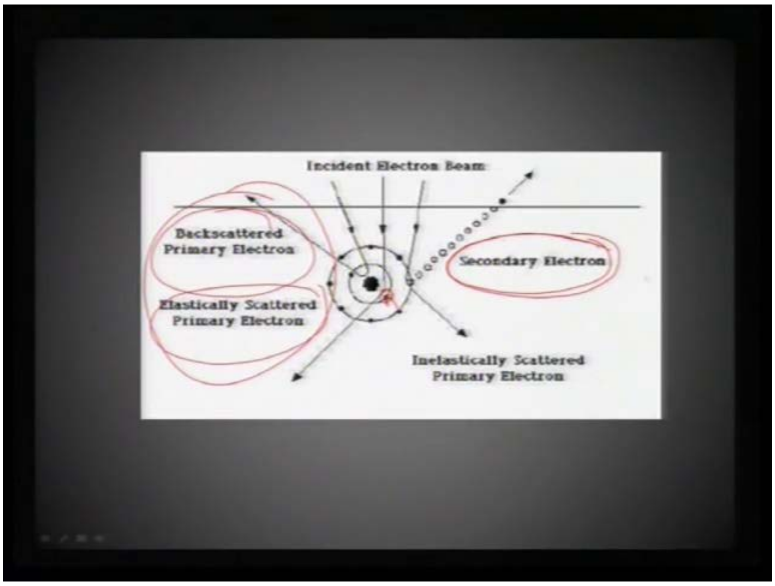

Now, what is the fundamental issue that that is involved in studying this SEM, TEM characterization tools is the impact or the interaction of electron beam with matter, how they interact and what is the secondary effect or what really comes out, that determines whether it is a TEM microscopy or SEM microscopy. Therefore, incident electron beam actually the way it interacts determines the nature of study that we are going to have and when we look at the incident electron beam, there is a minimum threshold that is needed to observe something significant and to quantify the result.

Electron beam when they interact with material, usually there are some secondary effects which happen and that can be used to convert into useful information. As, you see here first of all there is a backscattering that occurs whenever, electron beam interacts with a nuclei or with the material, and that can be a primary electron the backscattered electron is a primary, electron or it could be elastically scattered primary electron.

So, we tag this process as backscattered process, so it does not really do any damage, it is reflected suppose small nuclei is there the backscattering is of a different nature compared to a larger or a heavily nuclei. Therefore, the way the backscattering occurs also tells with what sort of nuclei it is interacting with and the other thing is a secondary electron image, this is another process which can give us other information than the backscattered stuff.

And apart from that there can also be x-rays produced, because when a particular electron is knocked out from a inner core, then the outer shell electrons can come in and therefore, x-ray can be produced. So, three distinct processes happened when electron beam interacts, one is backscattered electrons, the other one is secondary electrons and the third one is the x-ray that is produced.

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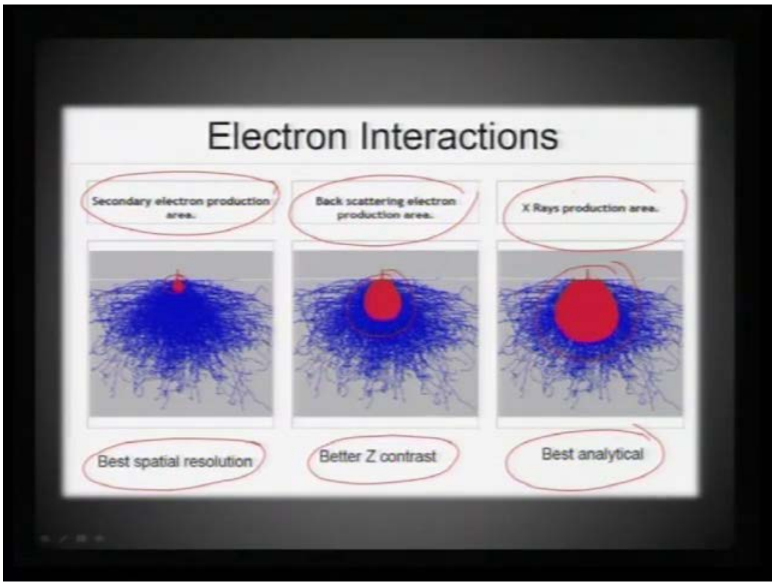

Electron Interactions

Secondary electron production area.

Back scattering electron production area.

X Rays production area.

Best spatial resolution

Better Z contrast

Best analytical

So, all this can be usefully converted into a image form and we can try to derive some information about the material, now the electron interactions have a depth, and that depth also determines what is that we are looking at select secondary electron the production range is of this dimension. Therefore, since the penetration is not too high and it is very much on the peripheral the secondary electron production is usually used for special resolution.

And therefore, predominantly any image that you see in SEM, you correlate that to a secondary electron image, but if you look at the backscattered electrons, the production area is much more deeper and broader compared to secondary electron. Therefore, this is used selectively because it the impact strength or the production area is quite big therefore, you can use this for a better contrast of the material that is already present. So, backscattered image is not a primary source information in SEM, rather it is a back up information that you would like to use other than the secondary electron image.

So, this is quantitatively the way we can picture about a scanning sorry, secondary electron image and the backscattered image, and then there is more impact which causes x-rays to be produced. And therefore, the x-ray mapping can be used for a analytical tool, so you cannot only look at the image, but you can look at the quantitative information about the element that is present, because of the x-ray production area is much more larger.

So, three important things happen in scanning electron microscope specifically, so when you look at a image from a scanning electron microscope, you need to understand that there are at least three major information's that you can get. One is the secondary electron image, backscattered image and the x-ray that is coming out of it the electron.

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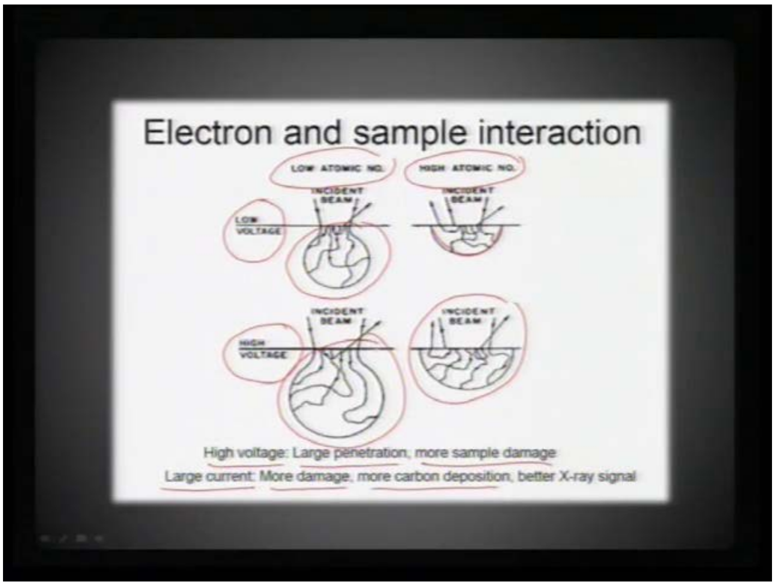

Electron and sample interaction

High voltage: Large penetration, more sample damage

Large current: More damage, more carbon deposition, better X-ray signal

And the sample interaction also has it is magnitude which depends on the atomic number therefore, if you looking at low atomic weight atoms, usually the response or the phase contrast is very, very less compared to heavier metals. So, if we have heavier metals the interaction will be very distinct and therefore, the mapping is much more easier. For example, you have iron and nickel in a material then it is very difficult to get a image contrast between iron and nickel, because they are very close in atomic number.

Whereas, if you have iron and rhodium or platinum or palladium, because of the difference in the mass or because it is a heavier, one is heavier than the other, then the phase contrast will be easy. So, when you have low atomic weight the incident beam propagates this much even at low voltage, and for high atomic number the penetration or the interaction is only minimal when you have a low voltage situation.

Therefore, if you need to have more information or more contrast for higher atomic number then you have to use high voltage, and the impact area is much more for a low atomic number elements. So, high voltage means large penetration and therefore, the sample damage will also be considerable larger current means more damage and more carbon deposition, but you get better x-ray signal.

You do not really resort to large currents always, because of the carbon deposition, but then if you’re looking for x-ray mapping then we need to go for higher currents. So, x ray analysis and backscattered analysis is usually kept as a backup characterization methods, but predominantly you look only for scanning secondary electron images.

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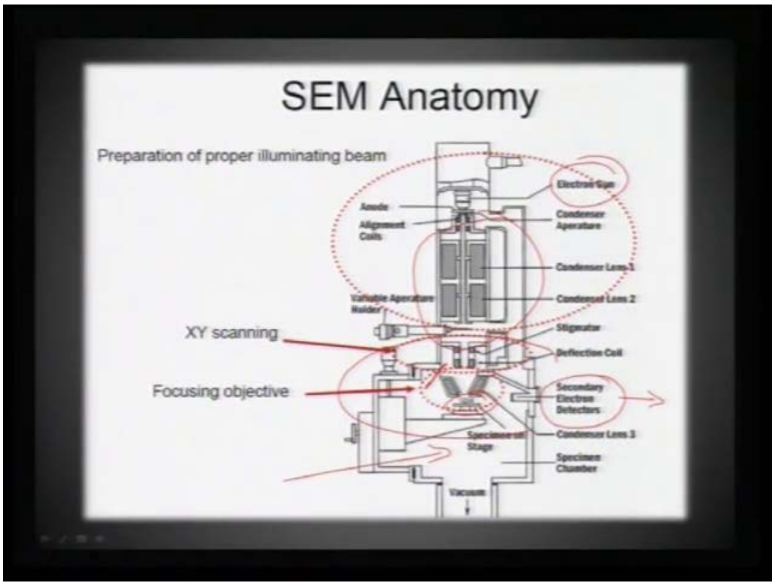

SEM Anatomy

Preparation of proper illuminating beam

XY scanning

Focusing objective

Now, this is the SEM anatomy of a microscope, where a you have a complicated lens arrangement which really brings in to focus the electron beam that you are shining on the sample. And as you see here you have the electron gun which is taken through a series of optics, and electron beam is made to fall on the specimen here. And what happens when the electron beam interacts with the sample is what is the optics that is in this region, and as you see you have detectors, which will sense the secondary electron.

And this is almost kept perpendicular to the sample surface, therefore, you can collect enough of this secondary electrons. And secondary electrons are then sent to another photomultiplier tube where you can transfer that into a image, and we also have backscattering which is collected closer to this region, we will see that in the next slide. So, what you see here is more of the collection area, whether it is a backscattered electron or a secondary electron that is actually mapped, and in this sample specimen chamber you also have another important addition, which is called a fluorescence screen, in case if you are using a TEM microscope.

So, the design is more or less the same between a SEM microscope and a TEM microscope, but the sample position and how you image will differ otherwise, the principle by and large remains the same.

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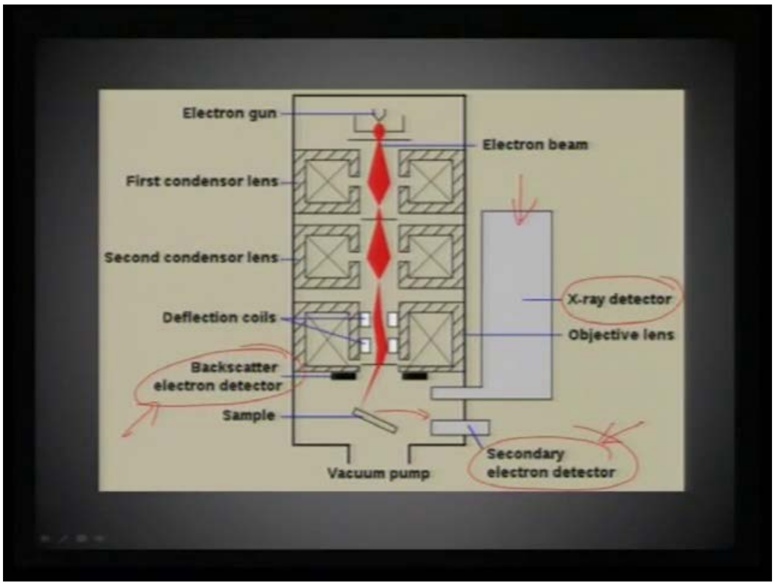

This cartoon tells us the process that we are referring to one is the secondary electron image, which is almost kept perpendicular to the sample orientation. Therefore, you get enough of the secondary electrons falling into the detector here is the x-ray detector that is kept mainly for x-ray analysis, but here again the x-ray detector is kept in a liquid nitrogen chamber. So, this is a extra attachment that usually comes with the main SEM microscope, and what you see here is the backscattered electron detector, which will preferentially collect the backscattered primary electrons.

