Chemistry and Physics of Surfaces and Interfaces
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Lecture - 11
Examples of PVD and CVD

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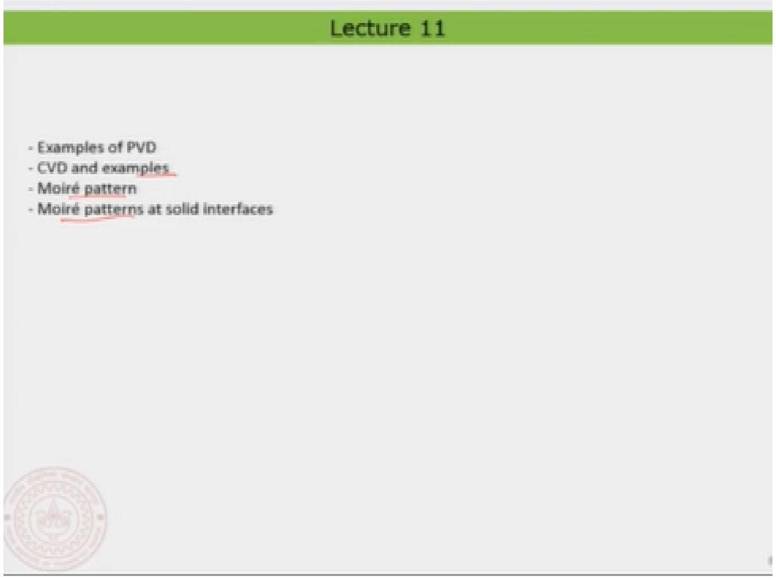

Lecture 11

- Examples of PVD
- CVD and examples
- Moiré pattern
- Moiré patterns at solid interfaces

Hello again. Welcome back to the lectures. Today we have lecture 11. And in this in continuation to what we have been doing in the previous lecture. I will show you some of the examples that are made using physical vapour deposition and will try to understand what are the capabilities and certain aspects of physical vapour deposition itself. And then we will look into the chemical vapour deposition and also familiarize some examples out of that. And then I will also introduce to you something called the Moiré pattern. I think it is better we discuss that when you see that for the first time it is a different and interesting pattern that you normally observe at solid interfaces. Well, that is also observed in daily life you will see basically the examples. And now let us look at the examples from physical vapour deposition.

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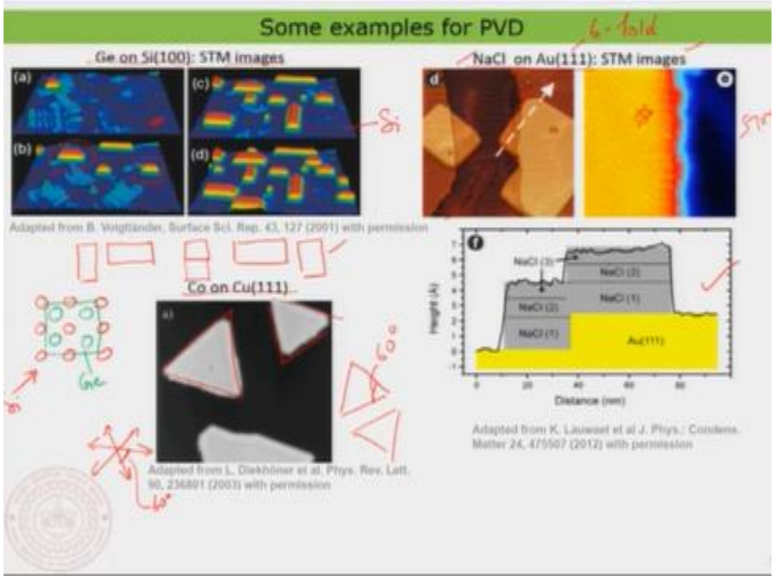

Some examples for PVD

Ge on Si(100): STM images

NaCl on Au(111): STM images

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Co on Cu(111)

