Chemistry and Physics of Surfaces and Interfaces
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Lecture - 05
Hexagonal Lattice and Miller Bravais Indices

Hello everyone, welcome to lecture number 5 and in this lecture what we are going to look at a few more examples of reconstruction.

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Namely some complex reconstruction so this is of course much more time consuming to understand it clearly, but I would like to show you a few examples how complex the reconstruction can be on surfaces, then we will familiarize today hexagonal lattice, and in the hexagonal lattice the surfaces are represented by something called Miller Bravais indices and not just with Miller indices. And of course, you can also represent it with Miller indices, but Miller Bravais lattice is a more common practice, and we will also finally conclude with the two-dimensional Bravais lattice. Because that is what is very important for us as you have seen in the three-dimensional Bravais lattice, we had fourteen different group and then here we are going to just have like five indeed.

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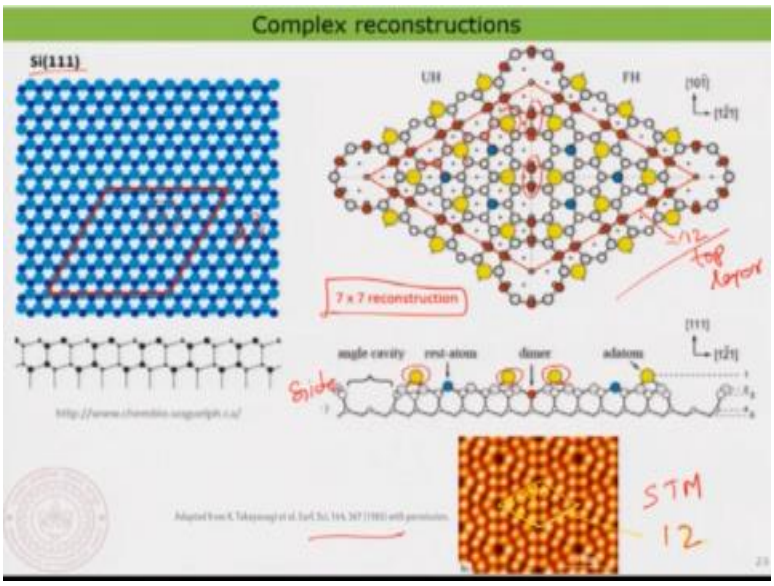

So, let us have a look at the silicon 111 surface. So, this is again a type of bulk crystal and this what you are seeing is actually the idealized silicon 111 surface or what you would expect to see basically. So, the light blue atoms are the one on the top layer and the one with the dark blue is basically the one just in the second layer, so that makes it although it looks like a hexagon, the symmetry of the surface is three-fold and not sixfold as in the fcc 111 surface. Now that is the key but this is what is expected but the interesting thing is, when you look at the surface in reality, this is what you actually just end up this you have like an extremely complex reconstruction on the surface. Well, It is hard to first understand but let me try out to make you understand this. So, what you have to follow is this red line here that is actually the unit cell which is being converted finally to the reconstruction. And that is why finally it is known as a 7 by 7 reconstruction, because the periodicity after the reconstruction is basically seven times of the original unit lattice vector of the silicon 111 surface in an ideal case. Now what you notice here is that particularly in the side view what you realize is that there are these yellow atoms which are actually known as the adatoms or adatom in this case it is actually said because it is not looking like kind of an atom which is absorbed on the surface. But ideally this is nothing but the silicon atom, this is actually in the topmost layer, but look here in this case the ideal case the number of top layer atoms was actually about 43. You can basically count it including the one in the corner and at the edge it is about 43 atoms, and now after the reconstruction the number of atoms on the top layer is actually now reduced to just 12 on the top layer, this is quite interesting.