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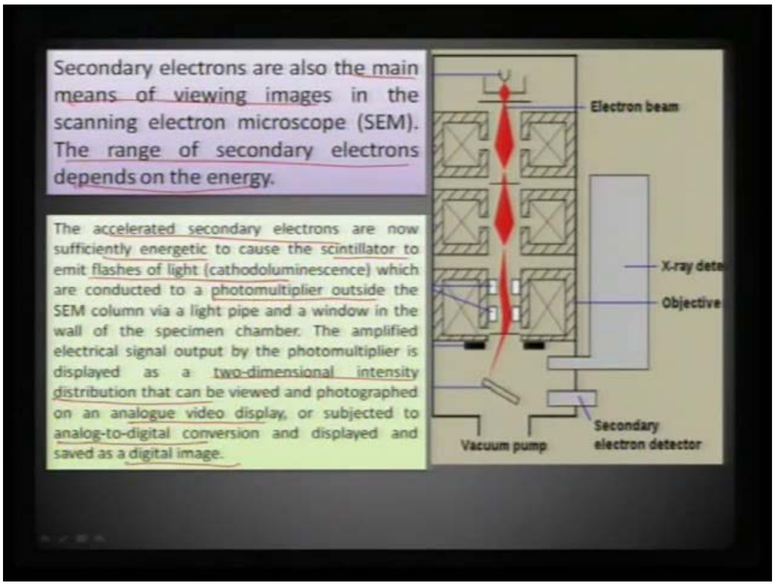

Secondary electrons are also the main means of viewing images in the scanning electron microscope (SEM). The range of secondary electrons depends on the energy.

The accelerated secondary electrons are now sufficiently energetic to cause the scintillator to emit flashes of light (cathodoluminescence) which are conducted to a photomultiplier outside the SEM column via a light pipe and a window in the wall of the specimen chamber. The amplified electrical signal output by the photomultiplier is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected to analog-to-digital conversion and displayed and saved as a digital image.

So, this is a primary process this is a secondary process that happens, so both are kept very close to the sample environment and we can translate that into useful information. Just to highlight what this secondary electron image means, the secondary electrons are the main source of information in terms of viewing images and the range of secondary electrons usually depends on the energy.

And for secondary electron image we usually resolve to very high voltage, we cannot work at low voltage because the number of secondary electrons that you that you collect has to be very large for a very good topography. Therefore, you usually work at a very high voltage the accelerated secondary electrons are sufficiently energetic to cause the scintillator to emit flashes, and that is exactly the collector and this phenomena is actually known as cathode luminescence.

And this cathode luminescence is now picked up by a photomultiplier tube, because that would harvest all these signals in a very sensitive way, and this is actually now converted into a two dimensional intensity distribution which finally, comes to a digital image. So, the secondary electron image is actually transferred in the form of a cathode luminescence by a photomultiplier tube, and then it is transferred to a analogue video display and then there is a analogue to digital conversion, then you get a digital display, so this is quite a involved process, but it all happens.

So, therefore, if you need more of the secondary electrons to come then you need to make sure that the sample preparation has to be proper. And therefore, the surface of the sample is preferably a flat surface, if it is a three dimensional one then the range of or the orientation of the secondary electrons will be on different directions. Therefore, you get more useful and sharper images or contrast when you deal with the flat surface that is why sample preparations have to be rather very intricate for secondary electron images.

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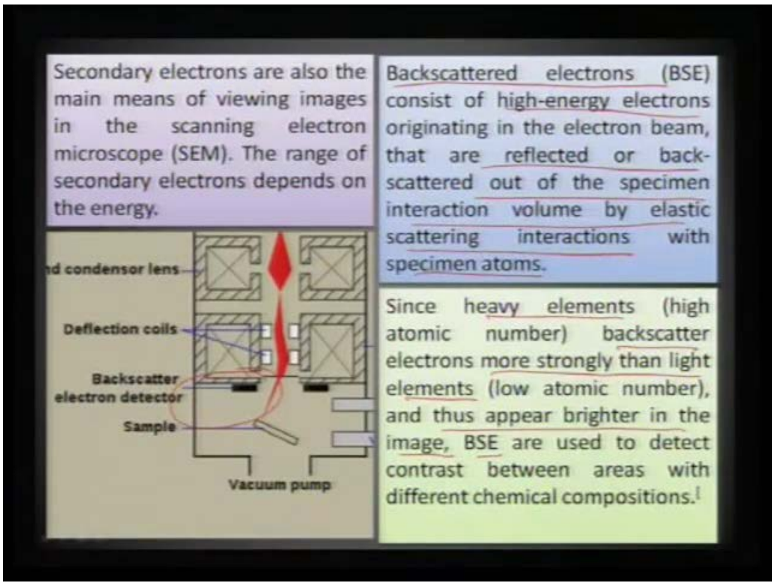

Secondary electrons are also the main means of viewing images in the scanning electron microscope (SEM). The range of secondary electrons depends on the energy.

Backscattered electrons (BSE) consist of high-energy electrons originating in the electron beam, that are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms.

Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image, BSE are used to detect contrast between areas with different chemical compositions.

Now, compared to secondary electron image which I said the backscattered process is another complimentary information, backscattered electrons consists of high energy electrons. These are the ones which are reflected or backscattered out of the specimen and this is mostly the primary electron, which is backscattered and this is a scattered out of the specimen interaction volume by elastic scattering interactions with the specimen atoms.

Since, heavy elements are backscattered more strongly than lighter elements, the thus they appear brighter in image and therefore, backscattered image is used as a contrasting technique. So, when you have a secondary electron image the same area can be twisted in to or verified as a backscattered image and because the level with which the backscattering occurs is different you can get a contrast. So, if you are not sure about the chemical homogeneity of a particular area it is always better to focus there, and switch from a secondary electron mode to a backscattered mode.

And if there is no difference between the secondary electron image and the backscattered, then you say the composition is the same, but if you see two different contrasts then you say that the chemical homogeneity differs in that particular region. So, this is therefore, a very crucial mapping between chemical homogeneity, in samples by choosing a secondary electron image or a backscattered image.

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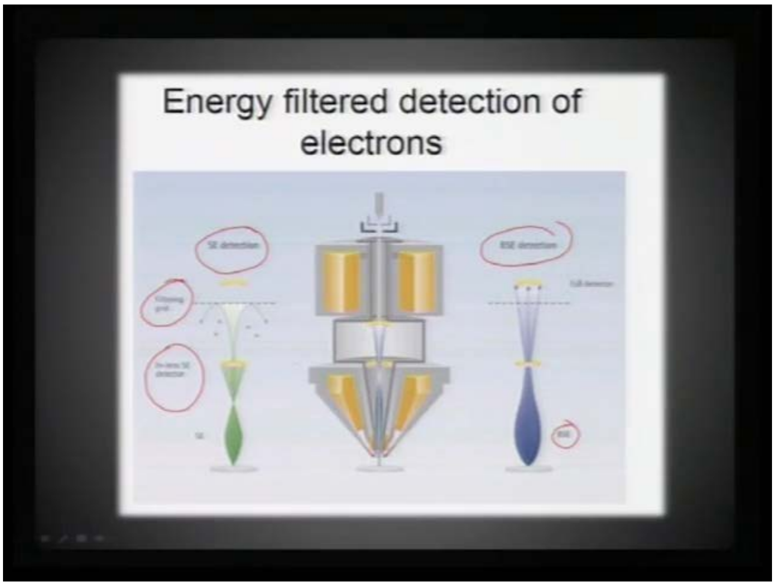

Energy filtered detection of electrons

And the way the secondary electron detection and backscattered detection goes, it is totally different and you usually have the preferred optical alignment. So, that the filters are used properly in order to only sense the secondary electron and the backscattered electron, and this is the way the backscattered images are viewed and this is the way the lenses are arranged just to collect the secondary electron images.

So, the optics is very crucial in the SEM to differentiate between these two process, this is one of the very old technique, very old instrument that has been used. As, you see here the digital image in those days at least ten years back was lacking and therefore, all the conversions were usually taken in terms of photograph, we never had a analogue to digital conversion. Therefore, when you have those images usually the those are taken as a photograph and then we develop those images, but now a days we have everything digitalized therefore, we have much sharper images can be recorded.

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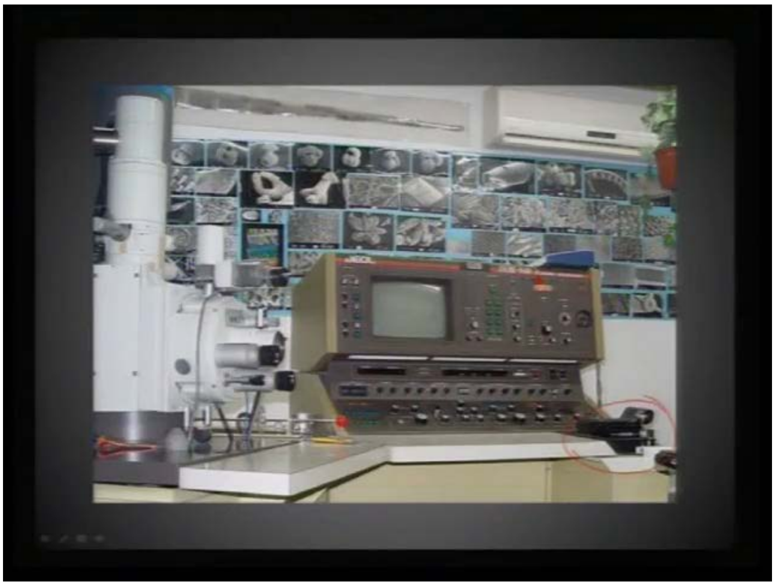

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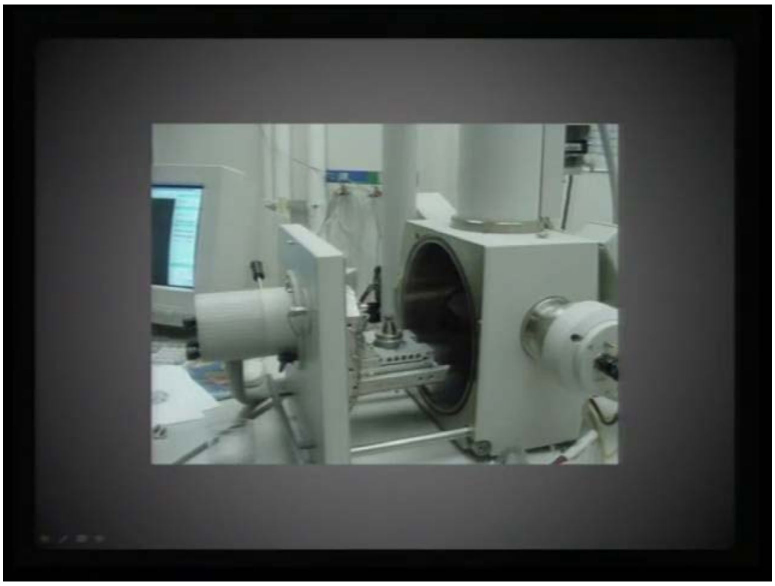

And this is one of the old instrument that you would see in any institutions, this is a new generation SEM instrument, where you see a picture of how the sample chamber looks like. In fact, we can actually mount or we can even bring down the electron gun much closer to the sample, we can try to position the right sample everything is now arranged with a camera that is fitted right inside the sample chamber.

So, lot of improvements have come with the new generation instrument, typically this is a field emission SEM and I will come to this later. And say why field emission SEM is much more preferred these days than ordinary SEM, because of the advances in electronics, now we have more refined picture of this SEM microscope.

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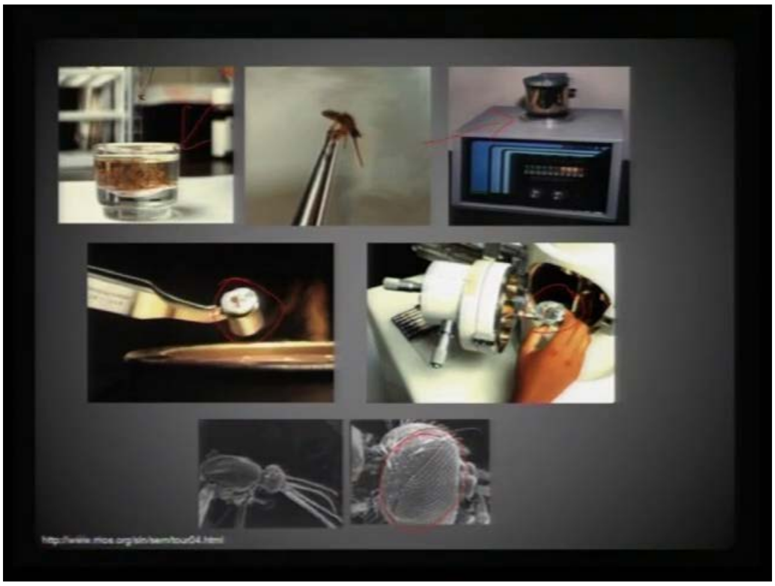

http://www.mos.org/sln/sem/tour04.html

Just to touch on a minimum protocol that is needed in terms of sample preparation, I have just put some cartoons here to just take you through the course that you need to do in order to get a SEM image. First of all take any sample that you want on a stub mount it here, on the stub and then this is actually gold coated any conducting sample you do not need to gold coat, but if you are going to use a non-conducting sample.

Usually, it needs a gold coating, because any material that is interacting with the sample has to have a conducting area, otherwise there will be charging of the sample you cannot see the image you cannot see the conversion of this into a useful image pattern. Therefore, a very thin layer of the order of one to two micron thick gold coating is usually preferred on any non-conducting surface, for metallic samples we usually do not do that in any form it can conduct. So, once you have done the gold coating, now this is ready to be mounted here in a sample stage, and once the instrument is ready we can actually get useful pictures.

