Chemistry and Physics of Surfaces and Interfaces

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Lecture - 13
Growth Modes of Adlayers

So, hello everyone. Welcome back to lecture number 13. So, in this lecture we are going to look at an interesting aspect about the growth modes of adlayer.

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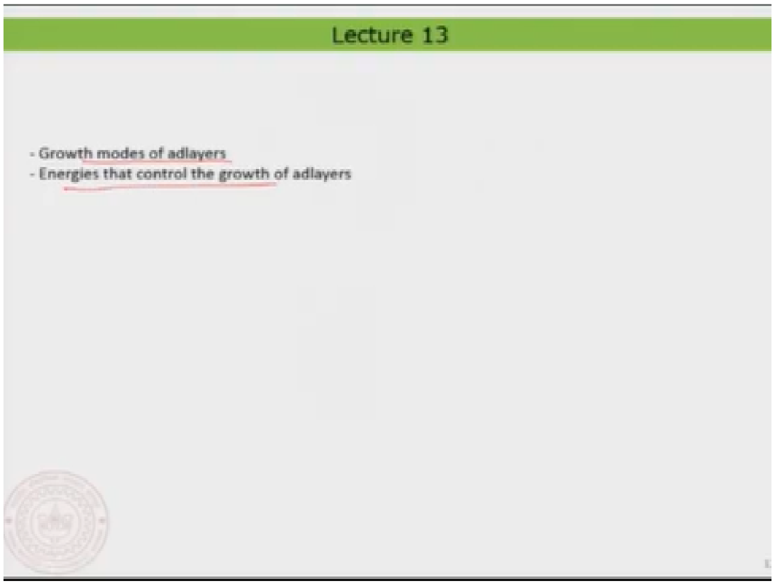

Lecture 13

- Growth modes of adlayers
- Energies that control the growth of adlayers

We have already seen that by depositing atoms on surface we can indeed form adlayers and there are when you start to grow more thicker layers. There are certain different ways that the adlayers are growing in the third dimension which is actually the layer formation. So, we look into to the different type or the general classification of adlayer and while we understanding that we will try to also just have a look at the energies that is controlling the growth of adlayer.

We have already talked a little bit about that in the previous class when we discussed so-called adsorption. And there we also familiarized it as something known as adsorption energy. So, but now you will see it in greater detail because a different coverage regime the energies that are going to energies that get involved in controlling the growth is going to be different and they have different weightages and we have a qualitative look at that in detail. Now let us look at the growth modes itself.

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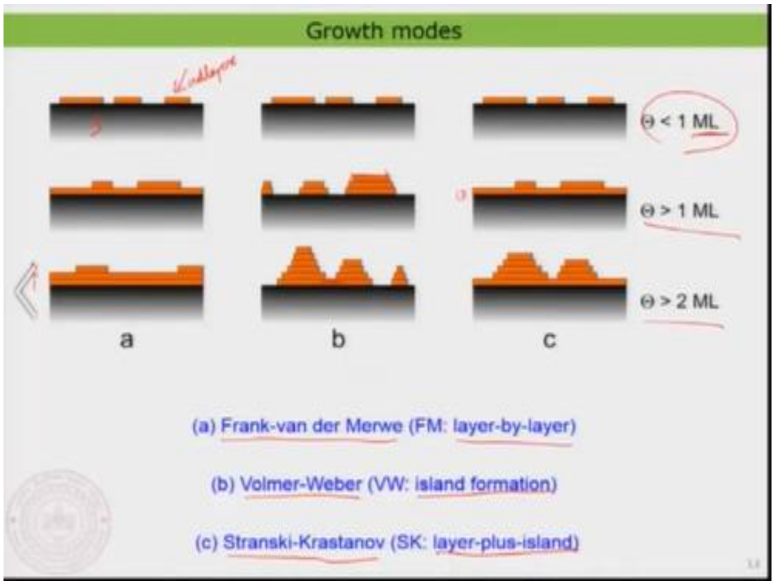

Growth modes

(a) Frank-van der Merwe (FM: layer-by-layer)

(b) Volmer-Weber (VW: island formation)

(c) Stranski-Krastanov (SK: layer-plus-island)