Now, you understand the philosophy behind the reconstruction of the surface that the surface actually reconstructed in a way that the total number of surface atom is actually reduced almost by you can see about one fourth of the original. So, this is quite striking that finally the number of surface atoms are actually reduced and the advantage now if you look at the second layer which is basically represented by this light color and those ones you can see they all get more coordinations now. You can see all of them are getting much more coordination that you would have actually expected in the normal case, so that is the whole point here. And at the same time the spacing between the atoms are also changing compared to the ideal case. Then you also see something called as dimers which are actually particular atoms that are also seen in between. So, that at the end of the day what you are seeing here is actually the surface is reorganized in such a way that the top layer atom number is reduced. And every other atom which is below in the second layer is actually getting a higher coordination. So, that is the philosophy basically that effectively the total surface area or surface energy is basically reduced in this case compared to the silicon, so this is known as a silicon 7 by 7 reconstruction and it took about 20 years for the surface science to completely solve this or it was a long unsolvable problem for about 20 to 25 years. And then with the discovery of scanning tunneling microscope people solved it will come to that story a little later. Now if you look at the scanning tunneling micrograph that means topography, you see basically again this oblique here, this is exactly the same as the one which is represented here in red. So, I am just going to use a different color here just, so that you can visualize it better. And now if you count all the bright atoms inside you can see here that there are 12 bright atoms that are inside the cell. So, that is again 12 atoms and the 12 atom is exactly what we have just said in this case that is the top layer atom. So, what you are seeing in the STM image is 12 surface atoms and the unit cell you can see it looks very different compared to what you would have expected for the ideal case, so this is an extremely complex reconstruction. So, the reconstruction can be as complex as this one that is what I wanted to show you. You can see more details in this reference.

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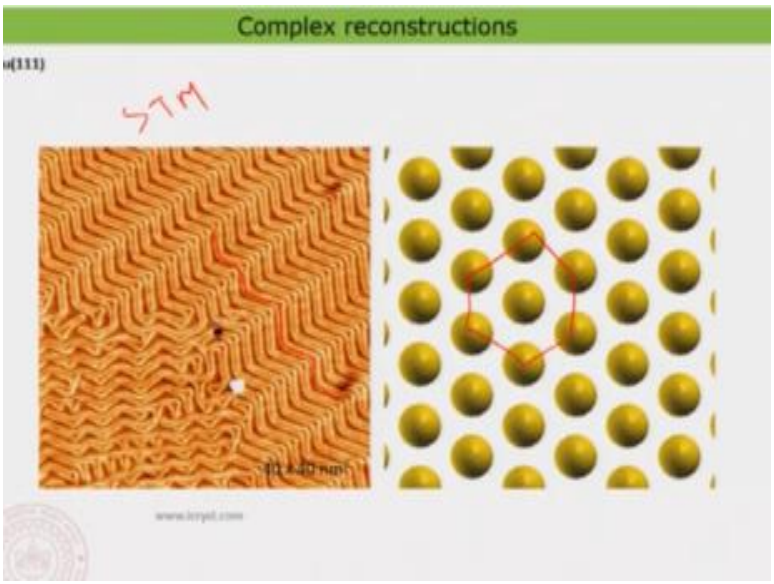

Now let me show you another example which is a gold 111 surface. This is the gold 111 surface you would have expected, a hexagon a perfect arrangement of the atoms, but that is not what you observe in reality. In STM image so this is again an STM image basically there you see that these are the surface atoms that they actually just form some kind of a herring boundary construction. So, this is known as a herring boundary reconstruction.

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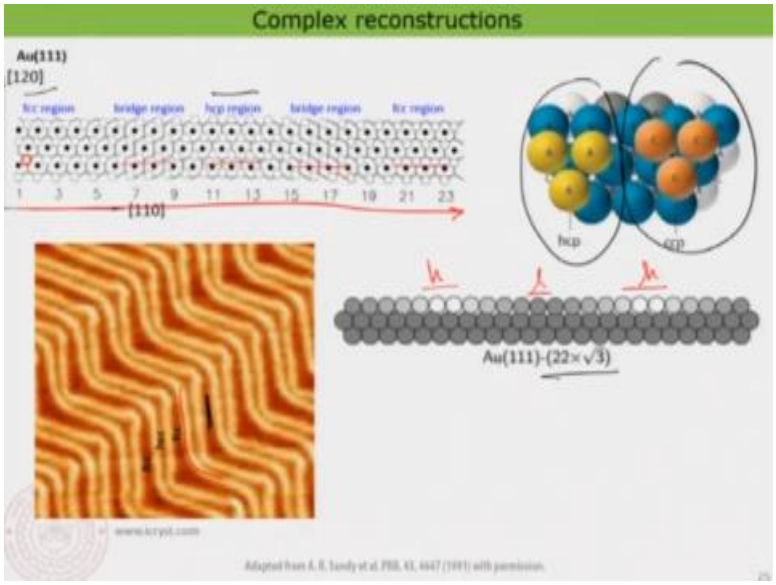

