

**Materials Chemistry**  
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**Module - 3**  
**Lecture - 5**  
**Applications of Scanning Microscopy STM and AFM**

In the previous modules, we have seen the preparation and in the third module we have so far seen how the materials can be characterized. And basically we have grouped it group the techniques into 3 different groups namely diffraction techniques, and spectroscopic techniques and microscopic techniques. In the spectroscopy, we have specially looked at two important characterization tools namely x-ray absorption, and x-ray.


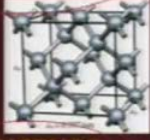
In the microscopy techniques we will be specially looking at the range of methods that are available, which can be mapped under microscopy namely scanning electron microscopy, transmission electron microscopy, scanning tunneling microscopy and atomic force microscopy. All these are basically imaging techniques, they are quite different from these spectroscopic tools, but it is impossible to cover all these in one lectures. So, I am going to just give some idea about the tunneling microscopy and force microscopy. And in another lecture we can look at the most prevalent spectroscopy tool that is SEM and TEM which is widely used.

Just to recap on what we have seen already, in materials characterization, we basically look at chemistry related tools to evaluate the elemental composition, titrations are the best chemistry approaches to ascertain whether we are making the right type of material or not. But, when we come to the structure we look at the x-ray diffraction as a major tool both for those working with molecules, and those working on solids they heavily relay on x-ray diffraction.

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### Materials Characterization

- What is the Elemental Composition : **CHEMISTRY**
- What is the crystal/local structure: **STRUCTURE**
- What are the defects: **MICROSTRUCTURE**

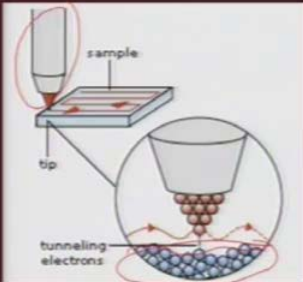


We have already seen the principle of x-ray and also when we want to look more carefully into the microstructure, then we look at the imaging tools. In today's talk I will be first talking about almost the first invention on imaging tools that is scanning tunneling microscope, which almost brought a new focus into material characterization. Because, until 1986 SEM and TEM, where the only tools which were popular to study the microstructure of any given solid, one of the major benefit of this microstructure analysis is to see how the defects are orientated in a given sample.

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### The Scanning Tunneling Microscope (STM)

**The STM is an electron microscope that uses a single atom tip to attain atomic resolution.**

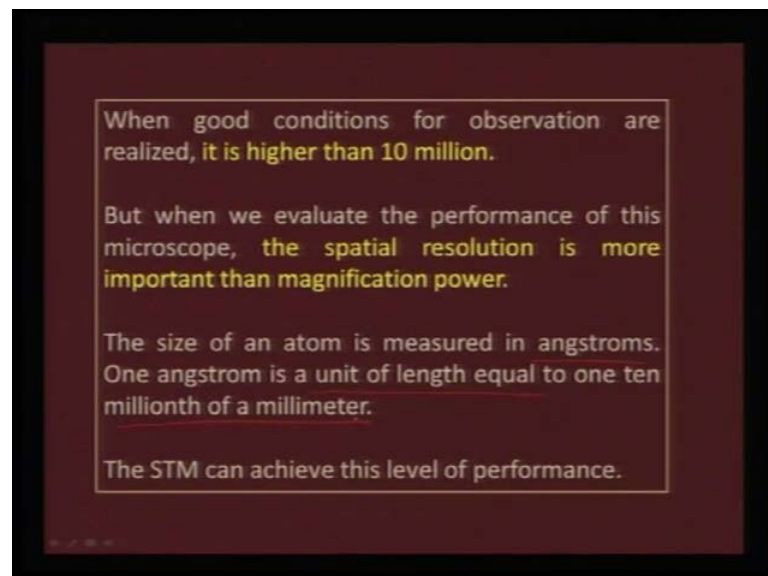


So, mainly the defects in a solid can be mapped using the microscopic tools, so we will look at the principle of STM, in this slide I am just giving you a brief outline of what this technique is it look simple from this diagram, but it can become the most complicated technique, in terms of attaining the tunneling condition. What you see here, in this is a tip and this tip is actually made to scan in x y direction, and when you scan this in x y direction then you should be able to map the atomic level arrangements.

And to achieve a atomic level mapping of your material, you need to have a material or a tip which will also bring about such a resolution. And as you would see here from for a naked eye it may look like a pointed tip, but the tip in essence should almost be reduced to a single atom tip and that is the most governing principle of this STM.

So, when you bring this tip into such atomic level dimension, then a process of tunneling is possible between this tip to the surface which you want to scan, and as a result when you attain a tunneling condition, then it is possible to generate a topography of the material that you want to study. So, STM is an electron microscope essentially that uses a single atom to attain atomic level resolution therefore, this is certainly a more refined technique compare to scanning electron microscope.

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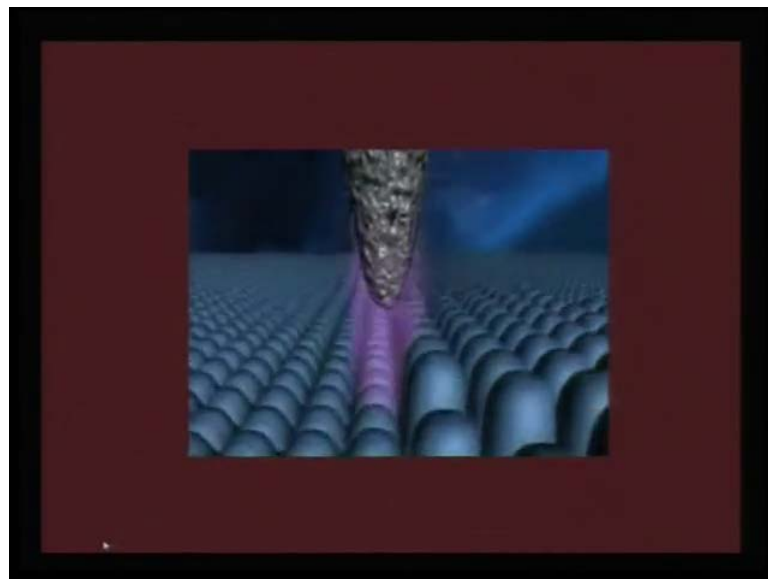


When good conditions for observation are realized, the magnification that you can achieve is of the order of 10 million times, so when you talk about 10 million times you are talking about looking at a atom, through this probing technique. So, this is one of the

most richest information, that anyone can get out of scanning tunneling microscope, so the order of magnification that you can achieve is of atomic level dimension, which is about 10 million times.

And what we also look here is for a spatial resolution, which is far more important than a magnification power, because when we talk about optical microscope or scanning electron microscope. We usually look at the magnification, but here we are looking at spatial resolution therefore, this is entirely a different notion altogether in the microscopic techniques. The size of an atom actually is measured in angstrom, and therefore, one angstrom is a unit of length equal to one tenth of a million of a millimeter.

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So, we are actually going to look at the material in angstrom dimension, and this can be achieved by STM, this is an animation that I just want to show in the beginning itself, which can give you some idea. As, you would see here this is a tip which is actually scanning through an array of ordered atoms, and this can actually go back and forth into any prescribed area.

And as you would see here there is a tunneling, that is achieved between the tip and the surface, and this can map and if there are any edges or steps that are possible the tip can actually adjust itself to probe. Therefore, in a predominately flat surface any corrugations, any step edges that are there everything can be mapped, once you attain or achieve a tunneling probability.

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So, the machine although it looks very simple, in reality the machine is a pain taking effort, because this is a ultra high vacuum chamber which is actually having the STM features, so get a STM image it is a very costly probe. Now a day's, different forms of scanning probes are coming, where you can even use a scanning probe in a ambient condition in a laboratory and in a cleanse clean room atmosphere, but STM essentially calls for a high vacuum environment.

Therefore, it is called UHVSTM that is ultra high vacuum STM, and in ultra high vacuum STM most of the time it is only done at room temperature. But, today as we are addressing this issue in 2011 we have much more refined techniques where even you can go to liquid nitrogen temperature to probe scanning tunneling microscopic images.

So, the instrumentation has become very, very extensive and more improvisations are coming, and as I go through some more slides you will understand, that now this STM or scanning probe has become a family of techniques. It is not just STM it is taken upon itself many modifications therefore, STM is not a standalone technique, but it is a group of techniques that can be used. So, just to impresses upon you that STM by itself is actually a ultra high vacuum probe, but we can also try to do that in ambient condition by modifying this technique.

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Scanning Tunneling Microscope

Tunneling current starts to flow when a sharp tip approaches a conducting surface at a distance of approximately 1nm (10Angstrom).

The tip is mounted on a piezoelectric tube, which allows tiny movements by applying a voltage at its electrodes. The electronics control the tip position to keep tunneling current and, hence, the tip-surface distance constant, while at the same time scanning a small area of the sample surface.

This movement is recorded and can be displayed as an image of the surface topography. Under ideal circumstances, the individual atoms of a surface can be resolved and displayed.

Heinrich Rohrer  
Gerd Binnig  
Nobel Prize 1986

$I = K \cdot U \cdot e^{-2\kappa \cdot d}$

The slide features a graph showing an exponential decay of current (I) with distance (d). A schematic diagram shows a sharp tip approaching a surface, with a piezoelectric tube and a computer monitor displaying a topographic image.

Now, what is this STM all about we can start with some simple definitions just to highlight the point, but let me single out the 2 Nobel laureates who are responsible for bringing this technique and they were awarded Nobel prize in 1986, Heinrich Rohrer and Gerd Binnig both this scientist were awarded Nobel prize for designing this STM. In this scanning tunneling microscope tunneling, actually tunneling current starts to flow from a sharp tip to a conducting surface at a distance approximately of one nanometer.

