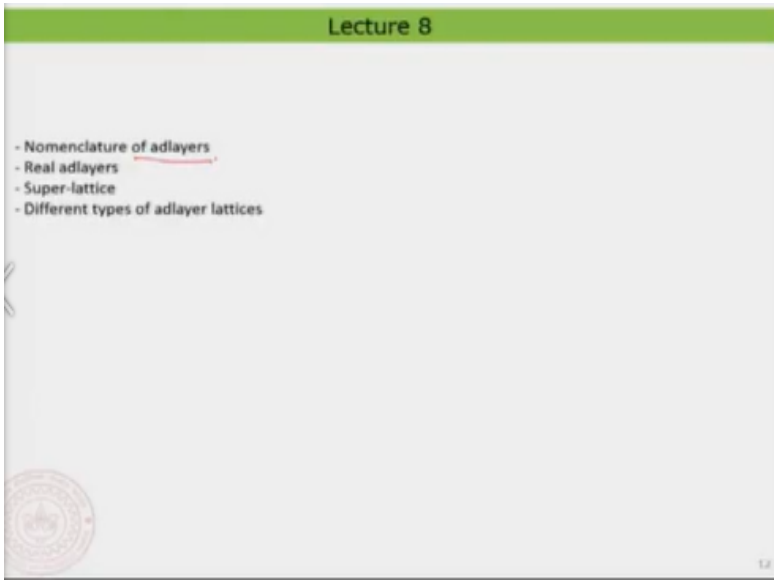
Chemistry and Physics of Surfaces and Interfaces
Prof. Thiruvancheril G Gopakumar
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 08
Nomenclature and Types of Adlayers

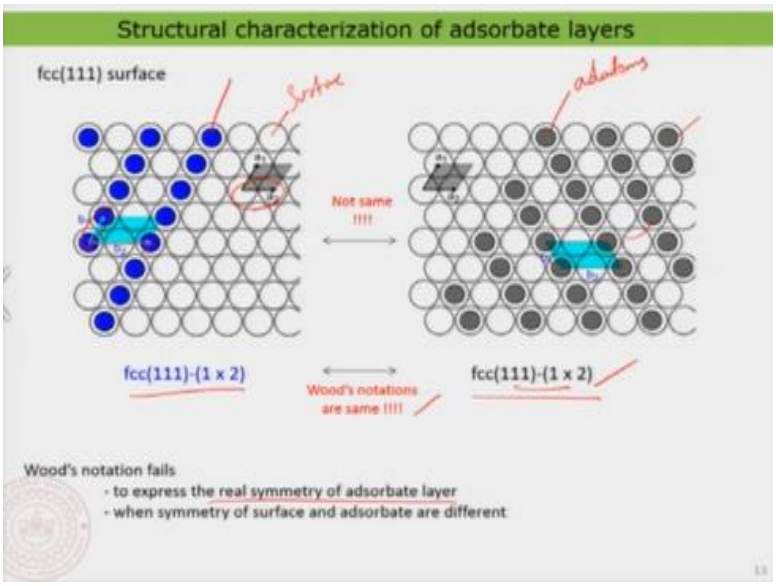
Hello everyone. Welcome to lecture number 8. And in this lecture, we are going to continue first with the nomenclature that for the adlayer.

(Refer Slide Time: 00:23)