So, what is going on inside is quite interesting that the reconstruction go over a very very large number of atoms of about 23 times of the original unit cell. And during this journey you can see the original atoms are actually getting displaced at the position it comes to something called an fcc region, then it go through an a bridge region again, an hcp region then a bridge region and

finally again to fcc region. What causes, this one causes basically kind of ripple on the surface. That means some of the atoms are slightly higher and some of the atoms are lower than again higher and so on. You can see these region which is represented are high they are actually high in the topography, and then these region are basically low in topography, that actually makes the corrugations looks like up and down and this is exactly what you are seeing in the STM image, that some regions are appearing brighter and some region are actually just appearing darker. We can represent the darker region with the black color. So, this is actually appearing as darker region and these regions are appearing as red. So, this is basically due to the fact that the atoms are actually corrugating on the surface. But now you see the reconstruction is actually about 22 times root 3. It is very very large reconstruction that means the surface atoms are not just reorganizing just with its neighbor but it is actually reorganizing together with about 23 atoms along a unit lattice direction. This is extremely complex and this I have actually just brought to here is just to show you the different type of regions which I have used here called the hexagonal close packing region and the face centered close packing region where the packing is basically in like an ab ab type and in the ccp it is basically an abc abc type. And that is what the fcc region and the hcp region basically meaning. Just keep a look you can try to look that in in greater detail. So, just for your understanding the circles are actually representing the top atom and the dots are representing the atoms below. And the hexagon is basically to just guide you through the symmetry of the surface.

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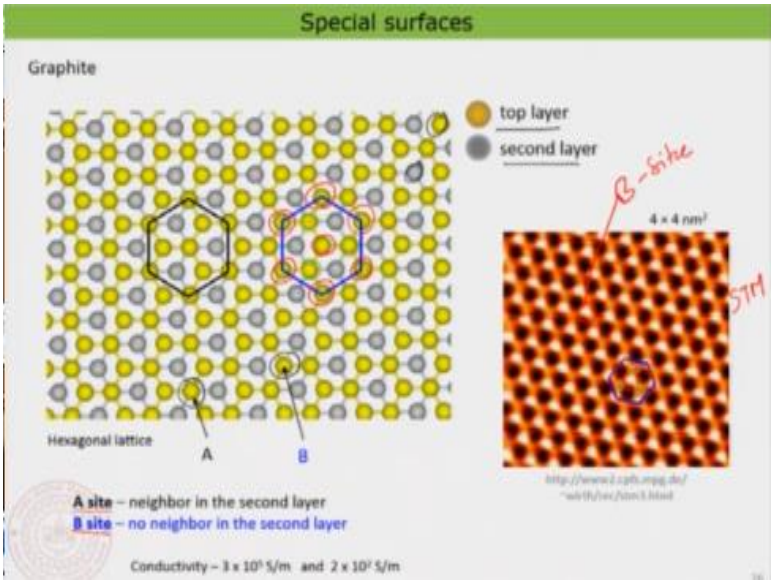