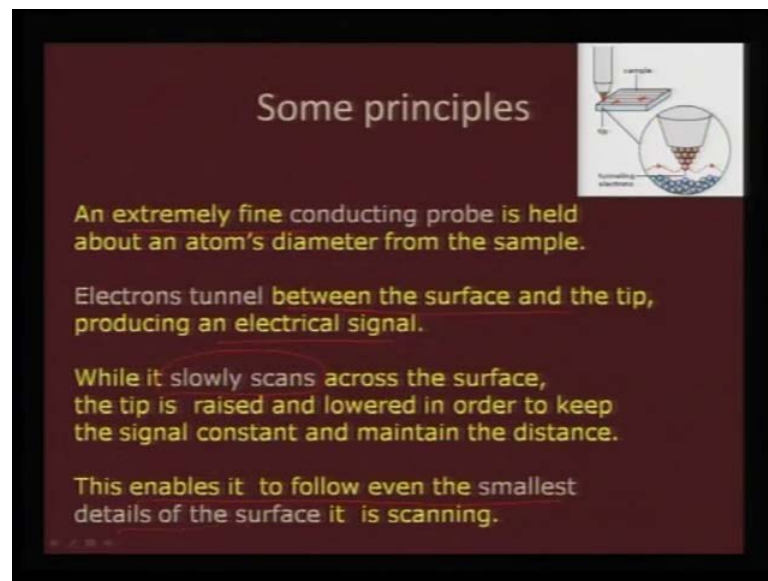
So, that is the tunneling distance and if you look at this graph you would find out that you can play around with a range of current, which is your tunneling current and that depends on a very small width of the distance. So, within the small distance you can achieve, so the tunneling current is exponential to the distance between the tunneling tip and the surface. And if this tunneling has to happen you need to have both the tip and the surface that you are probing, which has to be metallic, you cannot have a non-metal or a insulating compound.

And therefore, if you have a insulating compound or a biological sample then you need to come out come up with another probe, which will help you to do the same atomic level mapping, and incidentally that what is AFM is able to do atomic force microscope is mainly meant for non conducting surface. So, we will go more into this detail as we progress through this lecture that tip is actually mounted on a piezoelectric tube, which

allows tiny movement by applying a voltage at its electrodes and the tip position can actually be therefore, maneuvered.

And the tip to a surface distance actually can be kept constant, we can vary the tunneling current or we can keep the tunneling current constant and vary the distance. And this is actually governed by this notion, so based on this tunneling probability it is possible to engineer different types of STM arrangement.

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**Some principles**

An extremely fine conducting probe is held about an atom's diameter from the sample.

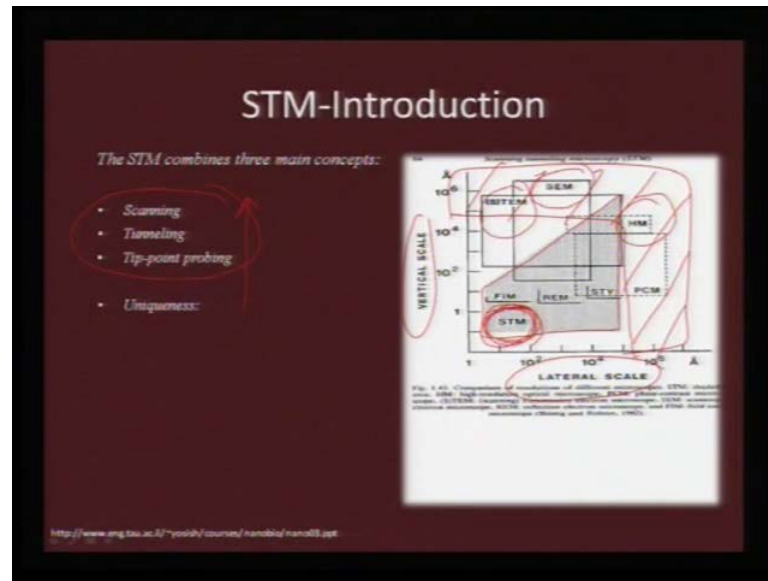
Electrons tunnel between the surface and the tip, producing an electrical signal.

While it slowly scans across the surface, the tip is raised and lowered in order to keep the signal constant and maintain the distance.

This enables it to follow even the smallest details of the surface it is scanning.

So, this is the basic principle by which this works out, so some important features that we can get to know about this STM is the tip has to be extremely, and then the electrons actually tunnel between the surface and the tip producing an electrical signal. And while, the scan is going on which has to be very, very slow it is not a rapid scan it has to be a very slow scan, and when you do that you can actually trace the topography of this surface. So, this enables it to follow even the smallest details of the surface as it is scanning.

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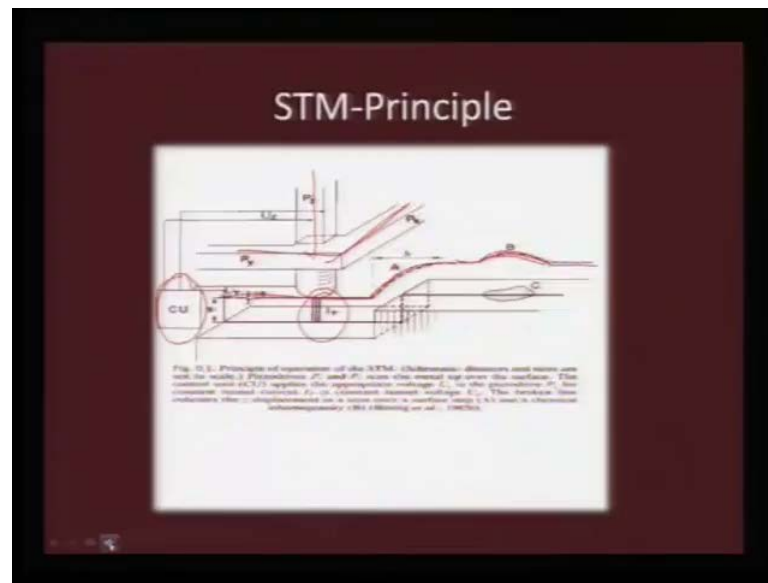


So, three principles that we can come out with one is scanning one is tunneling and the other one is tip point probing, so actually the protocol in a scanning tunneling microscope is on the reverse order. First you try to bring the tip in closer proximity to the surface, and then you establish a tunneling and once the tunneling is established then you do the scanning. So, these are the three important concepts that you work out during the STM and what is the uniqueness of this STM, why we need to take such a costly procedure for mapping, because we have already the well established once that is optical microscopy.

And then you have SEM we have TEM, all these are available at a much cheaper rate compared to STM, but if you look at the vertical scale and the lateral scale you can only map those which are above ten power 6 angstrom. So, anything in micron scale the STM TEM or optical microscope can easily mapped therefore, we have so far been more interested or we are adopted more to materials characterization along this domain. So, SEM TEM optical microscopy has helped us, but more, so in the recent years the shaded area this has become point of focus and more, so you can find out the spatial resolution that you can achieve from STM is of the order of angstrom and that is why this is positioned somewhere here.



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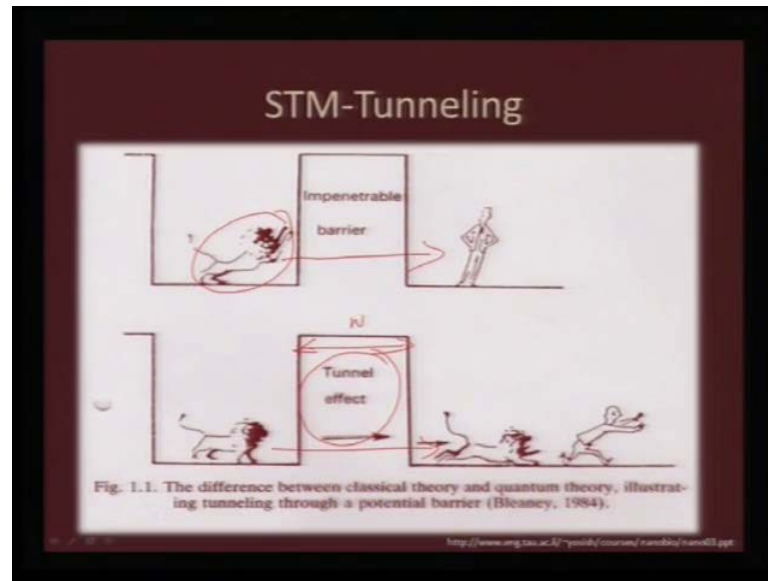


So, in comparison to SEM and TEM and other microscopy, STM stands out because you are almost taking it near to a atomic resolution, so what is the principle here the principle of operation of this STM is given in this cartoon. Where, you can see that this tip here is actually mounted on a piezoelectric table with the x y arms, so you have x y and z position. So, this piezoelectric table actually can move this tip in x y direction, and this y z direction is given for the tunneling to be established.

So, once you established the tunneling, then you can actually move in the x y dimension to any part of the sample what you are looking for, and then the control unit actually will take care of applying the current the required voltage. For the for sustaining the tunneling to proceed and this is the map, which tells you what exactly will happen when this piezoelectric table is moving in the x y direction.

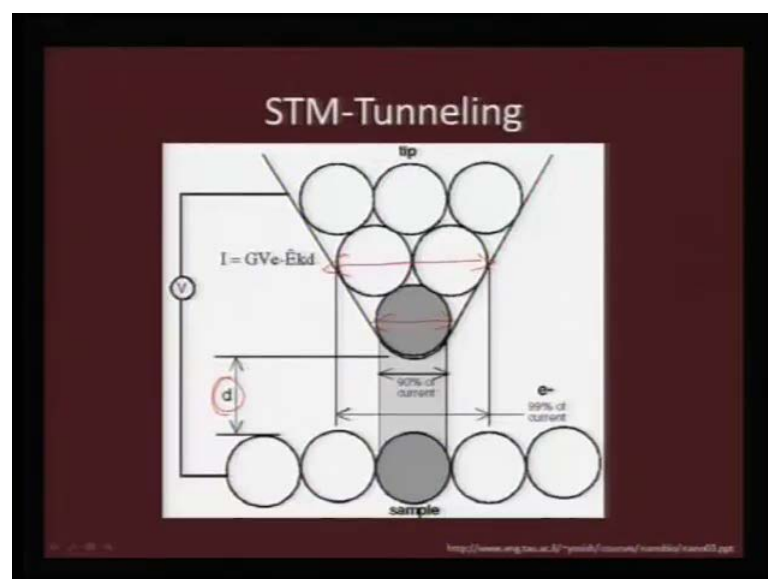
So, if this is actually flat terrace then this dotted line will tell you that the surface is smooth, and suppose the crystal has a step edge then the position of this of this tip will move this way. And if you see this sort of movement then you understand that the crystal has a step edge, and if you see a bump here a small one then you understand that the surface is inhomogeneous is not flat or something else is there. So, the way the tip moves will give you all the related information with respect to the surface that you are probing.

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Now, the principle of tunneling actually we understand that this is totally a quantum phenomena, because if it is a classical picture then if there is a barrier and the object, which is suppose to tunnel. If it is a macroscopic object then it will not tunnel through this barrier, but if it is a microscopic particle like electron, then there is a tunnel effect even through a barrier then it can tunnel through. So, this is the difference between a macroscopic stuff and a microscopic object of, so tunneling is possibly even if there is a barrier, and this barrier actually width of this barrier has to be very small for the tunneling to sustain.