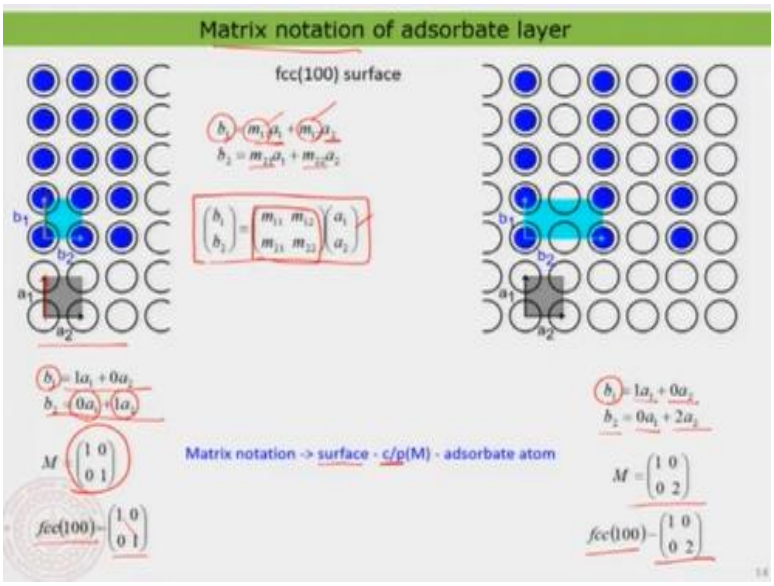
So, you remember last class, we have actually just familiarized something called Wood's notation and now I will actually take you to another type of notation which is actually known as Matrix notation which is of course a more methodical and systematic method that is commonly used. And then, we will look at something called real adlayers and something called super-lattices due to the fact that not all atoms are necessarily adsorbing on the same site. You can actually have something called super-lattice. And then finally, we will also just familiarize the different general classification of the adlayer lattices.

(Refer Slide Time: 01:04)



So, now let us look at the matrix notation. But before that let me just show you these two examples here. So, this is like an fcc 111 surface, where this is the surface atom and the blue or the grey atoms are actually the adatoms or the adlayer in general. So, the interesting thing when you look at this adlayer so both of them are looking same ideally and if you would write down the wood's notation of both of them, you would write down it is to be 1 by 2 because you can see that the adlayer lattice is basically two times that of the surface lattice along one direction and along the other direction it is exactly same as that of the surface unit lattice vector. So, that means it is actually 1 by 2 adlayer and both the names are basically the same. But now the interesting thing, if you look carefully the woods notations are the same but the adlayers are not the same. You can see that there is truly a difference in the symmetry of the adlayer with respect to the surface. You can see here the oblique of this particular adlayer is basically facing to this side and the oblique of this adlayer is basically facing to this side. So, ideally these two are just nothing but mirror adlayers. But that is not reflected in the wood's notation. So, the wood's notation is basically not representing the real symmetry of the adlayer. So, that is the reason why we need to now look for another type of notation which is basically a clearer and a more methodical type of notation, which is actually known as the Matrix notation.

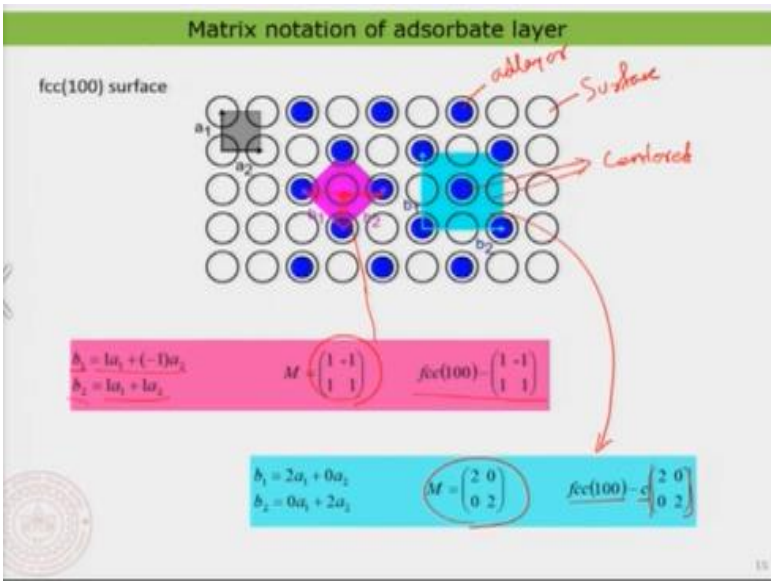
(Refer Slide Time: 02:56)