Now let us have a look at some special surfaces, the graphite surface because we are also going to look at a few examples later where you will be using graphite. Graphite is also nowadays quite interesting after the discovery of graphene, because graphene is nothing but just a single layer of graphite. Graphite comes under this hexagonal Bravais lattice. Here the yellow atoms are actually the top layer and the gray atoms are actually the second layer. So, what you are seeing here in this image is the arrangement of the atoms. So, the atoms are basically arranging in a hexagonal manner and they form one the top layer and the bottom layer are slightly just shifted with respect to each other, that is making the two different type of atoms on the graphite layer. One is known as a B site and another one is known as an A site. What is an A site? A site is actually having the carbon atom with a neighbor in the second layer and B site is the one which is having no neighbor in the second layer. That is basically the A and the B site, now if you look at the STM topograph, so that is again the micrograph with which you can actually just get the atomic resolution where the bright so you can see basically that the whole thing is going like a hexagonal lattice. The bright lines if you connect you can see I can form a hexagon with something in the middle. Now when you look at the graphite itself, it is not very clear why we should see basically like a hexagonal lattice in this. Because you can see like much more atoms or it is more like a honeycomb type of pattern rather you see in this case what is the reason for that? Now if I would connect basically the A type atoms together and the B types atoms together then you would find that well I can actually just draw two hexagons easily on the surface. Now the interesting thing is that in the STM topograph what we are seeing or the bright dots are only the B site atoms. The atoms at the B sites are the one we see in the STM topograph. That means these are the atoms that we are seeing. So, now you can see, I can see all these bright atoms. These are the bright atoms and the one in the middle is again the bright atom. That is why when you look at the hexagon I can see six bright dots and in the center also I can see another bright dot, but now the atoms which are actually these ones which are the B site atom. So, let me just represent it using a different colour. So, these are the B site, sorry the A site atoms they are appearing rather weak in the contrast here you can see. So, they appear in the contrast but they are rather weak compared to the atoms at the B sites. The reason is very simple the atoms in the B site having no neighbor in the second layer therefore they are much more visible in the STM than the one in the A site. So, that is the typical surface. And now what I would like to discuss

with you is how you would basically name the lattices or the planes on this kind of surfaces like hexagons for example hexagonal lattice. This is the unit cell.

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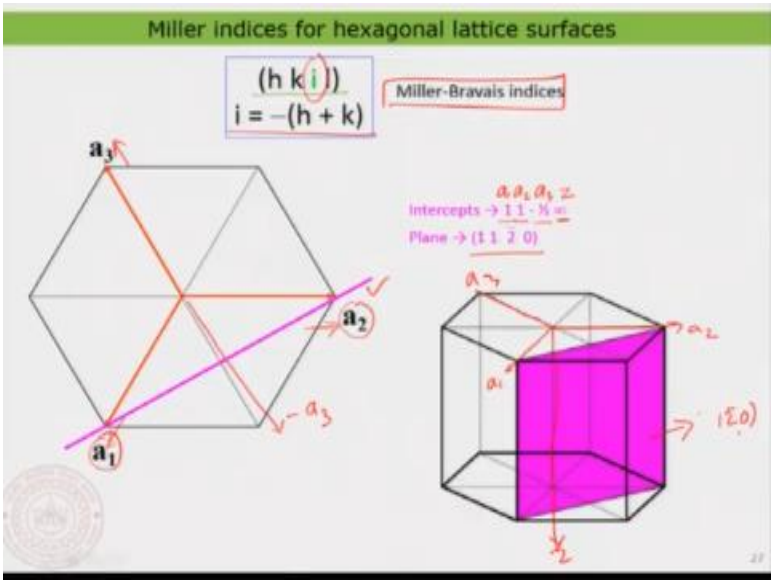

And now, let us do this for a hexagonal lattice. So, the difference of the representation of the hexagonal lattice compared to the one we have seen before is that here we use four indexes and not three like h k l we use an additional index namely i. And i should follow this particular rule which should be basically a minus of h plus k. So, this typical representation is known as Miller Bravais indices. And this is basically represented using four different indexes. Where are the four different indexes coming from? In the h k l, you were familiarized that the h k l coming from the x y and z directions. In this case it is not really. So, this is basically represented by a_1, a_2 and a_3. These are the three that is the h k and i and the l is basically representing the direction which is perpendicular to all these a_1, a_2 and a_3. That is how you can basically represent the entire unit cell of hexagon. Now if I would represent like this and if I want to basically just create a plane inside this. Now let us assume that I want to create a plane like this in the hexagonal lattice. Now what I all need to do is I need to look at the time at the intercepts of this plane along the different unit lattice direction. You can see along a_1, I have one intercept along a_2, I also have 1 intercept. But now the interesting thing is along a_3, this is the a_3 direction, but it is minus a_3 the negative direction of a_3, and you can see this is being cut two times. So, that means the intercept along a_3 is basically, so this is a_1, this is a_2, this is a_3, it is basically minus half and then along the other direction which is the z direction so there you can see the intercept is actually infinity. Now if

