Chemistry and Physics of Surfaces and Interfaces

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Lecture - 15
Kinetic and Thermodynamic Control in Adlayer Growth

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Lecture 15

- Understanding interface with moiré pattern
- Kinetic and thermodynamic control in adlayer growth
- Molecules on surfaces

So, hello everyone. Welcome back to lecture number 15. In this lecture we will try to understand some interesting aspect about the interface using Moire patterns as I have promised in the previous class. We look and try to understand some interesting aspect. And then we will also familiarize while we work on this particular example will also familiarize something called the kinetic and thermodynamic control and then we will now switch at this point also to new type of interfaces called molecules on surface. So, far we have been talking about atomic adsorbates on surface. Now we will also look at molecular adsorbate on surface and there generally first we start with the preparation methodology and then we will go on in understanding the details of the molecules and surface interface. So, that also I will try to cover in this particular lecture.

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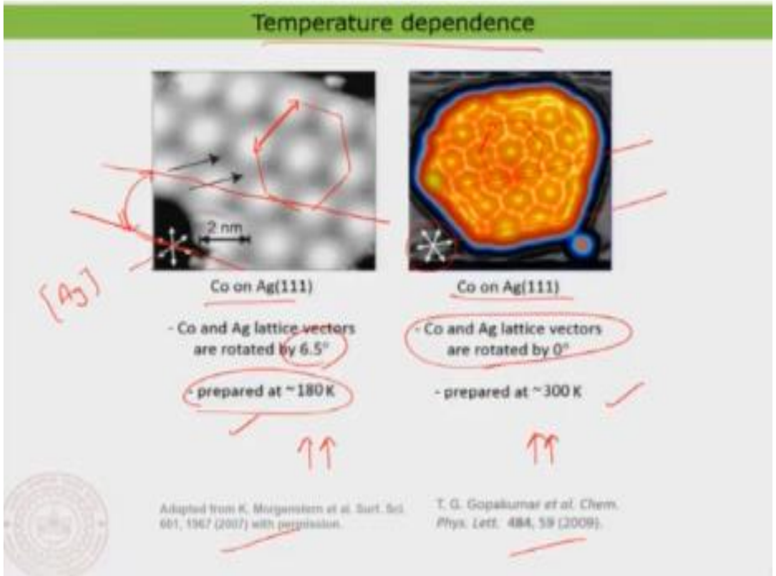

Temperature dependence

Co on Ag(111)

- Co and Ag lattice vectors are rotated by 6.5°

- prepared at ~180 K

Adapted from K. Morgenstern et al. Surf. Sci. 601, 1967 (2007) with permission.

Co on Ag(111)

- Co and Ag lattice vectors are rotated by 0°

- prepared at ~300 K

T. G. Gopakumar et al. Chem. Phys. Lett. 484, 59 (2009).

So, let me just get back to the same example that we have talked about before the cobalt on silver. But you remember that I have showed you when we were discussing about the Moire pattern itself.

Two examples of cobalt on silver 111 and so, you can find the details of these examples in these two papers. Please I encourage you to read these papers so, as to get the details. And now what the most important the major point is that the two different things are actually prepared two different temperature. So, that is the interesting aspect about it. So, now what you see is that the overall appearance of the cobalt island on the silver 111 surface looks somewhat similar to you because in both cases you do observe these kind of Moire lattice or the Moire super lattice in both case. In both cases it is looking like a hexagonal lattice as you can see here we can mark a hexagon over it and then also here you can see their hexagonal lattice. But the interesting thing when you look at the islands itself, in this particular case you can see that the Moire lattice and what you are seeing here is this with this double headed arrows indicate the silver lattice direction. So, let me just write it down. So, these actually represent the silver lattice direction. So, that means the compact lattice of the silver 111 surface. So, that means in this particular case so that the second example the Moire lattice and the silver lattice you can see they are actually just having no rotation with respect to each other. And that is what is written here, that the cobalt lattice and the silver lattice are actually aligned with respect to each other.