So, what is the growth mode itself? So, what when I talk about the growth mode, we are actually now going a little bit in a higher dimension. So, that basically means you are actually now growing more and more layers on top of surface. So, here again just note that what I am showing everything is basically monolayer so something like coverage below monolayer. So, that means I have my surface here. And then I am basically just adding my adlayer or adatom on top of my surface and then you can clearly see that they are actually just going to cover the surface. Now of course it is a crystalline surface so they will nicely put a layer. But since the coverage is less so you do not know how they grow. So, they would always form some kind of islands. So, that is what we have seen in the previous case if you recollect the cobalt and copper or cobalt and silver you have already seen that the island formations. But remember that all of them were actually just done at a very low coverage that means the amount of atom that you have deposited on the surface is basically enough to have like something less than one monolayer coverage. At that point every surface will look like that that you will always just see the different type of islands of the adlayer itself. But now the interesting thing happens when you increase the coverage.

So, that means you go above one mono layer or even further, you will start to see something interesting. Now there is a first type of growth which is actually known as layer-by-layer growth that simply means that the first layer is formed first. Now you increase the coverage, the second layer start to form on top of the first layer. Then you increase the coverage the third layer start to form on the second layer and so on which is simply known as a layer-by-layer growth and which is also generally known as Frank -Van Der Merwe type of growth. So, that is actually also named after the people who contributed in understanding this type of growth and then you can see that you form layers like 1, 2, 3 and so on. So, by increasing the coverage you can basically increase the layer thickness and that is exactly what you have also seen in the atomic layer deposition. Now comes something interesting. In certain other cases you would find that at lower coverage it is no problem everything looks same. So it is exactly the same as in this case. But when you increase the coverage instead of actually forming a complete layer what happens is that the layers start to form some kind of islands but they grow just in the third dimension that means along the height direction instead of spreading across the surface they just growing along the height. If you recollect basically the example that; you have seen for the case of germanium on top of silicon 1 0 0 surface.

You remember even when we increased the coverage whatever you have seen was basically that islands but they were growing basically in this height. So, that is some kind of island growth. And of course, if you increase the coverage very high then you start to see the first layer is getting connected. But nonetheless the overall nature of the surface would always look like that you have basically islands. Now you see we have a problem here that if you want to basically create the atomic layer deposition you need to basically also understand the type of growth. Therefore, you basically see that this type of understanding is quite important what is the growth itself? So, here you can see that the second type of growth is actually something known as island formation or is generally known as Volmer -Weber. So, that is a type of growth which is generally known as island formation. Now there is something interesting. So, there is another type of growth which is actually known as the layer plus island growth. So, now there is something else called layer plus island mode. So, what is this layer plus island mode? So, that one is generally known as Stranski-Krastanov. That is again the people who contributed in understanding this kind of epitaxy. Then what you see is that in the lower coverage everything looks same. But in the one monolayer coverage you first see that there is actually an island that is formed. So, there is a complete coverage of the monolayer and on top of the monolayer then you start to form basically islands. So, that means when the coverage is increasing you first form a monolayer and then on top of it or maybe after second monolayer you would find that always it forms an island. So, that is interesting. So, this is basically some kind of a mixture of the island and the layer type of growth. So, that is the whole point here that you can see that when you just deposit the atoms on top of another material it does not mean that it always grows like layer-by-layer. Layer-by-layer is something very important or something essential at the end because you know that finally you want to have like a proper hetero epitaxy where I have a perfect interface between two different type of materials but you see now there is a problem. So, depending on the material that you choose and you will also see that depending on the different type of interactions or energies that control the growth would leads to this kind of different type of growth generally known as the layer-by-layer growth island formation or so something known as layer plus island growth and so on. So, in the next slides we will try to understand each of these growth modes in a greater detail.

