Chemistry and Physics of Surfaces and Interfaces
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Lecture - 07
Adsorption and the Energetic of Adsorption

Hello everyone, welcome to lecture number 7. In this lecture what we are going to look at is the adsorption of atoms on clean surfaces.

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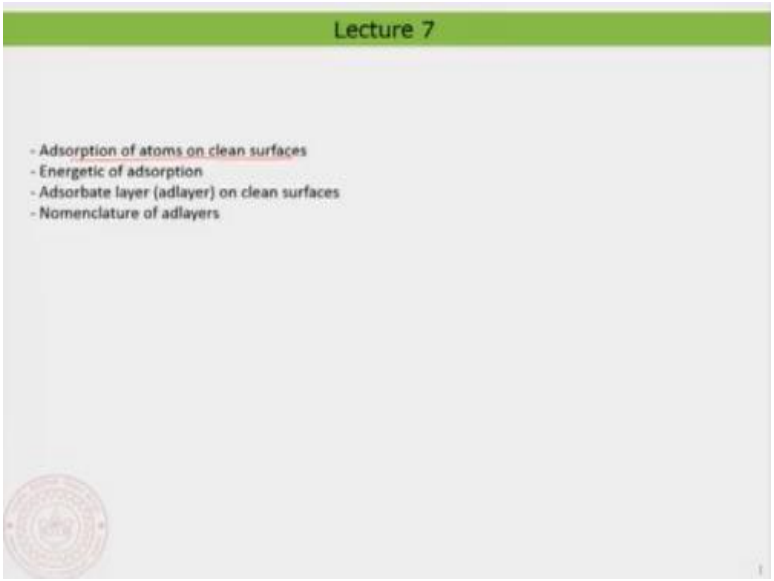

In the previous lecture you have already seen how to create a clean surface. So, believe me now onwards we are going to always work inside an ultra-high vacuum chamber, so that is something I have already told you. So, that means we are going to work always with a clean surface. Now adsorption of atom is actually the most important thing for us because with the adsorption of a single atom with the adsorption of many many atoms onto the surface we are going to create basically the thin film and finally the so-called interface. Then, we will also look at the energetic of adsorption? How basically the energy of adsorption is controlled? What are the important energies that we need to keep it in mind? And then we will also look at the adsorbate layers in general and mainly what we are going to do is the looking at the nomenclature of the adlayer. So, how do we basically call a name for this different type of adlayers. When I call adlayer, it actually means an adsorbed layer that is what it means.

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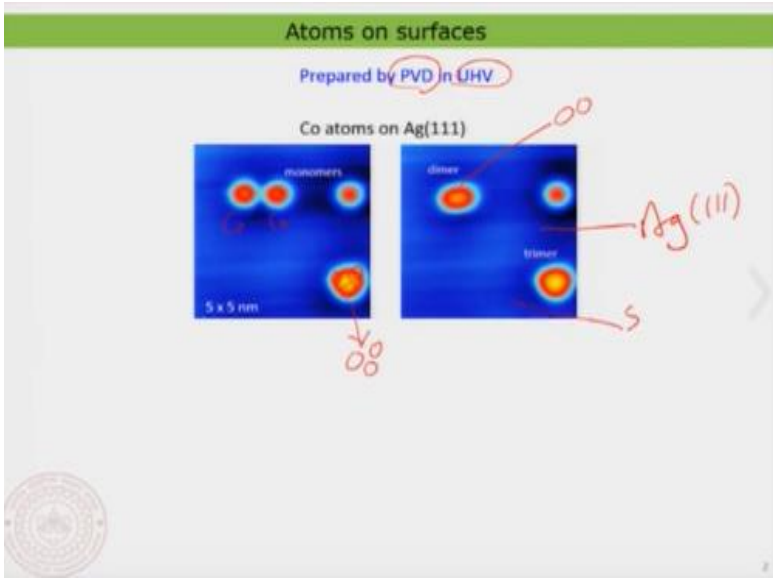