But when you look at that in the case of the cobalt on silver 111, this particular example you see that this is actually the lattice, the super lattice. And you can see the cobalt the silver lattice is a bit tilted with respect to each other. So, of course is not that obvious in this case like in my drawing. But they are actually just having a rotation and that rotation is about 6.7, 6.5 degrees. So, that means it is clearly two different type of arrangement of the atoms on the interface that is quite striking.

You would have expected basically that when you deposit cobalt on silver 111 surface, no matter what all the time you would have expected to have actually the same type of atomic structure at the interface. But this is strikingly different. That is something interesting because there is actually kind of temperature dependence. What is the difference is that this particular example everything is prepared at 300 kelvin that means at room temperature. And in this particular example everything is done at 180 kelvin that means the deposited surface while you deposit the atoms the surface is actually kept at a very cold temperature 180 kelvin, it is way below the room temperature. And on the cold surface this atoms are the composited. And then you allow the atoms to arrange and form this nice crystalline pattern. That is quite striking.
Let me also just clear this line and probably I can draw it a bit nicely. So, you can visualize this effect. So, you can see that there is actually an orientational difference between that. So, that is more clear you can use a ruler to clearly do that. And that is quite striking. So, the same material on same type of surface at two different temperature you see clearly a difference in the way they actually just arrange.

Now the question that you would ask is it really the way they are arranging differently or is it some kind of microscopic arrangement that is different within the interface.So, that is what we are going to look and how can we understand this. And that is exactly where the Moire pattern can be used because we can actually now there are two interesting parameters here we can measure the so called orientation of the Moire lattice with respect to the surface lattice and also the super lattice periodicity that means the distance between these two dots would be something known as the super lattice periodicity and if you recollect in my introduction to Moire pattern, I had showed you that D which is basically representing the super lattice. And that one is going to tell you a lot about what is actually happening at the interface. So, that is what we are going to do in a greater detail. Let us look at this example again.

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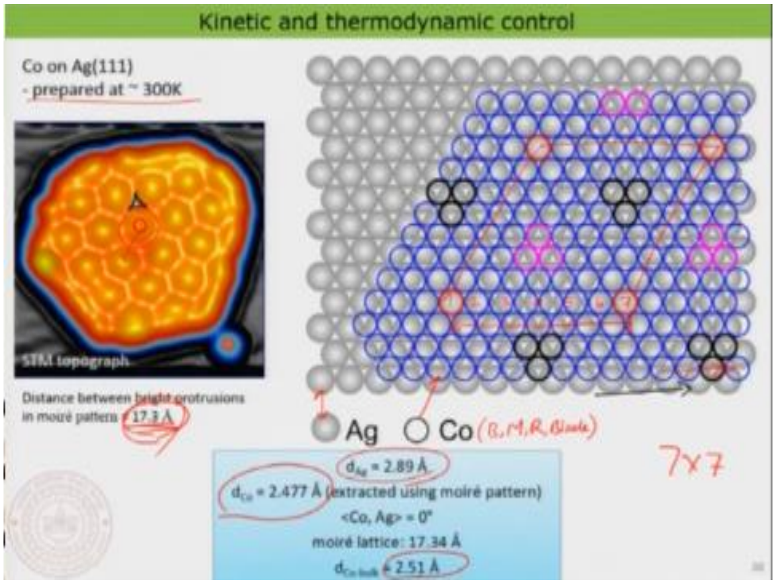

Kinetic and thermodynamic control

Co on Ag(111)
- prepared at ~ 300K

Distance between bright protrusions in moiré pattern: 17.3 Å

d_{Ag} = 2.89 Å
d_{Co} = 2.477 Å (extracted using moiré pattern)
<Co, Ag> = 0°
moiré lattice: 17.34 Å
$d_{Co\ bulk}$ = 2.51 Å

So, this is the cobalt silver prepared at 300 kelvin. Now the distance between these two spots that means the super lattice distance in this case is actually 17.3 angstrom and just you will see in the next slide that this the corresponding super lattice for the other case that means the cobalt film prepared at 180 kelvin, it is about 22 angstrom. So, that means you clearly see a difference in the super periodic lattice.