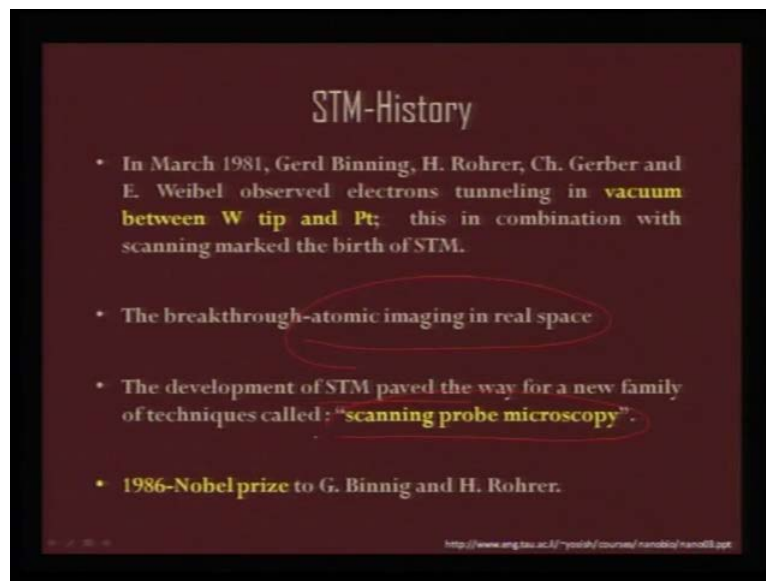
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So, that is the condition that we try to optimize or we try to achieve when we are doing the tunneling experiments. Now, if you look at this tunneling phenomena ninety percent of this tunneling current is actually, confined to one single atom and that is what we've see here. This distance D is very important and you will be able to achieve up to 90 percent here and 90 percent of the tunneling current can be confined to just two atom.

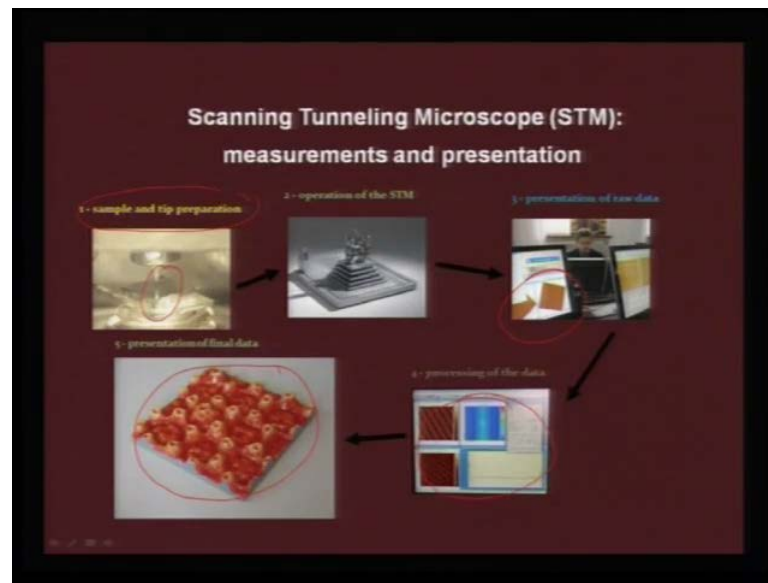
So, your probe that way has to be very, very sharp and it should be very well define otherwise tunneling cannot be a exercised, if you are tip is not properly done therefore, in STM technology tip preparation itself is a costly procedure. And if you understand the chemistry of the sample preparation or the tip preparation you will see that it is a simple electrochemical technique that can bring about great results we will see that shortly from now.

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So, just want to quickly recap what really has happened and how much this simple tunneling principle has been carried over, the first experiment that was done by this Nobel Laureates was in vacuum between tungsten tip and platinum surface. That was the breakthrough experiment, and we would shortly see some of the images which was brought out by them and. So, therefore, the path breaking discovery to atomic imaging in real space, and not only that the STM paved way to a new family of techniques called scanning probe microscopy. So, SPM is actually the normal way the microscopy is referred to, but it can also accommodate various other tunneling microscopic techniques.

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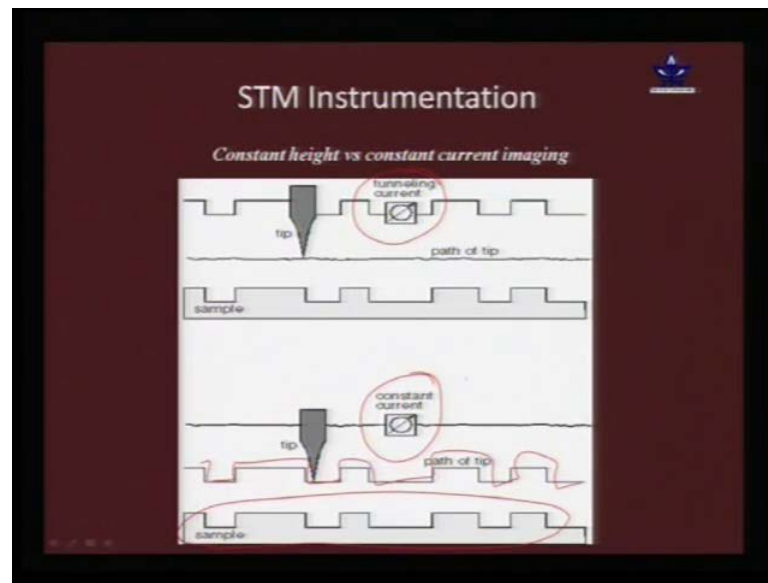


In the scanning tunneling microscope the protocol as I told you the first one is to do with the sample preparation, then tip preparation and this is real time photograph that is taken in a ultra high vacuum environment, where you can see the tip is actually approaching the surface of the sample. And you can this tip is actually seeing mirror image of the of it is own as you bring it closer to the surface, so with the optical microscope you can actually bring it as close as you can and then you can allow a auto approach for that tunneling to be established.

So, today's experiments allow that tip to do a auto approach, you can bring it as close as you can by following it through microscope, and then you allow the machine to do the auto approach. So, that the tunneling will be established once the tunneling is established then you are ready to go for mapping the surface.

So, what you precisely do is cover lot of frames of this sort of pictures and then you try to analyze, that you can you can try to estimate, you can try to verify whether the images are as expected. And then you can do variety of things that every frame that you are recording you can do line scan I will show some of the examples of what you can learn from such SEM STM pictures. And then finally, you can come to a presentation data in three dimension or in two dimension, so this is exactly the way you go about recording the STM pictures.

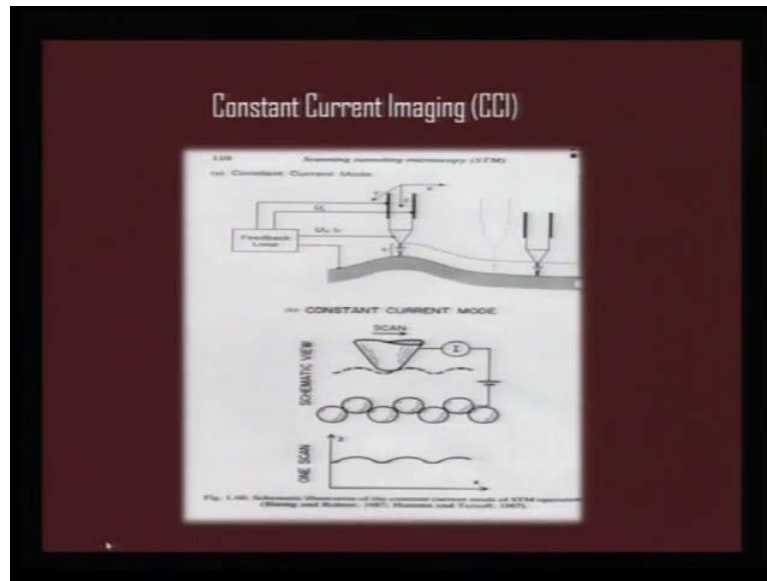
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In terms of instrumentation I have told you there are two approaches, one is constant height approach otherwise it is constant current imaging, so if your constant height approach then you are actually varying the tunneling current. So, just let the tip experience proper tunneling by varying the voltage that you are applying, so keep the distance constant and you only vary the tunneling current or you can have the tunneling current establish you fix it.

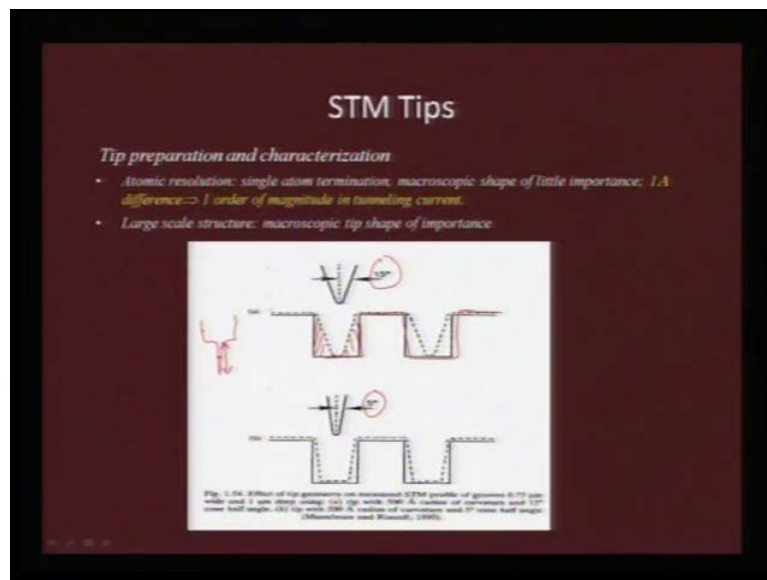
And let the tip go through the same contour as that of the sample, so if the sample is inhomogeneous, in this way the tip will actually be coming and going this fashion and we will exactly map the path of your atomic surface. So, both are predominant and sometimes it is always advisable to have a constant current tunneling current, and then you let it go through different heights. If your sample is dirty and if your sample is not very smooth, then in this approach what happens sometimes your tip can actually pick up some dirt or some islands of atoms, which otherwise will become very difficult to remove it therefore, it is always better to have a much cleaner surface.

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So, sample preparation that way becomes a very important issue, so this is another cartoon that shows the same idea of what this constant current imaging approach.

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But, there is another issue the tip that we saw here, this is the exactly the way tip will look for and if this tip is actually of a dimension like this, but then your cone angle, this cone angle if it is going to be 15 degrees or if it is going to be 5 degrees. You can look at the relative influence of your scanning microscopy images, because if you are cone angle is 15 then if the atomic surface is having this sort of patches. Then your probing will be

incomplete these are areas which will not be mapped by your STM tip, because of your cone angle. Therefore, the sharper the cone angle better the lateral resolution, so your atomic imaging will be very, very sharp, if you have a very short cone angle therefore, preparation of your tip is very, very important.

