Chemistry and Physics of Surfaces and Interfaces

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Lecture - 10
Different Types of Preparation Methods for Thin Films

So, hello everyone. Welcome back today we will have lecture number 10. And in today's lecture we will start to now focus on preparing the adlayers and thin films on different type of surfaces.

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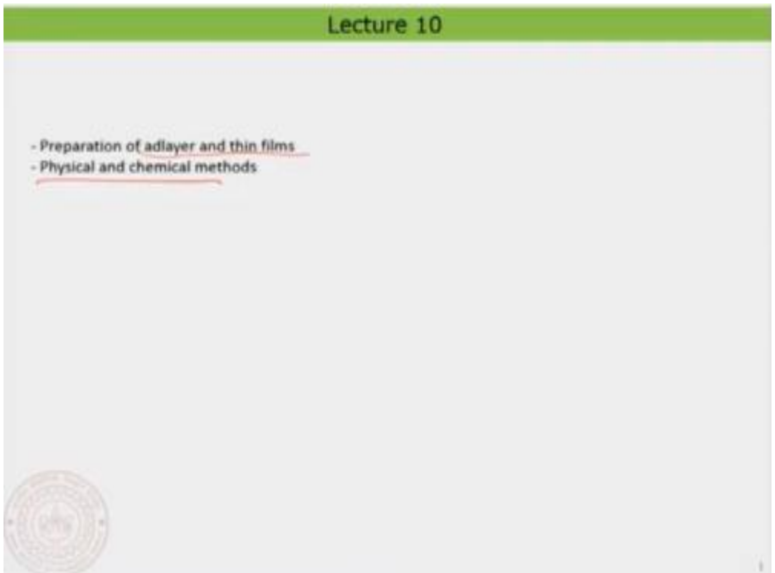

So, in the last class what we have seen is inside an ultra-high vacuum chamber, how to prepare a clean surface. And now we have the clean surface and we also have now an understanding about the structure of the surface and typically what should be the structure and properties particularly the structural properties of adlayer itself. And now today's lecture what we will be looking at is the preparation of adlayers and therefore finally the thin films because you put more and more adlayers on top of a surface you would eventually make a thin layer. And then mainly will have two different type of methods like physical and chemical methodologies that we will be focusing in this lecture.

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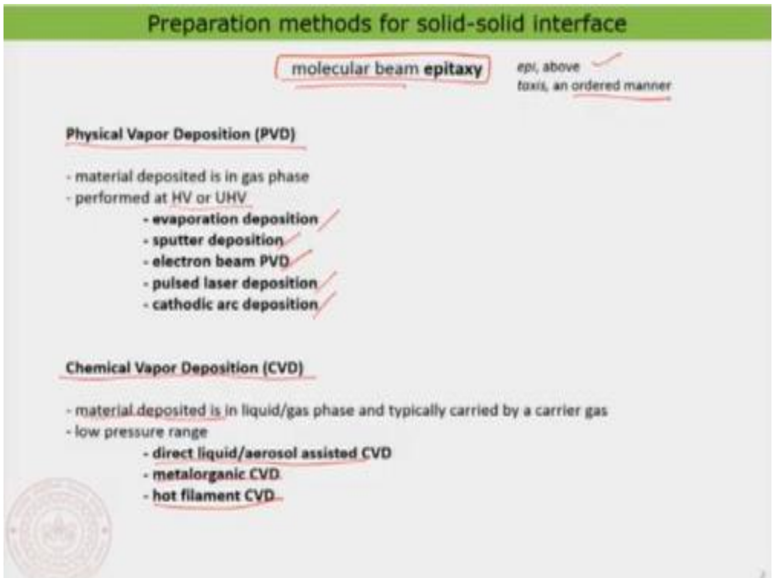