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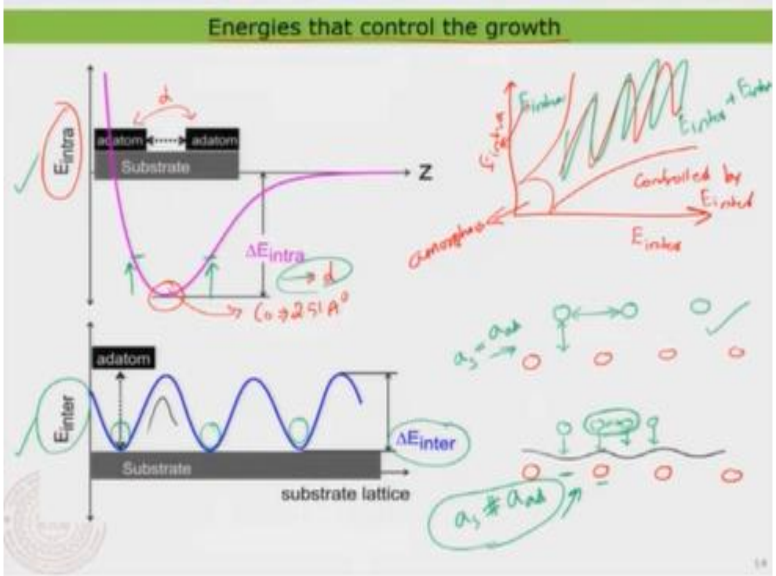

Energies that control the growth

But before that let me recollect the energies that controls the growth. This is quite important to first understand. Now you remember this periodic type of energy that that we basically have discussed when something adsorbs on top of a surface. So, this comes from the adsorption energy itself. So, I will just recollect it one more time. So, remember that you have a kind of lattice.

So, this is just the top layer looking from the side and I am going to add an adatom on top of it. So, just having an adatom here which is actually just interacting to the surface like that, but I have already told you it is not necessary that all the time the atom is basically adsorbing on top of a void side, it can actually adsorb at any site. So, for example the atom can basically adsorb at this point, the atom can also adsorb at this point here. But of course, the top side is normally the least energetically favourable and the so-called void site is actually the most stable site. So, therefore if you look at the energy profile of the adsorption of the atoms itself then what you would find is that there is a periodic way the energy itself looking like. So, that means here I have the highest stabilization or highest adsorption energy and at this point I have the lowest adsorption energy. So, that is basically something we have discussed. And that is exactly what I have drawn here in this diagram here which is basically a bit exaggerated in the y axis just for understanding it in a more clear way. But now you see that when we have many-many atoms that are actually sticking on the surface. So, let us assume that I have atoms sticking on the surface in this fashion. Now the point is that when the atoms are actually attracting to the surface it also should basically interact between each other. So, that means there is an adsorbate surface interaction and there is also something known as an adsorbate-adsorbate interaction. The adsorbate-adsorbate interaction also been captured within the so-called adsorption energy that we have talked about not really. So, that is what we want to look in detail. So, right now for just the understanding purpose I am going to call the interaction energy between the adsorbate atom and the surface to be E inter. The E inter is basically just saying the inter adsorbate surface interaction. Just for the understanding, and now you know that when the atom is basically absorbing on a very suitable site the adsorption energy is the maximum and if it is adsorbing on a non-suitable place, the adsorption energy is the minimum. So, typically the depth of this so that means the delta E inter or the difference itself is basically just telling you which adsorption site is the most favourable. So, you can see now the delta E inter is basically the highest for the so-called void site and the least for this place so, for the top side. So, that basically means that whenever you put an atom on the surface, the atoms are always going to get absorbed at these sites and that is basically the so-called void site or the site which is having the highest adsorption size. So, this could also be a vacancy site or a stepped or whatever but always the one with the highest coordination.

Now the problem is this that the moment you start to increase the coverage. So, this is basically the situation at very low coverage. But the moment you start to increase the coverage even you see below one monolayer in the previous slide you have already seen that you can already start to form the island. The island formation already represent that the atoms within the adsorbate layer are also interacting with respect to each other. So, that basically means we need to now understand the inter adsorbate interaction. So, that is something also we need to actually include in it. Now the question that you ask what should be the type of representation for the inter adsorbate interaction? So, I am going to represent it again using a simple potential energy diagram where I am just going to call the distance along this here, this is basically this distance is nothing but the adatom-adatom distance. So, this distance d is actually represented along this axis and that is actually the reason why I am calling it as z because I am just calling the z as actually the axis along which the atom is going to the surface, it is not extremely important at this case. Now you see the adatom and adatom are basically interacting. Now the intra interaction so that something I am calling it as E intra just to distinguish basically.
So, the intra interaction between the adatoms are actually also stabilized by some kind of a potential energy diagram where the minimum basically represent the most stable distance between the two adsorbate atoms. If you would take cobalt for example in the bulk you would find the cobalt atoms are actually spaced at 2.51 angstrom. So, this is basically for cobalt it would be something like 2.51 angstrom for cobalt.