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## STM Tips

- *Chemical composition of tip: oxide layer (jump to contact), atomic resolution - type of atom, higher resolution has been obtained by tunneling into or from d-orbitals (W).*
- Tip material does not 'dictate' atom at the tip !*
- *Tip material: hard, UHV-W, Mo, Ir, Au-Pt, Au (soft)  $\Rightarrow$  Pt-Ir.*
- *Tip preparation: Electrolytical etching (drop-off technique).*

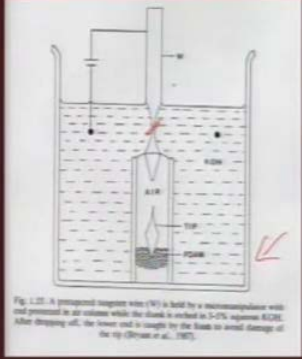
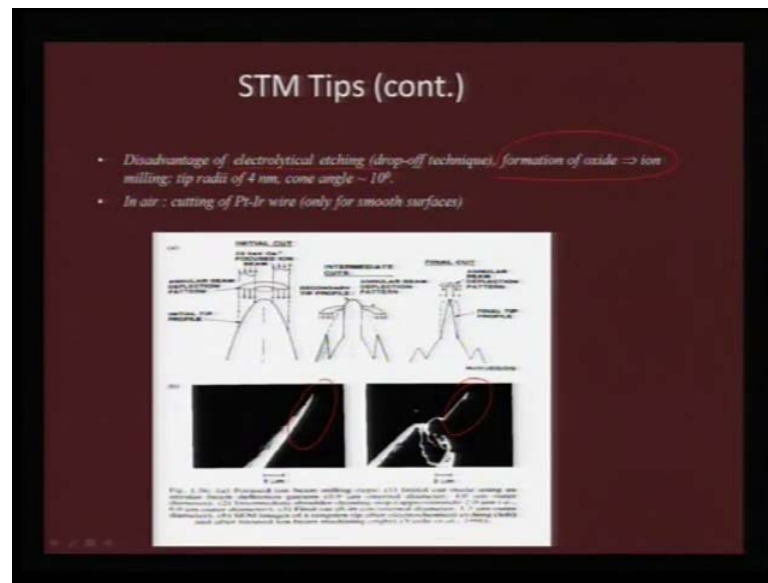


Fig. 1.27. A prepared tungsten wire (W) is held for a micromanipulator with and protected by an column with the leads is etched in 10% aqueous KClO<sub>4</sub>. After stripping off, the lower end is caught by the leads to avoid damage of the tip (Strat et al., 1987).

And this is how you prepare a STM tip, and the STM tip can be prepared by a simple electrochemical procedure, in this case what you see here is a prepared tungsten wire, which is held by a manipulator. And this is actually a n protected in air column, where as the leaching is done here then it will drop down, and you can preserve the tip this is the situation after this is leached and it is cleave.

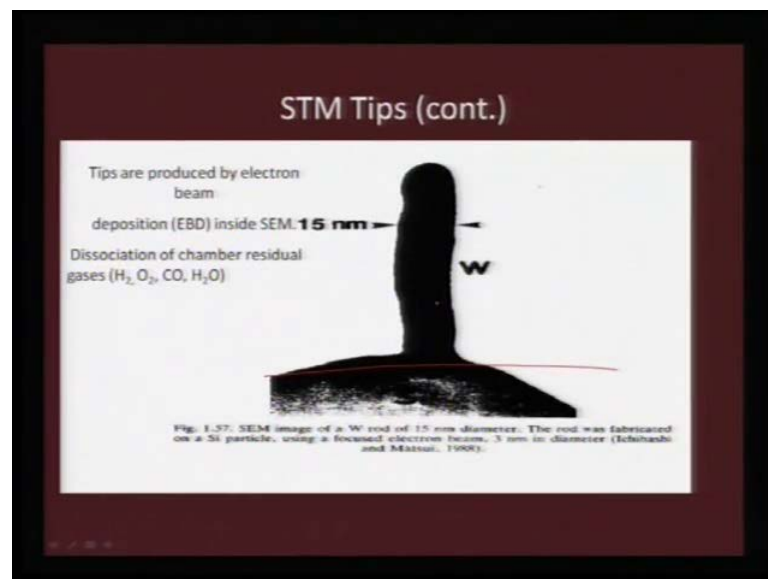
So, when it is actually this area is getting leached here, then you can see that you get a very fine tip, this side and this is almost near to a single atom tip, but in reality you never get a single atom tip. So, there are different ways that this can be done, but this is the simplest and cheapest way of preparing a STM tip, so this is usually engineered for variety of applications. For example, if you are working on a ultra high vacuum condition then tungsten, molybdenum, iridium are the preferred tips, if you are working in a air then it is platinum or gold, platinum, iridium, these are used for such procedure.

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And we also have other ways of doing this the disadvantage of your electro electrolytic method is that there is formation of oxide at the tip. So, usually ion milling is done, in order to prepare the tip you can see this compared to this tip you can get much sharper one by using ion milling. And ion milling can actually keep away from other oxidic impurities therefore, this is one of the preferred way of doing that.

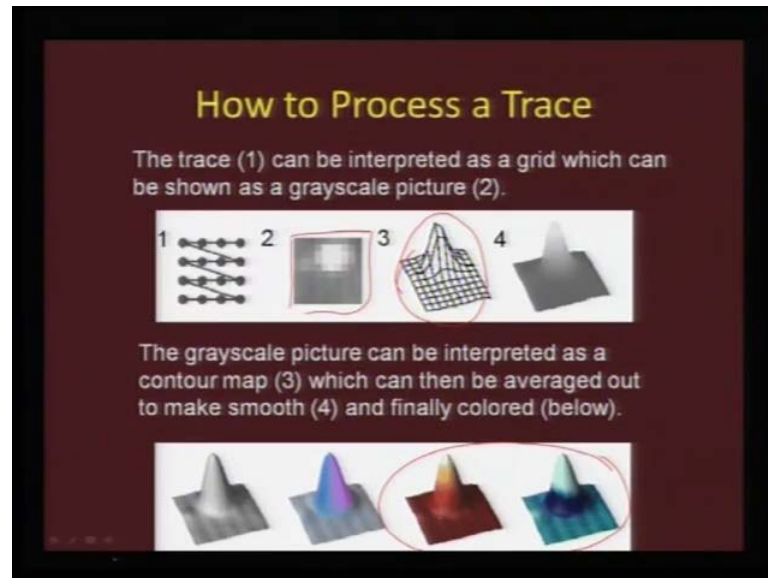
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This is another technique called electron beam deposition, where you can actually grow the rod on a silicon particle, you can grow tungsten rod which is very, very small the thickness of this can be 50 nanometer, so you can artificially grow STM tip.

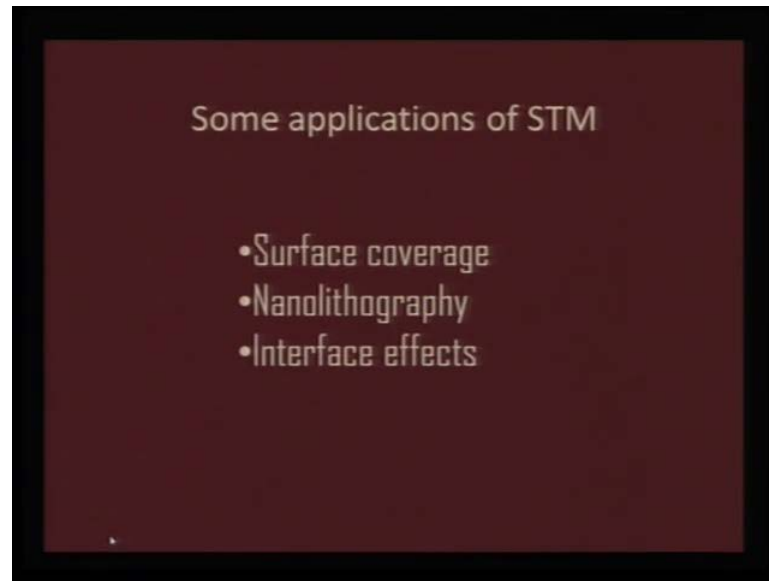
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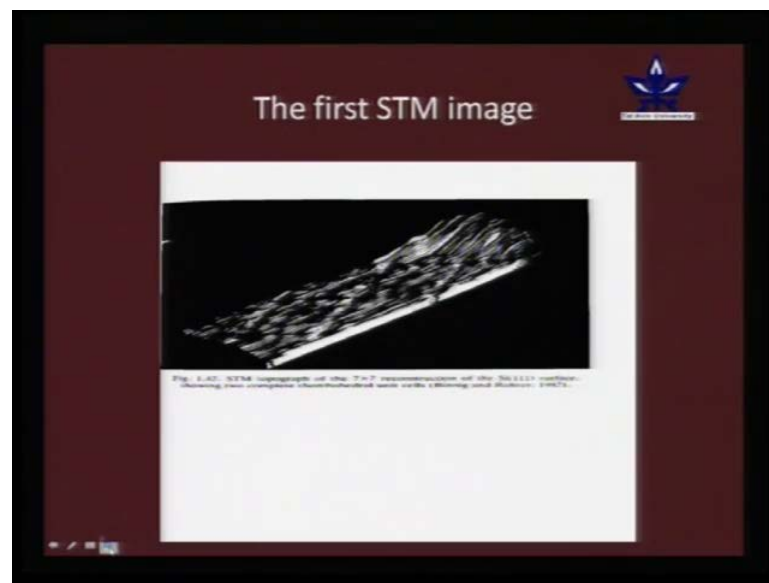
This is the protocol that you usually use when you try to map a surface, first the trace can be interpreted as a grid and then this converted into a contour map like this, and after that this you can try to get images of desired color or shape. So, once you scan through there is a procedure by which we can try to map the imaging therefore, this is coming out as a software we will not be looking at those details, so each of this scanning is started up with a software procedure, which will give you the pictures the way you desire.

There are some calculations that also can be made on every STM topography that we make, I will give you some idea about the applications of STM. Once you probe what is all that you can look for and from our own experience I would like to quote a few details, one of the main application of STM is actually in ultra high vacuum environment, where you try to control depositions in atomic level. I have already discussed this these slides in module 2, while discussing about molecular beam epitaxy, but today I am going to show some of those results again, but will tell you how to map those depositions. So, the first application is on surface coverage and another popular area, where STM is playing important role is in nanolithography, and also we can look at interface effects, so we will go by some of the applications of this technique.