So, let us look at the preparation. In general, when you prepare a molecular or an adlayer of any material be it a molecule atom whatsoever on top of another crystalline surface. Normally that methodology itself is known as molecular beam epitaxy. I will come to that in a minute and in general epitaxy means that something above something and in an ordered manner. So, epitaxy itself generally represent that you form some kind of an ordered layer of ordered something. So, that ideally means what we are now making is actually a solid-solid interface both crystalline and generally that process of making the interface is known as an epitaxy process. And molecular beam, why is it molecular beam? Because in the epitaxial process itself you are now going to generate a beam of molecules or atoms that are going to eventually get deposited on the surface. So, that is the reason why it is called molecular beam that means atoms are coming actually one by one or molecule if you are depositing molecules and surface molecules are coming basically one by one on to the surface and therefore it is actually called as molecular beam epitaxy. So, we look into two different major methods that people generally use in making these kind of adlayers or finally when you put many adlayers together you have a thin film on top of a surface well that is what we do. And the general and the most simplest method that you can think of is actually something known as a physical vapour deposition or PVD in general. And physical vapour deposition is done that is the most important thing it is done either in high vacuum or in ultra-high vacuum chambers. So, that itself tells you that physical deposition is a kind of an extremely clean methodology in preparing adlayers.

Well, therefore in the modern technology people do prefer actually just making physical vapour deposition. But the physical vapour deposition in general so as that you have to create the high vacuum and also the ultra-high vacuum in order to create extremely clean epitaxial layers. It is much more expensive than the chemical methods that we are going to follow in a minute. Therefore, the physical vapour deposition is actually still not the most preferred one although that actually provides you the best. But in a moderate regime like if you would for example like prepare these things in high vacuum for example that is neither like more expensive not low quality. So, you can actually prepare also epitaxial layers in high vacuum. So, therefore the physical vapour deposition is also generally conducted in high vacuum so as to make the process quicker and also if you want to make larger areas of epitaxial layer so, that is the point. Now what do you do in physical vapour deposition? As the name suggests it is a simple vapour deposition. So, it is very simple methodology in terms of the method itself it is not complex as you will see in the chemical methods, it is rather very simple. So, what you need is a clean surface, a crystalline clean surface that we have already seen how to prepare a clean surface and once you clean the surface you can actually just start evaporating materials, one type of material on other type of material. So, generally you use something very simple called evaporation deposition that means like you heat the material and deposit or you use other method called a sputter deposition. You have already seen in the previous class what is the meaning of sputter itself. So, we can use that same technology sputtering itself to deposit materials on top of another material. So, you will see that in greater detail in a minute. And then you have like the electron beam physical vapour deposition and then you have pulse laser deposition, cathodic arc deposition and there are enormous different type of methods that are existing. Today I will just in detail I will basically explain you the evaporation deposition, the sputter deposition and the e-beam deposition. So, that is basically what we are going to do. And before that let us also look at the other major methodology that people use in preparing the epitaxial layers or adlayers on surfaces that is actually nothing but chemical vapour deposition. So, when chemical itself comes you are clear that there is actually some kind of chemistry that is going to happen. But you still see that the vapour deposition is still present there. So, eventually the deposition, it is extremely important to have the vapour of the adsorbate coming into a gas phase and then finally the gas of the adsorbate is getting deposited, be is the chemical methodology or be the physical vapour deposition in both cases you are basically depositing the vapour deposition. But well out of this there are also a few other different type of methodologies where you directly deposit a layer from a solution. For example, that you can create from solid-liquid interface that is also possible. That we are not going into the details but these are actually the most celebrated and the best clean technology that one use in preparing epitaxial layers or these are the methods that is being implemented to generate different type of heterostructures that you use in your electronic devices. For example, because you need to have actually highly pure and clean interfaces need to be produced. Well, very simple essence of the chemical vapour deposition, what you need is basically like I told you the material that need to be deposited should basically be carried by a gas in either in a mixed form or in pure form. And then, you can basically just use that kind of a gas carrying the material to be deposited and then you can finally deposit it on the surface. Within that itself you can have like you know direct liquid aerosol assisted chemical vapour deposition or metal organic chemical vapour deposition or hot filament chemical vapour deposition and so on. So, a few of them we will look in detail and we will also see how to prepare a chemical vapour deposition-based epitaxy, we will also see a few examples. Now let us have a look at look in detail about a few physical vapour deposition methods like I have told you.