So, how do we do that? It is very simple. Again, we are going to write down we are going to write down a small mathematical expression for the unit lattice vector of the adlayer in terms of the two-unit lattice vectors of the surface itself, and they will be connected using two integers and the integers particularly along the direction of the adlayer lattice. And that is the reason why you would find this is actually called as m1 and this is actually called as m12 and here you have an m22 and then your you have an m21. That is a connection basically. You will see that now when I do an example. So, let us try to do that for this particular example. So, this you remember was a one-by-one supercell of an fcc 100 surface. Now well then finally if I would write down, so I can basically just represent my b_1 and b_2 that is actually the adlayer unit lattice vectors in terms of the surface unit lattice vectors using a matrix, that is the point. Now let us do that. So, for example if I want to write down b_1, you can see that b_1 is actually one time a_1, one time a_1 and 0 times a_2 and that is the first equation to represent the b_1. And for b_2 it is basically 0 times a_1 and then it is plus one time a_2. Now, I can write down the matrix is basically a 1001. So, that means the surface can actually be named as fcc 100, that is a surface and this is basically the Matrix notation corresponding to this particular adlayer. Here, it is not huge surprising but you can now see for more complex surfaces you will see that it is actually becoming more interesting. Now, let us look at this one this is basically a_2 by 1 super adlayer. Now if I want to write down the Matrix notation, I have to express basically the unit lattice vector of the adlayer b_1 in terms of a_1 and a_2. So, this is basically $1a_1$ plus $0a_2$ and b_2 is basically $0a_2$ and $2a_2$.

So, that means the matrix is basically 1002 and then I can write down the expression or the name of the surface as fcc 100 then 1002. The one and two is actually telling you it is a 1 by 2 or in this the 1 and 1 basically telling it is a 1 by 1 so for these ones it is very simple. But let us look at more examples, but before that the general expression is basically that you have to write down the surface, then you have to write down whether it is a centred or primitive and then you have to also basically write down the Matrix notation and then finally the adsorbate atom.

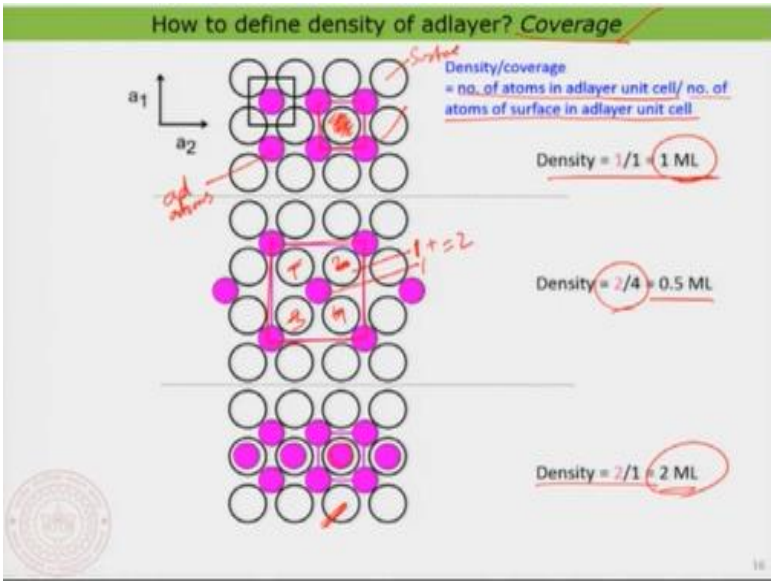
(Refer Slide Time: 06:12)