Now this here is actually kind of a physical vapor deposited. We are going to see after couple of lectures you will see what is a physical vapor deposition meaning. It is a simple evaporation method of an atom inside an ultra-high vacuum chamber. So, what you are seeing here is actually cobalt atoms, isolated cobalt atoms and this what you are seeing is actually a trimer of cobalt atom. So, that means three cobalt atoms are coming together like that. And then here you have a dimer that means two atoms together like that. So, what you are seeing is a clean, silver 111 surface. So, this is actually the silver 111 surface and I have deposited cobalt atoms onto this. So, you can basically now work with atoms alone. So, that is the interesting thing about that and with this scanning tunnelling micrograph I can actually image them nicely and resolve at their atomic level.

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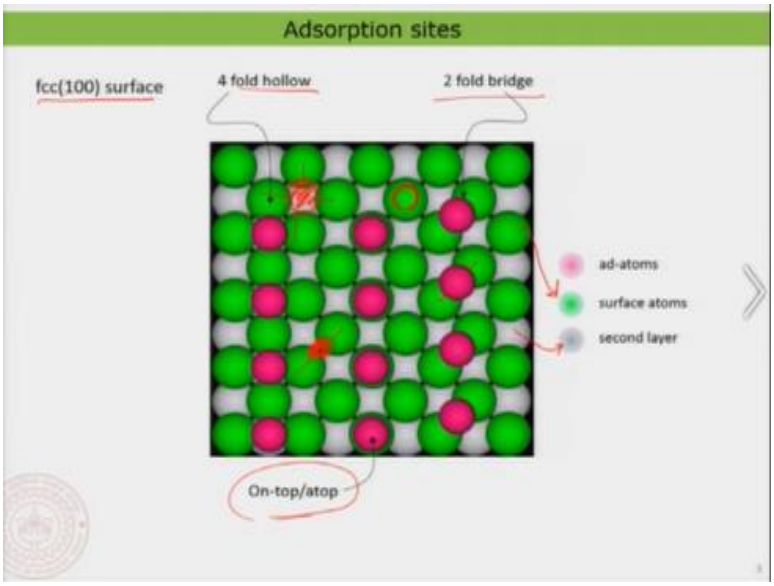

Now when it comes to the adsorption of an atom onto surface, there are certain important things that you have to keep it in mind. Now remember that we are going to always discuss or deal with atomically flat crystalline surface. So, that means there is a particular symmetry for the surface there is a particular way the atoms on the surfaces are arranged. Therefore, it is extremely important for us to define something called adsorption site of the atom that is actually getting stick to the surface. So, here is an example, I have here an fcc 100 surface and the green ones are basically the first layer the surface and the light grey is the second layer and you have already seen this fcc 100 surface that is actually a four-fold symmetric surface. Now when the atom goes on to the surface it has many different choices but where does the atom really go and that is the question. Of course, it can go on to this part here which is actually a four-fold symmetric site or the atoms can go directly on top of an atom or it can also go on in between two atoms here. So, these particular absorption sites are namely known as two-fold bridge site or four-fold hollow site and then you have something called on-top or atop side. So, the name itself suggests what it means so this is actually a four-fold hollow site. Because you can see here there is no atom in the first layer the atom is actually in the second layer. Therefore, it is actually a hollow site and this for example is a very very favoured side for the adsorption. You would imagine why is that because when the atom basically adsorbs this side you see there is actually four and then one coordination to the atom at the bottom. So, there is actually about five coordination that this atom can have when it basically adsorbs on the fourfold side. But when it adsorbs on the two-fold side as you see here in the twofold side the atom is actually having a two coordination basically. So,

the coordination number is less and when the atom is actually absorbed on top of an atom then you see this only has a coordination just with the atom on the surface. So, that means the number of coordination is finally going to define where these atoms are going to finally adsorb. Because that coordination will define how strong is the adsorption and that is what we are going to see in the next slide and then, that will decide where the atoms are going. But you will see that you will encounter all these sites will be occupied or the adsorbate would use many different sites of the surface to get adsorbed. It is not necessarily that you always hit this so called most stable or most energetically favourable four-fold hollow site for example. Let us have a look at first familiarized the possible sites in different surfaces.

