Concepts of Chemistry for Engineering
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Lecture 49
Surface Characterization Techniques

Hello and welcome to this new segment of Surface Characterization Techniques. My name is Arnab datta and I am an assistant professor in the chemistry department, IIT Bombay. So, let us take a look into different methods by which we can actually visualize the surface, even for a very small material.

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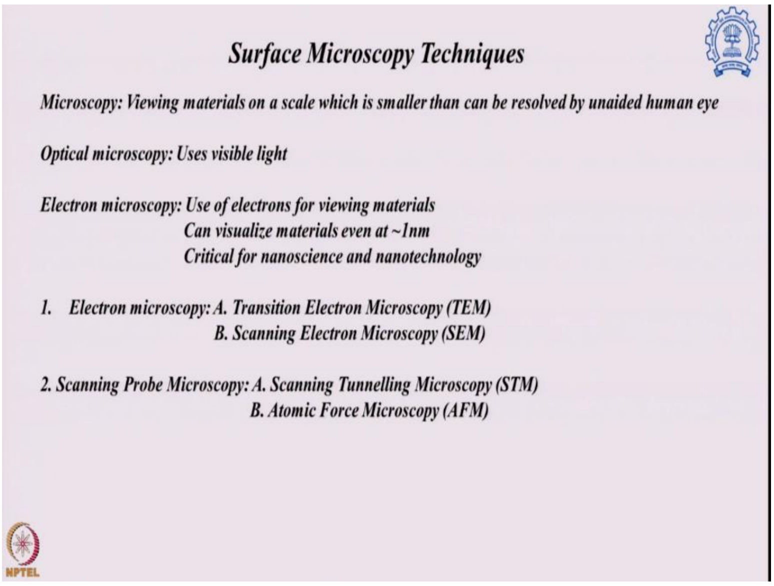

So, when we talk about surface analysis technique, one of the important techniques that comes to our mind is actually the surface microscopy. So, what is microscopy? Microscopy generally means that we can view a system or view a sample, in such a scale, which we cannot see by our naked eye. So, optical microscopy is quite common and it has well developed over the years by which, we can not only define the biological systems, but also material system.

But with respect to the time, we also developed some other microscopy techniques. So, for example, over here, we are showing you the electronic microscopy technique, which actually use electrons for viewing the material, whereas the typical optical microscopy uses the visible light. So, the electron microscopy has an added advantage over optical microscopy.

Because the light that we use for optical microscopy that has a wavelength in the region of nanometer, so, to find out anything lower than that is very tricky. Whereas with the electron microscopy, we can go further down and we can visualize systems even below 1 nanometer. And this particular electron microscopic system and their evolution was very critical for the development of nano-science and nano-technology, because over there, we generally handle samples, which actually plays around nanometer or sub nanometer region.

So, electron microscopy has two different versions, one is transition electron microscopy and one is scanning electron microscopy. On the other hand, recently, some scanning probe microscopy have been also developed, which also allow us to have an idea about the surface of different materials. And over there we have these two particular techniques scanning tunneling microscopy, and atomic force microscopy. So all these four systems, transition electron microscopy or TEM, scanning electron microscopy or SEM, scanning tunneling microscopy or STM and atomic force microscopy or AFM, will cover one by one in the following session.