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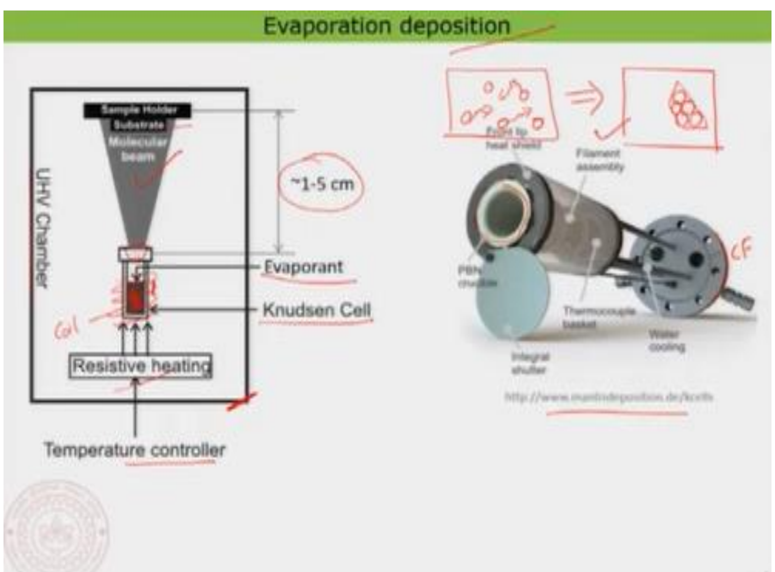

The first and most important is actually the simplest one which is just the evaporation deposition. So, the name itself suggests that you are basically evaporating something and then that gas or that so called molecular beam or atomic beam is basically getting deposited onto the surface. So, how does it work? It is very simple. You need to have of course the ultra-high vacuum chamber or a high vacuum chamber as I have already told you. So, that is the most important requirement and this black box basically represent it just to depict that we are doing everything in an ultra-high vacuum chamber or in a high vacuum chamber. Now what you need is actually the material that you want to evaporate. So, typically the evaporant need to be kept inside a cell and the cell is generally known as Knudsen cell that is actually named after the name of a scientist, Knudsen cell. And you put the material of interest inside the Knudsen cell. And the Knudsen cells are generally prepared by either high melting metal or for example molybdenum tungsten and so on or you can also prepare it using silicon. The idea is very simple that during the evaporation or during the heating process you do not want to have a mixing of the material of the Knudsen cell to react with the evaporant itself. So, therefore people need to be careful that the Knudsen cell should always be prepared with materials that are having very high melting point and also like having an inert nature. Inert nature is not necessary in reality, you can still actually use something with a very high melting point. So, that is the point I said. So, once you do that then what you need is actually a coil that would just go around this Knudsen cell. And then that coil can actually be just connected to external power and then you can pass electricity through that and then you can basically heat the crucible and once you heat the crucible. So, I am basically just doing a coil here, so the coil is basically to heat and then you can do the resistive heating. Using the coil, you can basically pass current and then you can do the resistive heating. The idea is very simple that depending on the current passing through the coil you can actually control the temperature. So, there is always a temperature controller also associated to the heating itself. So, you can control nicely the temperature and once you now control due to the fact that the front part of the Knudsen cells having a very small opening which is more or less looking like a corn, the molecule or the atom that is being evaporated from the Knudsen cell will basically form a molecular beam, a beam itself. And why is it molecular beam? It is actually because atoms and molecules inside the beam is actually just separated to each other. So, they are not coming as coupled you understand, this is extremely important. Once you have the molecular beam you can basically have the substrate and substrate is something generally known for the surface onto which you are basically putting your adsorbate. So, you this is your surface and you put your adsorbate on top. So, the point is like generally this is not a substrate. So, now the substrate can actually be also heated while you are adsorbing the metal but metal or whatever material that you are putting but it is not necessary so, depending on the and the requirement you can basically do that. And then usually the Knudsen cell and the substrate is kept in the order of about a few centimetre and that is the distance that the molecular beam need to travel. And once you have the molecular beam then you basically can deposit the molecular beam onto the surface. So, now what you have is actually that you have the surface and, on the surface, atoms are actually coming one by one at a given rate. And now what happens is actually over the time these atoms would start to move around on the surface in a random fashion and then as soon as it moves. And then it meet basically another adsorbate atom they start to cluster together and then form an adlayer. You can now see that I have formed a small island of the adsorbate, adatoms together and I have formed an adlayer. So, this is how you do it. So, you send atom by atom onto the surface and then you let the atoms to move because the atom that are coming on to the surface has a certain energy because they are coming out of a heater. So, this has a certain high thermal energy and thermal energy is good enough to move around on the surface. And once they move around, they would finally form this kind of adsorbate layer on top of the surface. Now this is how a typical Knudsen cell look like. So, this is just taken from a real example what you have here is actually like a ceramic crucible and then that is the crucible where you deposit your molecule. And then the molecule is basically just molecular atom is actually kept and then the and this heater is actually now. You can see here the CF flange as I have already told you, so, this is CF flange and this flange is what is connected to the vacuum chamber. So, you can ideally control everything from outside and then you can basically evaporate the atoms and then they go on to the surface. So, this is what a real example is. Normally you also have something here called a shutter and the shutter is used to kind of control the flow of the molecular beam out of the Knudsen cell. So, that is also something you can control externally. So, whenever you want to shut the flow of the molecular beam you can basically also control it externally. So, that is the general definition of the evaporation by deposition. So, we are going to look at a few examples how the outcome looks like and then you can get the understanding more clear. So, now we do the sputter deposition or sputter coating it is generally known as. So, you remember in the last class we have discussed about sputter sputtering itself. Because sputtering is a method that you use for cleaning surfaces. So, to clean the surface and then to generate basically atomically flat surface you were basically using the sputtering and heating, sputtering and heating. So, cycles of sputtering and heating would generate a clean surface. So, I hope you recollect what we have done in the previous class.