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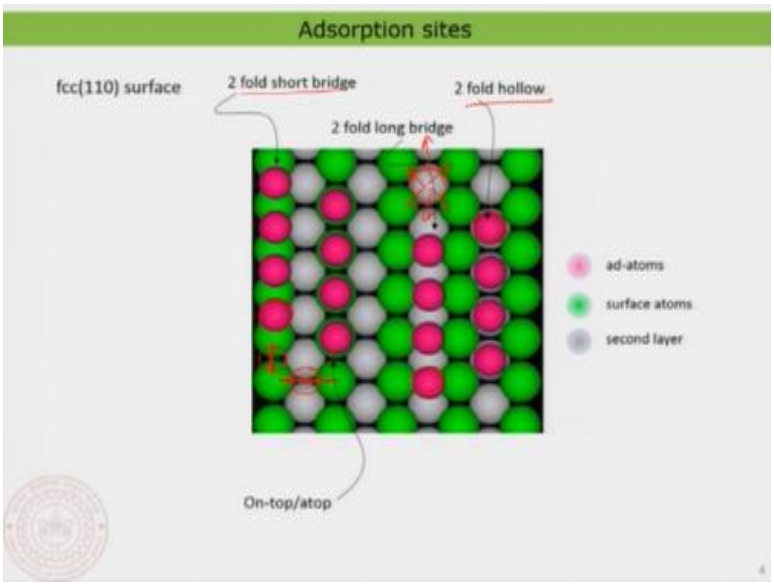

So, for example, if you take the 110 surface you know the symmetry of the surface is different this is actually a rectangular site. Therefore, your hollow site that means this site here looks similar to the one on the 100 surface but now you see that they actually have a weaker coordination along this direction. There is no atom there is only a coordination along this site. So, this is mostly going to have a coordination like this. Then, you have something interesting a site like this and also a bridge site like this and then finally an atop site. So, these sites are actually called like that of course this particular site is actually known as the two-fold hollow site because this is not the four-fold symmetric surface it is a twofold symmetric surface. Therefore, the hollow sites are basically known as the two-fold hollow site and then, you have here something called an atop site that is the top of the surface atom then you have two different types

of bridges. One is called as a short bridge because you can see the distance between these two atoms are much shorter compared to the distance between these two atoms. So, that means when an atom goes here it is actually adsorbing on a short bridge and when an atom goes here it is actually adsorbing on a long bridge. Now you see the difference the surface as the surface getting much more complex or getting more rougher you are going to get basically like more possible adsorption site.

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And now if you look at the 111 surface that is one of the surface we talked about is the least corrugated surface of course atop site is always an option. But you now see that I have basically here two different types of hollow sites. A hollow site where I have no neighbour in the second layer and another hollow site here which is actually having a neighbour just below that, and these two sites can actually just occupy atoms, and they are actually known as the hcp hollow site and the fcc hollow site. So, this is something you might also have studied in previous classes or earlier solid-state related courses where hollow site is actually known as something like an ABAB type packing and fcc sites are actually having something called an ABCABC type of packing. So, that is the basically the point. So, these sites are not energy in terms of their adsorption depending on the material they can be slight differences in the energy. But they are very close in terms of the coordination because both sites would offer basically three coordinations to the atom that is adsorbing on the surface. So, that is the key point here. Now once you have understood the adsorption site.