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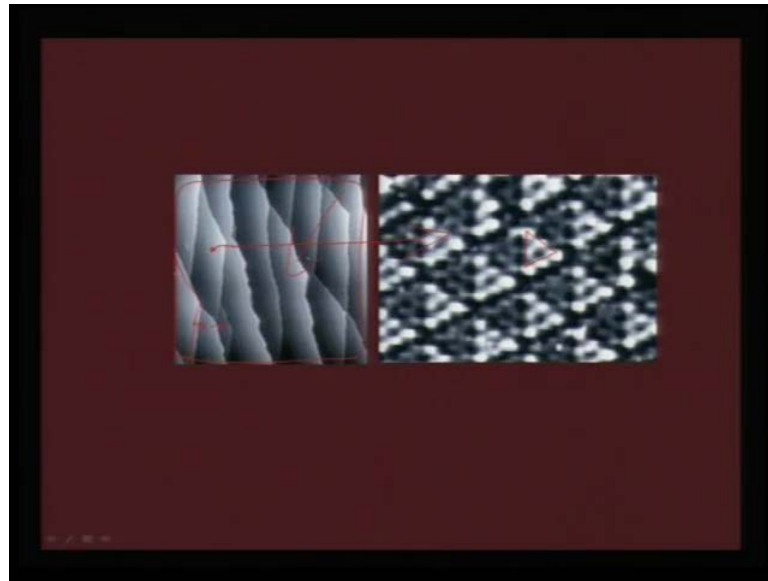


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This is the first STM image that was mapped by the Nobel Laureates or the pioneers Binnig and Rohrer, they actually try to scan the silicon 1 1 1 surface and this is a gray scale image which shows that they could find a 7 by 7 reconstruction of a silicon 1 1 surface later with the lot of improvements.

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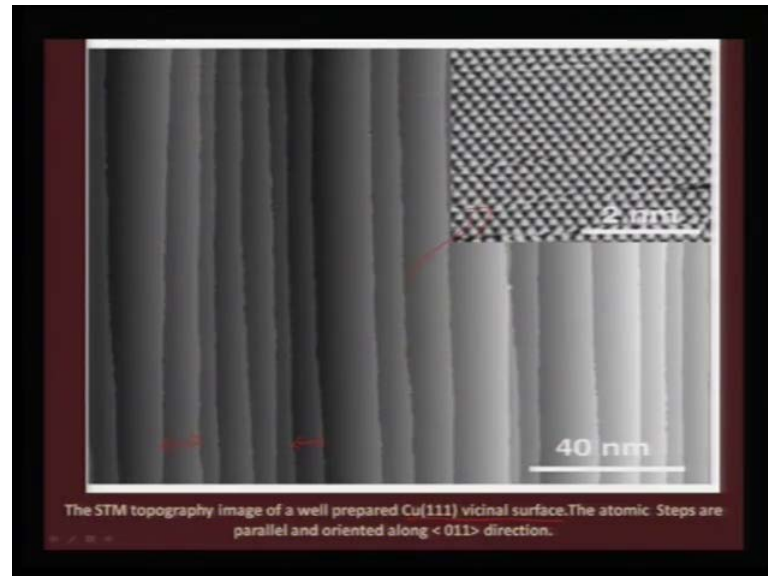
You can see a much better topography of the same surface, what do you see here is nothing but the step edges of a silicon 1 1 1 it is cut like this, typically when you take a STM picture you will get this sort of contour. And what you see here this is one edge, and just below that in one nanometer scale you would see another step edge, and below that is another step edge. So, each one is a step and if you suppose go to a small point, and then try to look at the atomic level resolution, this is what you would observe.

So, what you are observing is in a very small area of this terrace, you can go to very higher spatial resolution, where you can see a typical 7 cross 7 reconstruction of silicon in 1 1 1 surface. So, this bright spots are nothing but this 7 cross 7 reconstruction that that you are saying, so what in essence you can see is not only a macroscopic image of your crystal. You can also go down to a spatial resolution, where you can see atom by atom the periodicity, and if you if you see any of this reconstructions disorder.

So, you can look at the defect ordering in those structures. Not only that, if we try to deposit something on this surface, then it is possible for you to understand how the deposited material is growing. So, you can look at the coverage, so this is a clean surface of the silicon, so when you deposit some material then you can map, how to understand the growth mode and how much layer thickness of the deposited material is grown on the surface. So, all this can be verified with the in situ to STM probing, sometimes it is possible to deposit some material and retract the deposition gun, and then immediately

bring the STM probe and look at the coverage, sometimes it can be taken in situ to another chamber where you can do the coverage calculation.

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This is one of the viewgraph which I have already shown in module 2, but just to reinforce what information that we can get out of STM, I am showing this copper 1 1 1 vicinal surface. This is a very important protocol that one has to follow, when we specially try to make new materials, this is a very clean surface of copper 1 1 1 with the step heights. If it is a vicinal copper 1 1 1 surface, you would actually see the breadth of the terraces are of this dimension, roughly of the order of 10 to 15 nanometers.

So, with this sort of vicinal surfaces, you are almost forcing different growth mode for different materials, that is the reason why we go for copper 1 1 1 the same materials. Suppose, I want to grow iron film on copper 1 1 1 the terrace, and the morphology of your copper 1 1 1 surface will initiate a very different growth process compared to copper 1 0 0 growth process.

So, if you want to understand atom in atomic scale how this growth process proceeds then you need a very good understanding of the STM, so STM place a very important role therefore, to dictate the growth mode. And what you see here in the inset is nothing but the atomic resolution of this copper 1 1 1 surface, as you can see here typically this is 5 cross 5 nanometer image and you almost see no defects in atomic resolution.

Therefore, this surface is quite good, and we can proceed with depositing any sort of a film on this surface, that is the message that you take from this viewgraph.

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And what can I do with this from the cartoon that we saw in the earlier slide, we can use the same information and then try to calibrate how the iron is growing on this copper 1 1 1 surface. As, you see here this is iron on copper grown using a thermal deposition, and when you put some iron atoms, there is a step decoration that is happening only at the edge of this traces, iron atoms are going and sitting. Therefore, those who are interested in the magnetism of this iron films it becomes a very, very important information, because you are almost successfully making a one dimensional iron stripes.

So, in this you can see what is the nature of the magnetism there, but from STM point of view I do not want to discuss the magnetic information, but you see here it is a line that can be drawn on this topography, which is post analysis. You do not usually do this when you are scanning the STM, you can save this frame and on this frame, you can actually draw a line here like this and that is what you see here this is a line drawn, and this line scan is what is given here in the inset.

So, what do you see here is this is the line, that is drawn and on this line you can see, sorry this is the line, that is drawn here, and what you see here is some troughs and these troughs mean between two iron islands there is a break, which means the iron atoms are not actually fused together there is a discontinuity. So, I cannot call this as a iron stripe,

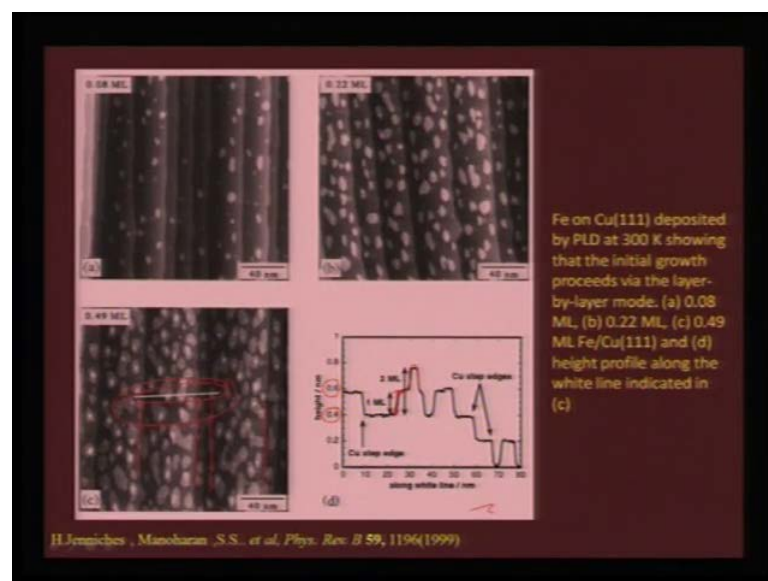
but it is a one dimensional wire, but with discontinuity, so if I keep on depositing then this sort of troughs will be missing.

So, then I can say it is a one dimensional wire, but now it is simply remaining as a one dimensional stripe, but it can become a one dimensional wire, and as you would see here the length of these wires can be as long as 1000 angstrom or 2000 angstrom depending on the continuity of the stripes. Now, what other information that you can get here, when you draw the line you can see some sort of white spots there and these white spots clearly say, that on the first ion layer. There is a second ion atom going and sitting on the top, and that can say whether it is truly a one dimensional wire or it is a one dimensional wire with a double layer of ion.

So, this mapping cannot do any otherwise other than with STM therefore, it is important for us to do a line scan, in this case now if you improve little bit more on the thickness then you can see that this is only a continuous layer second layer from growing. So, all this information, that you can get out of a line scan from a post calibration that you can do while saving these images.

Now, the same example we can take, but we can try to deposit the ion layers instead of using a thermal deposition technique, where you get this sort of one dimensional stripes we can use a different deposition technique called PLD that is Pulsed Laser Deposition.

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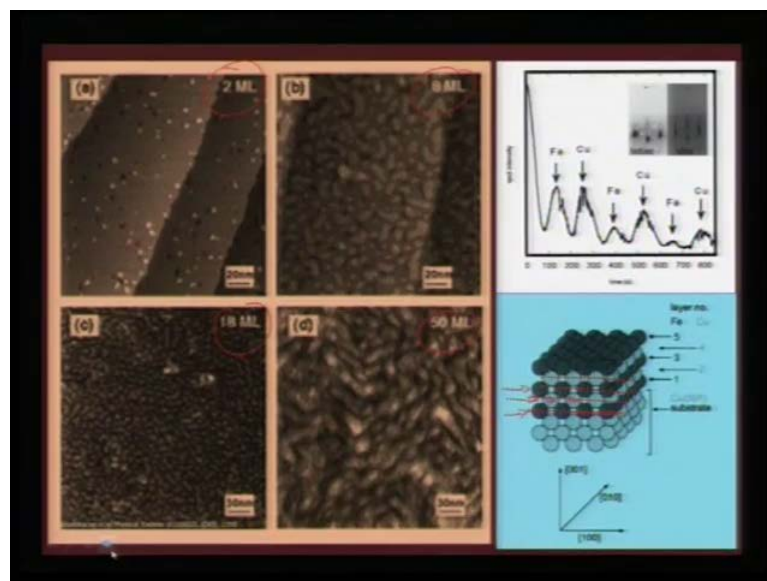


And if you try to deposit ion atoms then this is the picture that you get, and STM clearly shows that the way the ion atoms are deposited is entirely different from the previous slide that we saw. So, the growth mode depends on the growth technique that you follow, from thermal if you go to a more dynamic deposition technique, which carries your ion atoms with extra kinetic energy.