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So, in the previous class we have discussed how to do the physical vapour deposition. And I have actually convinced you that in the physical vapour deposition the best methods are actually the electron beam evaporation and also the normal thermal evaporation methodologies. Because with that we can precisely-precisely control atomic layers and you can even control at atomic precision. That is the important fact here. And this is extremely important because if you want to make an interface and you want to apply in technology, you want to also have high reliability of the technology itself. And then of course if you are actually just messing at the interface you are actually just going to have a bad working device. Therefore, it is extremely important that we actually end up in an atomically precise interface. And as we go actually down with the feature size that today you can actually here that the transistor size is actually going down to below 10 nanometre. When you want to have a transistor which is below 10 nanometre it is extremely important to have atomic level precision for the interfaces that you actually make in creating a transistor. We have already seen transistors are actually just created by different types of interfaces and if the transistor itself is extremely small then the atomic level precision is very important. And that is actually the reason why this kind of physical vapour deposition or you will also see the chemical vapour deposition in general are extremely important in developing thin films and heterostructures which are directly applied in technology. Now let us take a few examples and we try to understand a few aspects of it. Now what I am showing you is actually germanium deposited on a silicon 100 surface. Now you see something interesting is happening. Now we are actually just getting close to real examples silicon 100 surface. Now you all know how a silicon 100 surface looks like. It is a fourfold symmetric surface. Now Germanium when you deposit on silicon 100 surface so these are actually nothing but STM images. What you are seeing here in a, b, c, d are actually some kind of a coverage dependent image. So, you have here the blue area is nothing but silicon so, this is basically the silicon surface itself and what you are seeing here in this green and orange colour is nothing but the different layers that are deposited of Germanium on the silicon surface. Now interesting thing is as you increase the coverage or that means as you increase the amount of atoms that are actually bombarding on the silicon surface you can basically see the amount of Germanium that is actually getting deposited on the surface increases. That is no big deal. That is very good. But now something interesting you mark here that the islands are actually forming like rectangular islands. Each island if you look at the islands are basically looking like different shapes but they are all different types of rectangles that you are forming on the surface. What is that? You can actually think about that while you are listening to the lecture. We will come back to that in a minute.

And you see that as the coverage increases the different types of rectangles are forming and now rectangles are also forming in two different directions. So, they are also forming like this or maybe another one is actually getting extended and so on. So, the rectangles are actually forming in one direction like this another direction like this. Now of course the height is also increasing you can basically see the height of the islands are increasing, it is not just a monolayer of Germanium on top of silicon. It is actually many layers of Germanium is actually getting deposited on top of the silicon surface. Now let us look at another interesting example. It is actually sodium chloride. So, the examples I am showing here is actually to make you familiarize with the variety of materials that you can actually deposit, here is salt. The question is can you relief deposit salt? Of course, we can deposit. We need to use the electron beam evaporator because to evaporate sodium chloride you would need a lot of temperature. So, if you can actually achieve that temperature, you can easily evaporate sodium chloride for example. Now look at this, you have basically sodium chloride on the gold 111 surface. So that is the surface you know what is a 111 surface, gold is of course an FCC type of packing it is a 111 surface. And again, what you are seeing is actually the STM images. Now at low resolution what you are seeing here is actually if you carefully look in the images you can basically see that herring bond type of reconstruction. That is just showing you that it is a gold surface and on top of that you basically see islands that are looking more or less like square and rectangular shape or you can say with the rectangular or square facets. We will come back to that in a minute. And if you zoom into that you can basically see the atomic resolution. That is what I said STM is always good for resolving atomic level structures and this is basically the edge of the island and you can see now within the islands you can see atoms are basically arranged in a square manner. So, that is nothing but the sodium chloride atoms. Now you can also take a cross sectional profile along this white dash line that is given here and that is a cross sectional profile which is given here. And now from the cross-sectional profile you can also basically calculate how many layers of sodium chloride are basically getting deposited. You can already see that here in the beginning I have only three layers and then this is actually another step edge of gold. Therefore, I also have about three layers of gold. So, this is what it is and just keep thinking about why it is looking more or less like a square or a rectangular facet at which the sodium chloride is growing. We can look at one more. Now you may actually understand.