But now the question again you ask well we have seen for example in other examples of super lattice that if you have a lattice mismatch or if you have a difference in the lattice you would, always should have expected to have the same kind of periodicity in the super lattice because you take two different type of super lattice. Now you keep it in mind that in this particular case the orientation between the silver 111 lattice that means a compact lattice of the silver 111 surface and the cobalt is basically zero or they are basically aligned. And in the other case it is about 6.5 degree. So, that means you would expect basically a difference in the periodicity because there is actually a difference in the orientation of the lattices of the surface and the adsorbate layer. Now what I can do is I can using this parameter and also using the bulk parameters, the bulk lattice distances of the cobalt and also the silver, I can actually generate a model and bring up the so called Moire pattern by a scheme, this is what it is. So, I have here the silver atoms are represented by the light grey atoms and the blue atoms the magenta and the red atoms, red rings are basically representing the cobalt. So, this is basically the cobalt. So, cobalt is either blue magenta or red and black. So, all these are basically the cobalt atoms. Now what I did is basically that looking at the lattice parameter. So, the bulk super lattice parameter which is basically the distance between these two point that means the atom of the add lattice or the add layer is actually on top of a silver atom. So, you can see now if you move along this lattice what you find is that the atoms are basically changing their position and only at about 1, 2, 3, 4, 5, 6, 7 surface atoms. So, it is basically some kind of a seven by seven superstructure. Now this distance is something I obtained from the Moire lattice so, that is about 17.3 angstrom. And then I can basically back calculate what should be the distance between the cobalt lattice because I am basically arranging them.

Now in order to accommodate it nicely on the surface so, I would basically recalculate the d cobalt-cobalt distance and by keeping the d of the silver. So, the silver lattice I am not changing it is basically as it is from the bulk because I am expecting it is a silver surface. So, therefore I am expecting the silver atoms are not relaxing. But I am expecting it is the cobalt atom because it just one layer I am expecting the cobalt atom to relax.And now you find that by slightly adjusting the bulk cobalt lattice as you know it is 2.51 angstrom in by adjusting it slightly to 2.477 angstrom, I am nicely able to accommodate this kind of a super lattice and then finally I can make a 7 by 7 supercell. Now you find that all these red spot would correspond to the red spot in the image and the black and the magenta spots are actually corresponding to this point here.

So, there of course you can see the absorption of the cobalt atom is basically on an HCP site or an FCC side and the atoms at the red point is basically that the cobalt atoms are absorbing on top of an atom of the silver. Now what I am basically doing by slightly adjusting the cobalt lattice by keeping this surface lattice is same. I recalculate or make a model in order to satisfy the experimental parameters.Now you can see of course the silver lattice and also the cobalt lattice are aligned. So, that means their orientation is 0 that is an experimental input and the super lattice distance is also an experimental input and by putting that into account, I can basically just regenerate and what is most important is that I can now recalculate the modification in the cobalt lattice. It is now basically compressed very, very slightly compared to the bulk lattice. So, now keep that in mind, we will get back to the discussion.

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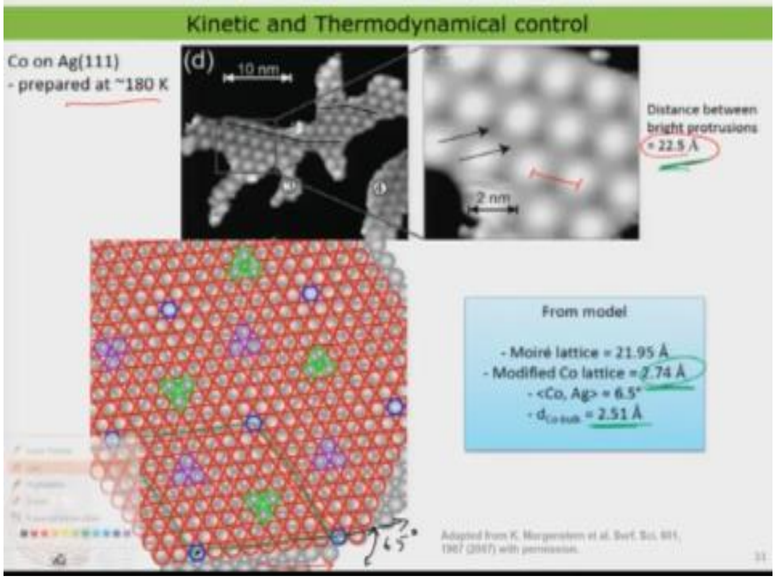