Then the growth morphology changes and here is another line scan for such a ion grown film on copper 1 1 1, where you can see if I draw a line scan across 2 3 steps. This is one step and this is one step and then there is a small step there and then comes another step, so I am drawing a line scan across 4 steps, then you can see here the step edges are marked by this.

So, this might on the whole may look as though it is a inhomogeneous surface, but it is a homogeneous surface, but you can get lot of information about this, so as you go through this you can find out this is your step edge and then whatever that it is happening here. This shift corresponds to one monolayer because that variation is from 0.4 to 0.6 nanometer, which means only one atomic layer is growing, but there is also another small hump there which corresponds to one more monolayer over one of the ion I length the second layer is also trying to grow.

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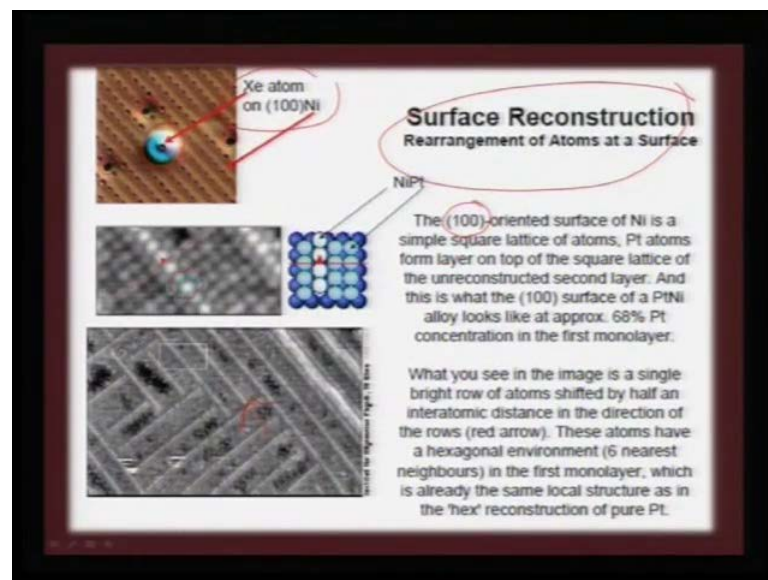
So, this information you can get out of a line scan for ion film, that is grown using pulsed laser deposition this is another example, which I have briefly mentioned in module 2,

which I want to revisit. Suppose, I want to make a artificial alloy where I am going to put one layer of iron one layer of copper one layer of iron, alternatively and keep on growing a artificial alloy because iron and copper are immiscible alloys.

Then I can easily map whether such a alloy can be formed, because the first layer what I what I have deposited here as a ion can be seen here. These small dark spots are those first layers, which is fully covered by the second layer that is copper. And this gray scale is nothing but the second layer. So, in the initial growth mode we can try to map, whether it is a continuous growth or whether it is a column growth.

So, if it is a two dimensional growth then it is easy for us to map, so as we are trying to deposit such Bilayers of iron and copper you can see from 2 monolayers to 8 monolayers or 18 to 50 monolayers. We can keep on stopping at every region and try to see whether you are able to grow such flat atomic layers to build up a equiatomic iron copper alloy composition. So, that way STM becomes very useful in terms of coverage calculations, we can also try to deposit a variety of other stuff and try to see in atomic resolution whether a periodic ordering is there.

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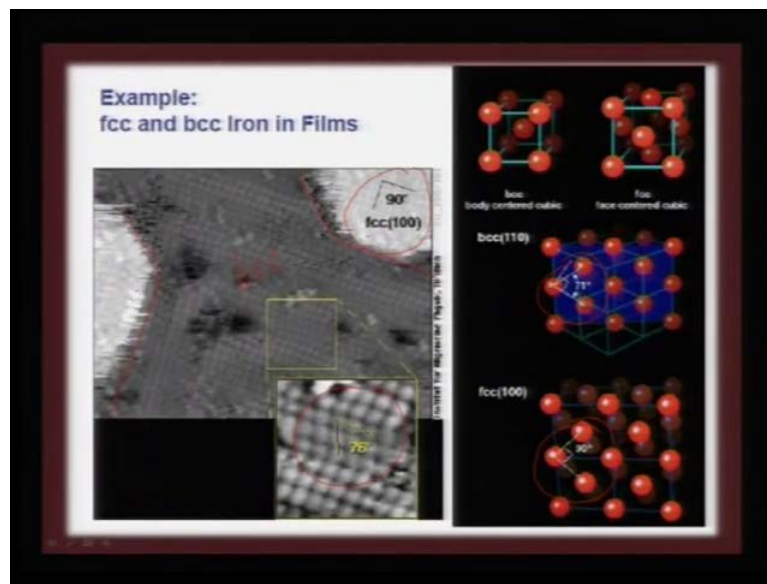


This is a surface reconstruction of nickel platinum alloy on nickel 1 0 0 surface and as you know this is a FCC lattice, and you can easily map whether this is a iron platinum sorry, nickel platinum which is growing epitaxially on nickel 1 0 0 surface. As, you could clearly see such ordered nickel platinum alloy can be made in a nickel surface, it is



also possible to map some absorbed atoms on nickel, this is a one of a good picture which shows how xenon can be absorbed to nickel 1 0 0 atom at very low temperatures. It is very difficult to deposit xenon, but xenon when it is when the substrate is cooled at very low temperature, it is possible to trap xenon atoms. So, this sort of mapping can also be done, and you can also see that on nickel 1 0 0 surface there are some defects which can also be tracked.

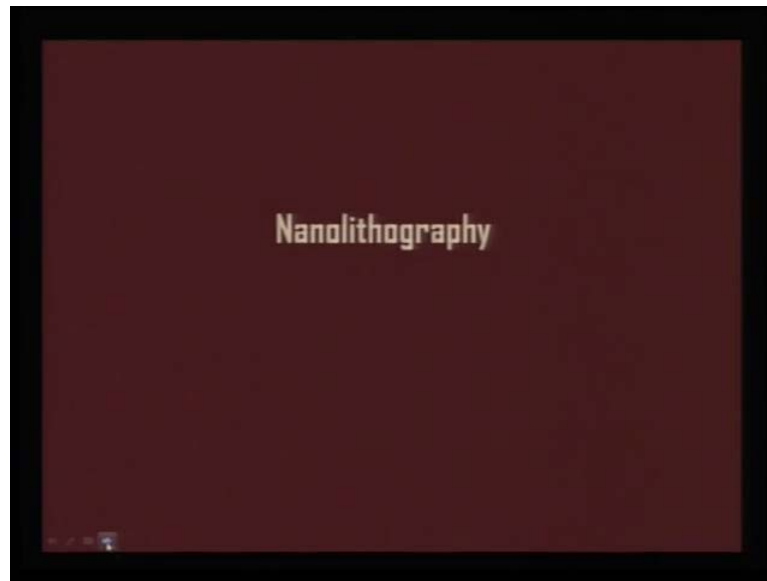
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When you look at phase transformations between iron and iron BCC and iron FCC as you know BCC iron is magnetic FCC iron is non magnetic, when you are trying to map the iron films you can easily find out whether there is a transformation from FCC to BCC. As, you would see here the angle for this BCC atoms is 71 degrees whereas, for FCC it is a 90 degree stripe and therefore, if you map this region and this region in atomic scale, you can find out this patched region whatever you see here is totally a BCC iron compare to FCC iron.

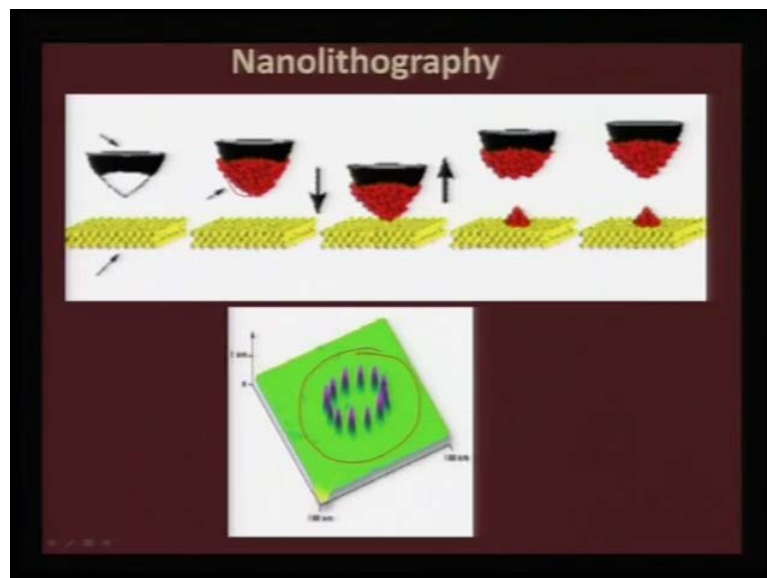
So, when you grow such very thin layers it is possible not only from phase contrast, but you can easily pick out from this lattice arrangements and pinpoint, which are the regions which have converted from FCC to BCC.

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So, such conversions can be easily mapped using this resolution nanolithography most of the time this view slides are shown.

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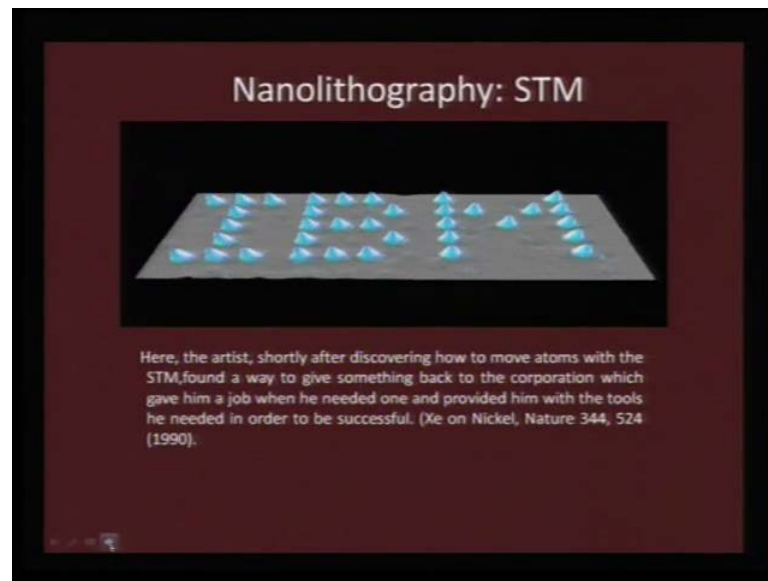


As an example, where you can actually try to decorate any surface the way you want therefore, this is one of a very useful technology by which lithography can be engineered. As, you see here in a surface you can bring your STM tip you can actually capture some material and then you can go and with forward or reverse bias, you can try

to dump that material on to a surface that you are desiring, by this way you can actually grow a corral or a decoration on a particular surface.