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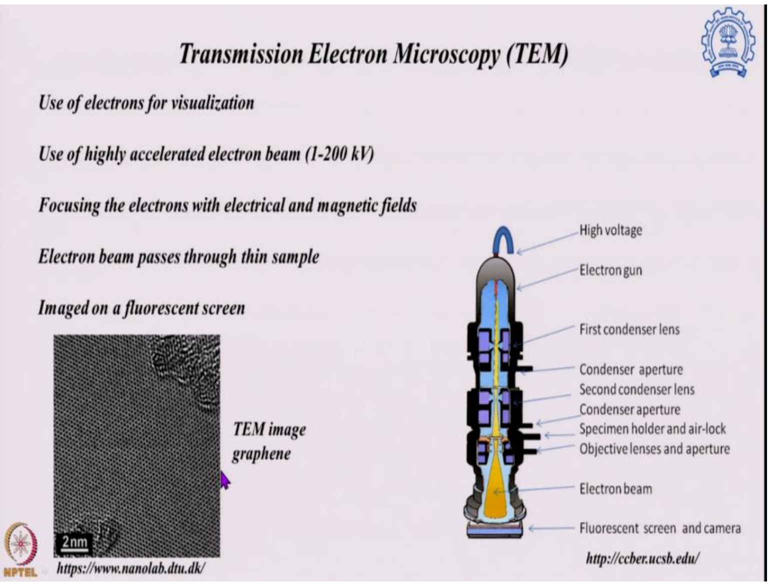

Let us start with Transition Electron Microscopy. So, this is a system where the transition electron microscopy is done. This is the schematic diagram of that. So let us take a look into that slowly. Since transition electron microscopy, we use electrons as our visualizing aid. And not only we use electrons, we use highly energetic electrons, which has an energy around this region 1 to 200 kilovolts which is actually created outside and then through this electron gun, we actually bombarded through the system.

Now, when the electrons come through the system, this high energetic electrons, it can go any particular direction, without particular movement. And then we need to focus them towards the sample. In optical microscopy, we do that by lenses. Over here, the movement of the electrons coming from the electronic gun, is actually controlled by electrical and magnetic field, present over here.

So you can see those things. These are the electrical and magnetic field, which actually focuses the electrons coming from the electronic gun towards the sample. So that is why, this particular system which actually controls their movement, is known as the electromagnetic lenses, which acts almost in the similar effect of the optical lenses.

But over here we are using electrical and magnetic field to control the movement of the electron. So over there generally, two different set up of such lenses or uses, which are known as the first condenser lens and the second condenser lens over here. Then it interacts with the sample. Over there the sample, is actually created such a way that it is very thin. So sample preparation is a very important thing in TEM.

We have to make the sample very thin. So that the electrons coming through this electron gun and then condensed through this electromagnetic lenses, should be focusing only a very minute amount of sample. And when it hits the sample, the reactivity of the electrons changes and which is actually recorded over here, in the fluorescent screen, which actually record, what is the interaction between the electron and the sample. And that is what we actually look and try to find out, what is present there on that surface of the sample.

And over here, I am showing you a TEM image of a graphene. So, you all know graphene is nothing but a system where hexagonal C chains, are actually bound to each other in a honeycomb structure. And you can very clearly see over there the structure of the graphene, set up over here and look into the scale over there.

This is line defines is a 2 nanometer scale and over there we can see much lower than that. So, sub nanometer region we can see that pretty easily. And this is possible because of the electrons that we are using and we can condense that very nicely over here. And also the sample which should be very thin, otherwise, we cannot get such a high resolution picture. So, that is the beauty of TEM imaging, where we can get to even sub nanometer region.

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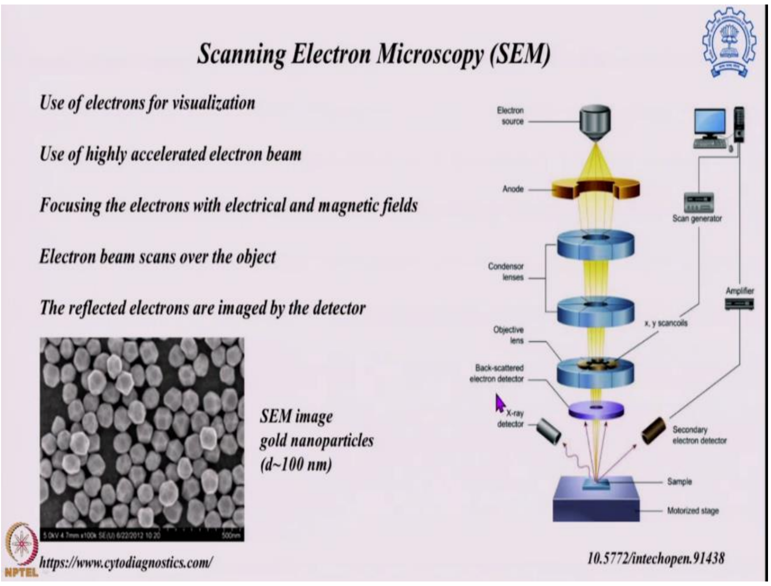

