Chemistry and Physics of Surfaces and Interfaces
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Lecture - 14
Energies that Control the Growth of Adlayers

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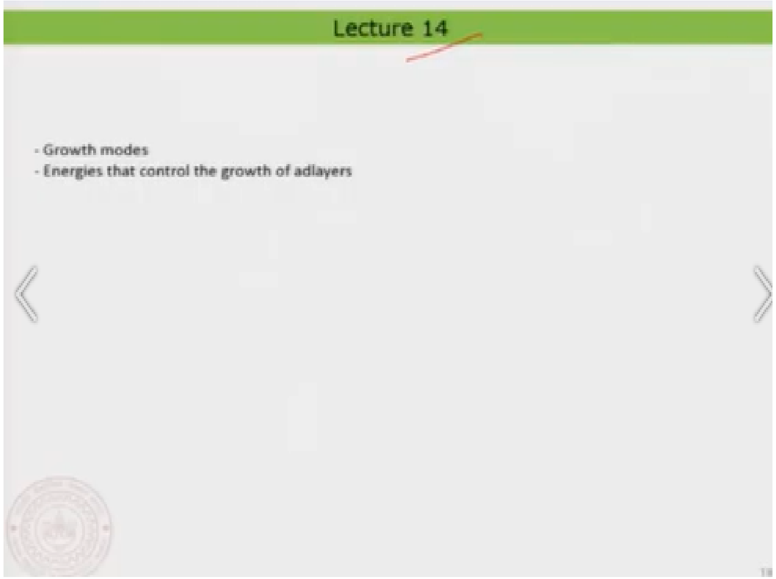

Lecture 14

- Growth modes
- Energies that control the growth of adlayers

Hello everyone, welcome back in today's lecture, lecture number 14. So, we look in this lecture a little bit more in detail about the different types of growth modes. So, we had already had a look in detail about the layer by layer growth. Then we look into the other two different type of modes of growth in further details. Finally, will have a summary of all the different type of energies that contribute to the growth of adlayers at different regimes including the lower coverage moderate coverage and as to very high coverage for example.

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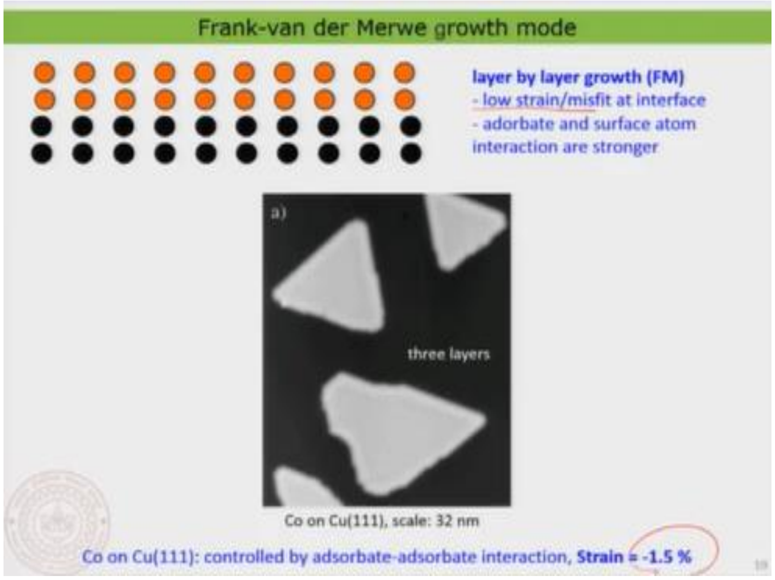

Frank-van der Merwe growth mode

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, so we have already seen this just only to recollect what we said. So, we said in the layer by layer growth what is most important is actually that you need to have a very low interface misfit or strain. That is basically in this particular case as an example cobalt and copper we have already seen that this is actually just in the order of a single percentage. So, that is very important and then the adsorbate surface interaction is also playing a very major role in this case. Therefore, we can basically just get this type of Frank-van der Merwe growth or the so-called layer by layer growth.