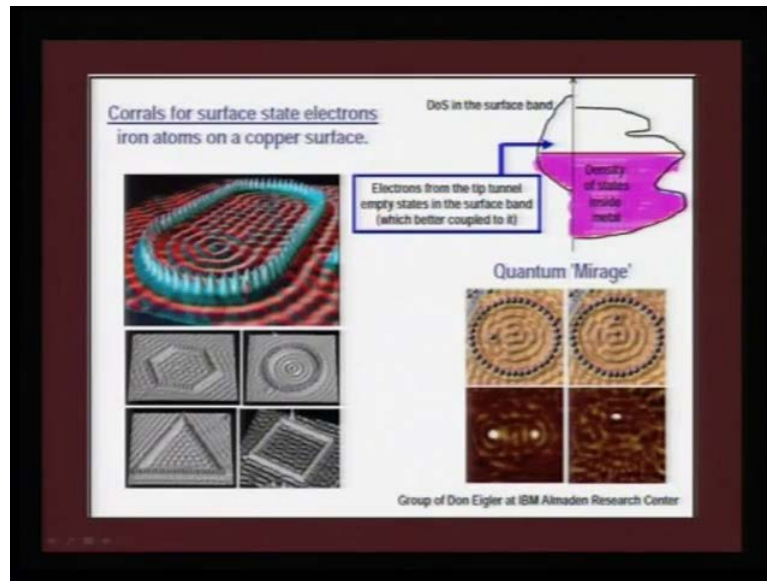
So, this is possible because you can actually takes some add atoms on to the STM tip, and then by way of applying the voltage you can dump those sticking atoms to the surface.

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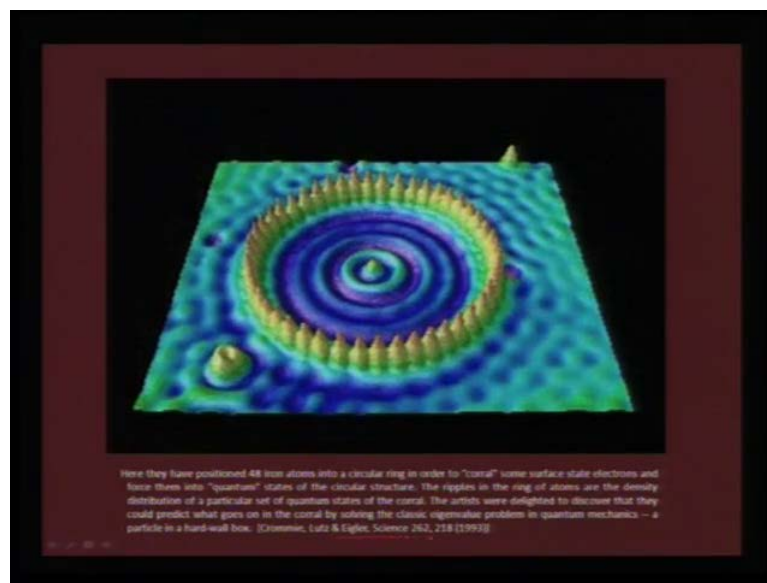


And such techniques are useful to make any sort of device applications and this is one of the example, where a guy who was hired by I b m was successful to capture xenon on nickel. So, this blue dots are nothing but xenon which he would just pick up from the STM tip and go and exactly decorate a IBM later on nickel surface, so this can play a very crucial role that way in doing nanolithography. And this is one of the most popular cartoon, which is shown in almost all the STM lectures here is one corrals surface, which shows how iron atoms can be grown on copper and each one is a iron island, which can be properly placed using a STM tip.

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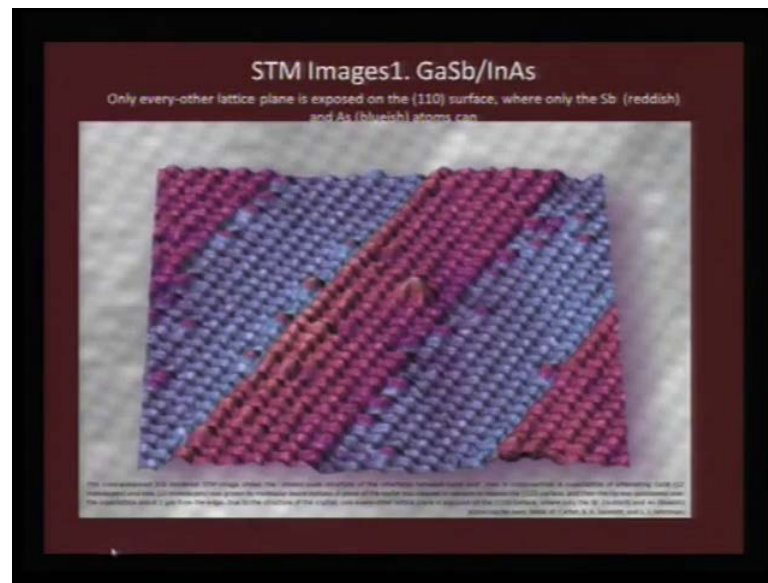


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So, several such things can be done this is a 48 iron atom corral, which is dumped on a copper surface and this is again done by the same group.

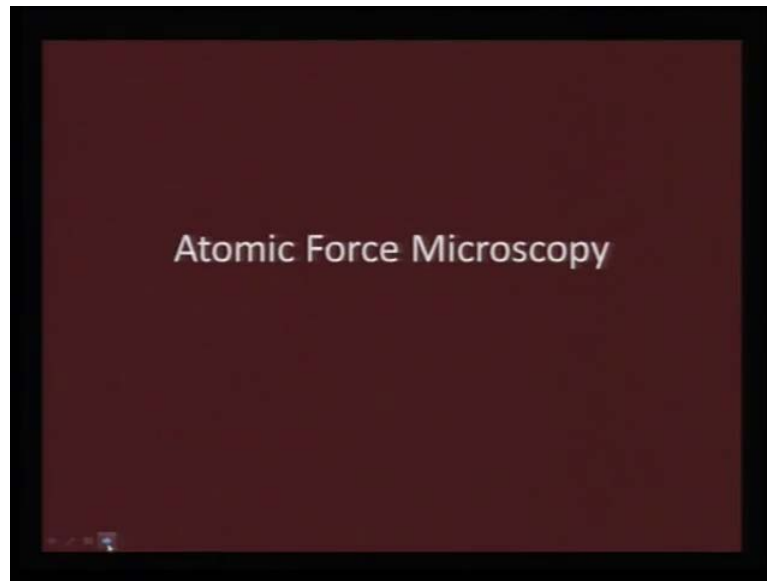
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So, several things can happen, we can also try to map how the interfaces are ordered in a situation, where you are growing two different materials. For example, you take a gallium antimonite and indium arsenide and when you are growing a multilayer, you can get a STM image of this contrast. What you are seen here is gallium antimonite, which is twelve monolayer stuff and this is packed between or sandwich between 14 monolayer indium arsenide. As, you can see here the repeat is 1 2 3 4 5 6 7, which corresponds to actually 14 monolayers of indium arsenide and 6 such maxima's are there corresponding to 12 gallium antimony layers.

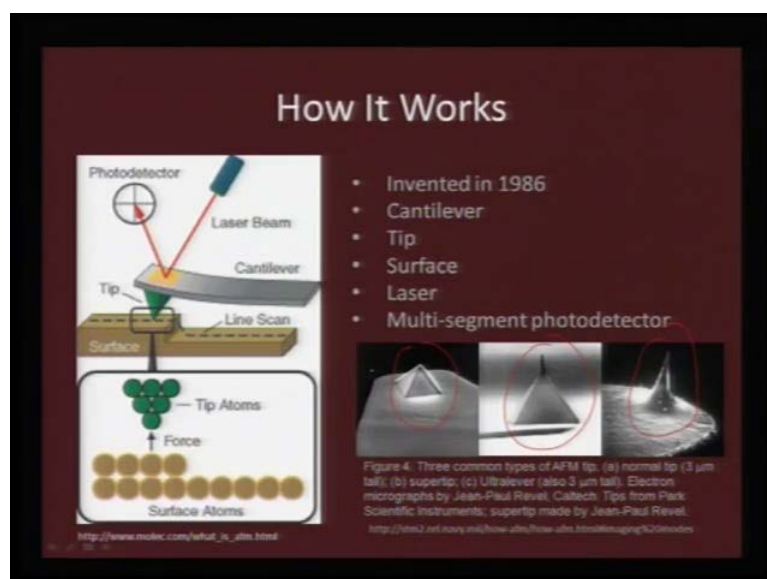
So, you can essentially map, how this interfaces are growing and you can see each one is a repeat, so you try to first grow gallium arsenide, then indium as a gallium antimonite indium arsenide and so on. And one can also find out sharp these interfaces are because you can see in some cases the antimony is actually coming out into the indium arsenide layers. So, specially in semiconductor physics this inter diffusion of antimony or arsenide is very, very detrimental therefore, STM can map and tell you whether you are growing sharp interfaces or not.

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So, this is very vital and in this case what is actually seen is not the gallium and indium ions it is just the arsenide and antimony layers that you can see here. Now, when we have a problem trying to study a non conducting materials, what we do in that case a another technique which comes handy is a FM. Now, a FM is there more than STM because most of the labs can offered a FM, main reason you do not need a ultra high vacuum condition. And second you can actually keep it in a very small place, it does not comment that much of attention as the STM, so atomic force microscopy was developed 2 or 3 years later after the STM was discovered.