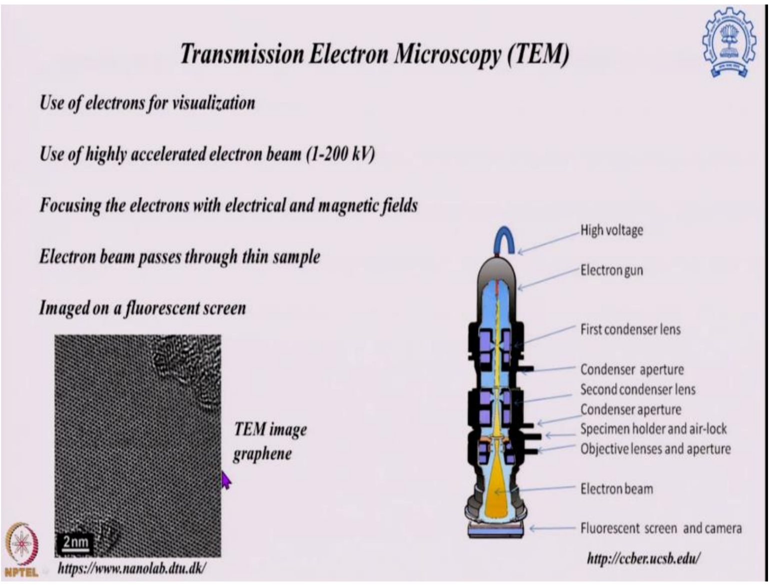

One of the complimentary electron microscopy comes after TEM is scanning electron microscopy or shortly known as SEM. Over here, we also use, the similar electron source. The electrons are coming over here. And over here, the electrons are also accelerated. So it is fast moving electrons, high energetic electrons coming in. And over there again, we are using our electromagnetic lenses by which we actually focuses our sample. And over there the electrical and magnetical field actually used through these lenses, where we actually convert a very widely coming electronic beam to a very focused electron beam.

And then we hit the electron beam over the sample over here. And then when the sample is hit by these electrons, there are three different things happens. First, some of them are scattered back, towards the electron gun, where the electrons are coming from. And over here, there is a detector for that of those back-scattering electrons.

And then some of the electron actually reflected and goes over here. And this is known as the secondary electron detector, where it actually is detected and their signals are amplified and analyzed over here in the machine. So, these reflected electrons are actually generally the main detection during the SEM.

And then some of the electrons actually comes out of the sample itself. Because these high energetic electrons are hitting and some of the valence and core shell electrons are actually comes out of the sample itself. And that actually creates an X-ray when core electron is actually shifted. So that X-ray is coming from the sample itself. The effectivity of it, we will discuss that a little bit later.

But now focusing on the SEM, we mostly look into this reflected electron. And not only that, we can also scan this sample. So, that is a very interesting thing we can scan this sample during this experiment. So we need not hit the same region all the time, we can scan over there and find out what is the surface behavior of this particular sample in different spaces of the same sample. And that is why the name scanning electron microscopy comes into the picture.

And when you look into that, we can very nicely find what is present there in the material. So over there I am showing you an SEM image which shows gold nanoparticles present with 100 nanometer of diameter. So, each of them are 100 nanometers in diameter.

So obviously, you can see there scanning electron microscope, although it gives us a very nice picture of all around the system. The resolution of the system is not as good as TEM. TEM we can easily go below nanometer level, whereas in SEM, we can go to almost 10 to 100 nanometers region that is where they actually acts better. So, that is the difference between SEM and TEM. They are both using the same kind of electronic beam, the both get focused by the electromagnetic lenses, but how it is interacting with the sample that is different.