Kinetic and Thermodynamical control

Co on Ag(111)
- prepared at ~180 K

Distance between bright protrusions = 22.5 Å

From model

- Moiré lattice = 21.95 Å
- Modified Co lattice = 2.74 Å
- <Co, Ag> = 6.5°
- $d_{Co\ bulk}$ = 2.51 Å

Adapted from K. Morgenstern et al. Surf. Sci. 601, 1967 (2007) with permission.

Now let us look at the other example that was actually the cobalt prepared at 180 kelvin now something interesting as I have already told you the bright protrusions are actually spaced by 22.5 angstrom that you can precisely measure that is something you can measure here. And that distance is now exact very different compared to what is observed in the other case. Now what I have to do is the exercise is that to regenerate a model for the microscopic arrangements of the atoms, the atomic arrangement at the interface.

Now we need to also keep it in mind that in this particular case the cobalt lattice and the silver 111 lattice is actually oriented by 6.5 degree. So, let us do that. So, now you can see this is my silver lattice and here you can see the cobalt lattice is basically going in this way. So, that means there is an angle between them of about 6.5 degree. So, there is an orientation. Now when you regenerate the model again. So, you have to keep it in mind the lattices are rotated with respect to each other. Therefore you would clearly see that the periodicity has to be different. Now you please look at these blue spots and the blue spots are actually the point where you have an atom of the cobalt sticking exactly on top of a silver. And these spots which are actually the green and the magenta part is the one where you have the cobalt atom sitting at either HCP site or FCC site.

Now with the rotation it is a bit more complex microscopic structure at the interface. You can now clearly generate the supercell as I mark here you can clearly generate the supercell. So, you can clearly mark that supercell and that supercell is basically that to 22.5 angstrom. So, what I am now doing to get this I have to also do a small modification in the cobalt-cobalt distance. So, that modification I do is about 2.74 angstroms. So, compared to the bulk lattice in this particular case what I do is I in order to get this microscopic model correct, I need to slightly adjust the cobalt-cobalt distance. And if I do that I can clearly reproduce the experimental parameters which are the angle between the atomic lattice and the silver lattice and also the super periodicity of the Moire lattice. If that is coming out to be correct the only thing the adjustment that I have to do is the change in the lattice parameters of the cobalt. So, that is quite striking. Why is it striking? Because now you can see to generate this model I need to relax now the cobalt atoms far apart with respect to each other. In the previous case, you recollect I had to compress slightly the distance between the cobalt atoms. But in this particular case I need to basically just relax the cobalt-cobalt distance in order to get the in order to get the microscopic arrangement correct as well as the agreement with the experimental data.

So, this is quite striking. So, now you see that the two different types of cobalt islands that you form at the interface are clearly different. Why is that? Their microscopic arrangement with respect to the surface layer is clearly different. This is what we talk about the microscopic structure at the interface. Although it is the same type of material on same type of material, you see there is a clear difference in the way the atoms are actually arranging at the intermaterials. That also means that the entire growth of the layers if you would actually just now go on generating different layers on the surface this is also going to be clearly dependent on the microscopic structure. You will also see later that the microscopic structure of the atoms at the interface is also clearly influencing the electronic structure. And the electronic structure is clearly something that you are looking at if you want to use these materials in electronic applications for example. So, therefore it is extremely important using the help of this kind of microscopy and empirical models we can clearly understand what is going on at the interface. Now I want to basically just tell you one more interesting aspect using these two particular examples which is the following.