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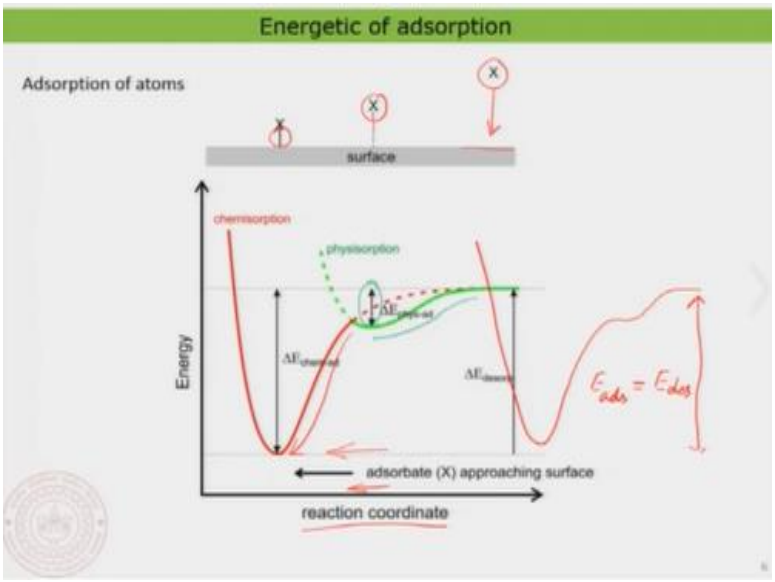

So, now what I want to basically just discuss with you is the energetic of the adsorption how or what are the important energies that we need to consider or keep it in mind when you understand the adsorption of an atom onto a surface. Now to understand this, we will do a small experiment where we take an atom namely x, it is any atom no matter what atom you would take, any atom and you adsorb onto a surface. Just keep it in mind that this surface is atomically flat. But now I am not at this moment looking at the specific sites to which the atom is actually absorbing, I am only just considering that the atom is actually approaching the surface. And you see that the atom is basically approaching as it keep on approaching there will be a point where the surface start to basically interact weakly with the surface, and that is where you would call that there is a weak interaction that is happening and that something you can call it actually a physisorption that means only a physical adsorption via but not strong interactions. Then if you push the atom a little further down then you can see there is true chemical bonds that can form which is actually typically known as a chemisorption. Now, when you look at the energetics that means how the energy of the adsorbing atom changes as a function of the distance between the atom and the surface. So, what I am plotting here is actually something known as reaction coordinate or this coordinate is actually right now just for the convenience, we use a one-dimensional coordinate of the atom moving towards the surface nothing more. It is just a one-dimensional coordinate. So, that means along this direction atom is basically approaching the surface. Now when the atom is approaching the surface you would naturally imagine that the interaction start to gain, and once

the interaction is actually gaining which would means that the total energy of the atom that is approaching is basically decreasing. And as a matter of fact, you can see that the energy is basically going like this, the energy is going down like this. Now the point is this is actually a physisorption. In the beginning the interactions are weak therefore the atom is going to get adsorbed physically onto the surface not chemically. In that case you can see that this so-called energy gain that the magnitude of energy with respect to the original energy of the atom the potential energy ideally is actually known as the energy gain due to physisorption. You can call it as actually as a delta E phis-ad or you can even call it actually as an E phis-ad which means like the energy gained during the physisorption but now the interesting point as you told, if you actually push the atom a little further on to the surface. So, then actually it can do undergo chemical reaction that means the interaction becomes stronger and stronger and if that is the case then the atom is basically gaining a lot of energy by putting them and chemically reacting them to the surface. It is not necessary that all atoms would chemisorb on surfaces it depends really on the nature of the surface and the atom which is adsorbing. For example, if you try to adsorb helium on metallic surfaces or any surfaces then you would find that mostly they are going to be physisorb and not chemisorb. But if you put oxygen onto gold or copper or whatever surface, you would find that most of the time they actually get chemisorb. So, it also depends a little bit but the overall picture is this that as you put the atom closer to the surface it first physisorb weakly interacting that means there is an energy gain and then, finally it goes down. So, the total energy diagram would be from a starting point like this a small energy gain and then further strong energy gain and then finally it goes like this in the path. And this energy, the magnitude of this energy is actually the total gain in energy which is something you call it as the adsorption energy. That is the same amount of energy that you also require to remove the atom from the surface therefore you can also call it as actually the energy for desorption. So, let us call this one as energy of adsorption and which is also equal to energy of desorption. You would find this terminology is slightly different but you can always call it as the energy of desorption and the energy of adsorption. But the only difference is that their signs are going to be changed. Because once the system is actually absorbed it is there is a gain in energy and because the gain in energy is always indicated by a negative sign so, the absorption energy is basically a negative quantity. And if you want to remove the atom from the surface you have to put in that much amount of

