Chemistry and Physics of Surfaces and Interfaces
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Lecture - 12
Moire Pattern at Solid- Solid Interface

Hello everyone, welcome back. In today's lecture I am going to discuss first a little bit on the thing that we have been discussing in the previous class. In the previous class we looked at the formation of graphene using chemical vapour deposition. So, I will just give you a few more information about the grapheme formation itself and a few important parameters to keep it in mind.

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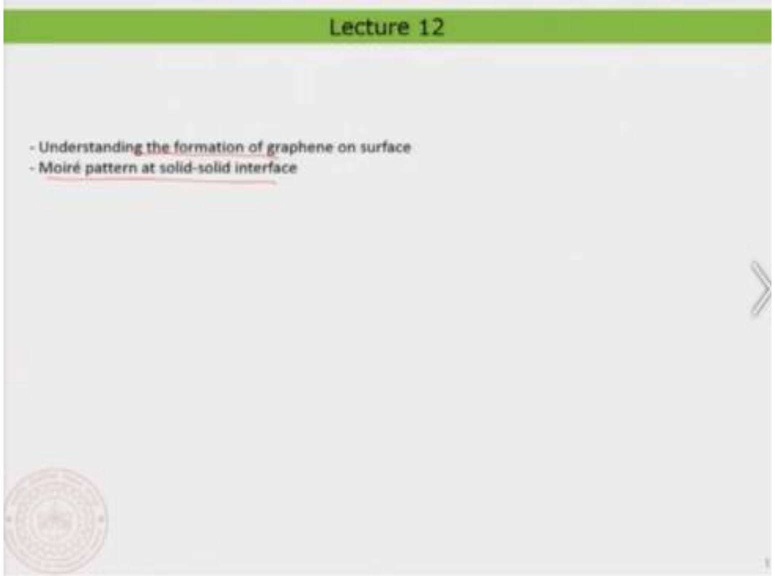

Lecture 12

- Understanding the formation of graphene on surface
- Moiré pattern at solid-solid interface

So, will try to understand that same a little bit further and then we; will come back to the moiré pattern at solid-solid interface. So, you have already seen when we looked into the high-resolution images of a graphene that is formed on platinum 111 surface. We have seen that there are also formations of super lattices and that is typically known as Moiré pattern and will also have a look at that. And then will try to understand a few important aspects about the Moiré pattern itself because that something you will always come across at interfaces. So, just that is also a good indicator for understanding a few important things at the interface so, we will have a look at that in greater detail.

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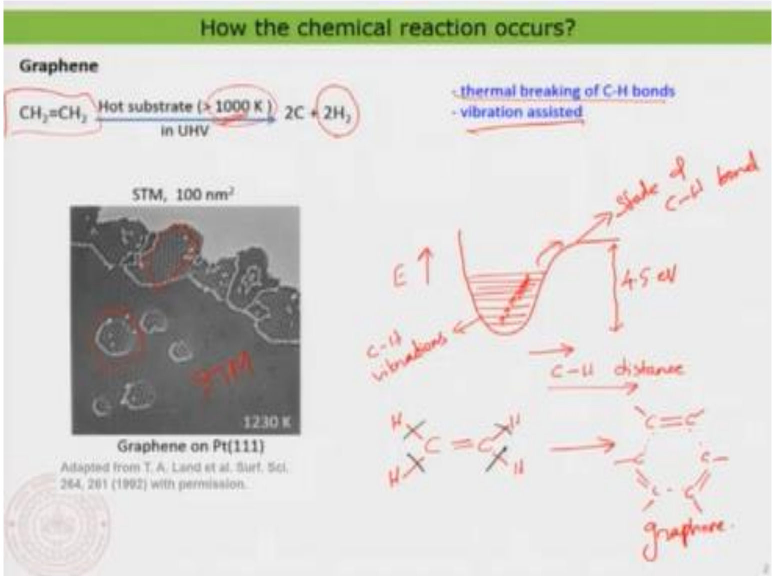

How the chemical reaction occurs?