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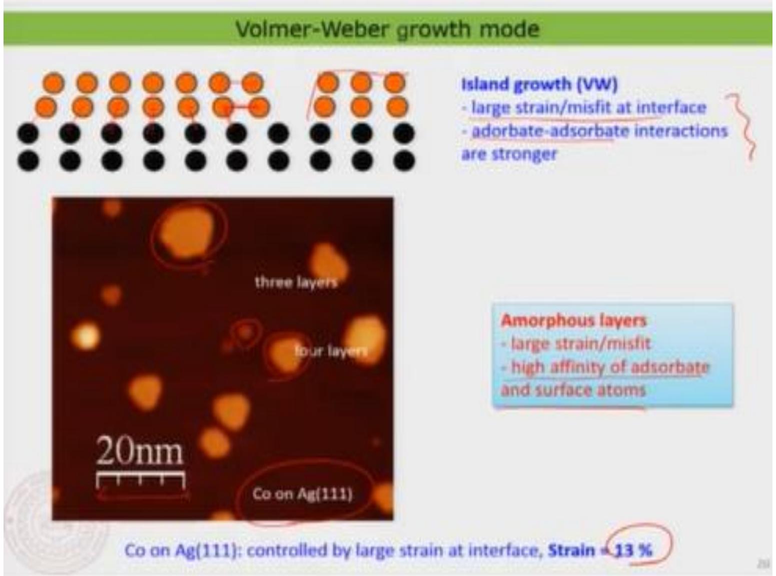

Volmer-Weber growth mode

Island growth (VW)
- large strain/misfit at interface
- adorbate-adsorbate interactions are stronger

Amorphous layers
- large strain/misfit
- high affinity of adsorbate and surface atoms

Co on Ag(111): controlled by large strain at interface, **Strain = 13 %**

Now, let us look at the other type of growth which is basically the Volmer-Weber growth and in that case, you already know that we have basically the island formation. So, what is actually the key behind the island formations and that is something very important that we need to consider here. So, the point at this particular case as you see at the interface or the so-called surface adlayer interface. You clearly see that they are not coming in very good registry with the surface. So, there is a huge misfit at the interface, so that means the large strain or misfit at the interface is actually the first and major reason for the so-called island formation. So, as soon as you see that there is a huge misfit then you clearly know that the adsorbate atoms cannot stay at the most preferred side of the surface. That is a key point here. So, therefore the adsorbate interaction is going to play a major role in this. So, the point is here the adsorbate and adsorbate interactions are also like playing a major role. So, that means it is actually interacting with respect to each other so that means our so-called e intra is actually taking part largely. So, now when the e intra take largely into account, then you would see that there is less relaxation at the interface. That is the reason why you can see that the interactions of the bond formation between the adsorbate and the surface is basically kind of tilted. And if that is the case then you would easily form kind of islands and then as the island height increases you can see that the distance between the adsorbate-adsorbate layer also relaxes back to its bulk lattice. So, that means at the interface the relaxation is actually much lower in this particular case. So, the adsorbate-adsorbate atoms are strongly interacting. So, therefore the relaxation of the adsorbate-adsorbate lattice is very low at the interface and therefore they prefer to grow like an island. So, this is an example here the cobalt on silver 111 surface as we have already seen that the strain at the interface is about 13% and the 13% is actually showing you a very-very huge misfit at the interface. And therefore, you clearly know that they are going to basically only form the islands and you please note here, the scale of this one is about 20 nanometre and each of the islands as you see are actually very-very small. So, this is in the order of 5 you can see here small islands large islands. But all the islands that you form are kind of 5 nanometres in size or 10 nanometre maximum. But you remember in the case of cobalt on copper 111 surface in the previous case we have seen that the islands are actually much larger. So, they were like about 30, 40 nanometre bigger. So, that is actually telling you that the cobalt and copper 111;

Surface is actually just growing in the lateral direction but in the case of the cobalt on silver this is actually basically growing in the z direction that means away from the surface. So, try they try to avoid the surface that is the basic key of it. So, these are the two major points that basically controls the island type of growth or the Volmer-Weber growth.