So, I have another material that is deposited cobalt on top of copper 111 surface. So, copper 111 surface it is also something you know it we have already discussed in the previous class that. Now I am depositing basically cobalt on top of copper 111 surface. Now the interesting thing is if you look here the islands here are looking more or less like a triangle or triangle of this shape or a triangle of this shape. That is interesting. And in fact, if you look at it more carefully you would even find that this angle that these triangles are forming are just 60 degrees. That is also interesting. Now the question here is basically what is actually controlling or why do we see this different type of islands? Why do we see this particular shape of the islands itself? Now look back into the symmetry of the silicon 100 surface. As we would recollect the silicon 100 surface is basically a four-fold symmetric surface. Well, a four-fold symmetric surface if I would basically deposit atoms on top of a four-fold symmetric surface. If this would be the way the atoms are arranged on the silicon surface let us imagine that this is basically the silicon. Now we take a different colour for the Germanium atom and now imagine the Germaniums atoms are basically getting deposited like this. What do you see? You see basically a rectangular or a square type of island on top of the surface. So, now as the Germanium atoms grows on top so this is Germanium. So, if I would basically just deposit the Germanium on top of silicon so silicon 100 surface. That is extremely important. On the silicon 100 surface the symmetry of the surface basically defines how the Germanium should grow. And that is the reason why we see these kinds of rectangular and square type of islands on top of that. That means it is completely influenced by the symmetry of the surface itself. Now when it comes to the sodium chloride on gold 111 so that is something much more interesting. In that case you would recollect immediately that the gold 111 surface is actually a six-fold surface. Gold 111 surface is actually a six-fold surface. It has a six-fold symmetry. But now when you look at the sodium chloride itself, what you suddenly see the island of sodium chloride. What you suddenly see is that the surface itself is basically some kind of a square or rectangular in shape. What is the reason for that? Now comes the interesting aspect to consider here. When an adsorbate go on to the surface there are two major interactions. We will look in detail in the next class when it comes to the energetics. When an atom goes on to the surface there is a strong interaction like we have already discussed that is the interaction of the atom onto the surface.

Now when there are two atoms next to each other two adsorbate atoms next to each other they also start to interact. That is actually known as the adsorbate-adsorbate interaction. Now there is a competition always between the adsorbate-adsorbate interaction and the adsorbate-surface interaction and that finally decides, what is actually the shape of the island that you form? So, it is very clear in the case of sodium chloride on gold 111 surface that the interaction between the sodium. And the chlorine atom is so strong that actually the gold symmetry is actually not observed in the final island that is formed. That is quite spectacular which is also something you might have intuitively thought because sodium chloride is known to be very strongly interacting, it is actually a strong solid that means the sodium is always ionically interacting together with the chlorine and forming the strong sodium chloride itself. So, that means it is no matter what is the symmetry of the underlying surface for materials which are having a strong adsorbate-adsorbate interaction everything is going to be controlled basically by the adsorbate-adsorbate interaction. But in the case of Germanium on silicon there is also a strong Germanium silicon interaction because both are semiconductors, they both strongly interact with each other. Therefore, the silicon Germanium interaction is actually very strong at the interface and therefore it actually grows on the same way. At the same time the symmetry is also maintained of the surface. That is the reason why you see that the Germanium islands are looking rectangular and the sodium chloride islands are looking also rectangular in shape. Now when it comes to the cobalt the copper 111 surface is basically six-fold symmetric. And that is exactly what you are seeing in the angle of the island. So, if this would be basically the different orientations of the copper lattice and all the different copper lattices will be basically rotated also by 60 degree. So, that means all the copper compact lattice is called as the atomic lattice on top of the gold 111 surface and that copper lattice is basically all the lattices are rotated by 60 degree with respect to each other. So, now when the cobalt is being deposited on the copper 111 surface you directly see the symmetry of the surface is implemented in the island that is actually forming on top of the surface. That is very interesting. At the same time, you also keep in mind that cobalt is basically forming normally an HCP type of packing. Therefore, the symmetry of cobalt itself is also kind of three-fold in nature. And that is the reason why you eventually see that the islands are actually forming in two different shapes like this either a triangle which is looking facing like this or a triangle that is basically looking like that. So, one is actually called as a folded half and the other is actually known as the unfolded half. Because on the copper 111 surface when atoms start to pack you can either pack all on the HCP site or on the FCC site.