Graphene

$CH_2=CH_2 \xrightarrow[\text{in UHV}]{\text{Hot substrate (> 1000 K)}} 2C + 2H_2$

- thermal breaking of C-H bonds
- vibration assisted

STM, 100 nm^2

Graphene on Pt(111)

Adapted from T. A. Land et al. Surf. Sci. 264, 261 (1992) with permission.

So, just before we start, let me recollect what we did in the previous class. So, we did basically the formation of graphene and we were discussing basically about this chemical vapour deposition itself. And then in this particular case I said that you take actually ethylene as the precursor and then depositing them on a hot surface about 1000 kelvin, you can basically just form the graphene itself. So, that was basically the recipe of formation. But I want to discuss is basically that if you look into the chemistry of how do you basically break this ethylene and then form graphene. There is an important question that you would ask how do you really dissociate the hydrogen atoms and then you basically form the hydrogen molecules and then how do you really do this. We can try to understand it using a bit of the energy to clearly understand what is going on. And then you also remember that we looked at this scanning tunnelling micro-graph image and then we have seen that we can form nice well-ordered areas or islands of graphene. And what you are seeing here these nice hexagonal patterns are nothing but a super lattice. We will come back to that when we discuss the Moiré pattern. But now let us have a look at how do we really break this bond and how do we really do the chemistry? So, although the temperature is there so, like if you look at you can basically say that this is actually like a temperature induced breaking of C-H bond. But the point is we have already just given a hint in the previous class, if I would look at the potential energy diagram of the dissociation of C-H bond. So, you can basically plot here the potential energy and along this axis you can basically plot the C-H distance in any unit that is no matter.

So, it is like a qualitative diagram. What is very interesting to note here is actually that in this potential energy diagram, if you look at the magnitude of the energy required to break a C-H bond, this is actually in the order of about 4.5 electron volt or in the order of about 100 kilo-calories per mole in the order. So, this is quite a lot of amount of energy and if you compare it just with 1000 kelvin, if you would convert the 1000 kelvin into the form of energy it would be basically in the order of only a few hundreds of mill electron volt. So, that is still way-way below the real magnitude or the energy required to break the bond itself. So, now we have actually to do the chemistry so we have basically the acetylene sorry we have basically the ethylene molecule. So, you have this type of geometry if you look into consideration. So, this is basically the molecule itself and what we want to do is actually what we want to do is basically to break this we want to break basically these bonds.

This is what we want to do. So, now the point is like you can see the amount of energy that is involved in breaking the 4 C-H bonds in this molecule in order to form basically the graphene itself. You have to break 4 bonds. So, that means the amount of energy that you require per molecule is about 18 electron volt. So, that is a huge amount of energy so that is not good. So, then how does this happen on the surface?

Well, we can complete the equation so, you go like that and you can basically get a C double bond C here another C double bond C here and another C double bond C and then you see like by connecting them together you basically form a graphene cell and then you have many-many different cells that are actually going in this direction and then you can basically complete the formation of graphene so, that is what it is. So, what we want to do basically is breaking of the C-H bond. Now the point is when you increase the temperature what happens is actually the C-H bond is started to vibrate. So, that means you are vibrationally exciting all the C-H bonds of the molecule. Now if you look at the; typical ladders or the vibrational ladders that are present within this electronic state of the molecule that is basically represented by this kind of mass potential. So, this is basically representing the state of the molecule, state of C-H bond for example. And so, this represent basically the C-H vibration so, this are actually the C-H vibrations. Now you can see that the energy required to basically just excite C-H bond. So, the vibrational energy required to excite the C-H vibrations are way-way below than actually the actual dissociation energy.