Now, one important thing here to keep it in mind that you would also ask a question what if I have large strain and misfit and at the same time the adsorbate atoms has a very high affinity towards surface. So, that means there is also a strong adsorbate surface interaction at the same time there is a large misfit. In that case most of the time you basically end up in forming some kind of an amorphous layer because the contribution of the so-called adsorbed surface is basically making them to really go and absorb at suitable sites or strongly letting them interact to the surface and due to the fact that they have a large misfit. So, they are unable to basically just relax at the interface the adsorbate atoms and therefore they cannot grow further and they start to form extremely tiny islands which is just constituting of a few atoms and therefore eventually when the island is formed it would look more or less amorphous in nature. So, that is also an extreme situation that you can consider. But just keep it in mind so these are actually some kind of a qualitative relations at the end of the day everything is basically nicely balanced by all these interactions. So, that is the point. So, you will also see that later there are two more contribution we need to consider and you will see that everything is nicely balancing and the nature does its own way. But for our understanding, we can kind of separate these interactions and then understand them qualitatively to predict which one which type of growth mode you would expect for a given set of material.

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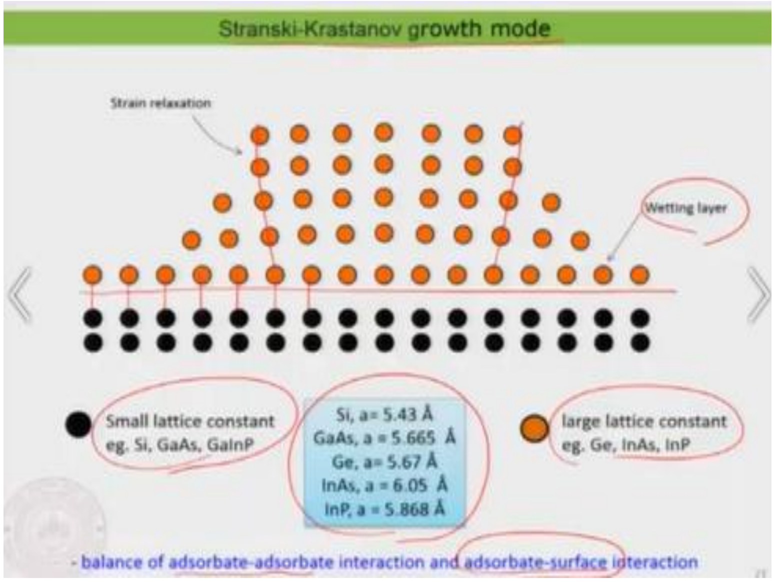

Stranski-Krastanov growth mode

● Small lattice constant eg. Si, GaAs, GaInP

Si, a= 5.43 Å
GaAs, a = 5.665 Å
Ge, a= 5.67 Å
InAs, a = 6.05 Å
InP, a = 5.868 Å

○ large lattice constant eg. Ge, InAs, InP

- balance of adsorbate-adsorbate interaction and adsorbate-surface interaction

Now, the most strange type of growth is basically the so called Stranski-Krastanov growth mode where you have basically the first waiting layer and then you have the island formation. So, what is really happening? So, that is a very special case here. The first layer that is just right at the interface is known as a waiting layer, so that actually means it would just act as a waitting layer. And then on top of the wetting layer you always find island formation.So, the interesting thing here in this particular case you have a nice balance of the adsorbate- adsorbate interaction and the adsorbate surface interaction. So, what happens you can see at the interface as I have shown in this microscopic image here microscopic scheme, every adatom is sitting exactly on top of a surface atom. That means the surface layer the interface layer is extremely relaxed that means at the interface everything is basically controlled by the so-called adsorbate surface interaction. But this is also an interesting point to note here, so even if the misfit between the different type of adsorbate layer and the surface layer is large, they would at the interface relax at a very large extent and they would all atoms would actually just sit on top of the surface and that way you form the first layer. But now the point is since the atoms in the adsorbate layer are more or less relaxed in the second layer what happens, the influence of the surface is actually getting reduced.