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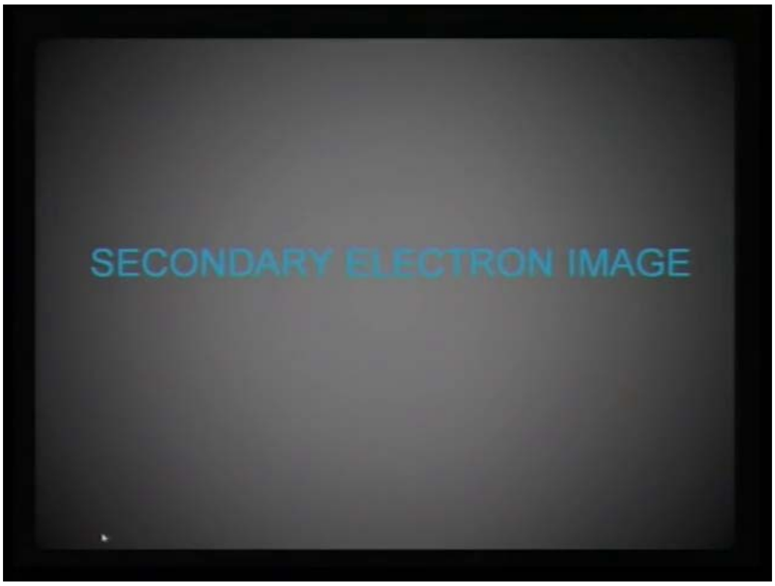

SECONDARY ELECTRON IMAGE

So, this is a simple protocol for recording SEM images, now I will just take you through a course of pictures, because it is very interesting to see a variety of samples through SEM. Not just for analysis or for understanding, but it is also very enlightening to see some of the stuff which is hidden to our naked eye comes to prominence, when you put it in a microscope. So, I will just take you through some examples of SEM pictures and tell you what are the ranges range of material that you can scan, and what information's that you can look for.

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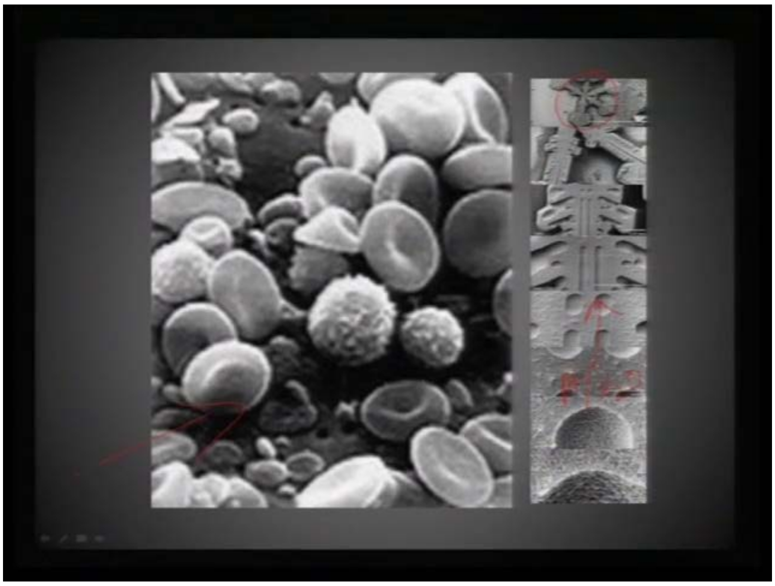

So, to start with I will show some examples of secondary electron images what you see here is in black and white, but you can actually do a colour mapping also to show the platelets present in our human body. And these are the platelets that one can see, which is present in our serum and on the right side what do you see is platinum coated snowflakes. Snowflakes have very preferred geometry as you can see here the symmetry of these flakes, which is actually coated with the platinum then you can actually retain that or you can stabilize that otherwise if the interaction with the electron beam the snowflakes will melt.

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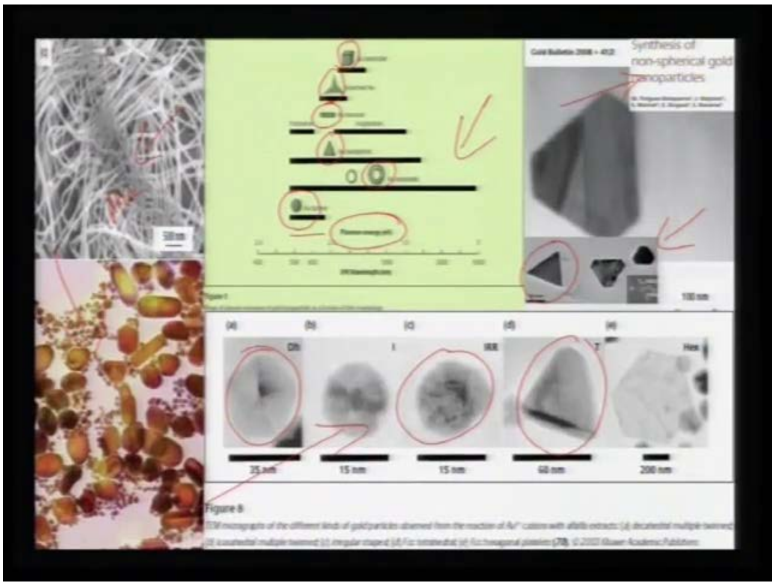

Therefore, these are platinum coated snowflakes which are frozen and they show very clear symmetry patterns, here is another cartoon, which gives us idea about the range of gold particles that I have been studied. What you see here on the left side this cartoon is bundle of gold wires, that has been prepared using chemical route and what do you see here is another viewgraph of a secondary electron image of gold particles prepared by another solution route.

We see here in this cartoon is a range of gold particles with different size, and with different size the symmetry of these gold particles also differ. And these are the gold particles that you can see from different extracts you can see tripodal decahedral or irregular shaped ones, and what do you see here it is a triangular shaped gold particles, and with each of this size and shape the plasmon effect also changes. And this is the cartoon which tells that with the size how the plasmon emission of gold particle changes, as you would know gold is not a photoluminescence, But they show surface plasmon effect.

And typically, gold particles of one to two nanometre they do not show the actual bulk colour which is gold colour they are actually purplish, and therefore, if you look at the size range and the plasmon effect with each size the plasmon energy surface plasmon energy also changes. So, the gold sphere has a surface plasmon energy confined in this dimension, then you can also have hollow spheres of gold or triangular gold particles you have rod shaped ones and tripodal shape gold particles or nanocubes of gold particle, each has a very preferred orientation of showing light intensity through plasmon effect.

So, there are several reports which talks about a controlled way to synthesize, there are also reports where researchers have used bacterial effect on controlling the size and shape of gold nano particles and we have plenty of literature data to support these cases.

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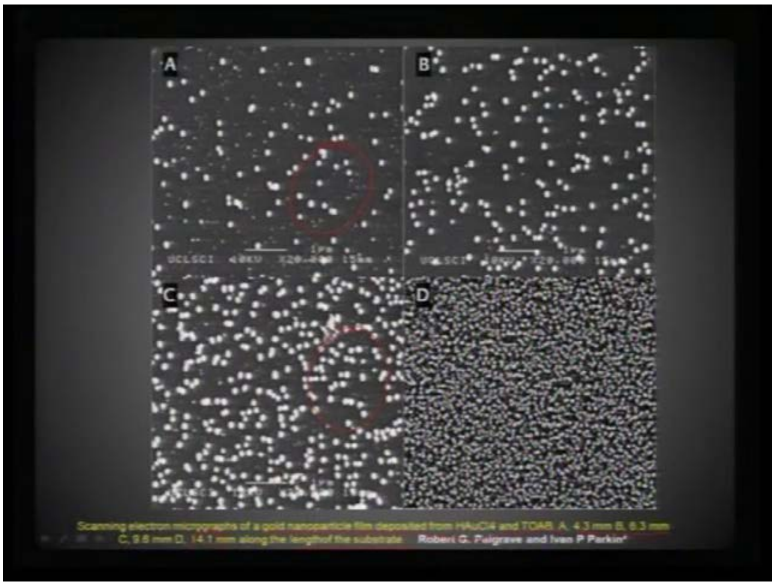

Scanning electron micrographs of a gold nanoparticle film deposited from HAuCl4 and TOAB. A, 4.3 mm B, 6.3 mm C, 9.6 mm D, 14.1 mm along the length of the substrate Robert G. Palgrave and Ivan P Parkin*

So, all this can be studied using a secondary electron image picture from SEM and here is another cartoon which tells about the gold nanoparticles which are deposited from auric chloride and tetraoctylammonium bromide. And these are different cartoons, which talks about the density and it is a shape control of the gold nanoparticles in a variety of or in different dimension of the substrate length. As, you see you can actually quote this in 4.3 millimetre substrate or you can go up to 14 mm substrate, so with the chemical approaches you can actually deposit in a very controlled way gold nanoparticles in a variety of substrates.

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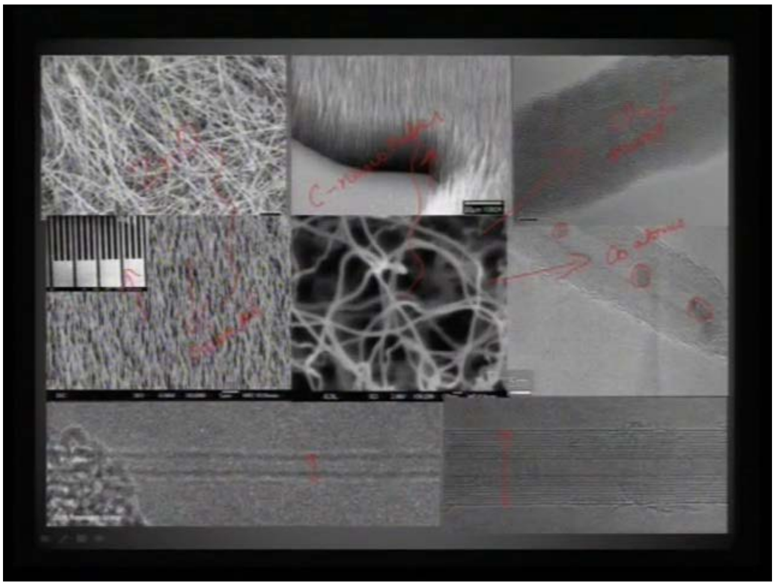

So, you can map those things conveniently using SEM microscopy, in these two viewgraphs you can study how zinc oxide can be prepared and these are zinc oxide bundle of nanowires as you see here. And these are irregularly oriented in a random way like a bunch of nanowires you can prepare whereas, in the cartoon that you see here you have oriented zinc oxide bundles and the inset shows how you can map that.

These are electrochemically grown zinc oxide wires with a specified orientation, and this also you can laterally see through a SEM micrograph and these two micrographs talk about carbon nanotube. And here is carbon nanotube in a in a random orientation, and here you can see carbon nanowires can be grown in a specific way, and just to compliment our understanding you can also see through the TEM images. These are TEM images of these carbon wires or fibres, where you can see preferred deposition of cobalt atoms inside carbon nanotubes information to study a particular system.

This is for cobalt atoms and here we can also incorporate silica in carbon nanotubes, this is silica in multiwalled carbon nanotubes and here the same TEM pattern can be used for studying a single wall or for a multiwall. There are multiwalled carbon nanotubes and these are single walled carbon nanotubes, so TEM and SEM can offer a combined approach can give very useful.

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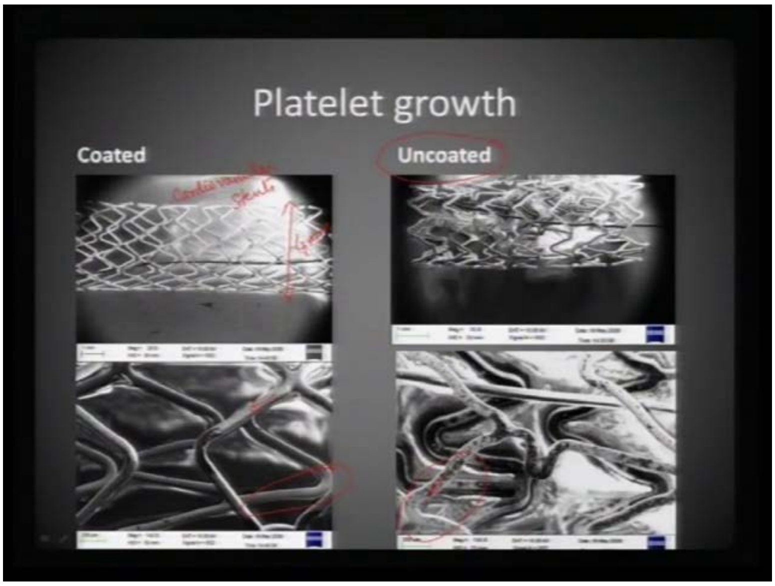

Platelet growth

Coated

Uncoated

SEM can be used also for several other materials here is a example of a cardiovascular strength which is coated with a polymer composite, and we can actually make the contrast between how a polymer coating can be made on thin specimens. As, you would see here the dimension of this is less than 4 millimetre, these are 4 millimetre dia cardiovascular stents.