So, if you would basically climb up this ladder like this that means something called as vibrational assisted. So, most of the chemical reactions are indeed happening like that along a given coordinate, this is the coordinate along which here for example the chemistry happens the C-H distance. Along that coordinate you have to basically find out a certain vibrational excitation that would basically help the chemical reaction. So, ideally by climbing up this ladder in small steps you can in fact reach somewhere at the dissociation point and then the bonds are basically breaking. So, like that you create a lot of you break all the C-H bonds and then finally you can kind of make the graphene. Now it is also very important that we do this chemistry on surface if you do not do it on surface there is a high chance that you can also make actually like different allotropes of carbon or you can even make amorphous carbon and so on. So, therefore it is extremely important that you do this chemistry on a crystalline surface because the crystalline surface actually help the C double bond C to actually just have a kind of template, and that template would actually just hold the geometry itself. As you see here it is quite important that the C double bond C bonds are actually present on the surface in a planar manner. Then they would basically do the chemistry nicely and then you can finally form the graphene. So, this is how most of the chemistry or the chemical reactions that you can actually induce on surface and in this particular case for us it is relevant because we can here make actually graphene and that is actually a very well-known two-dimensional material. Now we want to understand a little bit in detail so you remember that when you look into the graphene itself you do see that there are actually the super lattice formations. So, the super lattice formation is something that we have actually called as a moiré pattern so, will try to understand that Moiré pattern. So, this is actually a true effect that happens at the very interface of different materials. It is not necessary that you would find actually in thicker films of material because this is actually a true influence of the interface or the so-called interaction between the adsorbate layer and the very surface layer. So, therefore it is an important thing that you would observe at the interface.

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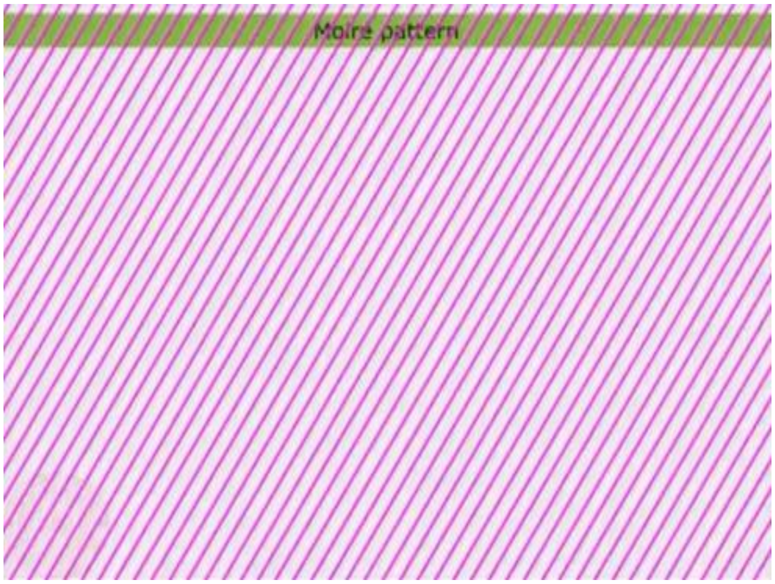

Now, let us look at Moiré patterns. So, what is a Moiré pattern? So, Moiré pattern is not necessary that has to do always with the lattices. It is also something that whenever you have two periodic lattices that are actually crossing with respect to each other. Depending on their orientation and also depending on the spacing between the two different lattices you can actually get super patterns.So, this is actually an illusion that you get because of the fact that the two super lattices or two lattices are actually just rotating with respect to each other or when the two lattices having different spacing for example. I will just show you an example. Here I have a lattice a single linear lattice so I have just lines and what I am going to now do is, I am actually going to put exactly the same top type of lattice on top of it and then I am going to rotate them with respect to each other. You can look carefully what happens that actually forms some kind of a super-periodic pattern inside and that is just due to the fact that these two actually just rotating with respect to each other.

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Now let us look at it so this is what is happening. So, now if you look very carefully, depending on the angle you can see that there is actually a pattern that is actually observed within these two lattices. So, this is exactly what is known as Moiré pattern. So, just due to the fact that two lattices are actually interacting. Now let us look a little bit in detail what happened.