That is actually some kind of an equilibrium adsorbate-adsorbate distance. So, that distance is basically something that you would find in the bulk of a material. Now you see that the moment there is actually now a combination between the adsorbate-adsorbate interaction and the adsorbate surface interaction. That is also something I have told you. If there is a huge mismatch between the lattice constant of the surface. And interface of the surface atoms and the adsorbate lattice then what happens is basically that there is a huge competition between the adsorbate-adsorbate interaction and the adsorbate surface interaction. Why should that be? Imagine a situation again that I have here the surface arums like this I place. And if the lattice parameter or the bulk lattice of my adatom is exactly matching with that of the surface then I would basically be able to place the atoms exactly in the most favourable adsorption site.

Where adsorbed on the ‘a of surface’ is equal to ‘a of the adsorbate’. But here you can see ‘a of the surface’ is not equal to a of adsorbate. In this case and here basically you can see they are matching. If they are matching then you can see you can actually just have the best combination of the adsorbate-adsorbate interaction and the best combination of the adsorbate surface interaction. So, that would mean if both are actually matching then the atom would always go to the most stable site but at the same time the atomic-atomic interaction within the adlayer will also be the most favourable. So, in that case both, energy would equally contribute in the final adsorbate layer formation and both quantities would positively contribute to the adsorbate formation. So, that means ideally in this case, I can call that the final absorption energy is actually nothing but a sum of the E intra and the sum of the E intra. That is the case. But now the problem is it is not the case for all the systems that you have been already looking at. You will see in in greater detail how the systems in the real case that you would find that this is something that you are going to encounter most of the time where the surface lattice is not equal to that of the adsorbate lattice. In that case what is going to happen? This contribution that means the adatom-adatom interaction is not going to contribute in a positive way. They are going to actually just contribute in a negative way. That means the stabilization is going to be not controlled by basically both the interactions together and stabilization is only controlling by one of the energy contribution. So, let us look at that in detail. Now assume that this particular case where you have the different type of lattice vectors for the adlayer and the surface.

Now you can see here that due to the fact that the atoms need to basically come to a particular site. They need to either be stretched at the interface or need to be compressed. So, that would means you would basically be this position or at this position. This axis as I have already told you that is actually the axis which controls the distance between the adatom. So, at the interface if the atoms need to be stretched. And then placed at the favourable adsorption site then you can see that there is actually this much amount of de-stabilization in terms of the E intra or if you have the atoms to be actually just pressed together in order to accommodate the adatoms on the most favourable adsorption site. Then also you can see that the adatoms are basically going to regain some energy. So, that means you can see if the atoms need to be compressed or stretched of the adsorbate layer.

Then the total adsorption energy is going to be basically lesser compared to that when the adsorbate adlayer lattice and that of the surface lattice is actually just matching well with respect to each other. That is actually a kind of qualitative summary of that and now you have to basically play with these two parameters to finally form the adlayer itself. Now you will see in the in the next slides that this is not the only contribution, they are also much more complex contribution that are going to come across when you start to grow the layers to a larger thickness. So, this is still valid at a lower coverage which is actually meaning that at extremely low coverage everything is controlled by only this. And as the coverage increases this contribution also start to get involved and when the coverage basically increases to a larger extent there are also few more contributions that are coming. So, we will see that. Now before leaving this let me also just do something like a plot of E inter and E intra. So, I am going to plot along this axis the E inter and along this axis I am going to basically plot the E intra. So, why do I do that if I would basically have a system so when I basically want to prepare an adlayer on top of a surface. I would basically have to look at these two contributions, which of the contribution is basically dominating or which of the contribution is contributing in a way that will control the final geometry or final structure that you form on the surface.

Now let me just show you that if I would basically have everything controlled by inter. So, that means if the adsorbate lattice is actually in well the lattice vectors of that adsorbate surface is just matching exactly with that of the surface, then you would find everything will be controlled basically by the E intra. But if everything is controlled by the E intra then of course you will say that the adlayer itself is formed fully controlled by the E intra.