you take the reciprocal of that then I get the plane so you have 11 and this is actually represented as bar 2. Typically, when you want to represent negative in indexes so you would call it as bar and then 0. This is the plane so the particular plane that you are seeing it is actually 11bar 2 0. Now, let us visualize how this looks like in the hexagonal lattice this is the hexagonal lattice where you can see this is my a_1, this is a_2 and this is a_3 and this direction would be the z direction. And now you can see how the plane is represented in the hexagon and this is actually nothing, but the 11bar 2 0 plane. This is the way you basically index the surface.

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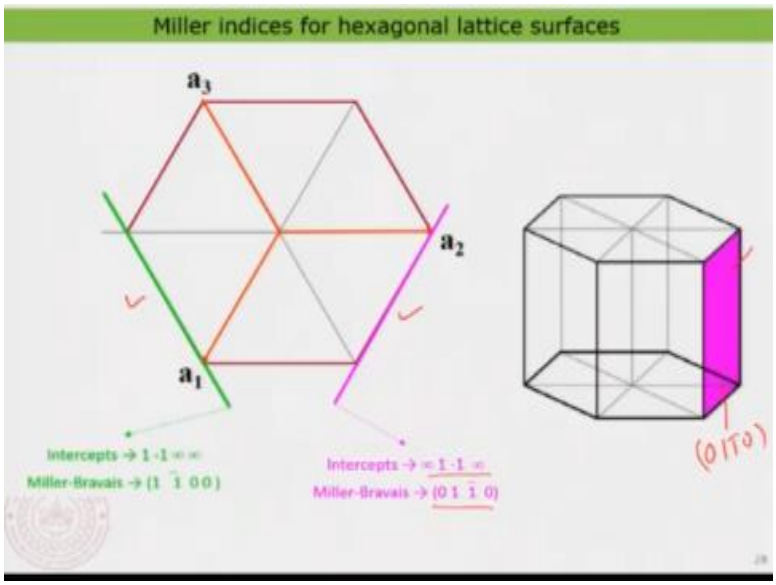

Now let us have a look at a couple of more examples. Like the Miller index again for a different hexagonal lattice. So, this is the two different planes that I would just like to represent. You can first of all look at the intercepts and from there you can calculate or understand or represent the Miller Bravais lattice. And this plane is nothing but 0 1 bar 1 0 and this one is actually 1 bar 1 0 0. The planes are actually the similar type, it is just facing the different sides of the hexagon and of course if you look in the crystallographic plane they are actually oriented in a different direction. Therefore, they have different name but once you create a plane out of that it is actually unimportant from which plane you have actually just cut. All the different type of planes that comes under the similar family is going to actually just give you out the same type of surface. Now, if you look at that surface so this is basically the surface and that surface is nothing, but 0 1 bar 1 0, you can actually create as many surfaces as you want, please do it as a

couple of exercises, you can try to understand and create different type of planes using the Miller Bravais lattice for the hexagonal lattice.

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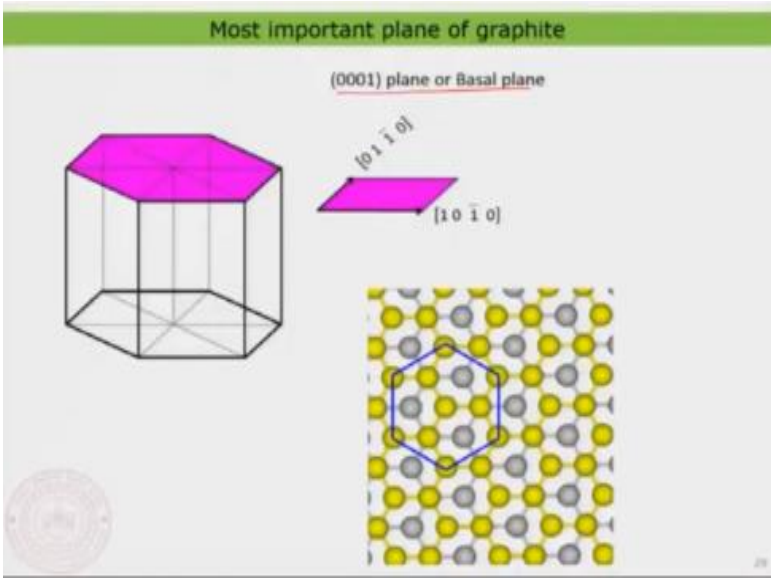