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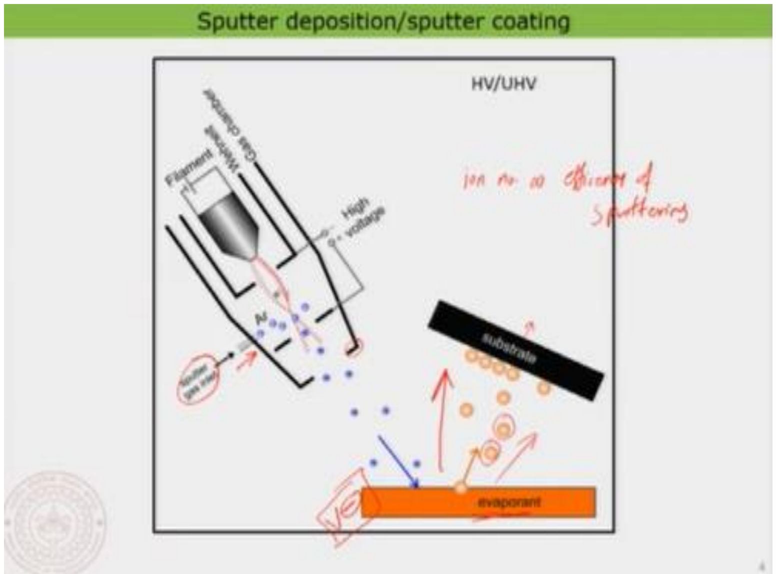

So, what we had was again just to recollect we had a beam of electron beam that is coming out of a filament. And the beam of electron is basically bombarding with noble gas molecules that are actually going into the beam of electron. And once to the electron beam bombard with the argon ions it is not necessary that you work always with argon ion you can use any noble gas that should work. And now you create actually a beam of positively charged noble gas molecule because your electron is basically bombarding the electron knocks out, an electron out of the system and then you have basically a positively charged argon atom. And now the argon atoms are basically propelled by you can see a high voltage, rippled by a high voltage. And then it is also been attracted by, because always you keep a negative a negative voltage onto the sample, this is a sample. So, the beam of argon ions would basically get attracted to the surface. Now as we have already seen what would happen is like the fast moving argon ions would hit the surface atoms and also partly the bulk atoms and they basically just remove the atoms out of the surface. So, that is exactly what we have done during the sputtering. But now you see the interesting thing is that you are basically using the sputtering idea itself. Because now when the argon ions are actually hitting the surface you are removing atoms from the surface. Now imagine you have your evaporant here and that evaporant surface is basically now getting bombarded by argon atoms. So, what happens naturally is that the evaporate atoms are basically getting escaped from the surface. Now you generate ideally a beam of evaporant out of the surface by the fast-moving argon ions, this is quite interesting. Now you can use basically that evaporant which is coming out of the evaporate due to the sputtering can be collected on a substrate. Again, here you can see by controlling the speed of the argon bombardment, you can also control basically the amount of evaporant that is coming out of the surface and then you can see it is basically atom by atoms are getting evaporated from the surface or getting removed from the surface. And so ideally you create a nice beam of atoms and if you can direct those atoms to the surface or the substrate onto which you want to prepare the epitaxial layer then you can ideally get the surface to be decorated by the adsorbate atoms. So, that is the technique. Now just to point out here that compared to the evaporation technique sputtering deposition is a much more efficient process. Because you know and also sputtering is actually feasible for many variety of materials. The problem with the evaporation technique is actually that the evaporant material need to be not extremely high in their evaporation temperature. If their evaporation temperature or the so-called sublimation temperature is very high then the evaporation technique is not very effective because you need to really use a lot of heating in order to get a very high beam of the molecular beam or the very high beam of the atoms that you want to deposit. But in the sputtering case, it is much more efficient because you have the argon ion and now I can basically just control the amount of argon ions that are going into the chamber and now I can also control the speed of the argon ions that are actually coming and bombarding onto the surface. And these two things are extremely important, if can actually use more argon ions you can basically get more argon, more sputtering. So, ideally the ion number is proportional to the efficiency of sputtering. So, that is the interesting thing here, just by controlling the amount of ions I can basically control the efficiency of sputtering. The efficiency of sputtering ideally means I get more and more evaporant. So, therefore for making extremely thick layer people do prefer actually the sputter deposition over the evaporation technique. But the evaporation technique is actually much more cleaner in a sense because you are actually not bringing any additional materials than the evaporate into the chamber. But in this case, you can see you actually bring argon and the purity of argon is very important and so on.