So, that means in this regime you would basically find that all the adlayers that you form are typically controlled. So, let me just erase this, will be typically controlled by E inter and, in this regime, everything is controlled by this one. But the interesting thing imagine a situation where you have both E inter and E intra are not playing a major role or they are absolutely not matching and that will be a place here. So, where most of the time you will end up in forming an amorphous face because neither E intra is contributing or neither or E inter is actually contributing to the formation or the stabilization of the adatoms on the surface. So, in that case you would basically find that you have basically formed in this region something like non-crystalline or amorphous layer. Now in this region here everywhere you can still form something. But that is the region where you have to now take into account both the E inter and the E intra. So, they are going to now contribute with respect to each other and then you would basically form the crystallite. So, that in summary what I want to say is that here everything is going to be E inter plus E intra. And in this regime, everything is E inter and this regime everything is basically E intra. So, that is basically it, and now here at this low regime where none of the energies are actually contributing enough. So, that the adatoms can actually absorb and then form a crystalline surface. So, what in that case happens is actually the formation of an amorphous layer at that site. So, that is the general thing so just keep this in mind so, you need to exercise a little bit further for your own understanding and now you will actually just see a few examples. And then you can actually just understand this, a little better.

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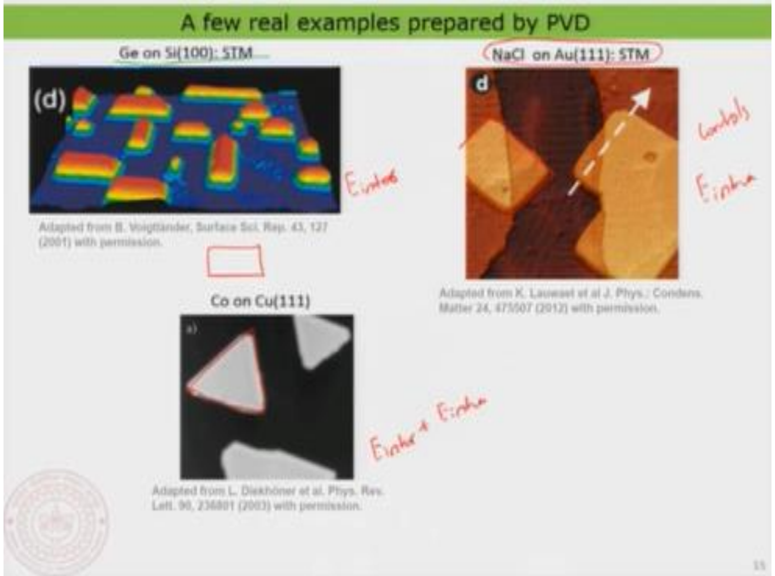

A few real examples prepared by PVD

Ge on Si(100): STM

Adapted from B. Voigtländer, Surface Sci. Rep. 43, 127 (2001) with permission.

NaCl on Au(111): STM

Adapted from K. Lauwaet et al J. Phys.: Condens. Matter 24, 475507 (2012) with permission.

Co on Cu(111)

Adapted from L. Diekhöner et al. Phys. Rev. Lett. 90, 236801 (2003) with permission.

Now if you recollect in the previous class, we have actually just seen this case. This is again germanium on silicon 100 surface there I have told you the symmetry of the silicon 100 surface is being implemented clearly in the formation of the islands itself. So, that means finally whatever you are forming is clearly implying the symmetry of the silicon 100 surface. So, that means these particular islands are completely not completely majorly controlled by the so-called germanium silicon interaction. So, that means the adsorbate surface interaction or you can call it actually the E inter is actually controlling this. Now when you look at the sodium chlorate on gold 100 surface you remember that we have already discussed this in the previous class in this particular case what you find is that the islands that are forming is looking more or less square in shape. So, that means the symmetry itself tells me that sodium chloride is actually just playing a major role in the final adlayer formation. So, that means the surface is not playing a major role, because you do not see the influence of surface in the island formation itself. So, what we want to emphasize here is actually this particular island that means the sodium chloride on gold 111 surface is completely controlled by the adsorbate-adsorbate interaction and in this case it is actually sodium and chloride. It is also very clear and this is a particularly an extreme situation.