We will actually just give you some of the assignments here to just to grow materials on different types of materials. So, there you can basically start to understand this in more detail and then you can actually just see from the symmetry of the island formed itself what is basically going on at the interface. Good, then any combination of materials may be used. So, that is also the interesting thing about physical vapour deposition that you can just evaporate any metal on top of any material. So, that is the idea.

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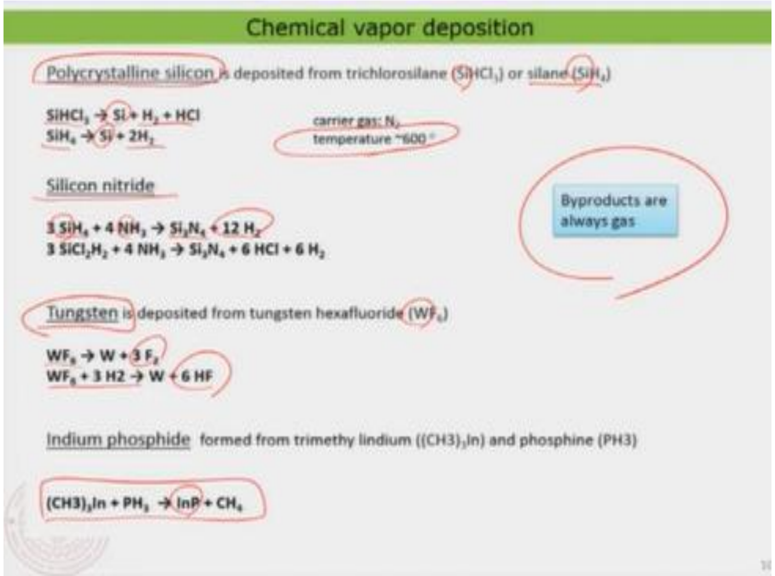

Chemical vapor deposition

Polycrystalline silicon is deposited from trichlorosilane ($SiHCl_3$) or silane (SiH_4)

$SiHCl_3 \rightarrow Si + H_2 + HCl$
$SiH_4 \rightarrow Si + 2H_2$

carrier gas: N_2
temperature ~600 °

Silicon nitride

$3\ SiH_4 + 4\ NH_3 \rightarrow Si_3N_4 + 12\ H_2$
$3\ SiCl_2H_2 + 4\ NH_3 \rightarrow Si_3N_4 + 6\ HCl + 6\ H_2$

Byproducts are always gas

Tungsten is deposited from tungsten hexafluoride (WF_6)

$WF_6 \rightarrow W + 3\ F_2$
$WF_6 + 3\ H2 \rightarrow W + 6\ HF$

Indium phosphide formed from trimethy lindium ((CH3)$_3$In) and phosphine (PH3)

$(CH3)_3In + PH_3 \rightarrow InP + CH_4$

Now come to the chemical vapour deposition. So, in the chemical vapour deposition it is actually working in a slightly different way than the physical vapour deposition because there is some chemistry going on here. So, there are impurities chances of having impurities are much higher in this case and also like by-products can be present in this case and so on. So, therefore, the preparation or the material that is actually prepared using chemical vapour deposition is not necessarily as clean as the one which is actually prepared by physical vapour deposition.