energy so therefore normally desorption energy is actually counted as a positive quantity. So, that is basically the general energetics of an atom adsorbing onto the surface.

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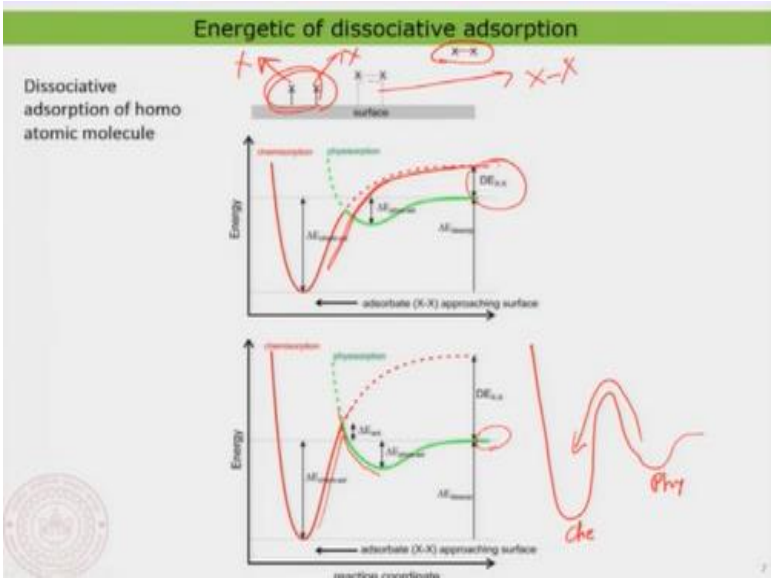

But now what is interesting that we can look at a special case which is actually a diatomic molecule. A molecule that is connected so let us call it actually as a homo atomic molecule, heteroatomic molecule would also do similar but let us take actually homo atomic molecules and I have a molecule now. And the molecule a diatomic molecule is now absorbing onto the surface so everything works the same way. But the only interesting thing here or the most interesting thing that you have to keep it in mind when the interaction of the molecules start to increase then you can see the interaction between the molecules are actually starting to weaken. That means if this would have been the molecule while it adsorb it basically start to also just get separated. And then finally, when they chemisorb on the surface these atoms are truly separated, not necessarily completely away but they are actually separated not as in the case of the true molecular situation. So, if you look at the energetics of that it looks slightly different the overall picture is same, the picture look the same as you have seen before. But the difference is now that when looking at the chemisorption particularly, the chemisorption is basically leading to a different point in energy compared to the physisorption. The reason is very simple that this extra magnitude in energy is nothing but the dissociation energy of the molecule itself. Because the molecule when it physisorb without any dissociation it actually can just go on the surface. So, there is an energy gain when a molecule just goes on to the surface. But if I have to dissociate them, I need to

supply an extra amount of energy and that is reason why your chemisorption curve would reach to a higher point than the physisorption. Because in the physisorption when you remove the molecule the molecule go as a single molecule, when you remove from a chemical state that means a chemisorb state you can see the atoms are actually separated it goes like x and x but from the physisorb state when the molecule goes it is going as x_2. That is the difference. So, because of that you will see that there is actually a difference in that. Now the interesting aspect here is if you would take molecules that are having extremely large dissociation energy. Then, what is interesting is that because of this extremely large dissociation energy of the molecule itself you would find that you create basically some kind of a barrier between the physisorption and the chemisorption. It is actually due to the fact that the crossing of the physisorption and the chemisorption actually is going to happen at a higher point than the physisorb state. Therefore, you ideally create some kind of a barrier. So, that means you have a physisorb molecule and then the molecule need to overcome a barrier finally to reach to the, so this is actually the physisorb state and this is the chemisorb state and the molecule need to basically cross this barrier in order to come to the chemisorb state. So, that is the difference in this case compared to the general physisorption or generally atom adsorbing onto the surface.