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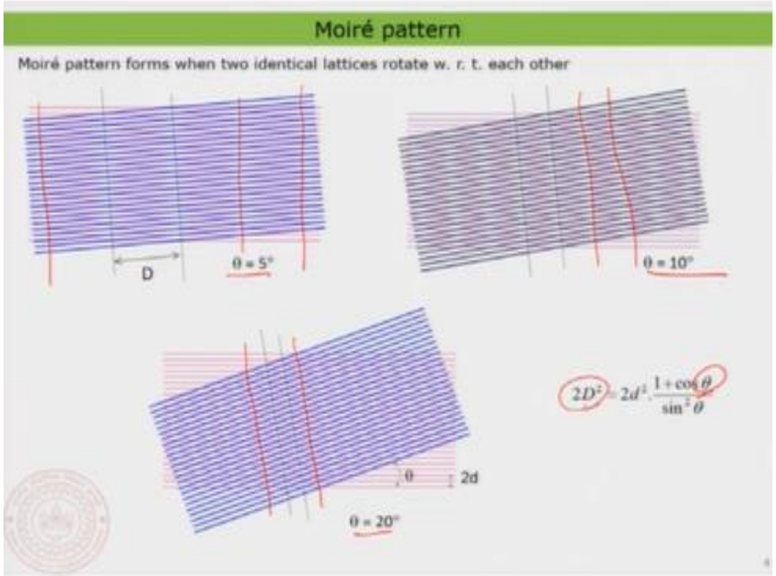

Moiré pattern

Moiré pattern forms when two identical lattices rotate w. r. t. each other

$$2D^2 = 2d^2 \cdot \frac{1+\cos\theta}{\sin^2\theta}$$

So, these are actually like the snapshot of the same what you have seen in the previous animation, where I have actually just, took a snapshot of the rotation of the two lattices at different angle of rotations. Now you see clearly that if the angle of rotation is very large then the super-periodicity that you can now see, that the two dashed lines are representing a kind of super lattice.

You see, I can see a super lattice that is actually forming between the two different lattices. And the spacing between the super lattices are actually much larger and if you now increase the angle, you can see the super lattice is basically just getting smaller and smaller. And if I would make actually the angle much larger then you see that the super lattice is basically getting smaller and smaller. So, that means there is a clear relation between the angle of rotation between the two lattices and also between the super lattice periodicity. So, this D would be the periodicity of the super lattice. So, that also means if you would eventually have the Moiré pattern and if you know the super lattice you would even come up with the angle of rotation between the lattice and you need to also know the distance between the lattices of the original lattice that you are actually using for it. So, you can actually now make it more quantitative.

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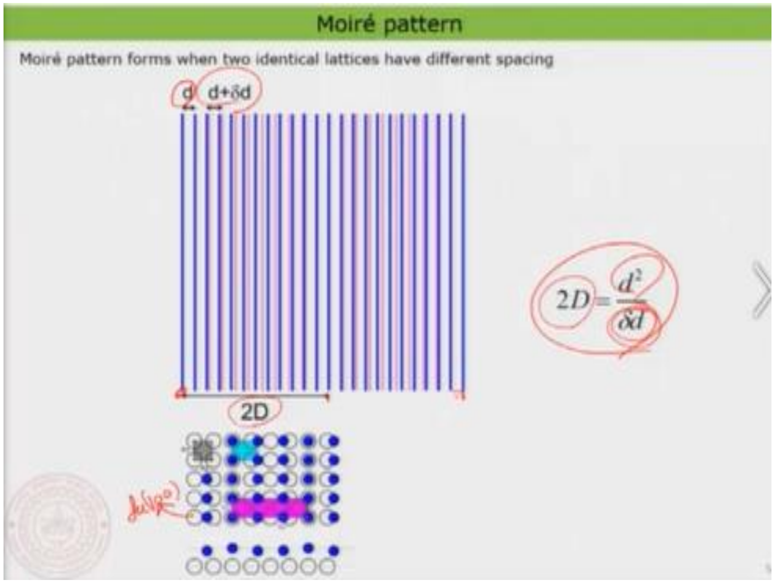

Moiré pattern

Moiré pattern forms when two identical lattices have different spacing

$$2D = \frac{d^2}{\delta d}$$

Now, let us look at a few more examples. So, here for example is the same type of lattice where what I have done is I have taken one lattice and the other lattice that I am going to put on top of each other. I am keeping it actually at the same orientation but I have actually just made the lattice to be a little bit larger compared to the original one. You can see d is the original lattice and the new lattice that I am putting on top of the other is actually having slightly larger lattice parameters between the adjacent lines. Now, something interesting happens.