And this is the expanded stent once you put it in the artery you can expand this, and these are uncoated stents and what information we can get out of it. If we try to expose these cardiovascular stents to human platelet for a preferred time period and then try to look at the surface, as to what has happened to the coated and the uncoated cardiovascular stents.

Here, is the viewgraph that tells clearly that the platelets are totally kept away from the surface in the quoted stent whereas, the platelets are adhering to the surface of a uncoated stent. So, this information can give us some idea whether the platelet which is sticking to the surface of the cardiovascular stent can initiate a thrombogenic activities. In the case of the cardiovascular stent which is coated with polymer you do not see any platelet adhesion, which means the thrombogenic activity will be very, very minimum in other words it is anti-thrombogenic, so such useful informations you can get out of it.

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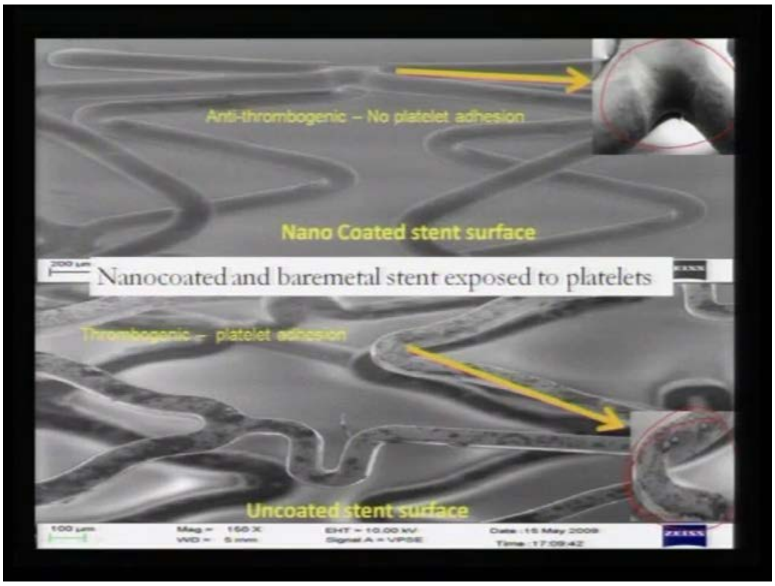
Nanocoated and baremetal stent exposed to platelets

Here is another view graph of the same what I had shown here if you take a close look at the surface of these coated stent you see almost practically you do not see any platelet there whereas, the whole surface is plagued with platelet adhesion in a uncoated surface.

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Suppose, the platelet adhered surface is there then it is possible to see the influence of another coating of the polymer composite and here is another view graph which tells how SEM can go hand in hand with your deposition process. And if you take this platelet adhered surface and then you try to coat the polymer once again this whole surface, now gets transformed almost as a unadhered surface. So, this shows the influence that you can map even very thin coating of the polymer on the surface of the stent, so SEM can be used for such intricate analysis

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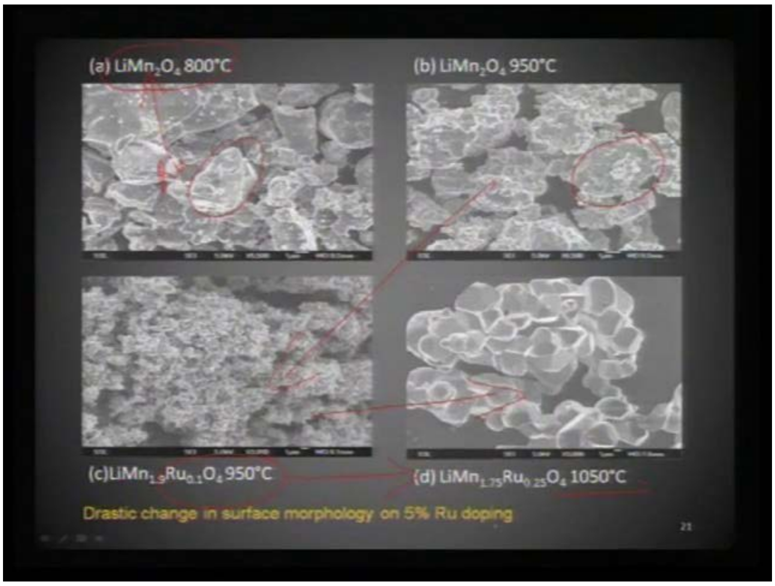

Drastic change in surface morphology on 5% Ru doping

Here, is another range of material which gives us idea about the influence of the particle morphology specially with adhesion of ruthenium, this is a well know battery material which is called a lithium manganite it is a layered material. Suppose, you prepare this using solid state method at 800 degree C the particles, usually show this sort of morphology. And if you further heat this sample then you can see they are coalescing together into larger particles, and if you try to substitute ruthenium into this Li Mn 2 O 4.

And if you look at the morphology just with little amount of ruthenium, you can see the whole morphology of this particle changes, what does that has to do with this, because these battery materials have to be compacted loosely, but in a battery and the particle morphology. Therefore, becomes very, very important and you can see from irregular or rocky type of material, you can bring down the particles considerably even with little amount of ruthenium doping and you can see a very monosized uniform grain growth of this materials when you go from 950 to 1050 degree C.

So, you can get some understanding about the particle morphology not only with respect to temperature, but also with respect to the elemental composition, so it gives you a indirect clue that ruthenium is actually playing a role on the particle morphology. So, it is very useful even for preparing, for devices to have a closer check using SEM micrographs.

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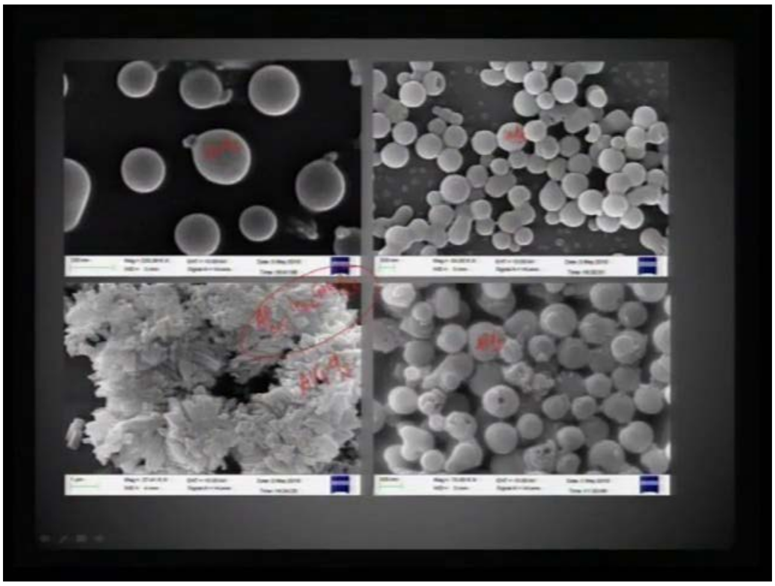

Here is another view graph of quinoline precursors, if you take gallium q 3 or indium q 3 or aluminium q 3, you can see that the morphology of this aluminium, gallium and indium are more spherical in nature when they are formed as a precursor complexes. Whereas, if you take aluminium 0.5, indium 0.2, gallium 0.3 q 3, if this is the composition which we can refer it as Ai G q 3 complex then the morphology of this solid solution changes entirely from the respective morphology pattern.

So, this also gives us some idea about whether the solid solution is indeed forming or not, so SEM can prove very useful to understand how the influence of this substitution affects the morphology of the samples. We will look at the backscattered image and see what information we can get out of backscattered image processing, and we will see that in the next few slides. Let us take the case of magnesium which is doped in zirconia system, and then it becomes very easy to understand how backscattered image can give us information.

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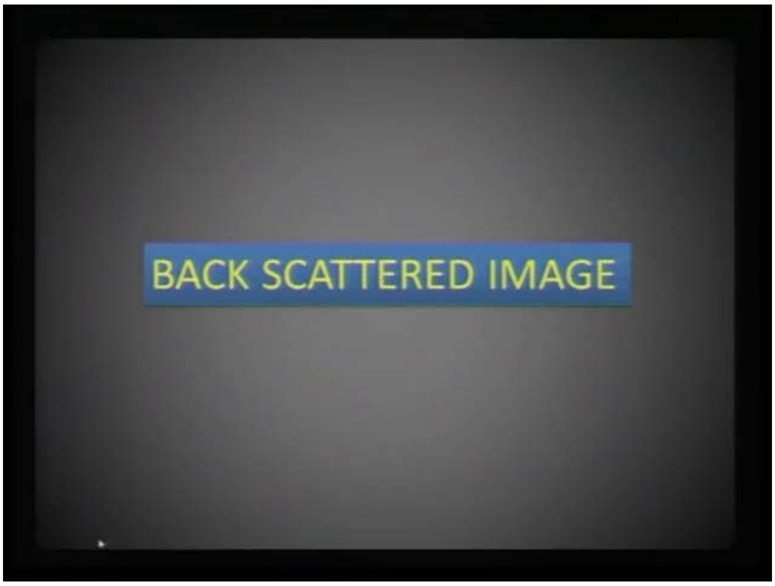

BACK SCATTERED IMAGE

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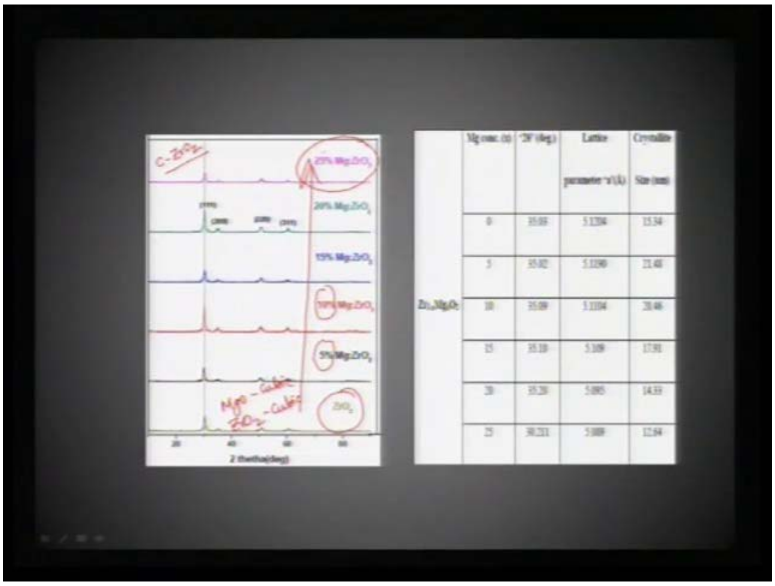

	Mg conc. (x)	2θ (deg.)	Lattice parameter 'a'(Å)	Crystallite Size (nm)
$Zr_{1-x}Mg_xO_2$	0	35.05	5.1204	15.34
	5	35.02	5.1190	21.48
	10	35.09	5.1104	20.46
	15	35.10	5.109	17.91
	20	35.20	5.095	14.33
	25	30.211	5.089	12.64

For example, if you take zirconia system and then keep on increasing the substitution with magnesium, the idea is to reinforce more strength, because zirconia is a toughened ceramic it has a very high mechanical strength. So, if you put little bit more of magnesium, it is reported that you can increase the strength of the zirconia particles, as a result we can actually go through a range of substitution to increase the solubility of magnesium into zirconia.

And as you see here from the x-ray pattern the magnesium does not seem to be coming out as a Mg O impurity, because Mg O is a cubic system, and zirconia is also a cubic system. And fortunately you see here only the cubic zirconia pattern that we can infer from the X r d. So, magnesium oxide is actually absent in other words magnesium is getting substituted, so with this information one can go ahead trying to sinter this and make it into a very strong solid.

But what we should understand is when we heat it to high temperature, these solids can disintegrate or the phases can come out, so the only way that you can characterize that is using SEM. So, I will give you some information about how backscattered image can give us a clue about their limiting composition as well as where to limit the sintering temperature.

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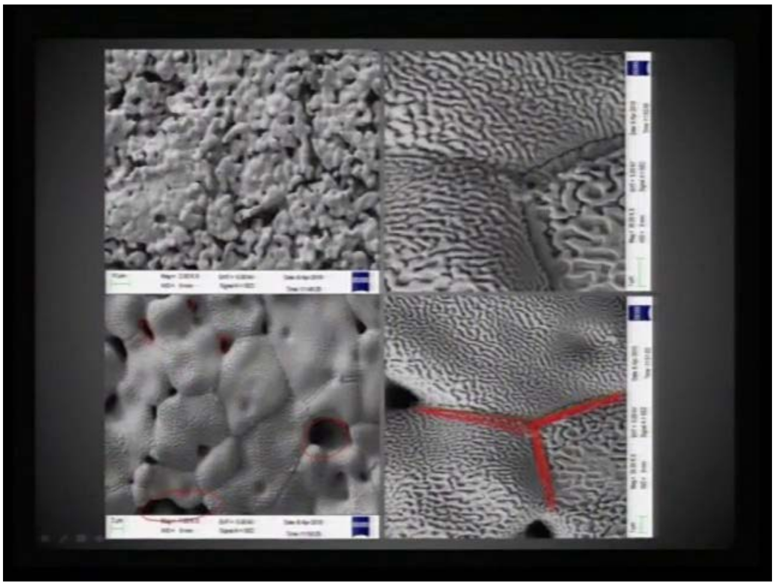

This is a viewgraph that shows a fine grained grain growth for zirconia and these are not polished surface, as you see here there seems to be hole, but this is not hole this is the surface defect, because it is not a polished surface. But, once you polish you would actually see almost this sort of small pittings are not there, which means even at 1100 degree C, these nanoparticles of magnesia doped zirconia can be sintered almost to 99 percent theoretical density.