But nonetheless the practices are much more optimized now a days and therefore people actually can prepare very well ordered adlayers of different types of materials one on each other using chemical vapour deposition. Here the chemical vapour deposition is also very interesting because of the efficiency of the process. It is actually a process through which you can actually produce a much higher quantity of thin films compared to a general physical vapour deposition. So how does it work? In every case of chemical vapour deposition, I will show you a couple of examples. But I want to do here in this case is I want to generate a polycrystalline silicon. I want to generate a deposition of polycrystalline silicon on any given surface, that is my task. So, what I need to think about is I need to have a molecule that is having silicon as one of the ingredients. As you see here if I would take trichlorosilane or silane itself you can see that I have silicon as one of the ingredients.

So, that is the most important thing. Now you take these precursor molecules and mix it with some carrier gas and then let these molecules with the carrier gas to travel on to a surface at which the reaction actually happens. What is the reaction? It is normally done with the help of temperature. So, you get deposit the material and while you deposit the material you basically just do some kind of heating. And the heating would cause the silane or the trichlorosilane to basically dissociate and then you can see atomic silicon is basically produced. Now the interesting thing here in both cases the by-products are gas molecules. That is the interesting thing. So, the carrier gas that actually brought the precursor molecule will actually carry the by-product away and then finally the silicon is getting deposited on the surface.

Well, I take a little bit I make you understand this by taking a few examples if I want to generate for example a silicon nitride layer that is something quite important in technology. So, there what I need is again silane but I also need now nitrogen because in the final product I want to have silicon and nitrogen. So, I want to have a precursor of silicon, I want to have a precursor of nitrogen. So, I use silane and ammonia and basically this will be carried by a carrier gas and getting deposited at a hot surface and then you form the silicon nitrate and hydrogen molecules are actually evaporated or removed and this is basically carried by the carrier gas itself. So, then you have another example. For example, I want to deposit tungsten. Here I just want to deposit pure tungsten on top of any surface. So, again I need to have a precursor hexafluoride I can take with tungsten as an ingredient inside. Again, you can see the reaction is very simple. You take the tungsten hexafluoride and let it pass on to the surface where you want to deposit heat the surface and then you can actually eliminate fluorine. You can also take another mixture where you do a little bit of chemistry in a sense you take actually the hexafluoride tungsten, hexafluoride and hydrogen. You mix it and then you basically just remove the by-product as hydrogen fluoride. More examples you can actually just look. So, this is very important indium phosphide. It is basically a semiconducting material which is very much used in the silicon industry or in the semiconductor industry in general. You can actually see how the equation happens. You can basically just prepare again an indium phosphide layer. So, what you always need to keep in mind if I want to deposit something I want to have actually a molecule which is having that particular element as an ingredient. Then you actually just mix it with some liquid then mix it with the carrier gas, let us send it to a hot surface, it basically reacts. So, that is the way it works and they always the by-products are gas. Therefore, the chemical reaction is actually not yielding anything which is getting deposited onto the surface finally which is not the real requirement. That is the important thing. So, when you choose the precursor molecules you just make sure that the chemistry will finally lead to a by-product which is a gas.

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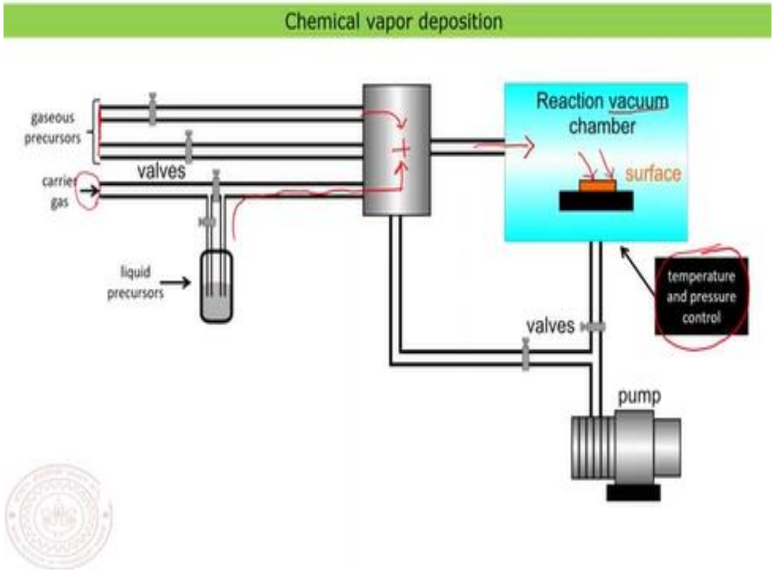