You can see that in the beginning the two lattices are actually coinciding with respect to each other. But then after a long time about 2D distance you can see that again they are actually merging and after along distance again they are merging. But in between the lattices are not matching with respect to each other. So, you can also now see that in this image you also create some kind of a super periodic pattern with 2D being actually the lattice parameters of the super lattice.

You can also now calculate basically the 2D, if you know the d square and also if you know the delta d. So, what most of the time you will actually find that when we apply that inside our case which is actually the interface case what you want to actually calculate is this delta d and 2D and d are actually something known to you and you can basically calculate the change in the lattice parameters because this is something going to really happen. I will show you an example now quickly. You see this example is something we have actually looked at in the previous case. Here, I have an fcc 100 surface and on top of that the blue atoms are actually kind of an adlayer with a slightly different lattice parameter than the surface. So, this is basically the surface and the blue is basically the adlayer. Now you see that there is actually some kind of a coincidence of this lattice and this lattice point, which means that is kind of a super-periodicity. So, this is something that we have already discussed in the class and when it come to our case that means the solid interface this kind of super lattices are actually very good that something you can experimentally observe. And if you know, the super lattice parameters then you can ideally calculate the change in the lattice parameters between the surface lattice and the adlayer lattice. So, that is why it is actually interesting for us.

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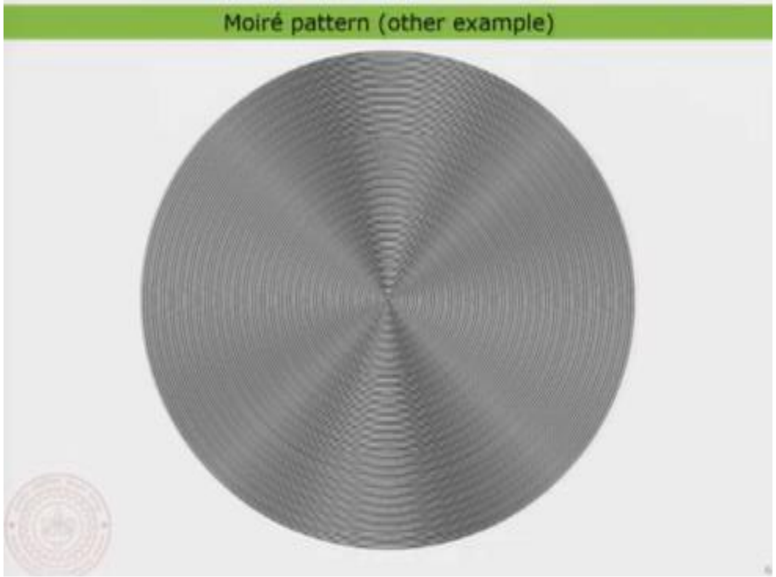

Moiré pattern (other example)

Now, let me also show you a few examples just to see how important it is so, here it is not necessary that the lattices need to be always like lines or grids or whatever it can also be something else. Like look at this this is actually some kind of a circular pattern and I am going to basically just move or stretch the circular pattern on top of another circular pattern. You can see what actually happens.

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Now, you see as I stretch the other circular pattern over the other you can see basically there is a pattern that is emerging in within that. So, there is a nice pattern that is basically emerging so, we can have a look at it one more time you can see that a pattern is basically forming. So, you can create this or we can actually look at a few different ways that you can create moiré pattern is by basically just shifting different type of circular patterns across each other.

You can actually just move them like this and then you would always whenever they go around so they would create basically some sort of some sort of a pattern with respect to each other. So, that is typically what is known as Moiré pattern.