You will not find this kind of situations more often, but sodium chloride is a very special situation or an extreme situation where everything is controlled basically by the adsorbate-adsorbate interaction. So, that means the surface actually plays no role at all because also the symmetry as you can see. The symmetry of the sodium chloride is a fourfold symmetry and the symmetry of the surface is actually a sixfold symmetry, you see there is no way you can match the atoms on top of each other. So, that is the most important emphasis here. So, that means here everything is basically controlled by the E intra, E intra controls everything and in this case, it is basically the E inter so that means the adlayer surface interaction. Now you can see here another island which is actually the cobalt and copper 111 surface. So, there you can see the islands are always forming some kind of a triangle and that is a very clear indication that the surface and the interface is basically in registry with respect to each other. And at the same time the symmetry of the cobalt also is matching very well and therefore here it is basically mediated by both E inter plus E intra. So, that is just to give you a kind of understanding how the adlayers are basically controlled with respect to each other.

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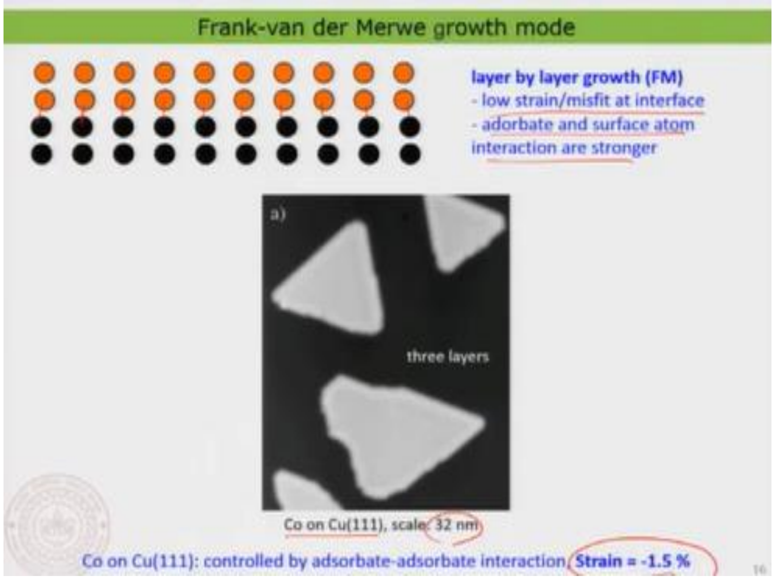

Frank-van der Merwe growth mode

layer by layer growth (FM)
- low strain/misfit at interface
- adorbate and surface atom interaction are stronger

Co on Cu(111), scale: 32 nm

Co on Cu(111): controlled by adsorbate-adsorbate interaction, **Strain = -1.5 %**

Now what we are going to do is we are going to look a little bit in greater detail why we have seen basically the Frank-Van Der Merwe growth or the so-called layer-by-layer growth. So, as I have already told you if I want to basically make a complete layer type of growth then it is extremely important that the strain or the misfit at the interface due to the lattice mismatching between the surface and the interface should be minimal. That is exactly what happens probably in the case of the cobalt on copper 111 surface because the lattice mismatch is just about 1.5% there what happens is basically that each atom is able to match with that of a surface atom. You can see it is almost like a one-to-one epitaxy that is because the mismatches between the lattice parameters are very small. Therefore, they could relax at the interface in terms of the adsorbate-adsorbate distance or they can even do an interaction in this fashion. So, they can basically get accommodated on the surface. So, in this particular case what always happens is kind of a layer-by-layer growth. And that is the example that we have already discussed in the previous case that this is basically the cobalt and copper 111 surface. So, this is of course a very low coverage the total number of layers are just three layers here. But you still see that they actually have the island size is very large. So, that is indicating that they are basically just kind of in a layer-by-layer growth. So, that also means that here the adsorbate and surface atom interactions are basically kind of strong in some sense. But of course, I also told you that some kind of a balance also happens. But at the end the strain that is like very-very small in this particular case and that is the reason why you can basically form this kind of a layer growth. I am trying to conclude this lecture here. But in the next class what we are going to first look is basically the other two different type of growth modes and then we try to understand basically the reason behind the island type of growth and then the island plus layer type of growth. And then we will also look at with the help of a few examples. But in general, you see that everything is basically controlled by the so-called lattice misfit and also the adsorbate-adsorbate or the adsorbate surface interaction. And that is basically controlling everything at the interface, particularly at the lower coverage region because you will see the other contributions playing majorly in the other cases. Thank you very much for your attention and I see you in the next class.