Chemical vapor deposition

Now let us have a look at the typical setup you require for doing a chemical vapour deposition. Of course, what you see here is a very schematic representation and of course a variety of designs would be available. But in general, what you need is something of this sort. Well, you have the inlets for the gas precursors and then for the solid precursors what you generally do is you mix them in a solvent and then you make a solution and then using a carrier gas you basically just bring them to the reaction site. And then now it actually just mixes with the gaseous precursors that are coming from here and then finally you let them into the reaction chamber. Now in the reaction chamber so typically the reaction chambers are also always under vacuum in order to basically create an inert atmosphere and then also to remove the by-product. And now the precursor molecules would get deposited on the surface and on the surface which is kept at higher temperature the reaction would occur. And of course, you have to have a better control of the temperature and the pressure of the reaction chamber which is quite crucial for controlling the quality of the epitaxial films that you make. And then by controlling the temperature and the pressure of the reaction chamber you can basically form nice epitaxial layers on the surface. And this is a very generic scheme and of course as I told you can have a variety of designs for the chemical vapour deposition.

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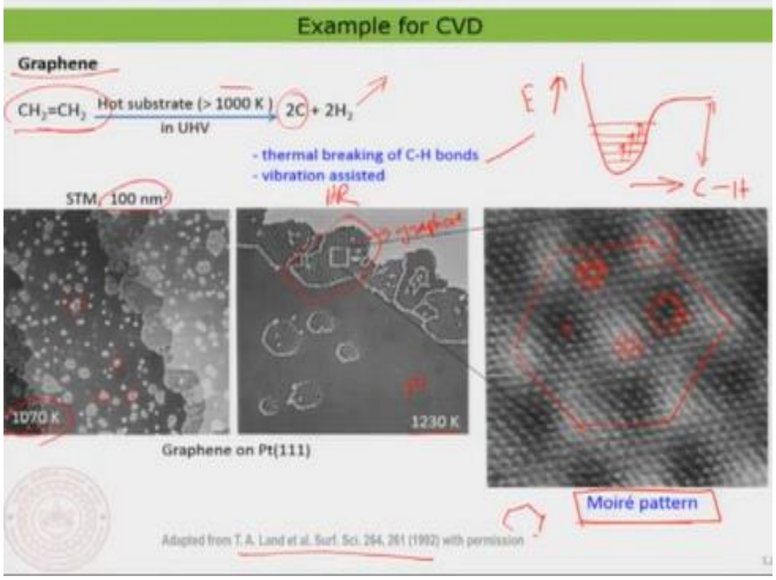

Example for CVD

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

Graphene on Pt(111)

Moiré pattern

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

Now we will have a look at a particular example. This particular example is also a very important example. It is nothing but graphene I just want to show you an example of the preparation of graphene on graphene. That is actually the kind of chemical vapour deposition technique to prepare graphene itself. So, what do we do? We have actually the precursor molecule which is actually nothing but ethylene where you have CH 2 double bond CH 2. Now this particular example is of course done in ultra-high vacuum chambers but you can also do it in a high vacuum chamber or in normal chambers just to get the efficiency higher. And then what you do is you basically bombard the CH 2, CH 2 onto a hot surface. So, you keep the surface which is actually at about 1000 kelvin. And when the molecules go and bombard on the surface so then the carbon atoms are getting deposited on the surface and the hydrogen atoms are actually pumped away in the chamber. That is a very basic thing because carbon is the ingredient for graphene and now you have the graphene ingredient and now the carbon atoms go around and since it actually happens on a two-dimensional surface, a surface which is itself two dimensional in nature basically the carbon gets connected in a two-dimensional fashion or in a planar geometry. And the planar geometry is very important because that is what yields the graphene.