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Moiré pattern (daily life)

Images: wikipedia

Now not only here, Moiré pattern also is something that you would see in your daily life. For example, you see this kind of pattern in in the feather of birds or even in a polyester shirt of you can also see sometime there is actually some kind of a special pattern that appear. For example, here you can see some kind of a pattern that is emerging between two nets that is actually just kept between two different places. So, always when two different kinds of lattices are actually kind of merging or just overlaying with respect to each other you would actually find this kind of pattern. So, this you should not be actually just confused with an interference pattern this has nothing to do with interference. This is basically a true optical effect due to the fact that or a visual effect due to the fact that you basically have two different kind of lattices that are actually just overlaying with respect to each other. That gives rise to something like the presentation of a kind of a new pattern that would emerge. So, you can see here there are kind of strange wiggly patterns it all depends on the type of grid that you use because you know that cloth has actually like a kind of square pattern inside because you have like lines that are going like this threads that are going like that. That makes a pattern for example. So, this is what a Moiré pattern is.

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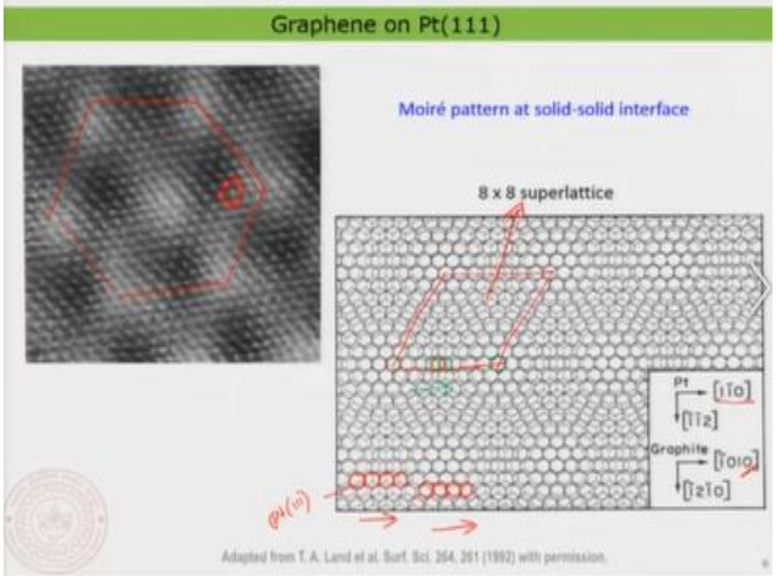

Graphene on Pt(111)

Moiré pattern at solid-solid interface

Adapted from T. A. Land et al. Surf. Sci. 264, 261 (1992) with permission.

Now how are we going to make use of it and that is also something you will see in this example also in a few other examples that I am going to show in the next lectures. So, this is basically the graphene that we have already seen in the previous class deposited on platinum 111, surface. So, I told you already that these spots are nothing but just graphite atoms or the graphene atoms. And you can see this graphene atoms would make a nice hexagon, that is a proof that it is basically a graphene atom. But now the thing is what is this lattice that you are seeing? Which also looks like a hexagonal lattice, what is that? That is actually due to the fact that you have a 111 surface which has again a hexagonal lattice and now the graphene is also some kind of a hexagonal lattice. So, you now take the two different lattices put one on top of the other and then you are actually just going to end up in a super periodic pattern and that is exactly what you are observing it. So, now we can look a little bit inside at the atomic level in a model and then we can try to understand what is really going on. Now, what you are seeing here is actually a model where all the circular you please follow these drawing very carefully. All the circular thing are nothing but the platinum surface, this is the platinum 111 surface the platinum atoms and you can see here everywhere some kind of a hexagonal mesh that is also put on top of the platinum atom and that is nothing but the graphene layer.

Now, most important thing that you note is one of the lattice direction that is actually the 11bar 0 lattice direction we have already familiarized that in the previous class. One of the lattice directions is actually in registry with the lattice direction of the hexagon. That actually means in very simple sense the lattice of the platinum and graphene are kind of aligned with respect to each other. That you can already see here if I would just make this sketch further you would see that the hexagons are actually going in this direction and also you can see the platinum atoms are also arranging in this direction. So, that is very important. Now what you see is somewhere at this part you can see there is platinum atom and the hexagon is basically merging with respect to each other.