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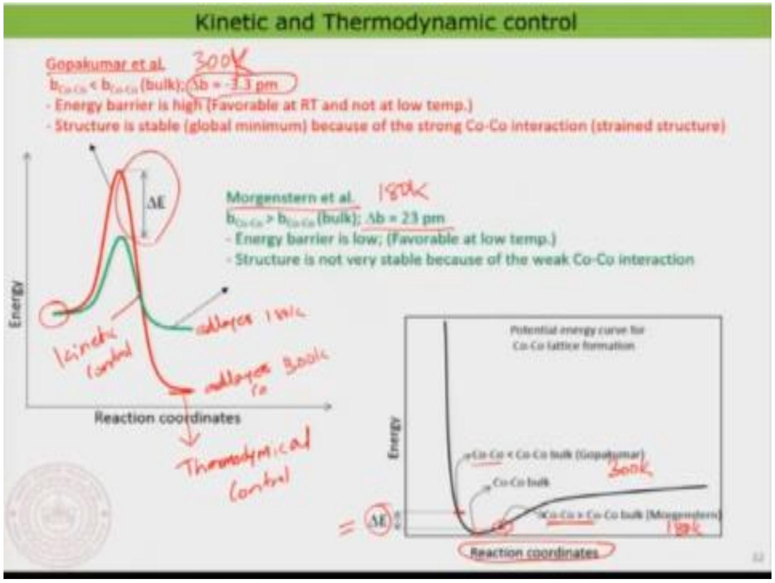

Kinetic and Thermodynamic control

Gopakumar et al. 300K

$b_{Co-Co} < b_{Co-Co}$ (bulk); $\Delta b = -3.3$ pm

- Energy barrier is high (Favorable at RT and not at low temp.)
- Structure is stable (global minimum) because of the strong Co-Co interaction (strained structure)

Morgenstern et al. 180K

$b_{Co-Co} > b_{Co-Co}$ (bulk); $\Delta b = 23$ pm

- Energy barrier is low; (Favorable at low temp.)
- Structure is not very stable because of the weak Co-Co interaction

Now let us take these two examples like the one which is prepared at 300 kelvin and the other cobalt islands which is prepared at 180 kelvin. Now just to put everything in summary, in the first example you can see that there is a compression of about 3.3 picometer of the cobalt cobalt lattice at the interface. In the case of the second example there is about an expansion of about 23 picometers for the cobalt-cobalt distance. Now one would naturally ask which one is the most favourable or the question is actually which one is the most thermodynamically favourable phase or thermodynamically favourable growth. Is it the one at 300 kelvin or is it the one at 180 kelvin? So, the point what is interesting in this case to understand that you can also just look at something known as the potential energy curve of the cobalt-cobalt formation. It is a very schematic model of course it is not really realistic. But just the potential energy surface is quite important. So, that actually shows the cobalt-cobalt distance, cobalt's are approaching at a certain point the cobalt would come to this so called potential energy minima and that corresponds to the cobalt-cobalt bulk distance. Then you can compress them further then the energy shoots up. Now if you look at the example that we have studied, in one case the cobalt-cobalt distance is actually much more greater than the equilibrium distance. And in the other case the cobalt-cobalt distance is basically much smaller than the equilibrium distance. So, what happens is that in this case you would basically just have a very high energy in terms of the cobalt-cobalt compression and that is what is basically represented by this delta E in this case. So, compared to the case of the 180 kelvin so this is actually the case of 180 kelvin and this is the case of 300 kelvin.

You can see that there is between them there is a huge energy difference. Because you can see that the different cobalt-cobalt distances are actually you can see it in the potential energy diagram. So, compared to the; equilibrium position in the 300 case that there is actually high energy than compared to that in the case of the 180 kelvin. So, the influence is this. Now let us try to form the whole assembly. So, imagine that you are actually just starting here. This is the beginning of the self assembly. So, the beginning of the assembly of the adsorbate atoms and now you want to finally go and form actually the adlayer. So, this is the adlayer at 180 kelvin and this is the add layer of cobalt of course at 300 kelvin. Now you see the energy that you need to cross the barrier that you need to cross in order to form the add layer at 180 kelvin is definitely lower than that at the 300 kelvin. The reason is very simple.