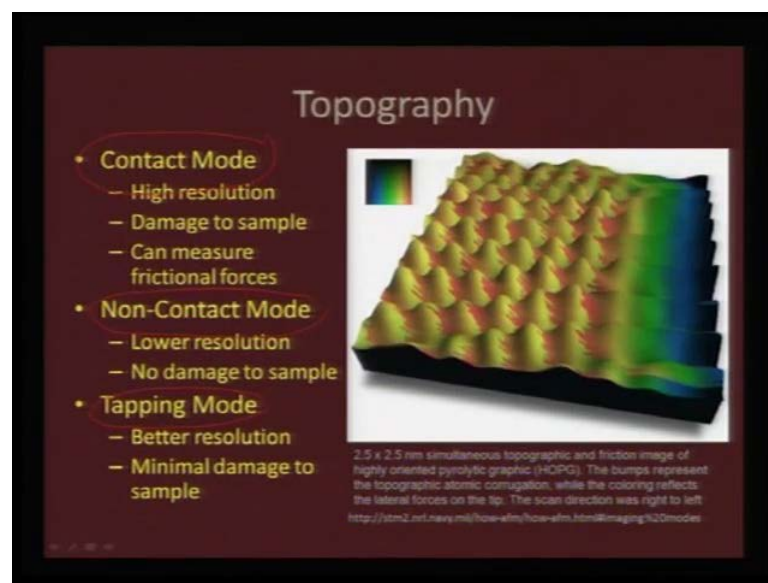
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Now, here the principle is very simple where you are trying to use a cantilever, where which houses a tip and this tip actually is scanned across the surface, and if there is any ups or downs in the surface. Then the deflection in the cantilever is photo detected using a laser beam, a laser beam is actually following on the cantilever and any deflection that is actually seen, and this can actually be traced as a topography.

Therefore, the same information that you get from STM you can also get out of a FM, only thing here we do not look at the tunneling probability, there is no tunneling here. It is just a simple micro tip, which is actually scanning across a surface and the way the topography is contoured here is based on a laser beam deflection, which is monitored by a photodetector. So, this is the principle. So, this gives a luxury for most of the experimental people to study their materials, and specially if they want to look at the atomic scale resolution. There are several things that we can talk about the way the S A F M tips, that are made also is equally important and it is a challenging task as that of STM.

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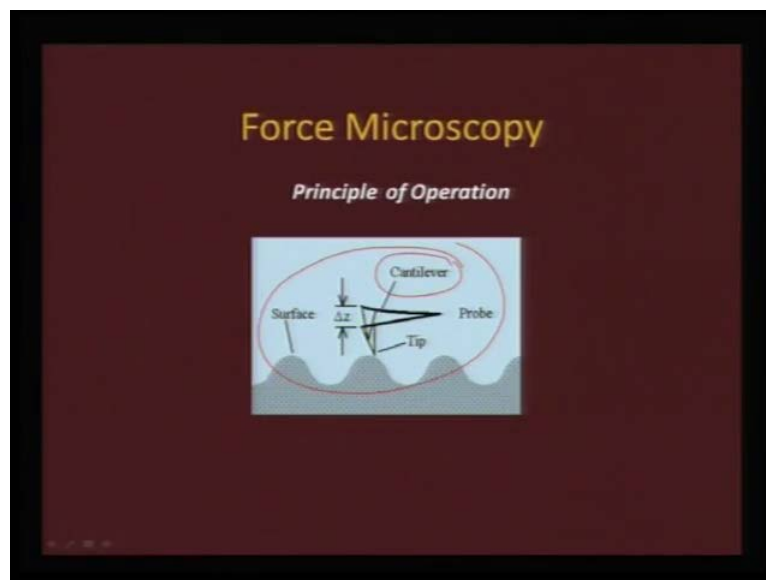


This is typically a contour that you can generate out of a FM microscope, what you see here is a pyrolytic graphite structure, and this tip actually scans through and there are different ways that you can scan this topography. One is using a constant mode or a sorry contact mode, another one is a non contact mode or the other one is a tapping mode.

Usually, the tapping mode is preferred or which was the first generation AFM, which actually keeps tapping and mapping the atomic arrangement.

One problem with the contact mode is that, it although it has a high resolution it will destroy or damage the sample, non contact mode gives a luxury of not corrupting your sample, but then suffers from resolution. And tapping mode is better resolution, but with minimum damage, but during tapping mode or contact mode you can also get many other information's, which is actually based on frictions. So, when you have a tip and then you scan through it will actually drag through the atomic periodicity, but because of the frictional exercise, you can actually bring about more information's on the atomic arrangement.

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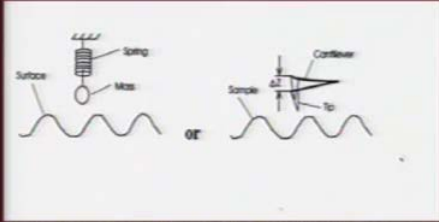
So, we will see that example later the principle of operation, as I have told you is based on a cantilever. So, this can be used for atomic level imaging, and then this is the basic principle of your force microscopy, we can actually detect the forces between a mass attached to a spring that feels some force, when it is brought very close to the surface, ideally the mass would not damage the surface. And the sensor that responds to a force and a detector that measures it.



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### Force Microscopy

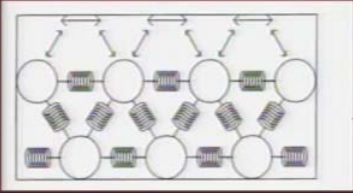
- *Basic Principle of Operation: detecting forces between a mass attached to a spring (cantilever), that feels some force when it is brought very close to the surface. Ideally the mass (tip) would not damage the surface.*



- *Sensor that responds to a force and a detector that measures it.*

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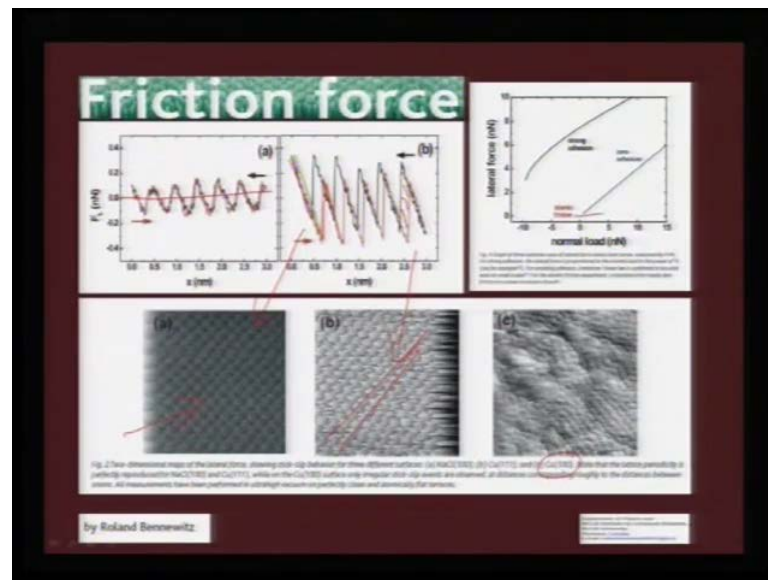
### Force Microscopy



- *Frequency of atoms vibration,  $\omega$ , at room temperature  $\sim 10^{15}$  Hz*
- *The mass,  $m$ , of an atom  $\sim 10^{-30}$  kg*
- $\Rightarrow$  *The effective spring constant,  $k$ , between atoms is*  
$$k = \omega^2 m \approx 1 \text{ N/m}$$

In this force microscopy the numbers that we need to understand is to do with the force constant, so the frequency of the atoms vibration is roughly of the order of 10 power 15 hertz and the mass of an atom is of this therefore, your spring constant is roughly of 1 Newton per meter.

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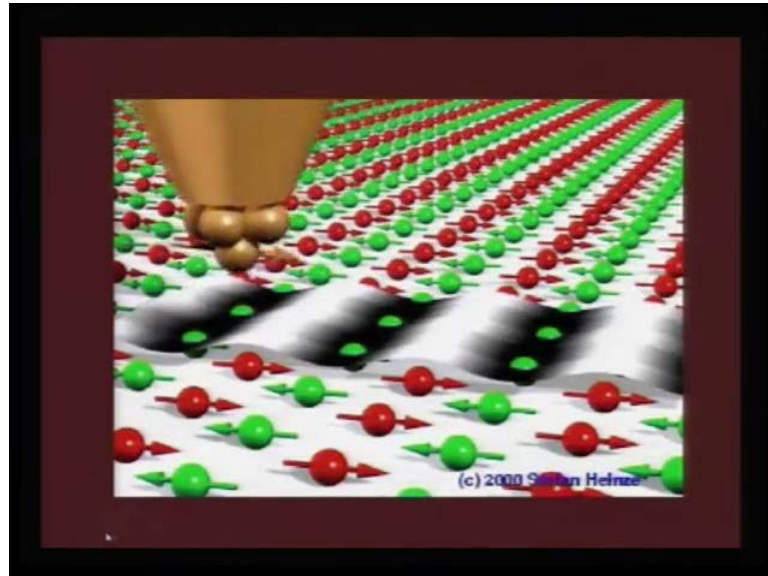
We also can extend the same AFM principle to understand, how the lattice arrangements are places, and this is an improvised technique of your atomic force microscope, which is called friction microscope. If you scan through a sodium chlorite lattice, you can actually see the kinetic friction is actually averaged out therefore, it is 0, but once you place a load on your cantilever. Then you can see that, when it is actually placed on a on the top of the atom, then it will actually take a frictional force until it is moved to the other atom which will come out as a jump.

So, either you scan it from left to right or right to left, you will actually almost generate a hysteresis and this is the principle of the frictional force microscopy, that you use to contour how the atomic arrangements are placed. For example, if you take the sodium chlorite you can see that the atomic ordering is periodic and therefore, you get a image out of this using a frictional force microscopy. And for a copper 1 1 1 again you see a similar periodicity, but whereas, if you go for copper 1 0 0 you see a irregular lattice spacing.

So, that clearly represents what sort of atomic agreement that you can sense lastly, I just want to cover with one animation, this is a another improved SPM probe, which is called as spin polarized scanning tunneling microscopy where the tip you can see has a magnetic tip. It is not just a metal, but it is a magnetic tip and this will keep sending the conduction electrons to the surface, and the surface here is nothing but a manganese anti-

ferromagnetic surface, where every other manganese atom is antiferromagnetically rearranged.

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So, the way the conduction electrons goes from the magnetic tip to the atomic periodicity is different, so as a result if it scans layer by layer or every atomic arrangement. Then bit will easily map the regions which are ferromagnetically arranged to the magnetic tip, and antiferromagnetically aligned to the magnetic tip. As, a result you will get a topography, similar to this the brighter areas represent the ferromagnetic alignment with respect to the tip, and the darker areas will actually represent the antiferromagnetically aligned reason. So, if you have a magnetic tip then it is possible to you to map a antiferromagnetic image and this is how it will proceed finally, you will get a topography, like this which will give you a dark and white pattern which will clearly say that your surface is a antiferromagnetic surface.

So, this much information you can get and just to sum up I want to say that there are different phases of scanning probe microscopy, one we looked at the STM, another one we looked at the at AFM and then we looked at a frictional force microscopy. And there are lot more coming in the form of magnetic force microscopy popularly known as A M F M, we can study spin polarizing tunneling also. So, any sort of images can be made I have particularly avoided showing some classic examples, where you can even probe

biological samples, but for our course this is important to understand that any sort of inorganic materials can be mapped using STM.

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