So, let us assume this particular adlayer. So, the blue is again basically the adlayer and this is basically the surface. And now, we can check what is actually the Matrix representation for the blue and for this magenta unit cells or primitive cells that we have actually just representing this particular adlayer. Now let us look at, this so you can basically see here that the b1 of this one can actually be represented. So, you can see that the b_1 is actually one time a_1 and minus a_2, one time minus a_2. So, that means you move along a_1 once and then you actually go in the negative direction along a_2 then you would reach at b_1. That is basically the representation and then for b_2 it is basically one time a_1 and then positive it is actually one time a_2. So, you would get 1 a_1 and 1 a_2. So, that means the metric notation is basically 1 minus1 1 1, so the surface can actually be called as fcc 100, 1-111. Now, for the blue how does it look like? The blue would look like this where you basically have a 2 by 2 matrix that you are obtaining but here you see this is basically a centred this is a centred cell not a primitive cell. So, therefore you would call this one as fcc 100, then you write down the c for the centre, for primitive you do not write it and then the

matrix notation is basically the 2002 or it is a 2 by 2 cell. So, that is basically it. Now during the assignment time, we will basically just give you more assignments to work out and then you can basically solve more complex adlayer and you can get familiarized with this kind of notations, both the wood's notation and the matrix notation.

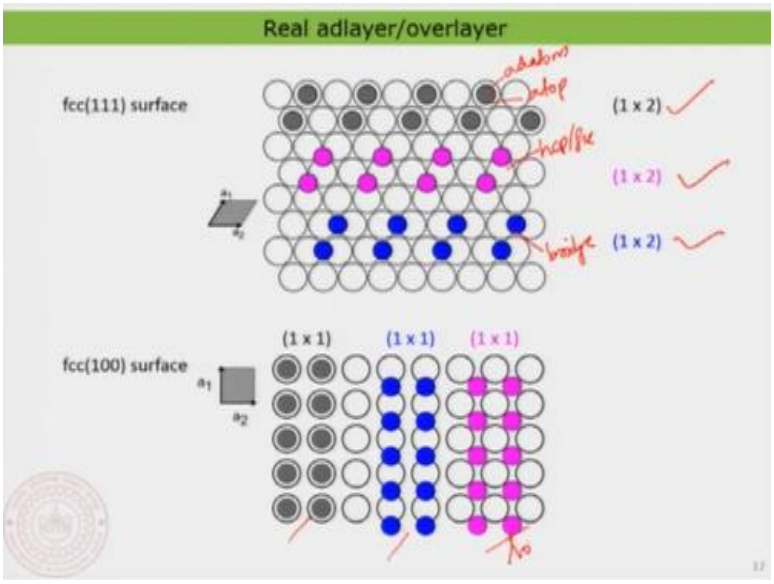
(Refer Slide Time: 08:24)



Now before we go into look into the real adlayers, let me just also introduce something to you called as coverage. What is the meaning of coverage? Coverage is something that you would use now to basically just see how dense is the adsorbate atoms on the surface. You remember we have actually familiarized something called the packing density for the surface atoms density. Similarly, for the surface for the coverage or for the density of the or the concentration of the adlayer atoms we want to basically just represented something called coverage. How can we define the coverage? So, coverage is basically defined by something called the number of atoms in the adlayer unit cell. So, now you see here this is my surface and the magenta is basically my adatoms or adlayer. Now you can see the unit cell of the adlayer is basically this one. And how many atoms are present in that adlayer? So, I have basically one atom in the cell; and then I have to calculate basically the number of atoms of the surface in the adlayer unit cell. So, that means I have to basically check how many atoms are there from the surface which is actually occupying the area of the adlayer lattice. Now you can see that this is just one atom is occupying the area of the adlayer lattice from the surface, so that means for this particular case the density or the coverage is 1 by 1 that means it is actually a one mono layer. A one mono layer or typically ml is