But, if you keep on increasing the annealing temperature say from 900 to 1000 to 1400, if you keep going the more you go the more you sinter it into a 100 percent theoretical density compacts. Therefore, you usually prefer a very high temperature, so having seen that there is a very clear grain growth, and you also do not see much of a phase contrast in this grain boundary. Because this can be detrimental for toughening mechanism meaning, if there is any phase segregation usually the tendency for that secondary phase is to be present in this grain boundary, so this particular image shows that there is no phase segregation.

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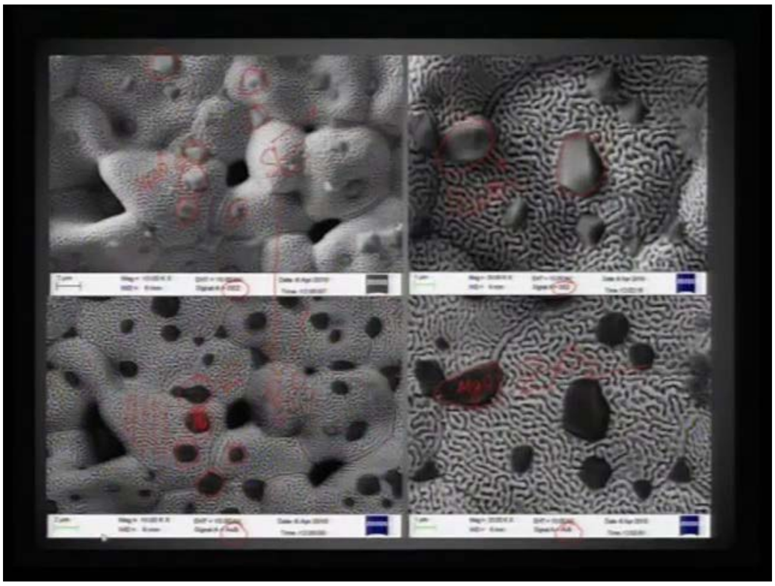

Now, let us go to the case of 1400 sintered sample if you look at a 1400 sintered sample suddenly, you start seeing this sort of grains protruding out of a uniformly grained situation which you can see from the previous picture. In this picture you do not see any such grains coming these are all uniform, but when you go to fourteen hundred you see several such things coming out of.

So, when you take a closer look at that and now instead of secondary image you can see here this is written S E, S E means secondary electron image from there, if you go to backscattered image that is what you see here it is written ASB this is backscattered. So, both are same only thing I have switched over from secondary electron to a backscattered image. Now, immediately you can see that there is a clear phase contrast between the macro grains and the ones which are segregating out.

So, what does this mean, that the chemical composition in this area and the chemical composition in this is entirely different, and if you carefully look at this these black regions are turning out to be Mg O and this region is relating to zirconia. So, what we infer from this backscattered images at 1100, there is no phase segregation whereas, when you go to very high temperature even though x-ray remains clean, it does not mean that there will be no phase segregation.

So, room temperature x-ray pattern is not a conclusive proof to say that there is no phase segregation, so when you sinter it usually the several things that happens inside the sample comes out and back scattered image can prove to be very, very useful to understand that.

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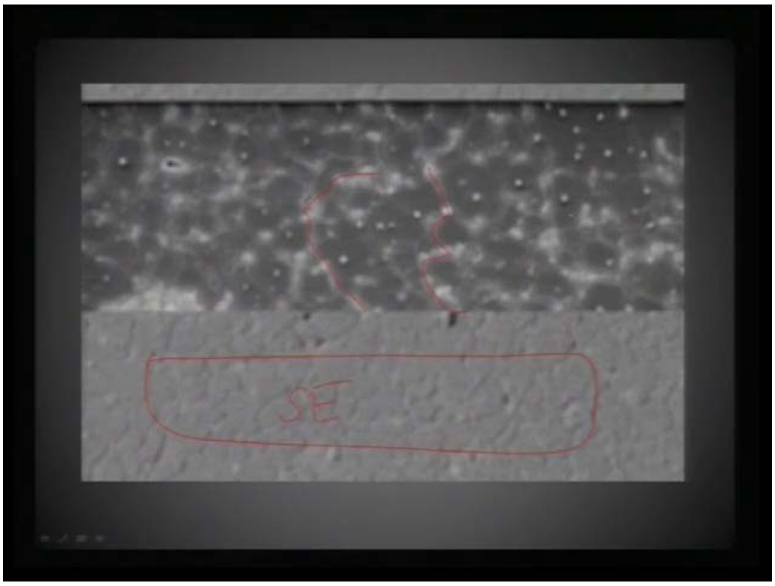

Here is another image where you see the secondary electron image does not seem to show any phase contrast whereas, back scattered image shows that along the grains there is a compositional difference compared to the macroscopic image, so backscattered image therefore, provides a very important clue to the chemical inhomogeneity or homogeneity.

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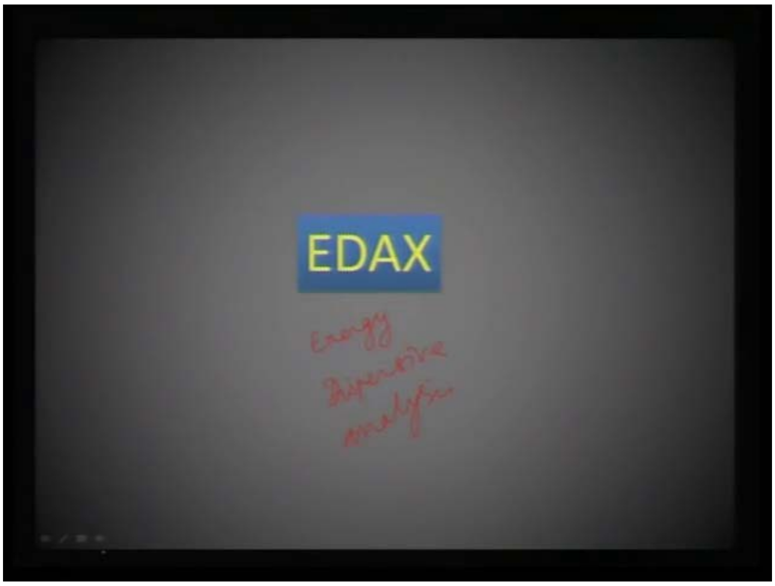

EDAX

Energy Dispersive analysis

Apart from that we can also look at the x-ray analysis, that is possible through SEM and EDAX is a very useful technique which is always attached to the SEM microscope and EDAX is nothing but Energy Dispersive Analysis of X-rays. So, whatever x-ray that is coming out can be used to quantitatively measure the amount of that particular element that is present, which is also present in the same area.

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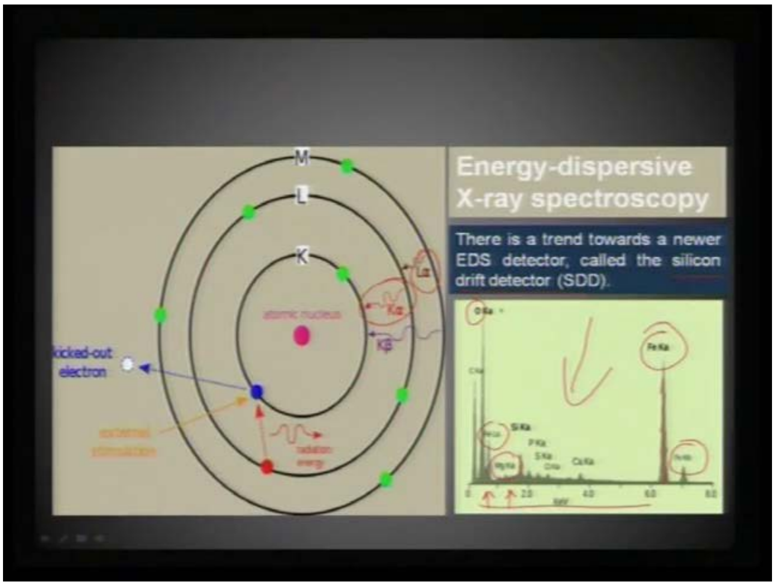

Energy-dispersive X-ray spectroscopy

There is a trend towards a newer EDS detector, called the silicon drift detector (SDD).

And this is the way the x-rays come out, and when the secondary electron is removed, then you have the outer electrons coming to the knocked out electrons. Therefore, you can actually get different sort of radiation one is k alpha radiation, k beta or l alpha and so on, if you are looking for very higher elements usually you get m alpha or l alpha radiation, but for smaller atomic numbers.

You usually look for k alpha or k beta radiation, if you are looking for lanthanides you usually go for l or m. So, in a typical energy dispersive analysis, you can find out that this sort of peaks do come. You can also get contrast for oxygen, but usually in EDAX we do not rely on anything less than oxygen, atomic number below 13 we do not really take that very seriously although they can still give contrast.

And specially from beryllium boron downwards we do not even do that therefore, we do not quantify any hydrogen that is present in the sample, hydrogen or helium or lithium we do not really consider that as a useful technique to quantify those presence of those elements. So, when we go for higher atomic numbers, then the contrast is more and for example, you can see typical iron k alpha k beta reflections do come here, and we have magnesium iron k k alpha.

So, each of these binding energies are given here and that the area under the curve gives the quantification of how much of that is present, but this is usually a semi qualitative image, because there are there are also surface impurities which can distort the elemental composition. One of the reason is that you do not have a very sensitive detector, but thanks to the advancement in electronics today that we have a detector which is much more sharper to pick up the signals, in the form of silicon drift detector it is called STD which is now a days coming in later versions of SEM.

Therefore, energy dispersive analysis can now be treated as a more quantitative measure, but usually it is used as a qualitative way to figure out, whether something is there. For example, if I have a gold coated sample then the sample if you analyze the x-ray, it will also show gold pattern, so it is, so sensitive even to very small or very small thicknesses of deposited elements. Therefore, energy dispersive analysis by and large we can say it is a qualitative measure, but with the sophisticated electronics today, we can call this more as a quantitative analysis. Here is another viewgraph just to show how magnesium doped zirconia can be treated and estimated, you can usually quantify the data and find out how much of magnesium is present in zirconia this is a reflection for Zr and this is reflection for Mg.

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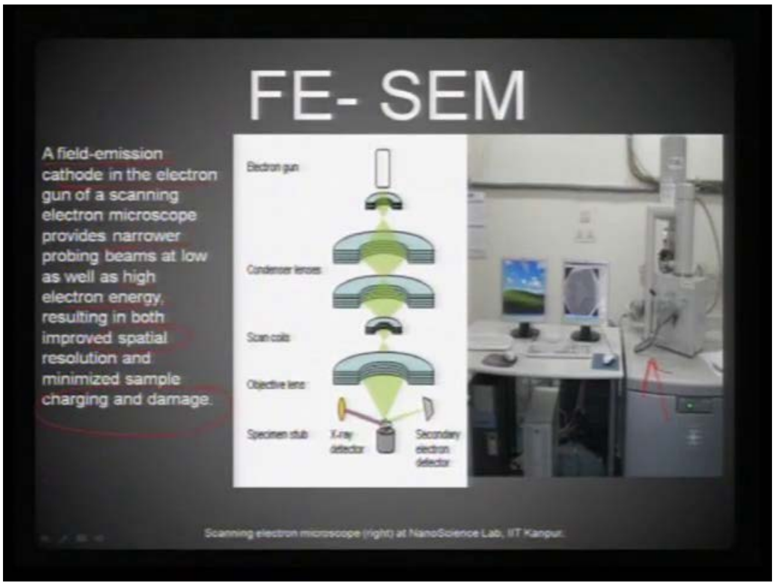

FE- SEM

A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage.

Scanning electron microscope (right) at NanoScience Lab, IIT Kanpur.

So, this can prove useful FE-SEM is another technique, which is much more refined compared to normal SEM, where a field emission cathode is actually replaced for a electron gun. And because this provides a narrower probing beams at low as well as high electron energy, you can actually get a more improved spatial resolution and the charging is very less and damage to the sample is very less.

So, field emission microscopes are much more convenient and it is used now a days compared to traditional SEM, one of the main reason is that you get a narrower electron beam, and it improves the spatial resolution and this is a FE-SEM that is available today’s market.