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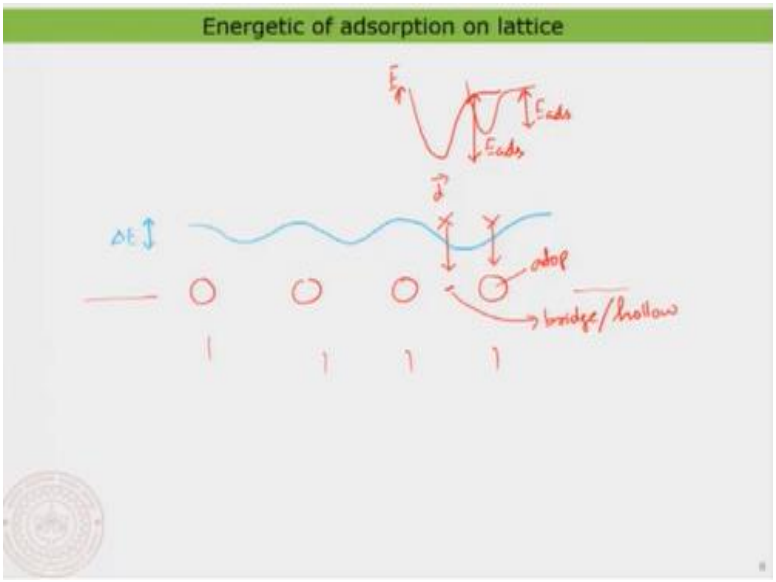

Now we understand this and now once we understand this, we can actually also have a look at the energetics of the adsorption of atom onto a lattice because that something we have not considered. How does the lattice play the role in the adsorption energy? For that we need to

consider a lattice. So, let me just draw a lattice so this is actually the top surface atom of the surface and of course the crystal continues in this way and of course the crystal also continues in this way. Now the point what I want to make here is actually now when the atom approaching onto the surface as I have already seen we have already discussed in the previous slide. That the atom could actually just approach along this particular point or atom can actually just approach along this particular point. In that case the atom is going to come in this case to an atop situation and here it is actually going to come to a bridge or to a hollow site. So, depending on where it goes. Of course, in the side view we cannot distinguish the bridge and the hollow but the atoms now can basically just come to do different sites. Now you see the point as I have already mentioned in the previous slide depending on the coordination number that the atom gain on the surface the adsorption energy truly be higher than the other situation. That means if you would consider that this is the point where it basically has the highest coordination. Then, the adsorption curve of this site would look somewhat like this I am not considering the physisorption in site. So, this would be the energetic. So basically, I have my energy here and here is basically the distance of the approach. And the magnitude is actually defined by how deep the atom goes. But now on the top site the interesting thing is the same curve if I would draw on the top site it would basically just look like that. So, what is the difference in this, the difference is basically in the magnitude of the E adsorption energy in the two different cases. So, here you can see that the energy E adsorption energy is actually much higher compared to that at the top site. So, now if you would have plotted basically the energetics of the adsorption of atom along the lattice you would find that the adsorption energy is low at this point, let me just take a slightly different colour to highlight this if this site. I have a very low adsorption energy and then when I come here I have actually a high adsorption energy. So, that means the profile of the adsorption energy would basically look like this as periodic as the surface and this is basically the typical magnitude of the energy difference between the absorption energy of a top site a hollow site or a bit site and so on. So, that means the surface itself is a kind of landscape of energy for the atoms to adsorb and the atoms at a lower coverage you will hear what a coverage means at lower coverage means lower concentration of the atoms on the surface the atoms would always go on to a hollow site or to a bridge site than on a top site because the energy at that point is actually higher.