actually the unit for this it is actually called as mono layer and one monolayer represent that the surface is completely covered or meaning that every single surface atom is actually occupying one adlayer atom. Now let us look at another surface. So, this is another surface which is a less dense surface you clearly see that. Now this is the unit cell of your surface, sorry the adlayer; and now you can clearly see that I have one atom in the adlayer lattice. But you can see I have 4 atoms in the surface 1, 2, 3, 4 atoms in the surface, sorry for the adlayer, I have basically one here and one here so total I have two atoms. So, that means 1 plus this 1 so which is likely equal to 2. So, that means if I now would calculate the density or the coverage you basically have 2 by 4 and that is actually something called a half monolayer. That means this actually meaning that the surface is half occupied by the adlayer atoms. Or you can actually have a extremely dense layer where you see now that it is the same as the first case but now I have an extra atom which is sitting in the middle of the adlayer lattice which is making that the density to be 2 by 1 that means it is actually 2 monolayer. But this is an extremely odd situation, this is not common this situation is not very common; but I just for the understanding I have basically just given you, you can basically calculate the coverage or the density of the adlayer atoms using this particular method.

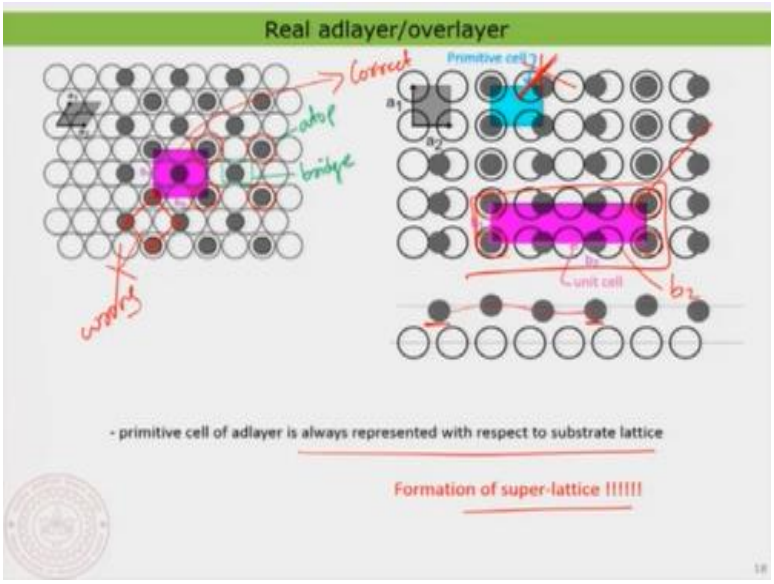
(Refer Slide Time: 11:57)



Now look at the real adlayers. So far, what I have shown you in the all examples I have always tried to stick an adsorbate atom adatoms on the top or the so called atop position of the surface. It is not true all the time because we have already seen in the possible absorption sides that there

are depending on the surface that is offered, I can actually have different type of adsorption sites. So, why did I do that all the time? It is just for convenience I did it but just believe me that the same adlayer can actually be represented also by occupying them equally at an hcp or fcc site or at bridge site. So, here I have an adatom atop sites atop site here at the hcp or fcc site and here at the bridge site. So, all possibilities are there. But now the question that you would ask, are they different? No, they are not different. They are all the same they will all be like a 1 by 2 supercell as you would imagine. But the point what I want to make is depending on the atom or depending on the reactivity or whatsoever factor that you would find out the atoms can actually occupy this variety of positions and it is not also necessary that all the time every atom would occupy on the same site it may also occupy on variety of sites. You will see that in the other examples. Here I have one more example from an fcc 100 surface there you also see that atoms occupying the atop site the atoms occupying the bridge site or the atoms occupying the hollow site. So, they are all same these are all one-by-one supercell. So, they are all technically the same but just occupying the different sites.