You can of course, go now about 8 platinum atom along this direction, 8 platinum atom along this direction. Now you can meet again another hexagon that is exactly on top of a platinum atom. That means only along this direction only every 8th platinum atom and every 8th hexagon of the graphene is actually on top of each other. Now, you see the problem is at many different locations. Therefore, you can see that at this location here, that to hexagon of the graphene is basically just staying on top of a platinum atom. I can actually just highlight it by the red colour, you can see here this is actually the platinum atom and now you can see two hexagon of the graphene is actually on top of a platinum atom. So, that means that point is going to be slightly higher in space and the other at where the platinum atom and the hexagon of the graphene is actually coinciding there, it is going to be a little like it a little bit lower in topography. So, that means if you go along the platinum direction you are going to get a small modulation in the topography. That is actually due to the fact that the atoms along the different directions are having different adsorption site. Now this makes it like that so you can actually now go along this direction 8 times in this direction along 8 times and this direction 8 times in this direction 8 times you basically make an 8 by 8 super lattice. So, that means the observed super lattice, you can also now start counting basically how many carbon atoms are along this and then you would basically find out that exactly. Then now you can see that the super lattice or the moiré pattern that you observed for the graphene on platinum 111, surface is actually just due to the fact that there is actually a super lattice formation and this of course, happen due to the fact that the graphene lattice and the platinum lattice are actually not matching.

The lattice constant of platinum and that of graphene are different. So, of course now that means you have actually two hexagonal type of lattices but their lattice constant are different and therefore they would basically just start to do this kind of a super lattice. So, that is nice.

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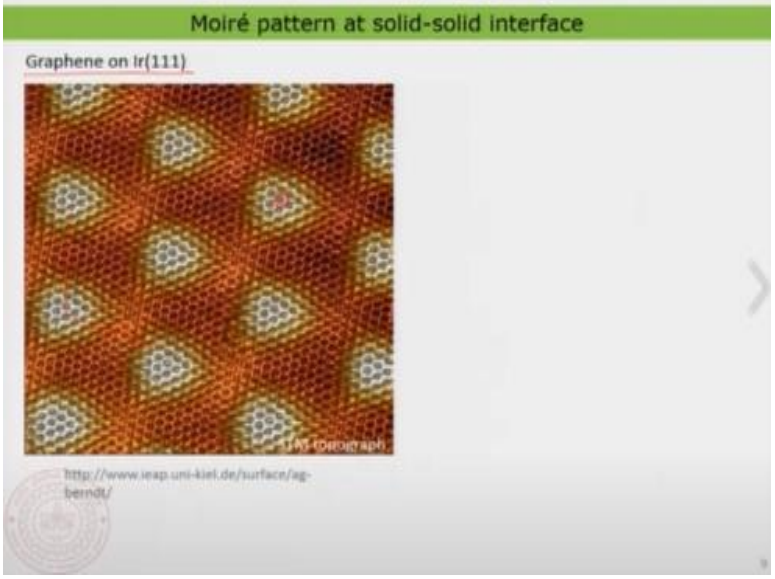

Moiré pattern at solid-solid interface

Graphene on Ir(111)

http://www.ieap.uni-kiel.de/surface/ag-berndt/

You can actually look at a few more examples, so, here again graphene on iridium 111 surface. Let us again a kind of hexagonal surface you can also see nicely the Moiré pattern. So, this actually represent the hexagon of the graphene and now you can see that is forming again a kind of nice super lattice that connects the graphene lattice and they are actually just forming this kind of a super lattice.