That is the reason why I said that there has to be a nice balance between the adsorbate surface interaction and the adsorbate-adsorbate interaction. So, as soon as you have the second third fourth layer and as the layers increases in the z direction the influence of the surface reduces. So, as soon as the influence of the surface reduces then what happens the adsorbate-adsorbate atoms would relax back to their original lattice or to their bulk lattice. And therefore, finally you can see the adsorbate lattice is basically just growing like this. So, it basically just goes like this. Then finally the top layer or the several layers after the interface you can see that the atoms on the surface is more or less relaxed and they would basically reach to the bulk lattice. So, that is an very interesting situation here, what we have where the interface layer would be completely controlled by the adsorbate surface interaction, and then as you grow further then the adsorbate-adsorbate interaction is basically controlling everything. So, this is a nice balance and that is the so called Stranski-Krastanov grow where you have typically kind of a layer mode in the beginning and then it is basically growing into islands. Just for an understanding I have given here, a set of examples and also the lattice parameters or the bulk lattice parameters of different materials. You can see typically you want to form this you can actually just choose different type of material. Materials which are having large lattice constant and materials which are having a small lattice constant. You can basically play with this table and using this table you can kind of create different type of layers and the moment you take actually this lattice mismatch to be the lowest then you would always form the layer by layer. And if you have the strongest misfit then everything is basically going to controlled by either the adsorbate-adsorbate interaction or the adsorbate surface interaction or both together. That is how we get this different three modes of growth and that is something very useful in understanding the generally the multi-layer formation in adlayer or in general the thin films.

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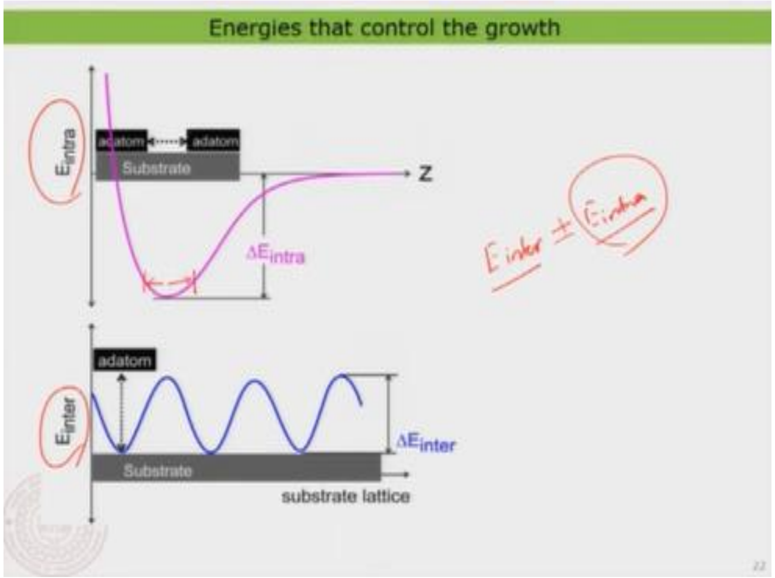

Energies that control the growth

Now, what we want to do is once again understand whether is it the only energy contributions that are going to basically stabilize the or basically controlling the growth of the adlayer on surface. So, let us have a look at the details in greater detail and we will try to understand the other energy contribution. So, these two-energy contribution we have already seen that we have basically the E inter and E intra and in generally both these contributions like the E inter plus E intra is going to contribute equally to the formation of the adlayer.