(Refer Slide Time: 13:51)



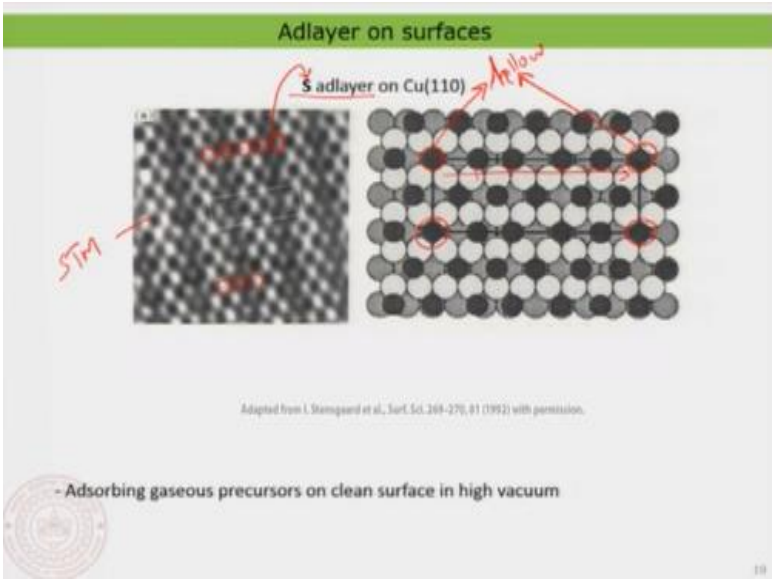
Now comes, the interesting aspect I want to put one more interesting aspect into the adlayer. But now, when you look at this very striking in it, not every atom as you would mark are actually just occupying the same side. These things that I am marking are of course occupying an atop site but this particular atom that I am marking with green colour is actually occupying a bridge site, I have a bridge site and here I have an atop site. So, you see that within a one single adlayer I am

going to get now variety of adsorption sites for the adlayer atoms and that giving rise to atoms with variety of adsorption site. Now something that you have to keep it in mind here particularly because now when I want to define the unit cell of this particular case it is not possible to represent using this type of unit cell. Because you see now that these atoms here are actually not the same as these atoms, you understand. So, which actually meaning that this cannot be used as a representation for the adlayer unit cell. So, the only representation that we can use is basically this one this is correct and this is wrong. It is all because the adatoms are not represented properly using this particular representation. Therefore, you please keep it in mind that when you represent for a real adlayer the adatoms that you choose for making the primitive cell or the so-called unit cell of the adlayer it has to be always with respect to the surface.

Well, that is the point what I have just mentioned. Now let us look at a bit more complex case where you can see now, I have an extremely interesting adlayer where not all atoms are actually just occupying the same site.You can see this atom is occupying of course the same site, this one after the fifth atom or after the fourth atom of the adlayer along the b_2 direction, I am basically able to occupy this. So, this truly because when you make an adlayer it is not necessary that always you make an adlayer of one material on the other is always different type of material and their bulk atom-atom distance are different. For example, if I try to make a silver adlayer on copper the copper bulk lattice is 2.5 and that of the silver lattice is basically 2.9. You see there is a difference of about 0.4 angstrom mismatch between the copper lattice and the silver lattice. So, that means when you occupy them on the surface the copper needs to relax or the silver need to relax but this is something what happens at the interface. We will look into that later in in special cases because of this reason because of these heteroatomic interfaces that you are creating it is not necessary that always they go on the same site. So, because of that now you can see that there is actually something that you are forming called as a super lattice. You are actually forming super lattices that means it is not very simple lattice, the lattice periodicity is actually much bigger you can see the lattice periodicity in this case it is b_2 which is actually much larger than that of the surface lattice. But now again the point is, please keep it in mind that this is not the representation of the surface. So, this cannot be used and this is the true representation of the surface because you need to always consider into atoms that are in registry with the graphite's with the surface lattice.

Now, the interesting thing about the super lattice is also that due to the fact that the atoms have variety of absorption site. You can see that they also have a variable height, they are also just changing their height that means the height is also getting modulated on the adlayer. So, that means they are not just atomically flat instead, they are slightly modulating their height because of the variety of adsorption site. And that is one example I would like to discuss with you here.