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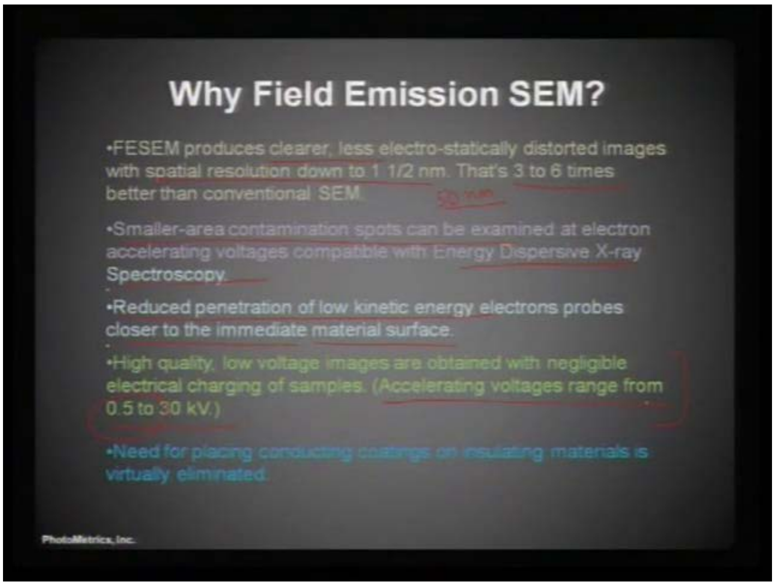

Why Field Emission SEM?

- FESEM produces clearer, less electro-statically distorted images with spatial resolution down to 1 1/2 nm. That's 3 to 6 times better than conventional SEM.

50 nm

- Smaller-area contamination spots can be examined at electron accelerating voltages compatible with Energy Dispersive X-ray Spectroscopy.
- Reduced penetration of low kinetic energy electrons probes closer to the immediate material surface.
- High quality, low voltage images are obtained with negligible electrical charging of samples. (Accelerating voltages range from 0.5 to 30 kV.)
- Need for placing conducting coatings on insulating materials is virtually eliminated.

PhotoMetrics, Inc.

Therefore, we can see some of the advantages why field emission SEM can be used it gives a clearer image spatial resolution and therefore, we can go down to even two nanometres which otherwise was not possible using SEM, conventional SEM you can map only up to say 50 to 100 nanometre thick particles. But, we cannot go down on the phase contrast, but now a days with the field emission SEM, the it is much more sharper by 3 to 6 times smaller area contaminations spots can be examined using field emission.

Therefore, even if the surface is not really flat it is possible for you to go down to a three dimension sample, and we can collect the x-rays also more easily in such samples. And reduced penetration of low kinetic energy electron probes closer to immediate material surface, as a result we can go in for even materials, which will demand very low voltage, for the inorganic samples usually you look for very high voltages.

So, we can actually play around with the voltage say from 0.5 to 30 kilovolts as a result even biological samples can be easily probed with much contrast, because your accelerating voltage can be brought down significantly. As, you see here it is impossible to operate SEM at 0.5 kilovolt, but because we can play around even with the vacuum, then it is possible to operate the SEM even at voltage, which is less than even 1 kilovolt.

As, a result we can go for a range of samples now, conventional SEM it is not possible to study any biological samples, because the moment you focus the electron beam it will immediately rupture the sample, but today's the field emission SEM is giving a very different landscape for studying materials.

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SEM – STM

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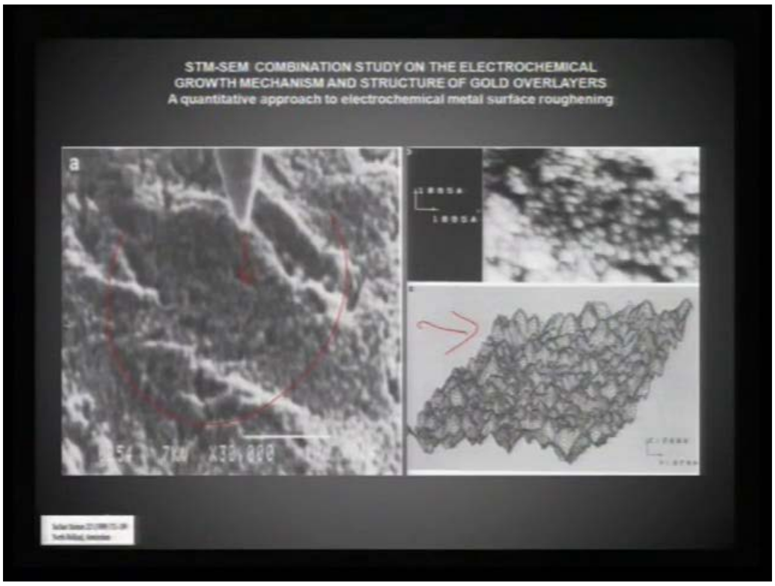

STM-SEM COMBINATION STUDY ON THE ELECTROCHEMICAL
GROWTH MECHANISM AND STRUCTURE OF GOLD OVERLAYERS
A quantitative approach to electrochemical metal surface roughening

Another technique which has emerged, but not very popular, but physicists really rely on is something called SEM, STM, suppose I want to do a scanning tunnelling microscopy on a particular area, it is impossible to take the STM tip to that particular area. Therefore, if you have a combined technique of SEM and STM you can first probe the macroscopic view from a SEM, and once you have spotted a particular region you can take your STM tip there.

So, this is called SEM, STM combined which is not very popular because of the sophistication it requires very ultra high vacuum atmosphere, and as you can see here this is a SEM image, where you can bring the STM tip to that particular desired region and you can get a STM image of that this for gold over layers. So, it proves very useful for you to bring down your focus to a particular point, but just left alone to STM, it is very difficult for you to take to the right locations.

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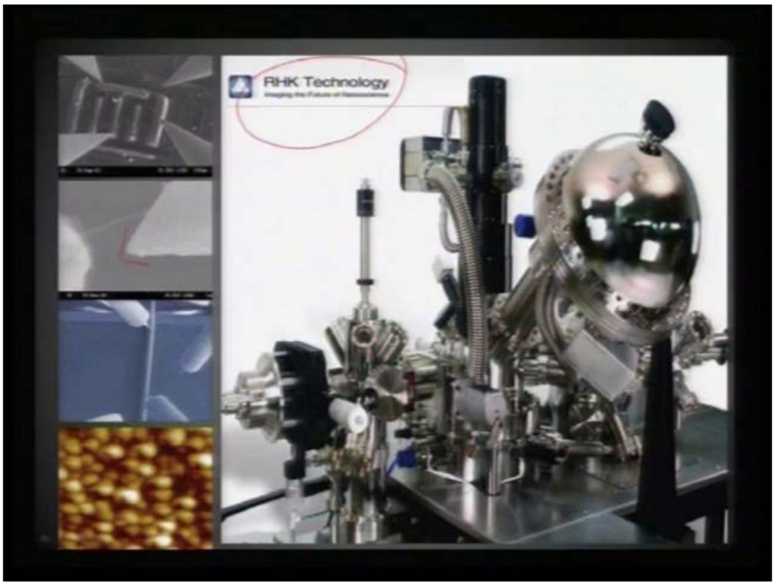

This is the viewgraph that shows how a SEM image can help you to take the SEM, STM tip to a preferred location, and this is another image of STM tip going to a preferred place. And not only that there are several companies, which are bringing a hybrid instrument and here is as 4 probe station which combines SEM, STM and XPS also all in one mode, so you can go for a in situ characterization using different techniques.

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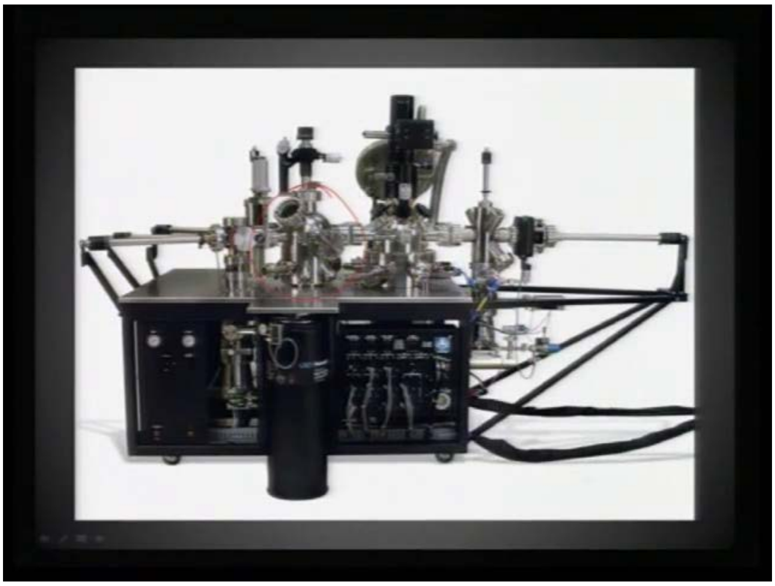

And this is the same viewgraph of this instrument where you have your SEM, STM and then you have the surface probe spectroscopic tool.

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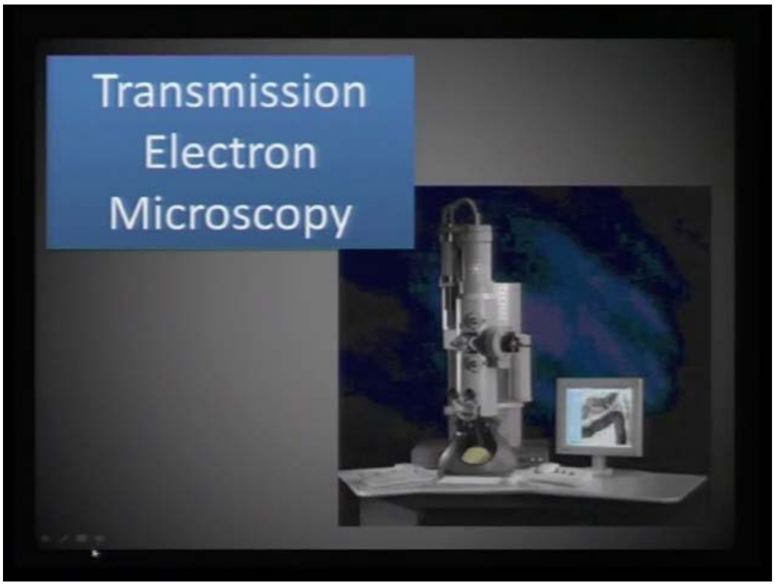

Transmission Electron Microscopy

TEM microscopy is another complimentary one, I may not be able to run through full details on the TEM, but just to tell you where we really differ.

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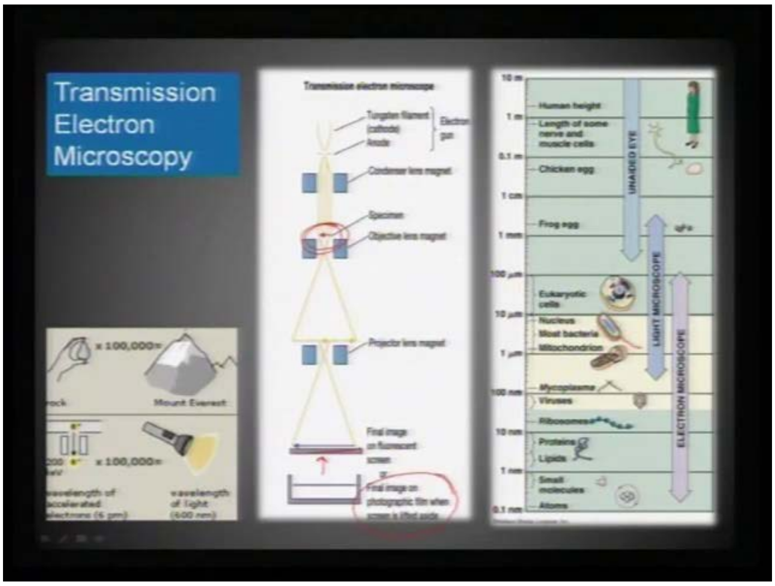

Transmission Electron Microscopy

If you think about SEM and STM the sample projection area and the way we harvest the image differs, in case of SEM sample is actually kept here whereas, in case of TEM sample is actually kept here. And the image of this sample is actually taken in a fluorescence screen, and when you try to take the image you remove the fluorescence screen and then you can photograph the image.

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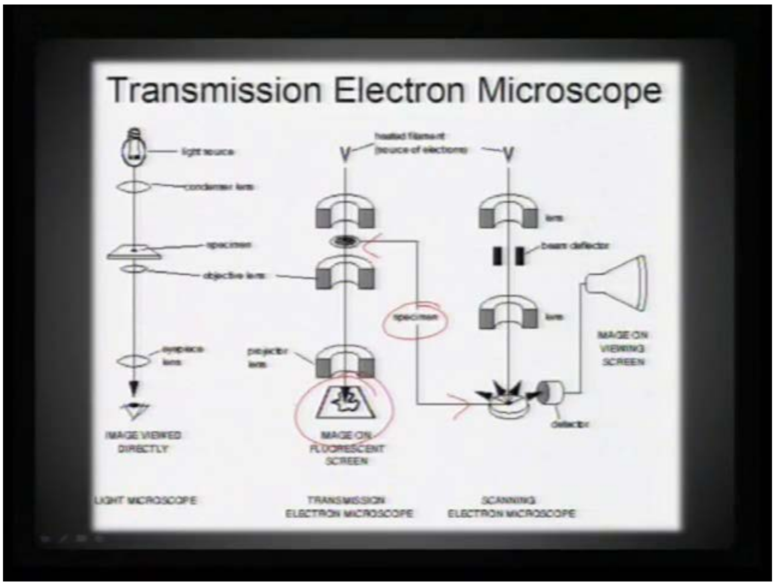

Transmission Electron Microscope

So, this is the main difference between a transmission and a SEM sample, but another requirement for transmission microscopy is the sample has to be very, very thin, so that the light can transmit through this one, whereas, in the scanning you do not look for the sample thickness. So, that is the main advantage, so you can see here this sample is placed here for a TEM whereas, here for SEM and then you capture than TEM image in a fluorescence screen here. And the TEM sample preparation is much, much more cumbersome than SEM therefore, we do not see TEM as popular like SEM.