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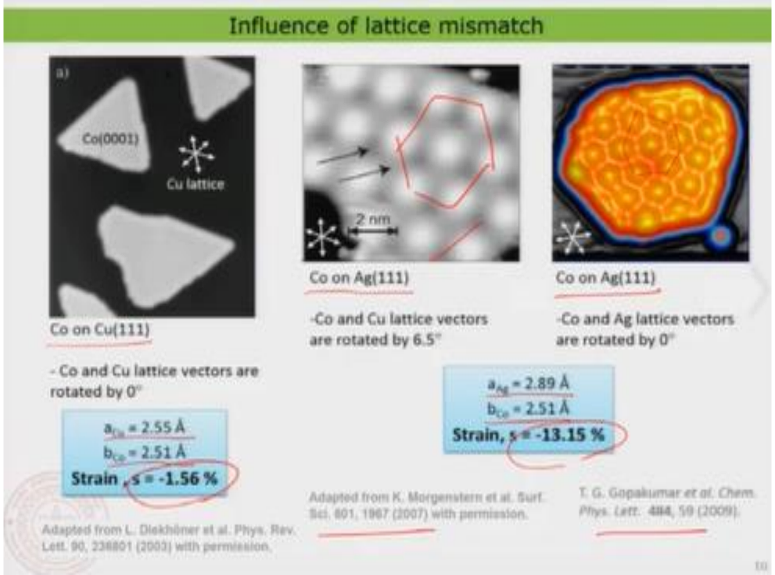

Influence of lattice mismatch

Co on Cu(111)

- Co and Cu lattice vectors are rotated by 0°

a_{Cu} = 2.55 Å
b_{Co} = 2.51 Å
Strain , s = -1.56 %

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

Co on Ag(111)

-Co and Cu lattice vectors are rotated by 6.5°

Co on Ag(111)

-Co and Ag lattice vectors are rotated by 0°

a_{Ag} = 2.89 Å
b_{Co} = 2.51 Å
Strain, s = -13.15 %

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

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

Good, then I just want to show you a particular example of kind of an influence of lattice mismatching. That actually happens in this particular case where you take actually a cobalt deposition on copper 111. So, this particular example I am going to show you is basically to understand the formation of moiré pattern and also the influence of the lattice mismatching for example. So, here, what you think is like the copper bulk lattice is about 2.55 angstrom but that of the cobalt bulk is actually about 2.51 angstrom. So, now if you calculate something like a strain at the interface which is actually given by the difference between the lattice constants of the two participating elements, divided by that of the surface you would basically just get something known as strain.

We will look also in greater detail later in some of the classes. So, you see the strain is about 1.5 %. Now in this case if you now deposit this cobalt on copper, you see that you can nicely see the islands and there is no moiré pattern for example observed in it. But now what I want to show you is actually a case of cobalt deposited on silver. These are two independent examples you can of course understand these examples in greater detail by reading these papers for example. And in that case what you find interesting is that the lattice parameter the bulk lattice unit cell of silver is 2.89 and that of cobalt is actually 2.51. Now you see there is a huge difference between the lattice parameters of silver and cobalt. And then if you calculate the strain, it is about 13%. So, this is a very-very large percentage in the strain that actually causing the interface. So, that means when you want to accommodate the cobalt atoms on silver surface the atoms at the interface of cobalt will have to undergo a very large strain. But that in the case of cobalt on copper it is relatively less. Now you see the interesting effect is basically that you can see a Moiré pattern in this. So, you are basically seeing again some kind of a super lattice in this case. Again, hexagonal in shape the reason is because the cobalt lattice and the silver light is there both hexagonal sorry silver 111 surface has a six-volt symmetry and cobalt is a hexagonal lattice. Therefore, you see eventually you see some kind of a hexagonal moiré pattern. So, this moiré pattern basically will tell you a lot of interesting aspects, so, that we will see in the next class. But what I want to say is that as soon as you have this large mismatch between the adlayer serve adlayer and the surface you are going to observe basically this kind of Moiré pattern. That is actually due to the fact that there is a huge mismatch between the lattice parameters.

Well in the next class I would show you in greater detail that you can also just understand a few more important parameters and details about the interface itself, by using the super lattice that you observe. Otherwise, this is a nice good example in getting an understanding of the influence of the lattice mismatch itself and the formation of moiré pattern. In cobalt case there is a small percentage, so that is that means the cobalt atoms are relaxed at the interface and you do not see any moiré a pattern. So, that means each cobalt atom is actually sitting on top of each copper atom or with respect to each cobalt atom, there is one copper atom. But in this case, there is a super lattice formation. So, that is the reason why you see this kind of Moiré pattern in this case. Good, thank you very much for your attention and I see you in the next class with you further details. Thank you.