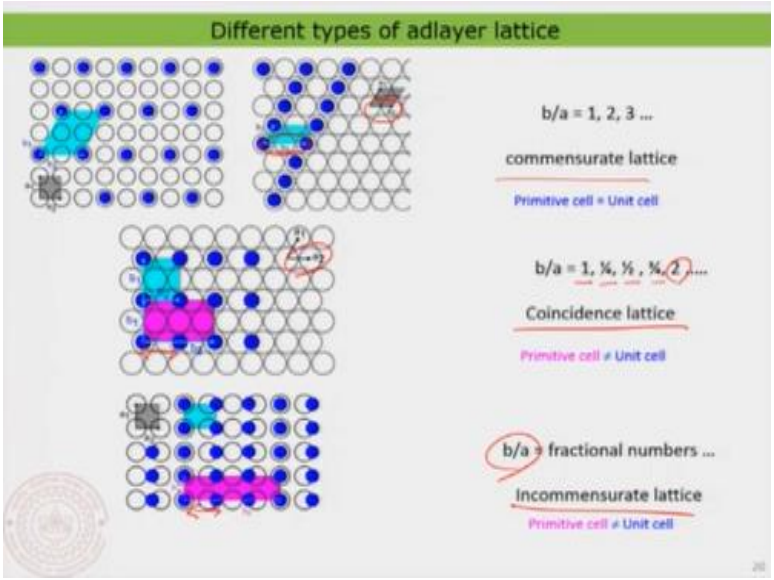
(Refer Slide Time: 18:32)



This is again an STM topograph of sulphur adlayer sticking on copper 110 surface. Well, whatever, what you are seeing here all these bright spots, every bright spots that you are seeing here are nothing but sulphur atoms. These are the sulphur atoms. But now you see that not all sulphur atoms are looking similarly bright, they are looking different. So, the question that you would ask, well why are they different? Well, then comes the real argument that I have put forward before. The real reason is because not all sulphur atoms are actually occupying the same site. You can see here, this corner atom sulphur atom is actually occupying the hollow site, but then after that about 8 atoms further so, that means along this direction if you count after 8 atom this is again occupying the same site. And now these atoms are actually occupying the same site; that means the hollow side but the atoms that are in between are not occupying the same site and that is the reason why they are actually appearing different. So, this is actually a true experimental result of a sulphur adlayer on copper where you can see this kind of real effect or this is something called a real adlayer mostly looking light. And also, it depends on the coverage because at the lower coverage you would find that atoms can occupy a more stable absorption

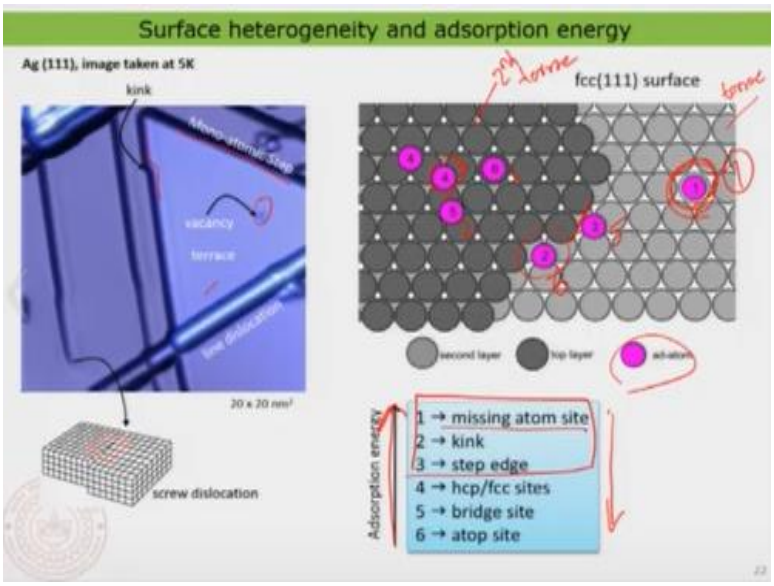
site. But as the coverage increases the atoms would start to occupy on a completely compact layer where you can actually start to observe this kind of real adlayer.