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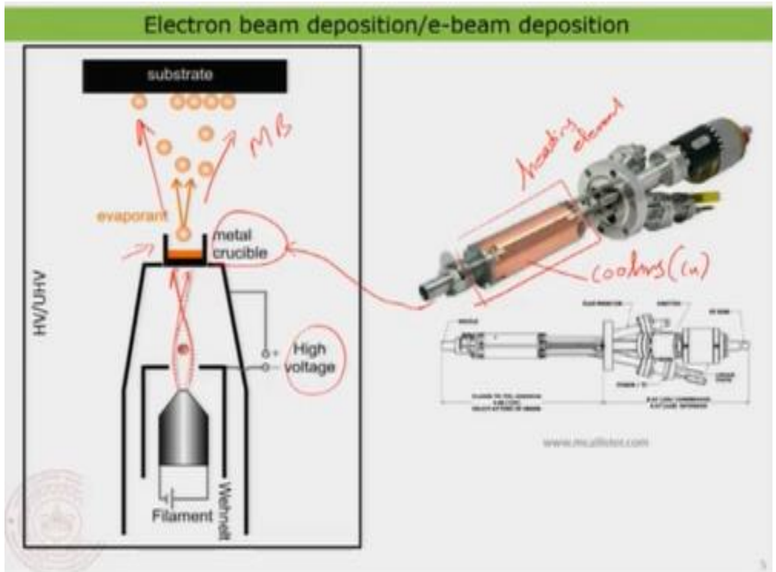

Now the next important method is actually known as the next important method is basically known as the electron beam deposition or generally known as e-beam deposition. So, what do you do in the e-beam deposition? Here again is a kind of evaporation technique ideally. But in this evaporation technique what is more important or what is more interesting is actually that you use or this technique is basically used for evaporants having much higher sublimation temperature. So, now how do you do that? You again have a metal crucible and the metal crucible here is actually crucible that are made up of molybdenum and so on which is actually having a very high melting point. So, therefore the stability even at very high temperature is good. So, you have a metal crucible and now on to the metal crucible what you do is you have actually a fast moving electrons that are actually bombarding the back side of the metal crucible. The speed of the electrons can be controlled by the voltage that you use here and also like the filament would decide how much electron should be emitted. You can basically use this electron bombardment to heat the metal crucible. So, once the metal crucible is actually hot then it is very simple, evapora molecules are actually evacuating out of the crucible and again you make ideally a molecular beam. So, this is quite important you have to make always this molecular beam where atoms are coming one by one and then they go on to the surface and get deposited. Just to show you how experimentally this looks like. So, this is basically the crucible so this is the crucible in the real case and this is actually made up of molybdenum. And this is actually the heating element are placed inside and also the electrons are getting actually bombarded from the backside through the heating element. Now you can also see that it is quite important that you will actually generate a lot of heat. So, just to cool down the exterior of the electron bombardment chamber, you also would actually just use some kind of a cooling system. So, that is the reason why you have here this copper plates. This copper plates are actually used for cooling the system. And once you do the cooling then you can also nicely do the evaporation itself. So, this is also a very efficient technique which is also used for evaporating materials which are actually having very high melting point for example. But nonetheless the sputtering technique is the one which is much more preferred over both the evaporation technique. Now you can actually just do something very nice with this e-beam evaporation. Because the interesting thing about the e-beam evaporation or the evaporation in general is basically that the control of the beam is very good in that unless in the sputtering case. So, now what I can do is something very interesting.