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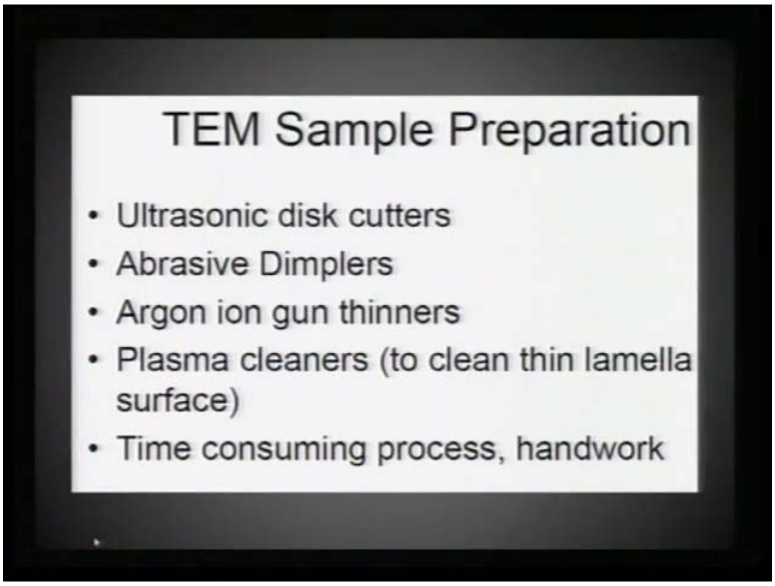

TEM Sample Preparation

- Ultrasonic disk cutters
- Abrasive Dimplers
- Argon ion gun thinners
- Plasma cleaners (to clean thin lamella surface)
- Time consuming process, handwork

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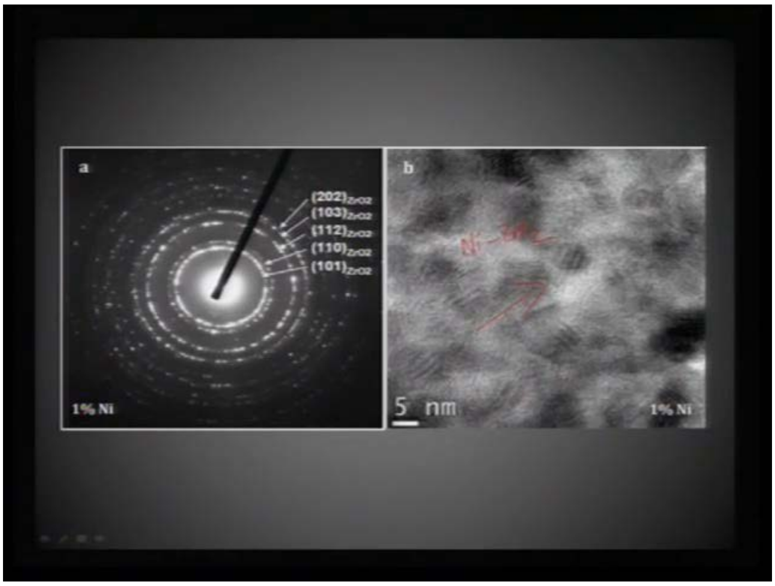

And here a some example f how TEM can be used for example, this is a sample with the nickel doped in zirconia, the transmission mode can be viewed either as a image in this form or as a electron diffraction spot. So, if you have a electron diffraction spot the information that you get here is that of a polycrystalline nature, but the spots really show whether nickel is actually coming out as a impurity or as zirconia, and you can see here zirconia does not show any nickel precipitates coming out.

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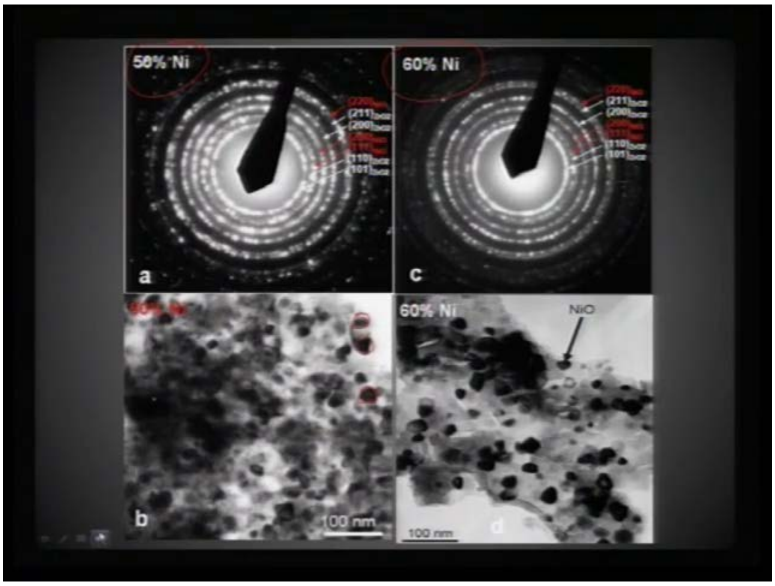

But, for nickel that is doped up to 50 percent and 60 percent you can clearly see that these are all the nickel oxide particles that are segregating out of zirconia.

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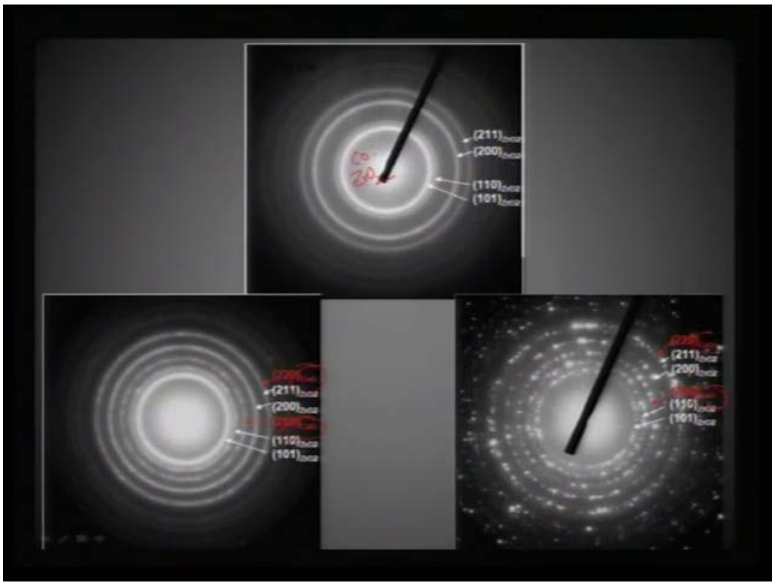

So, you can get very useful information from TEM and these are cobalt doped zirconia particles, you can see for up to 5 10 percent there is no phase segregation of cobalt oxide, whereas in the case of 20 30 percent you can see cobalt oxide that is coming out in a polycrystalline zirconia patterns.

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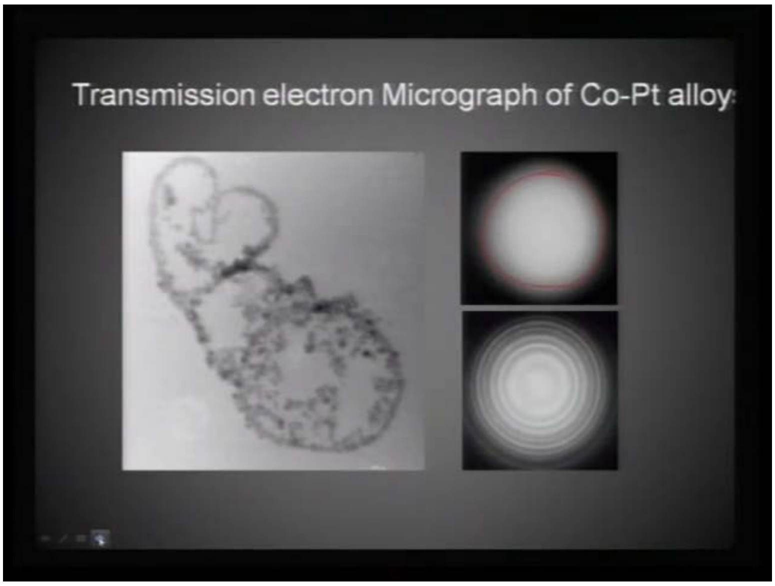
Transmission electron Micrograph of Co-Pt alloy

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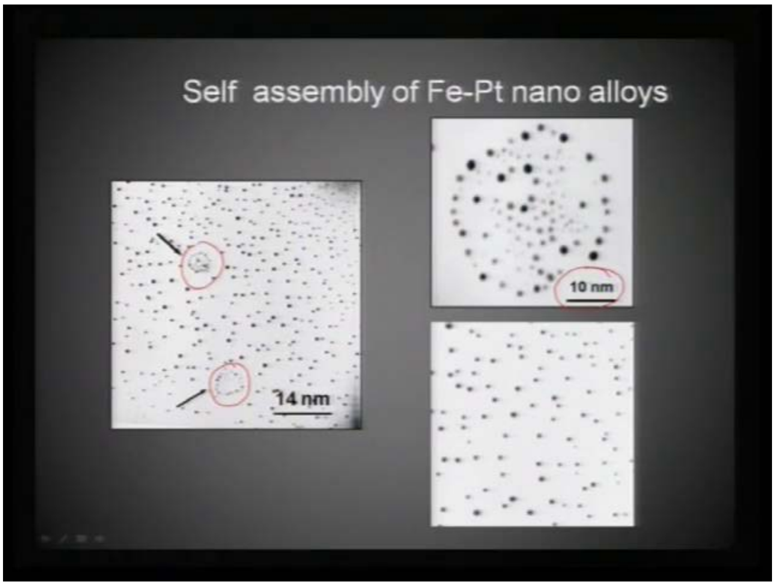
Self assembly of Fe-Pt nano alloys

We can also study a TEM for going down to nanometre size, and these are cobalt platinum alloys usually when you look at this alloy you see a amorphous picture in the electron diffraction, but if you keep on focusing the electron beam. You can see as you focus the particle actually goes from a amorphous to a crystalline pattern, so that you can see from here, so TEM can be used to probe nanoparticles.

Here is another example, of how we can use TEM this is for iron platinum nano alloys prepared by chemical route, as you can see here we can get the image of this iron platinum nanoparticles, which are much less than even 2 nanometres. So, with such contrast we can get the nano alloys mapped, and we can also get several interesting features about these nano alloys if you take a careful look at the TEM picture.

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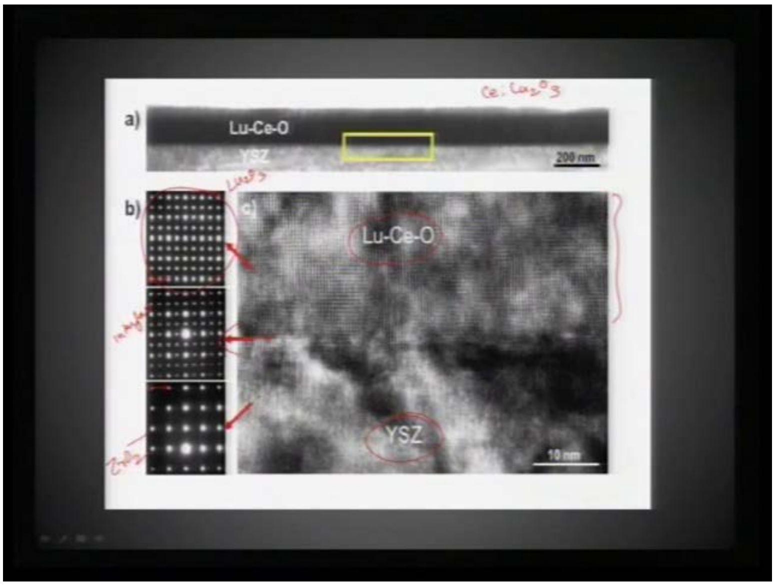

This is another example I have actually test upon this in module 2, when I discussed about multilayers TEM microscopy can be used even to look at the interface between multilayers that you grow using thin films. And here is a YSZ that is yttria stabilized zirconia, which is a substrate and on this substrate if you try to dope cerium doped lutetium oxide. You can find out how epitaxially this film can grow on zirconia substrate, this is the zircinia substrate diffraction pattern, and once you look at the interface where exactly the film is growing, immediately you see the pattern is changing.

But, once you go to higher thicknesses and look at it this is exactly the TEM pattern of lutetium oxide alone, and this is the interface, and this is the zirconia bulk substrate. So, you can clearly see whether a epitaxial growth is following or not, another thing you can see that the diffraction spot distances between these three spots is equal to that distance between these two. In fact, the the lattice constituent of this is actually half of the lattice constituent of yttria stabilized zirconia, so by mapping this we can find out whether we can epitaxially grow highly oriented films, so TEM can become very useful.