You can see here that the cobalt-cobalt distance is basically is much relaxed in in 180 kelvin case compared to that in the 300 case. So, that would basically means in order to pack the atoms in a compressed way you need actually to cross a much larger barrier than the other case. So, that is basically this delta E and the delta E is actually corresponding so, the delta E is in this diagram is somewhat corresponding to the delta E in this diagram. So, that means in order to com pack the atoms compressed on the surface you need to basically cross a large barrier. But if you want to actually have an atom relaxed at the interface you need to cross actually a lower barrier. So, that means at 300 kelvin you cannot form the red the structure as shown in the red curve because the barrier to cross is very, very high. So, therefore what happens when you deposit atoms when you form adlayer at lower temperature?

They would always go to some kind of a kinetically controlled structure than the most thermodynamically favourable structure because as you can see in the energy diagram, this particular case is the most thermodynamically favourable situation. So, this is thermodynamic control and this is basically the so, called kinetic control, thermodynamical control and the kinetic control. So, that means you have a most favourable structure to form which is basically the one definitely formed at 300 kelvin. But to form that you need a much higher barrier to cross. Therefore that structure can only be formed at 300 kelvin and not at 180 kelvin. So, the 180 kelvin structure is actually not the most thermodynamically favourable structure. So, that is the interesting thing about the kinetic and thermodynamical control. So, that also means in general when you do the adlayer formation not only just the different type of energies that we have talked about would contribute, also the temperature is an important factor. So, therefore the temperature at which you deposit the atoms on the surface is also an important parameter to be basically controlled to be considered in controlling the adlayer patterns for example.

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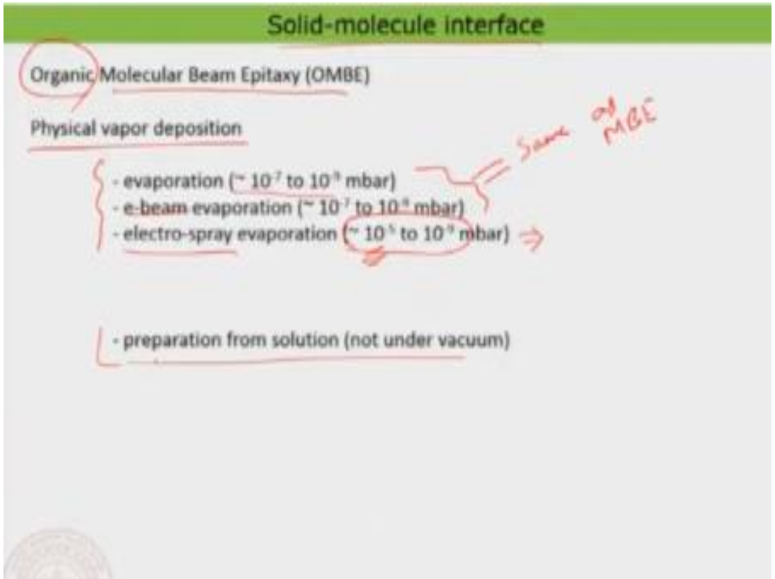

Solid-molecule interface

Organic Molecular Beam Epitaxy (OMBE)

Physical vapor deposition

- evaporation (~ 10^{-7} to 10^{-9} mbar)
- e-beam evaporation (~ 10^{-7} to 10^{-9} mbar)
- electro-spray evaporation (~ 10^{-5} to 10^{-9} mbar)

- preparation from solution (not under vacuum)

Now we move on to the next different type of interface that is basically the solid molecule interface. So, in this class I am going to just give you a very simple preview and then the next class we will look that in greater detail. So, the preparation methodology of forming the solid molecule interface is again something known as Molecular Beam Epitaxy or the physical vapour deposition. But since here we are using organic molecule so, we are actually just doing the so, called Organic Molecular Beam Epitaxy. The organic is basically representing that you are going to now deposit molecules really onto the surface and that is why the so, called organic molecular beam epitaxy or generally known as OMBE. And in the other case you remember this was typically the so called molecular beam epitaxy. The general preparation methodology for the molecular beam epitaxy or the organic molecular beam epitaxy is just the physical vapour deposition. And the physical vapour deposition is done like in the previous case using either evaporation or using e beam evaporation or even sometime you can use something known as electro spray evaporation that is the one which is different compared to the previous case.