Over there in TEM that actually goes through the sample and then in the fluorescent screen, we actually detect them. Whereas, in SEM, it actually hits the sample and the reflected electron is being analyzed over here.

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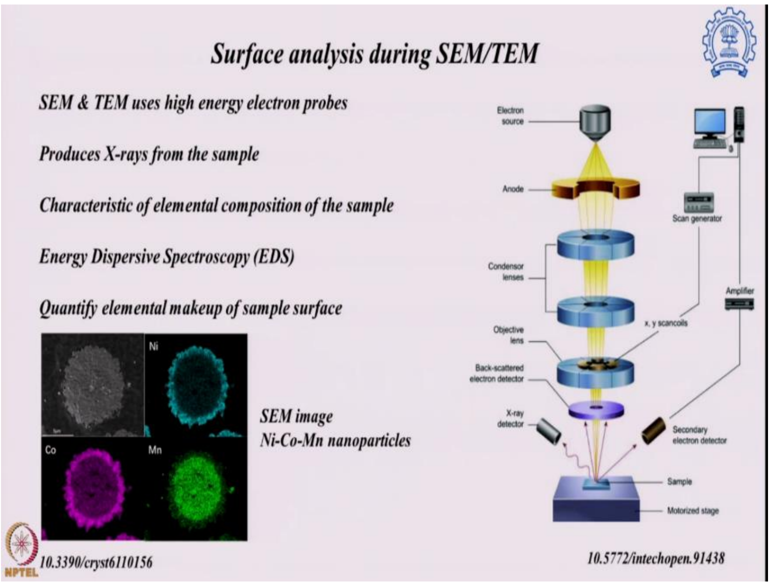

The good thing about SEM and TEM, as the high energy electrons are hitting these samples and as we just discussed a little bit earlier, it also takes out some electrons from the sample itself. And the electrons generally come from the core shell of the sample, so, they create a particular kind of X-ray, whose energy and signature will be very much different of which particular atom it is hitting there.

So, that is why we can not only detect which particular atoms or elements are present on the sample, but we can also quantify that by quantifying this X-ray. And that is actually known as the Energy Dispersive Spectroscopy or EDS, which generally comes as a complimentary segment for both SEM and TEM. So, with respect to that, we can easily quantify, what are the different elements present on the sample surface. Not only the identity, but also their quantity.

So, there is an example over here, I am showing you SEM data first. This picture over here in this gray region, which actually contains Nickel, Cobalt and Manganese. And then we did that EDS study along with that. And this particular bluish color over here showing you the presence of the Nickel and you can see the Nickel is mostly present on the edge, almost very negligible amount in the middle.

Then you look into the Cobalt through this violet color, you can see again most of them is present over there on the edge, but in the middle also they have quite amount of presence, which is much higher than the Nickel itself. Then the Manganese you can see it is mostly concentrated in the central area, the core area. It is not much present on the shell area.

So, by that we can not only find out the shape of the system by SEM, and through the EDS study, we can find out which of the elements are present, what is their quantity, and what is their overall spatial distribution. So, that is why SEM, TEM coming with EDS actually is a nice tool to find out what is the behavior of different nanomaterials.

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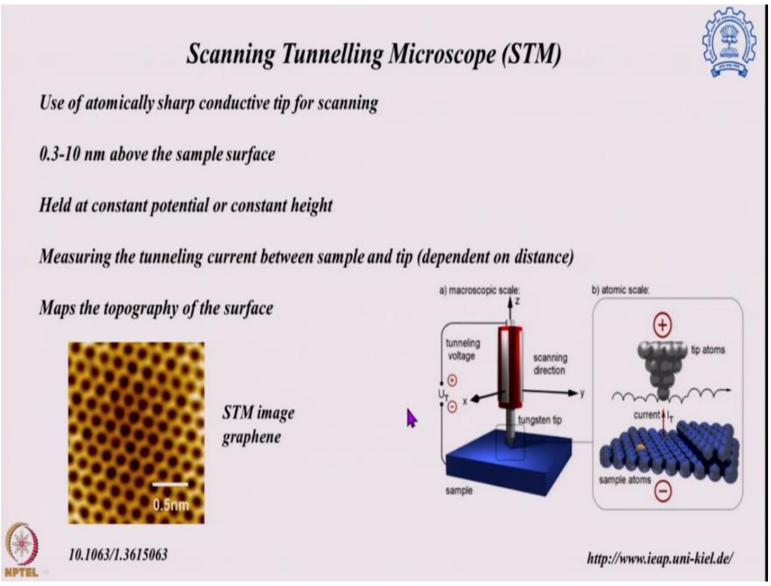