And in some cases, it will be controlled completely by E inter and, in some cases, it is going to be controlled by E intra or in some other cases it is a nice balance between these two cases. But just as I have already told you that this quantity is not all the time plus it can actually be plus or minus. Why is that? It is the reason because you can basically have also in some cases the atoms being relaxed the adsorbate atoms can actually be relaxed by moving the atoms away or by compressing the atoms compared to their bulk lattice. So, that it means in some cases the atoms can be relaxed in this way or in some cases the atoms can basically be compressed. So, that is actually also by you will see that there is actually called as a negative strain and a positive strain that basically represent either you compress the atoms at the interface or you relax the atoms at the interface. So, depending on the direction of the movement you would basically find that E intra would be more or less plus or negative. That is the reason why they are going to positively contribute to the adsorption energy or sometime negatively to the absorption energy. So, you will see that in in in greater detail in the in the next slide.

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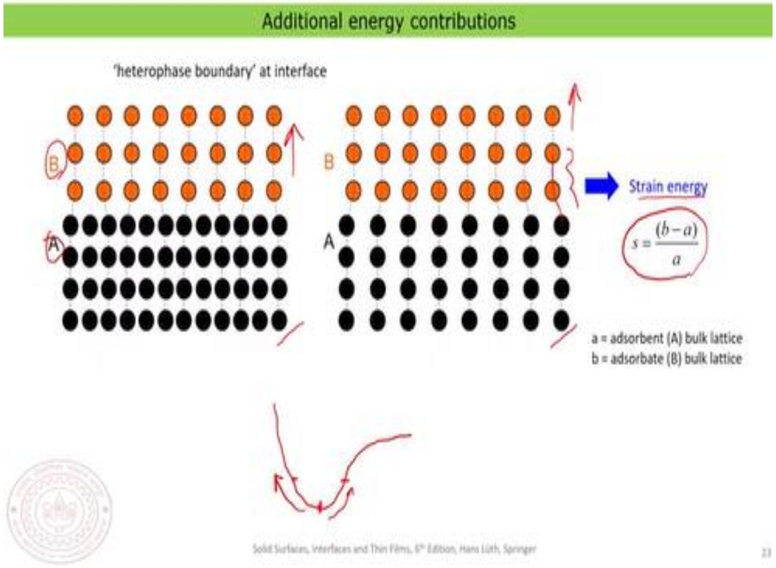

Additional energy contributions

'heterophase boundary' at interface

$$s = \frac{(b-a)}{a}$$

a = adsorbent (A) bulk lattice
b = adsorbate (B) bulk lattice

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So, now let us have a look at this energy contribution and its influence on the formation of multi-layer. So, that means when I grow my adsorbate layer along the z direction how does these energies particularly the strain energy, so that is formed at the interface how does it basically just vary as the growth occurs. So, here again A is basically the surface and we represent the adsorbate layer and I have here marking two different situation the first one where the lattice mismatch is very- very large. Then the second case where you can see the lattice mismatch is basically moderate. The lattice mismatch as we have already discussed in the previous slide. We can basically calculate it using this formula where we need to know the bulk lattice of your surface and also the bulk lattice of the adsorbate. Now we know that the strain energy at the interface can basically be contributed in two different ways and if you look at the potential energy diagram of the adsorbate-adsorbate interaction. So, the typically the adsorbate-adsorbate distances are the equilibrium distance and they would like to reside at the equilibrium distance. But, depending on the strain and the rearrangement of the atoms at the interface, so you can basically have either a situation where the adsorbate-adsorbate atoms are stretched apart or they are basically compressed together. So, these are the two possibilities and then the distances will basically be either a compressed situation or an expanded situation.

But now this strain energy is mainly at the interface. So, this is basically at the interface and as you grow along z direction so that means when the multi layers are formed this strain energy would basically decrease. We will see the variation more systematically in the next slides and you already see that the interface there are variation in the atoms and their arrangement and that basically because at the interface you have the highest strain energy deposited then as the layer thickness increases the energy basically decreases. But now the interesting thing is that of course you cannot have a very large strain energy, because if the strain energy is very-very large then of course it negatively contribute to the adsorption energy. In that particular scenario when the strain energy is very-very large something interesting occurs at the interface.