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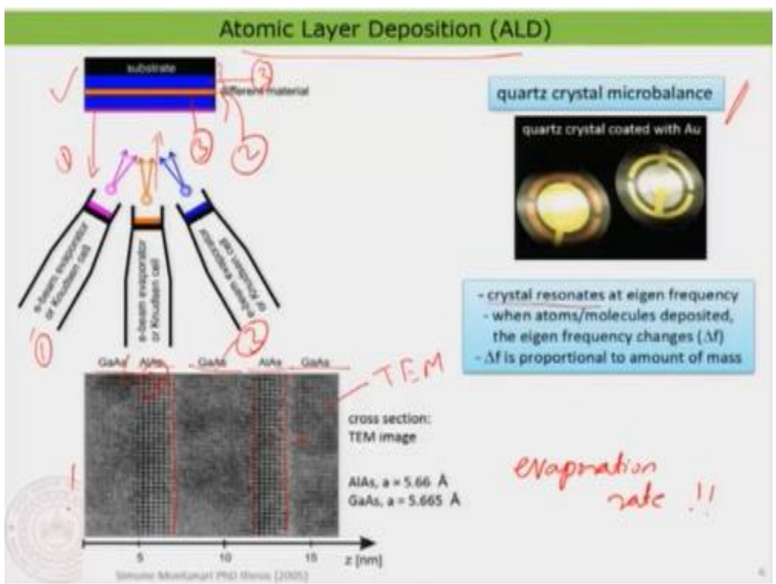

I can do something known as atomic layer deposition. This is extremely interesting. What is atomic layer deposition? Because I am going to now using this technique make just one layer of one type of material over another type of material. Now many of the devices that uses actually transistors and LEDs and things like that you have already seen that the entire construction is basically based on many different type of material deposited on one on top of each other. So, ideally what you do is you actually just make an extremely complex heterostructure. This is what you do. So, what you are seeing here is actually a heterostructure that is prepared for that what I need is three different type of material. Let us assume that I have three different type of material

1, 2 and 3. So, this is unimportant at this case what are the different type of material and imagine that I want to have different type of material deposited on a surface. Now this is what I want to construct. So, I will start depositing from three number three. So, I am basically just depositing three first and then I can basically control exactly the layer by layer and as soon as I create the layer by layer then I can start evaporating the second material that is actually evaporated. So, now you can see the second material is evaporated and then again, I evaporate the third material and then you can see finally I want to coat everything with the first material. So, this is only possible in this type of e-beam evaporation where you use several e-beams connected together to actually just focus and then to get different type of material deposited on different surfaces. So, here I have an example of an interface that is formed between gallium arsenide, aluminium arsenide, gallium arsenide, aluminium arsenide, gallium arsenide and so on. You can see how precisely. So, what you are seeing here is actually a TEM image that is actually transmission electron micrograph image and there you can clearly see the atoms. So, this each dot each bright dots here are nothing but the atoms of the different type of material and you can see here very nicely the atomic layers are precisely controlled. You can see there is almost no defect at the interface, you can use a ruler and scale a draw a line along that interface. So, that precise you can make and that is exactly the reason why it is known as atomic layer deposition and this type of deposition technique is actually a major type of technique that one uses actually in preparing a different type of interfaces. So, one more thing to be careful in this case we need something called a quartz crystal micro balance. And this is actually a technique that actually can use the evaporation rate. What you have is actually a crystal of quartz? That is resonating at its resonant frequency. And as soon as mass get deposited there is a change in the resonant frequency and the change in resonant frequency is directly proportional to the amount of mass that is deposited on the surface. So, that means using this quartz crystal balance I can also now control the evaporation rate and that is extremely important to control during the evaporation process. And once you can actually control the evaporation process of these three different types of material to be deposited and then you can exactly precisely form these kind of interfaces as you see in the image here. With this, I would like to conclude this lecture and I will come with more chemical methodologies to the preparation of adlayers in the next class. Thank you very much.