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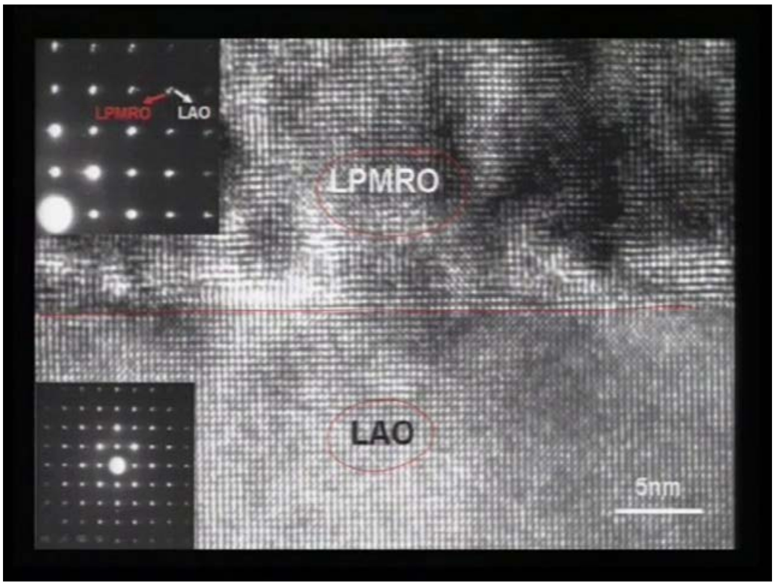

Again, in mapping the interface region whether you can make a epitaxially grown film, we can use manganite samples grown on lanthanum aluminate using a pulsed laser deposition and find out whether oriented films can be grown.

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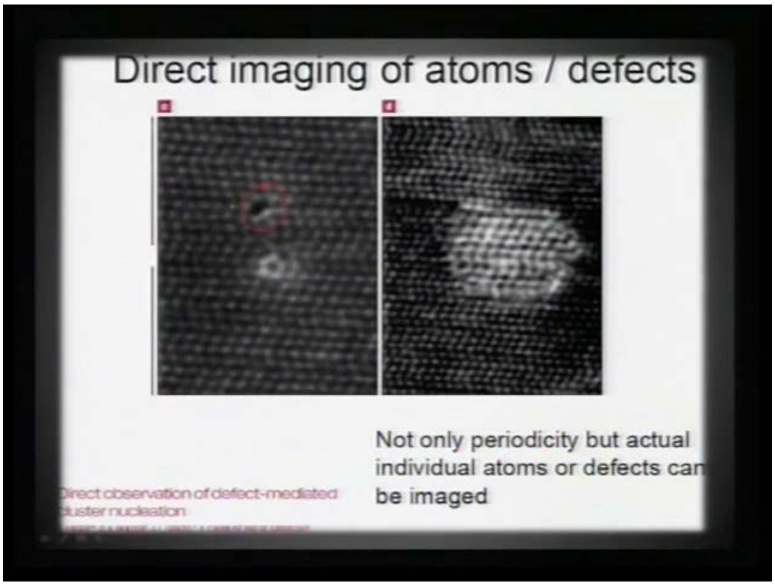

Direct imaging of atoms / defects

Direct observation of defect-mediated cluster nucleation

Not only periodicity but actual individual atoms or defects can be imaged

Also, TEM can be used for mapping, whether any atomic level defects are there which can be mapped.

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Focused Ion Beam
(FIB)

And another useful information that we can get now a days is using focused ion beam, focused ion beam is almost similar to SEM.

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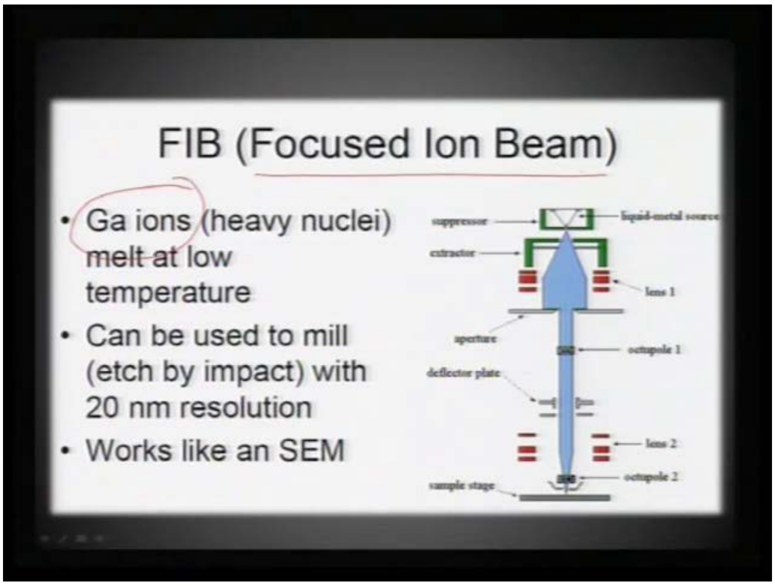

FIB (Focused Ion Beam)

- Ga ions (heavy nuclei) melt at low temperature
- Can be used to mill (etch by impact) with 20 nm resolution
- Works like an SEM

Even, if you look at today’s images of the instrument they look by and large the same and what you essentially do here is instead of using a electron gun, you are using gallium ions. And the gallium ions can be used in the same way to map the topography of your sample, not only that gallium ions can be used for making any impressions on you surface.

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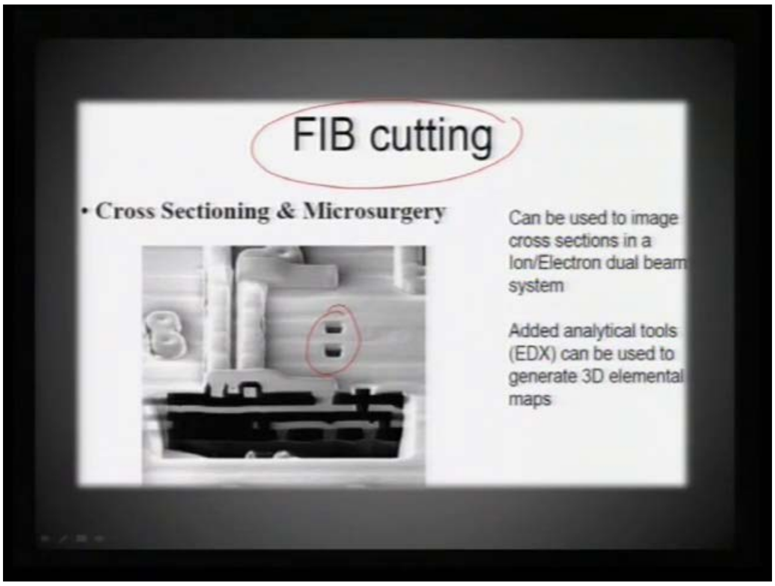

FIB cutting

- **Cross Sectioning & Microsurgery**

Can be used to image cross sections in a Ion/Electron dual beam system

Added analytical tools (EDX) can be used to generate 3D elemental maps

So, that is why it is called as focused ion beam because you're using a gallium beam instead of a electron gun to study the surface. And this is a example of how focused ion beam can be used in the place of SEM, not only for mapping the topography, but you can also preferentially do cutting this is possible.

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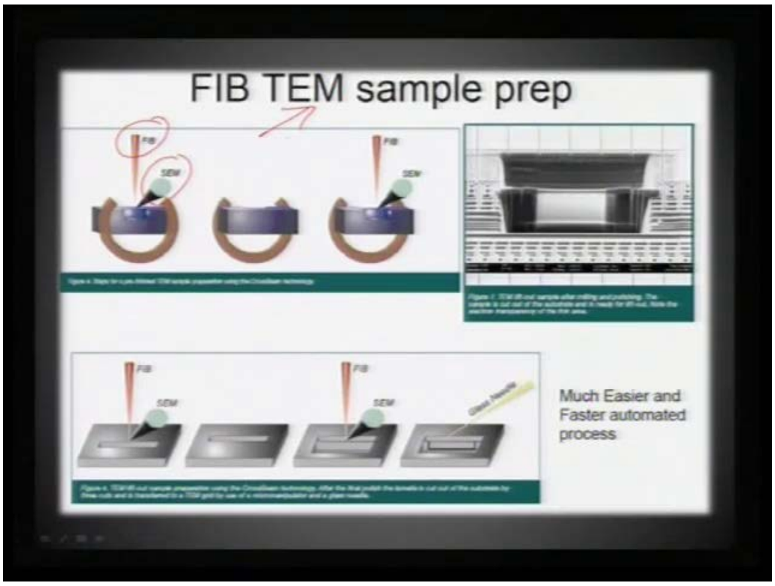

FIB TEM sample prep

Much Easier and Faster automated process

And we can use a combine of F IB and SEM to probe a particular place to prepare sample for TEM therefore, it has become a very useful complementary tool other than SEM.

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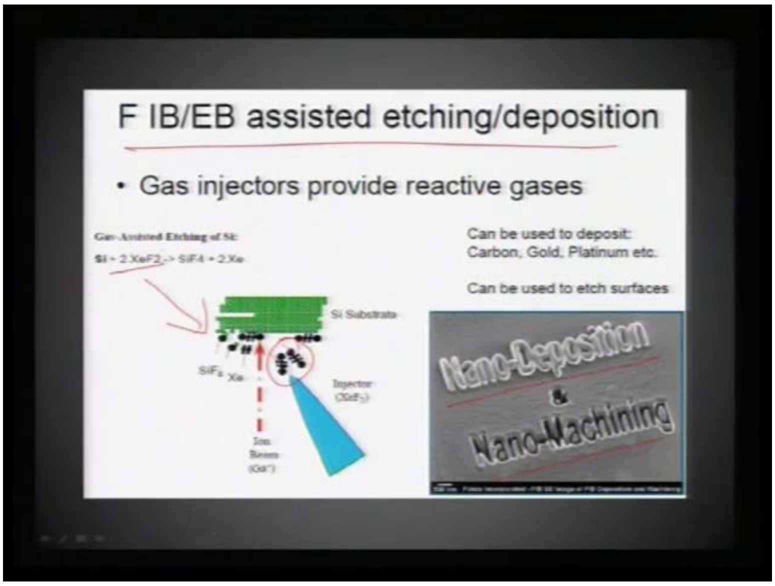


F IB/EB assisted etching/deposition

- Gas injectors provide reactive gases

Gas-Assisted Etching of Si:

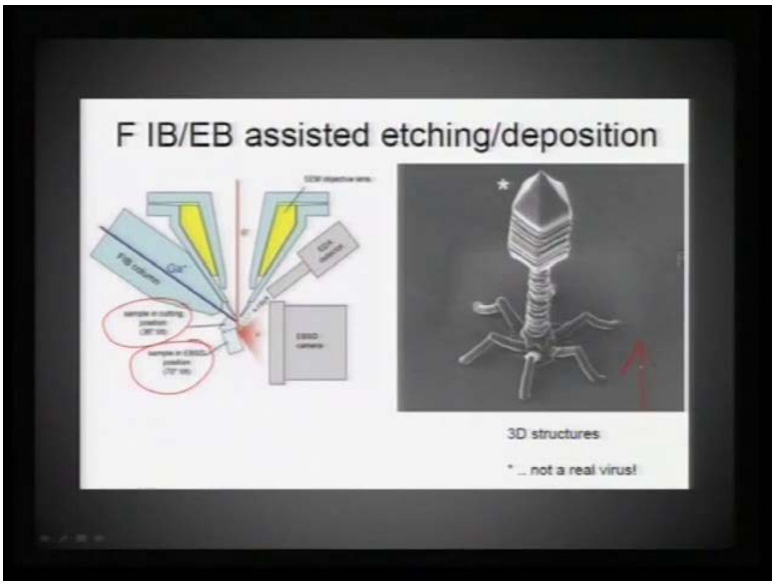
$Si + 2 XeF_2 \rightarrow SiF_4 + 2 Xe$

Can be used to deposit:
Carbon, Gold, Platinum etc.

Can be used to etch surfaces

And F IB can be used not only for mapping, but also for writing something or for etching, both can be done, and in this is a important viewgraph to say how on silicon we can we can try to do etching. So, you if you take xenon fluoride, then it will react with silicon and it will knock out silicon fluoride, and then you can actually etch those patterns, so a gallium assisted etching can be made using F IB we can make writings of this order.

(Refer Slide Time: 60:35)



F IB/EB assisted etching/deposition

3D structures

* ... not a real virus!

And this is the a contour of your F IB which involves gallium ion and this is the F IB column, suppose you are going to study the image, then this is the orientation that you do. And suppose you are going to cut it you tilt the sample orientation and essentially this is a new form of imaging technique that is coming, but the cost of the F IB is now three times more than the traditional SEM.

Therefore, this is proving out to be a very useful technique, as you see here this is not a virus image you can actually use F IB to not only map, but also to construct several structures, because you can do deposition, you can do cutting, and you can do imaging, all in one. And therefore, we have a new generation microscopy tool that is coming which is F IB that is focused ion beam, so we have seen in this lecture different examples where a combined technique of SEM, TEM and F IB can give you a very comprehensive analysis of the material that you are preparing. So, all these are useful for imaging your materials that you synthesize using a variety of techniques.