Then comes the probing microscopes. So far in the previous electronic microscope, we actually bombarded the system with electrons. Whereas over here, in the probing systems, we actually use a tip, a sharp tip, which actually can be handled in the atomic scale. And that is actually used for the scanning. So over there, I am showing you the picture that is how the instrument looks like.

And if I focus over here, we can see there is the tip which actually has only a few atoms present. And that is actually a conductive tip which can be transporting electrons. So, we can control its potential and the electricity passing through it. So, this particular tip is then hold at a very close to the sample surface. And we still keep a small distance between them, which is generally point 3 to 10 nanometer.

Within this difference, what we can expect that if the potential is correct, the electrons can get exchanged between the tip and the sample surface. And that electron is going through the space, so that is known as the tunneling current. And this tunneling current, it is dependent on what is the difference between the surface and the tip, what is the distance between them. And that is exponentially dependent on the distance.

So, amount of current we are going to measure over here that is going to give us a direct picture of the distance over here. And then this we can do in either X, Y or Z direction and find out the topography of this overall sample surface. So, we can find out exactly what is present there and how much it is present there and what is the spatial distribution. So, that is why the scanning tunneling microscope which actually measures that tunneling current is actually a very unique tool to find out the topography of the surface.

And that is how the STM image looks like. So, we are again looking into STM image of a graphene and you can very nicely see what is actually there. So, you can imagine when this STM is happening when it sees this bonding system that will be totally different than this pi-electronic back end system over here. So, that can be detected differently by this probe over here. So, that is the Scanning Tunneling Microscopy or STM.

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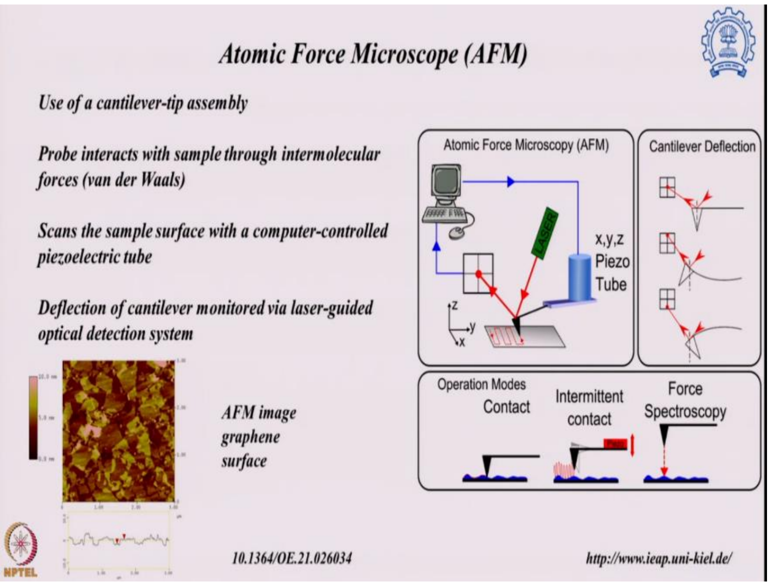

Then there is another microscopy known as Atomic Force Microscope. Over here, it is not only a tip, but it is also connected with a cantilever, which can actually move around. So, this is the cantilever shown over here by this blue line and there is this black tip. So, those are all connected. And this tip move different ways depending how it is interacting with the surface. And over there when this tip or the probe is interacting with the surface, it is interacting not through the tunneling current like the STM. Now it is connected through intermolecular forces like Van der Waal forces.