(Refer Slide Time: 20:21)



Now, the one more important point that I would like to mention here is actually there is a general classification of adlayer. If the adlayer lattice that means the adlayer lattice divided by the unit lattice vector of the surface. If they are coming to be like integer numbers like 1, 2, 3 and so on, then you would call this lattice as a commensurate lattice, that means the lattice is actually in commensuration with the surface. But there is another one where you can see the magnitude, this magnitude is actually kind of not really an integer number with in relation to the surface unit lattice vector. But if you are getting something like 1, 1/4, half, 3/4th, 2 and things like that then typically you call it as a coincidence lattice or if that is absolutely not possible if this distance is actually kind of a fractional number with respect to that of the surface lattice, then you would basically call it as an incommensurate lattice. That means it is not really in inregistry with the surface lattice and that is typically the surface that you would basically find in this case. This is a general classification, a general name that you would use and they can also have this modulation. So, you can also form super lattice.

(Refer Slide Time: 21:54)



And finally, what I want to show you is one more important thing. Although, we have actually considered so far only an extremely flat and smooth surfaces. But you see the real experimental result shows this is a silver 111 surface prepared using sputtering and annealing and after the preparation you find the surface is not looking extremely like flat as we have expected. It is actually looking much more heterogeneous. You would find for example monoatomic step edges; you would find vacancies, you would find terraces derivatives are good that is exactly what we have expected, you would also find for example kinks. These are actually small change in the step edges and you would also find line dislocations and you can even find screwed dislocation where the lattices are like basically just changing their orientation and things like that. So, the surface in general what I want to say is basically much more heterogeneous in the atomic scale and not as atomically flat as we have basically just expected or said in the ideal situation. So, this is the surface that we are going to work that means whenever you're gonna absorb atoms onto the surface you have to now come across these kinds of surfaces where you have actually like a variety of defects, kinks, terraces, vacancies and so on.

Well, in the next lecture we would try to adsorb atoms onto this in a real case and then basically we have basically we can understand the situation a little better let me all. So, now let me just try to adsorb atoms onto to the surface and this is basically can be understood as I have already showed you in the previous ah previous slide that we have basically these monoatomic steps kinks terraces vacancies and so on.

Now when I absorb atoms onto the surface it is not just going to absorb only on to the hcp, fcc and the top site, it is also going to adsorb onto the atomic steps, onto the kinks and to the vacancy and so on. So, let me just show you how it really looks like. So, this is a schematic of two surface layers. So, this is the first terrace and this would be the second terrace. So, these are the two different terraces and now you can see basically if I would absorb atoms.

So, these are basically the adatoms that I am going to put onto the surface. So, they can get basically vacancies, they can get they can get basically step edges, they can get kinks, they can get, then they can get bridges and they can get hcp sites and so on. So, there are variety of adsorption sites that you can get on the surface compared to what we have seen the ideal cases just in the previous slides. So, now the question that you would ask because we have already seen that depending on the site the adsorption energy is basically going to change, and we have already seen the hollow sites have the highest adsorption energy than the normal top site. So, now the point here I want to make here in this variety of adsorption site, but if you take actually the vacancy, this is where the atom is basically going to get occupy the largest because it has the highest coordination because you can see here, I have 6 atoms in the layer and one atom below. So therefore, the coordination is basically 7 here and if you take the kink atom, this has a coordination of 6, this step it just has a coordination of 5, the hcp site has a coordination at 2 coordination and this is having 3 coordination and a top side have just 1 coordination. So, that means the adsorption energy you can see is basically increasing as a function of the number of coordination that the atom basically would get and if that is the case then you would find that this site that means actually the vacancy site with the highest number of coordination is actually the one with the highest adsorption energy and then the adsorption energy basically decreases as you go along to this. So, just keep it in mind that these are the additional sites that we have just learned due to the fact that the surface is basically heterogeneous in nature.

And then we are going to really work with this kind of heterogeneous surface in the next classes. Thank you very much for the attention and we meet in the next class with how to determine the adsorption energy. Thank you very much.