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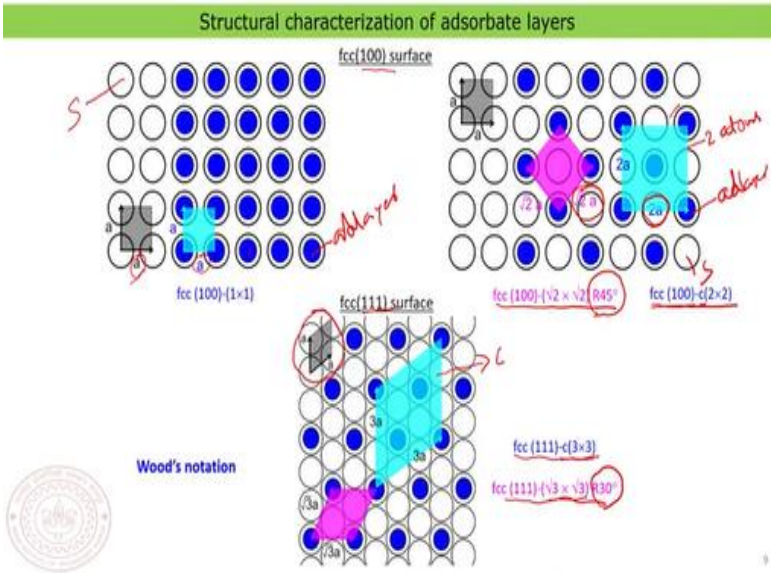

So, far we have seen the different possible adsorption sites on surfaces and also have seen the energetics. Now let me introduce to you the typical nomenclature or the naming convention of adlayers on surfaces. So, here I have an fcc 100 surface decorated with adatoms. So, here the black circles are surface atoms and the blue is basically the adlayer atoms. Now what you notice is actually that the unit cell of the surface is basically a square unit cell, as you have already seen for the fcc 100 surface and if interesting thing in this particular type of adlayer that we are showing where each of the surface atom is actually decorated with adlayer atom. So, that means it is a one-to-one adsorption basically which is meaning that the lattice parameter of the surface and that of the adlayer is basically matching. So, this you can call it as a one-by-one adlayer. So, the one by one is basically representing that along both crystallographic direction you would find the adatoms at the unit of one basically meaning that every atom is basically decorated by an adlayer atom. Now if you would take a little bit more complex surfaces here again you have the blue as this adlayer atom and this is basically the surface in all the cases that I am going to discuss it will be the same. Now I can basically represent the adlayer using two different types of cells. So, either the blue cell which is a little larger one or with the magenta one, so, in this case what you notice is that it is actually a cell which is having two atoms in the cells. So, it is not a primitive unit cell because here you can see this is a primitive unit cell where you have basically one atom in the cell. So, this is not a primitive unit that is difference. But you can basically represent the surface using either of this and you can generate the surface adlayer using any of these units.

Now, how do we basically name these unit cells. Well, I can basically calculate the unit lattice vectors of the surface with respect to the surface unit lattice vector which is a and this is basically root 2a in both direction because it is a square lattice. And in this case, it is basically 2a. So, if I would basically write down the unit cell corresponding to this blue one then I have basically a 2 by 2 units which is meaning that along both the direction I would basically require about two times to move to find actually an adatom. And I also need to basically represent that this is basically a centre type of cells. So, there you have already seen that in the two-dimensional bravais lattice and therefore I would also call it basically a c 2 by 2. So, you have to now, first name the surface which is fcc 100 c 2 by 2 would be the name of the surface the adlayer. Now the other unit cell is basically represented like this. So, you have the root 2 by root 2 that is a unit cell and it is an fcc 100 surface. And in addition to that, you also need to basically mention the angle that the adlayer is actually making with respect to the surface unit lattice vectors and that is 45-degree in this case and therefore you have to also represent the R. This kind of a notation of representing the adlayer is known as Wood's notation which is a simple notation. Now let me just introduce to you another surface for exercise. Here we have a 111 surface, and the surface unit lattice is basically represented using this oblique here. Now again the surface we can basically represent using any of these cells where the magenta one is basically a unit cell containing one atom and this is therefore a primitive cell and this is basically again a centred unit cell. So, you can basically just mark the unit cell as it is and depending on the magnitude of the unit lattice vector. You can actually now name them either a c 3 by 3 or a root 3 by root 3 but it is actually an R 30-degree. So, this is rotated with respect to the surface unit lattice vectors.