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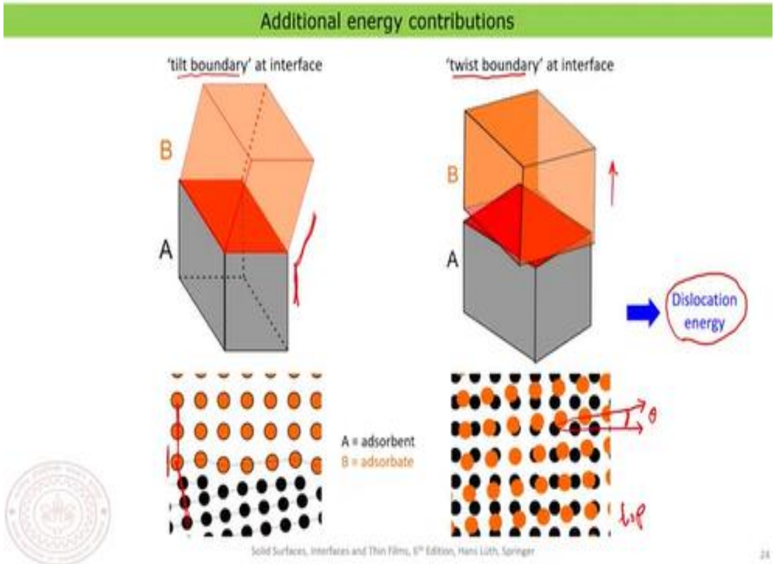

Additional energy contributions

'tilt boundary' at interface

'twist boundary' at interface

Dislocation energy

A = adsorbent

B = adsorbate

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That is actually an interesting scenario known as a tilt boundary. So, in this case we would call it as something known as dislocation energy or dislocation. It is not anymore compression or expansion of the equilibrium atomic positions of the adsorbate, instead what happens is that their orientation of the latitude would basically just change. So, here for example I have the surface lattice orientation and this is the orientation of the absorbate. And you can also see that same in this sketch here which is actually a microscopic structure or the atomic level picture a qualitative picture where you see that the orientation of the lattices are basically changing. So, in this case which is quite an interesting case where of course a lot of changes are occurring at the interface. But as you grow higher and higher the changes are very-very minimal and that is the interesting aspect about the tilt boundary. Similarly, one more scenario can occur. If the strain is very large that is actually known as a twist boundary. So, where the lattice parameters or the lattice orientation of the bulk surface and the adsorbate is basically changing. So, if this would be the orientation of the surface lattice and if this is the orientation of the adsorbate lattice and then you can see basically there is an angle theta between the lattice vectors of this surface and the adsorbate. So, this is obviously at top view right at the interface and now since this tilt boundary or the twist boundary is actually the changes are there at the boundary but as the layer the growth increases in the z direction the changes would become minimal and minimal. And that is the reason why this interesting scenario occur at the interface. If the strain energy is basically very-very large and that would be that we token it as a sort of dislocation energy either a tilt dislocation or a twist dislocation energy. We will see the details in the next slide.

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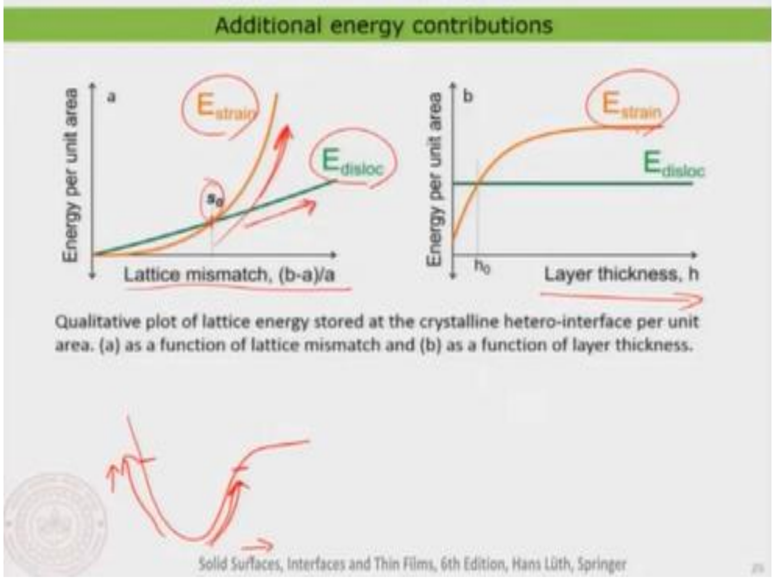