So, this is exactly the same as MBE, the molecular beam epitaxy of atoms. And in this case what you additionally need is some kind of an ionization technique. So, what you do is you have a beam of molecules a jet of molecules into a chamber and then you actually just bombard these molecules with some fast moving electrons to ionize these molecules. And once you ionize the molecule you would basically accelerate them using a kind of electrical field like in the case of the sputtering what we have seen is the molecules using electrons. And then accelerate them to the chamber. So, that is also some kind of a very famous technique currently people use. But you can see that due to the fact that you use actually a molecular jet in this case, the working pressure is could also be like very low, a 10 raised to minus 5 millibar compared to the one which is typically the evaporation technique where everything is much more cleaner than in the case of an electrospray deposition. So, that is actually a very popular technique that people use. And then you can also prepare the solid molecule interface also using solution technique that is actually known as clean as the one you prepare inside UHV. But this is also a very economic method because for the physical vapour deposition one of the conditions is that the molecule that you use should actually be sublimable. That means they should actually change from solid directly to vapour without any kind of decomposition or melting and so on. But that is not the case for all the molecule there are many examples of molecules that you can actually convert like that, but not all molecules are favourable for that. Therefore you also just end up in preparing in some cases using the solution based method.

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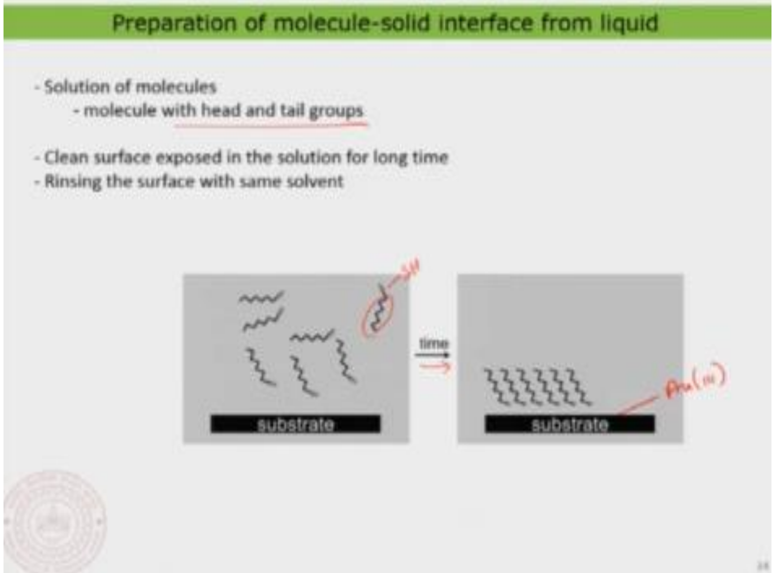

Preparation of molecule-solid interface from liquid

- Solution of molecules
    - molecule with head and tail groups
- Clean surface exposed in the solution for long time
- Rinsing the surface with same solvent

And in the solution based method what you do is also that particularly molecules with this head group and tail group. That means I have an example here where you have an alkyl chain connected to an SH group, ethyl group. So, what you can do is that you can basically just prepare a solution of this particular molecule. And immerse the substrate, the crystalline substrate that where you want to deposit the molecule inside the solution; And then allow them to stay there for some time. And then you would find that all the sulphur will start to link to the surface and then you can basically form a self assembly. So, this is particularly suitable for doing it on gold 111 surface. But even otherwise, if you have strong functional groups like acid groups or aldehyde groups or amine group you can basically use gold as a substrate and you can form this kind of layer or else there is other method which is also by basically simple drop casting of the molecular solution onto a surface, a crystalline surface.

And you can also end up in forming clearly nice adlayers. So, in the next class what we are going to do is we are going to basically just look at the preparation of a few molecules in greater detail. And then we will basically just also try to understand the energetics that controls. Because the energetics of the molecular adsorption is slightly different compared to the atomic absorption because here the molecule is a larger object. And also there are certain interesting interaction interactions the so-called molecule-molecule interactions are different compared to that in the in the atom like adsorbate. So, therefore the case of energetics is slightly different in this case. So, in the next classes we are going to look that in greater detail. But now let me just stop at this point. And I thank you very much for your attention.