If carbon would react in a non-planar geometry so then you might have actually just grown diamond for example. But in this case the graphene is actually just formed and we do it on a platinum 111 surface. So, this is actually an example you can also see the details of this preparation in this particular journal surface science. I always recommend you to basically just go and read these journals to understand the technique. And also the details of the paper in a much better way than what we discuss in the class because in the class we are only just trying to give you a small emphasis and not at the greater details. So, now you see I actually kept the surface at about 1070 kelvin and they deposit carbon from the precursor ethylene on top of the platinum 111 surface. And this is actually the STM image taken at a lower resolution and a higher solution image. So, what you see here is actually many-many small islands you can see around. So, that is not very clear but if you zoom into some of the region then you can basically see nice beautiful patterns you can see on the surface. So, this is actually platinum. So that is not the graphene but this is actually the graphene. This is the graphene and you see some kind of a hexagonal pattern inside. Now of course you can also see there is actually a post annealing. So, you deposit at 1070 kelvin and as soon as the carbon gets deposited you also do something like a post annealing. The post annealing is very important in order to rearrange the carbon atoms on the surface and then to form very-very ordered patterns on the surface. And now we can do, we can zoom into a small region there and then you can see basically that there is a very well-ordered pattern inside. And each of the small bright atoms that you see inside is nothing but the carbon atoms. And you can also see that these carbon atoms if you put them together it actually forms a nice hexagon as you have actually just seen in the case of graphite. We have actually just seen this example. There I showed you the graphene should have a symmetry looking like a hexagon. Now but what is also interesting if you look inside not all carbon atoms are actually looking similar. They are actually just kind of changing their intensity. For example, the carbon at this spot is actually looking not that bright but the carbon atoms at this point is actually looking much more brighter than the carbon atom at this. So, that is actually making some kind of a superlattice as you see here which is again another hexagon. That is actually a super lattice and that is generally known as a moiré pattern.

A moiré pattern is actually some kind of a superlattice that is forming between two different types of crystalline lattices. Not necessarily lattices between any different kind of materials. You will see some examples but in this particular case it is actually between the platinum which is a 111 surface. It is again a hexagonal lattice and you have graphene which also has a hexagonal lattice.

Now when these two hexagonal lattices go on top of each other they actually form something called a super lattice. We would look into great details in the next class about why is the super lattice forming or what can you learn basically from the super lattice generally it is known as a moiré pattern. We will discuss that in greater detail. But believe me that in this region the carbon atoms are not adsorbed at the same position as the carbon atoms at this region. So, the carbon atom in this region is actually adsorbed in a different position with respect to the platinum 111 surface compared to this position. So, that is the reason why you have this modulation of contrast, it is not only just the contrast modulation it is also just the topography is basically modulating because the atoms are actually just adsorbing at a different place. But now you can see in general using chemical vapour deposition you can actually prepare very high-quality materials. And the general mechanism known for the preparation of this graphene itself is the simple thermal breaking of the carbon and hydrogen bond. But generally, you know that the carbon hydrogen bonds are extremely more energetic than just 1000 kelvin. So, typically, if you have this as the potential well which represents let us say the potential energy and the distance between the C and H bond.

Then you can basically say that sorry for that, you can basically say that this is basically the depth of the potential well or the amount of energy required to break a C-H bond. But generally, this process is actually mediated by climbing across the vibration of the molecule, that means C-H bonds are actually getting excited as the temperature increases. So, that means the molecules are actually getting excited into different vibrational levels.

And finally, the molecule the C-H bonds get broken and then you form the C-C bond and that is how the chemical reaction happens. So, in the next class we will look into the different aspects of the formation of different types of adsorbate layers on surfaces and so on. Thank you very much for your attention and meet you in the next class. Thank you very much.