Additional energy contributions

Qualitative plot of lattice energy stored at the crystalline hetero-interface per unit area. (a) as a function of lattice mismatch and (b) as a function of layer thickness.

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Let us have a look at the qualitative energy contribution from both these cases. So, if you would plot basically the energy per unit area as a function of lattice mismatch. So, where again b minus a by a so that is actually the lattice parameters of the adsorbate minus the lattice parameter of the surface divided by the surface. So that is basically the lattice mismatch and if you look at the energy contribution so you are basically that much energy is being stored at the interface because it is a positive energy that you deposit at the interface. Now of course at a very low lattice mismatch. You can see that the energy that you deposit at the interface is very-very low. So, you do not almost do anything. But if the misfit increases then what happens is actually that the energy exponentially increases like this. The energy contribution that you basically deposit at the interface is actually exponentially increasing to a very high amount. So, that basically means that you cannot keep on doing increasing the strain so that actually going to mean that there is going to come some particular point where everything is going to actually just do something differently. So, now here comes actually the dislocation. But the interesting thing about the dislocation compared to strain is that, so the strain would basically just compress or relax things. So, there is actually a much more higher energy contribution coming from this strain field or the so-called strain energy that you deposit at the interface. But if you look at the dislocation it is not like that. So, that is actually either you tilt the interface or you basically rotate. So, that means the energy that you deposit due to the rotation or tilting of the surface with respect to the adsorbate is basically much less. And that quantity kind of goes linearly with the lattice mismatch. So, now something interesting happens at this point called s 0 which is actually some kind of a critical value of strain above which the surface actually not trying to relax the adsorbate-adsorbate layer is not getting relaxed at the interface, it is instead starting to tilt or to rotate basically. So, that is something interesting. So, that means if the strain is basically increasing so that means if the strain at the interface is very-very high the atoms in the adsorbate lattice will not just relax. The point is very simple, if you look back again to the potential energy diagram of the adsorbate-adsorbate distance and the potential energy, you would find that I cannot actually push the atoms all the way up here. If I have to put a large strain, if I want to accommodate a large strain at the interface what I have to do is I have to take the atoms further away very far away or I have to push the atoms very close. That is not possible because you can see that is going to basically contribute in a in a negative way to the total energy gain of the adlayer formation because you are actually having a very-very high strain at the interface. So, therefore what happens? If the atoms need to relax and accommodate a large strain then, what the adsorbate layer does is that they start to basically rotate with respect to each other or they start to tilt a little bit in order to accommodate this large strain. So, that is the relation between the E dislocation and the E strain. You can see after a certain critical value called s 0 that is actually the strain. The system would choose to go along this path and not along this path. That is the interesting aspect of it. It is better for the system the adlayer to grow with some kind of a rotation at the interface or some kind of a tilt at the interface than relaxing the atom to a larger extent at the interface. So, that means you cannot have you are going to get end up in kind of a different type of geometry of the interface as soon as you work with materials having very large strain.

Now, let us have a look at the energy per unit area again as a function of the layer thickness and if you look at the layer thickness the E dislocation is definitely independent of the E dislocation. But the E strain is basically dependent definitely on the layer thickness. Because we know that the strain itself is related to the relaxation of the adsorbate atoms at the interface, that would means if you are basically just growing more and more layer on top of each other. Then the influence of the surface is basically decreasing and therefore you can say that the strain energy that you store at the interface is also getting relaxed because as the thickness increases the atoms at the adsorbate layer also start to basically relax. So, that is basically the relation between the E strain and the E dislocation energy.