Now the most important plane in the hexagonal lattices are actually not the one we have seen. It is actually this particular plane where it is parallel to all the a_1, a_2 and a_3 and it only basically just intercept the z-axis and that particular plane is therefore known as the 0 0 0 1 plane or the Basal plane of graphite surface or even for other hexagonal type of surfaces this is known as a Basal plane. This is how the surface looks like and this is the lattice directions and this is typically what you would find in the case of the graphite that is also the reason why you can represent it like that. And now I can actually just cleave this surface along the basal plane that is very commonly observed in hexagonal lattices. For example, graphite if you take and you cleave a couple of layers out of the graphite you can basically just generate graphene for example. So, that graphene is actually coming along the basal plane or one of the basal plane is the graphene itself. Therefore, the basal planes are actually very important in the case of graphite.

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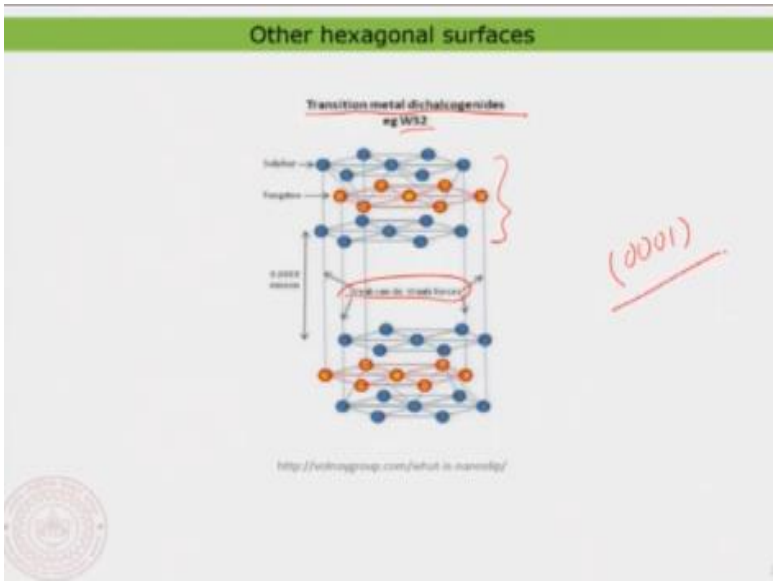

Now there are also couple of other examples about hexagonal lattice. For example, the most famous ones are the metal dichalcogenide tungsten disulfide as an example. There also you can see the whole thing is actually just looking like a hexagon where the adjacent layers are basically just displaced by a given atom and that looks like exactly what we have seen in the case of graphene. But now the interesting thing when it come to the graphite and also the tungsten disulfide, the adjacent layers are basically like interacting through a very very weak interaction namely the Van Der Waals forces, the layers are actually hold together by weak interaction like Van Der Waals interaction and that is also the reason why these materials are much more easy to cleave along the basal plane and cutting them through other planes are extremely difficult. Therefore, you would not find in the market a hexagonal or graphite, for example, which is plenty available is always the 0 0 1 surface and you would not find for example other complicated or other more complex planes are not really readily available because they are more difficult to obtain. But 0 0 0 1 planes are easily available in the market for purchasing.