So, we again bring this too close to the sample. And over there depending on the sample, their shape size, it actually starts interacting with the tip. And their interaction is getting recorded.

Depending on the surface and it is topography, this tip moves in different ways and the movement of the tip is actually followed by this unique laser and optical data detection system. So, the movement of this tip is actually monitored by this laser optical detection system. So, this laser actually hits on the top of the tip who is getting reflected and monitored in this optical detection system.

So, over here you can see very nicely. So, if the cantilever and the tip is like in this way, the laser is coming and it is hitting this particular position, in this optical detection system. Now, if it is moving upwards the reflected laser is also detected in a different region, showing there is an up region over there. If it is going down, it is again showing over there, by this laser guided system, which is actually shown over there at the bottom region of optical detection system. So hence with this laser and this optical detection technique, we can follow what is even the minute change is detected by this tip over here.

And over here, I am showing you again the AFM image of a graphene surface and you can see it actually shows the different topography and distances from the overall sample and their distribution over there. And over there this particular graph is showing, how the tip has been moved and that is actually detected by this optical detection system. And then this image is actually created from this distance from the movement of the tip. So that is how the AFM image has been created.

So AFM and STM, the difference is that the STM talks about the tunneling electricity so that means a tunneling current has to be present there. And for that generally a conducting surface is typically needed for a very good STM image. In AFM, it depends only on intermolecular force like Van der Waal force, even with different conductive samples, even non-conducting insulators, we can do AFM very easily.

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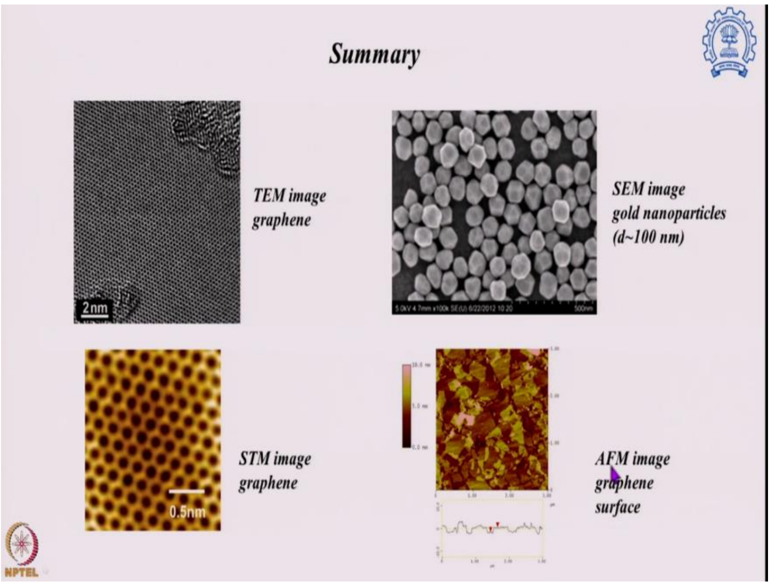

So, with respect to that, we will come to the summary slide of these systems. So, we actually detected four different, so over here, we discuss four different imaging techniques. Two of them are electron microscopy techniques which are TEM and SEM. Over there, TEM has a much better resolution compared to SEM, however, TEM needs a sample, which has to be very thin, whereas SEM does not need that much of a thin sample. So sample preparation is much easier in SEM. However, SEM cannot give us as good as resolution as the TEM.

Then, we also discussed two different imaging techniques, which actually used probes, like tips, one of them use tunneling current, so that is known as the Scanning Tunneling Microscopy. And the other one uses the intermolecular forces like Van der Waal forces which is known as the Atomic Force Microscopy. So, all these things we can use in tandem to get a very nice picture about the surface, even for a nanomaterial below one nanometer size. So, with respect to that, we would like to conclude this session over here. Thank you.