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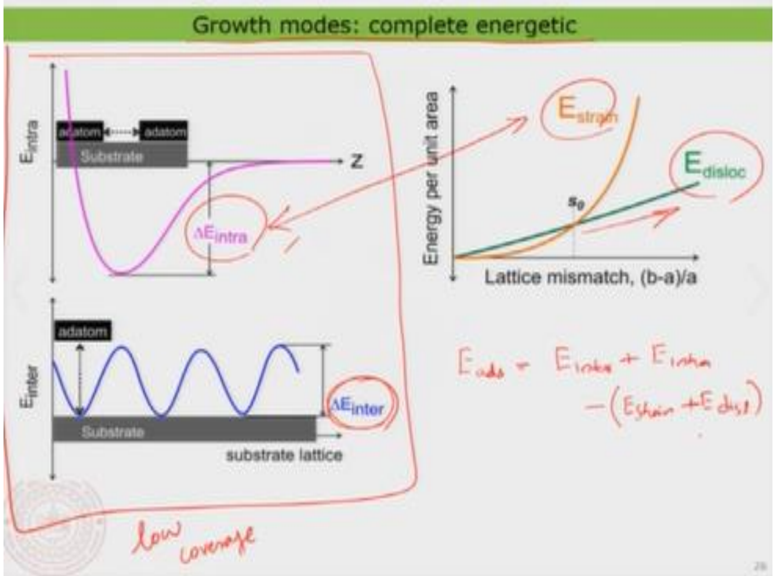

Growth modes: complete energetic

$E_{ads} = E_{intra} + E_{inter} - (E_{strain} + E_{disl})$

low coverage

Therefore, the final contribution of the energetics in the growth mode is basically coming from the E intra the E inter and also the E strain and the E dislocation. Well, you will see that the E strain and the E intra are closely related as I have already told you. But at the end of the day, you can still treat them slightly differently because I am going to treat that this part as for a case of low coverage.

And everything together in this slide is basically going to be considered for a general place or also for actually case where you have a several layer growth. Now, here you can see clearly the picture, so what you are going to gain here is an understanding about the energies that is contributing to the formation of the different type of growth and their influences. So, as I have already told you that this is strongly the so-called adsorbate surface interaction. And this is basically the adsorbate-adsorbate interaction and here is basically the kind of strain that you generate at the interface due to the fact that the adsorbate atoms would relax at the interface. And if the strain is actually increasing very large then instead of like relaxing the atoms at the interface what the system does is actually the system basically kind of do a dislocation either by rotation or by tilting the interfacial layer with respect to each other.

So, therefore you finally if you want to call something like an E adsorption energy of the atoms at the interface, you can generally call it as a sum of E inter plus the sum of E intra and you may also just call that this can actually be also negatively contributed by the E strain field plus the E dislocation part. So, generally at the lower coverage everything is going to be controlled by the E inter. And the E intra and as the coverage increases you have to also consider the so-called strain field and the dislocation energy and they are also going to negatively contribute. So, always your point is that this need to be as low as possible. If this quantity is actually as low as possible that is what the requirement is then you can actually just write down the energy expression for the adsorption energy as a simple sum of E inter and the E intra. They can actually be also plus or minus as I have told you and then you can basically just write down the entire adsorption energy. So, that is a qualitative description. Of course, one can quantitatively understand this E adsorption by doing as I have already told you the so-called desorption spectroscopy one can then understand this more clearly. But nonetheless the energy that you obtain from the thermal desorption spectroscopy does not tell you the real contributions to the total absorption energy. But this would tell you qualitatively what are the type of energies that are contributing to this E adsorption. I hope you understood and then we can also have some discussion in the tutorial. So, where you can actually also understand the things more clearly and get to know it in a greater detail. So, thank you very much for your attention and I see you in the next lecture.