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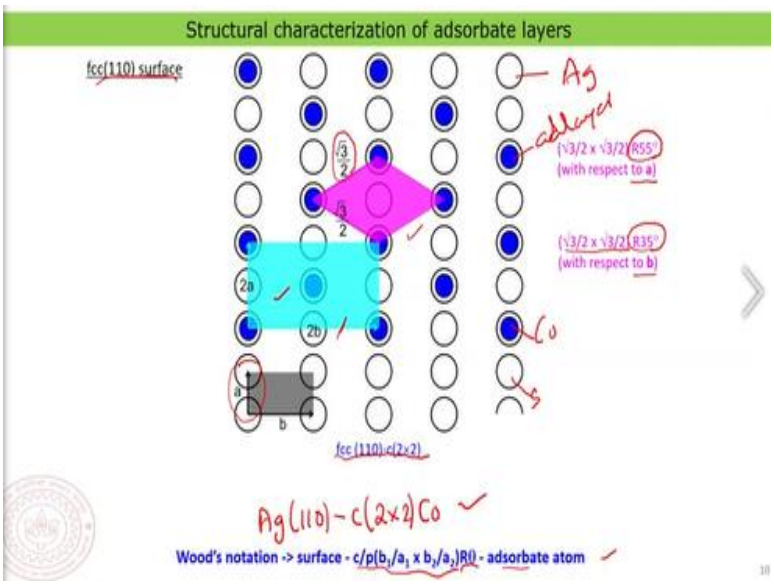

Now let us take one more example. So, this is an fcc 110 surface. Again, the blue basically representing the adlayer and the black lines are basically representing the surface. Now, the first representation which is basically this unit cell so which is actually a 2 by 2 unit cell and that is actually written as fcc 110, 2 by 2 adlayer. Now you can also represent the surface using this magenta unit cell where the lattice vectors are root 3 by 2 and root 3 by 2 with respect to a, because that is also something different for the fcc 110 surface that it is basically the units cell lattice vectors along different directions are different in magnitude. So, with respect to a, so the unit vector magnitude for this unit cell is basically root 3 by 2. So, you can now represent the unit cell of this adlayer using two different ways either you call it basically a root 3 by 2 by root 3 by 2 with respect to a. And in that case the angle of rotation is basically 55 degree or you can basically represent the same unit cell as root 3 by 2, root 3 by 2 with respect to b. Therefore, the angle is basically R-35 degree. So, that is the only difference. But the interesting thing about this wood's notation is that depending on how you represent you can have slightly different name for the different type of unit cells. Now in general this is how you write the wood's notation? You need to have the surface then you need to basically have the magnitude of unit lattice vectors for the surface and the adlayer and then the rotation and then finally the adsorbate atom. So, imagine that what you are looking at is a silver surface and the adatoms are nothing but cobalt. So, in that case we would be writing the surface as Ag 110 centred or primitive. So, now if I would basically take this one then I will have to use a centred 2 by 2 and then the angle. So, if there is no angle because this is basically with the same as that of the surface, so there is no angle and

then finally the adsorbate atom cobalt. So, this is how you are going to write the wood's notation of the surface. So, you can basically do this exercise for different surfaces and you can learn this further. With this I would like to conclude this lecture and in the next lecture I will introduce you one more type of notation for the surface which is a little bit more generic in nature and that is actually called as a Matrix notation. Thank you very much.