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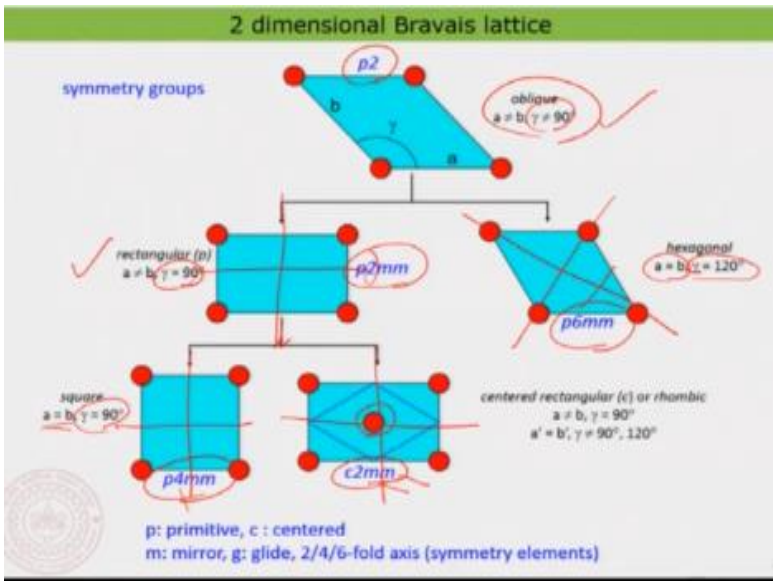

Now I come to the final slide of the lecture, this actually just summarize the two-dimensional Bravais lattice and in the two-dimensional Bravais lattice we have basically five different point groups. These ones are typically represented the first one is oblique, where the unit lattice vectors a and b are not equal and gamma is also not equal to 90 degree. That is basically is the oblique lattice or most of the lattices you can basically put it in the oblique. And now, if you would basically keep the gamma to be 90 degree and keeping the a and b not equal to each other then you can actually just form the rectangular unit cell. And then you can actually just by keeping the gamma 120 and a is equal to b you would get nothing but the hexagonal lattice. That is the classification. And now the rectangular unit cell you can actually just create two different type out of that where you keeping the gamma at 90 degree the same as in the rectangular. But now a is equal to b then you would come to something like the square lattice. Now out of this there is actually a very special group that is called as the centered group where you have the same classification of the same characteristics as in the rectangular one, but the only difference here is that that you have basically something at the center of this rectangular unit cell. So, now you can see that the entire different possible surface is actually like surfaces can be classified into these five different point groups, for example. Now the point group of these different things can also be just looked this is actually called as p2, this is called as p2mm, this is called as p6mm, this is called as p4mm and the last one is actually the centered one rectangle is actually known as the c2mm, where p represent primitive, that means it is a primitive cell it has only one atom in the cell and c represent basically that it is a centered cell. And two is basically

representing that it has as a two-fold symmetry, and six is representing for example it has six-fold symmetry, and four is representing that it has four-fold symmetry. So, the number basically representing the symmetry of the surface and the p or c is basically representing whether it is a primitive or centered and the last one m and m are representing whether there is actually a mirror plane or not. You can see here for the rectangle I have a mirror plane along this direction and I have a mirror plane along this. And also same for the hexagon so I have a mirror plane along this and I have a mirror plane along this and here also I have two mirror planes as you see here and that is why they all have like two mirror planes that is what is represented by the two different m's. That, is the summary of the Bravais lattice and as I have already told you we can classify all the different type of lattices that you observe in surface can actually be classified into any of this. And for example, our 110 surface was should be corresponding to the rectangle or p2mm and the 100 surface can actually be put in the p4mm to square and for the 110 of the bcc can actually be represented by c2mm, for example or the hexagon can actually be represented by p6mm and so on. So, with this you can classify all the surfaces and you can either represent the surface using the symmetry or you can actually also represent by the plane itself which we have already learned in the previous classes. What I wanted to also just summarize here is that these different types of surfaces are now commercially available and you can purchase them in the way you want and to maintain their cleanness and also to maintain the stability of the surfaces ultra high vacuum technology is very important and therefore next week before we go into understanding more about the surfaces, I am going to introduce to you to ultra high vacuum technology which is actually one of the major development that has actually just created the surface science into the current status. And also, where people could understand things at an atomic and molecular level. So, with this I would like to conclude this lecture and I will see you in the next lecture, thank you very much.