**Fundamentals of Materials Processing-2**
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**Module - 02**
**Thin Film Deposition**
**Lecture - 11**
**Chemical Vapor Deposition**

Welcome to lecture 11 of thin film deposition module of fundamentals of materials processing and in this lecture and the next three or four lectures, we will discuss about a process of thin film deposition called Chemical Vapor Deposition. Before we go to chemical vapor deposition, let us have a look at what we have discussed so far and differentiate physical vapor deposition from chemical vapor deposition.

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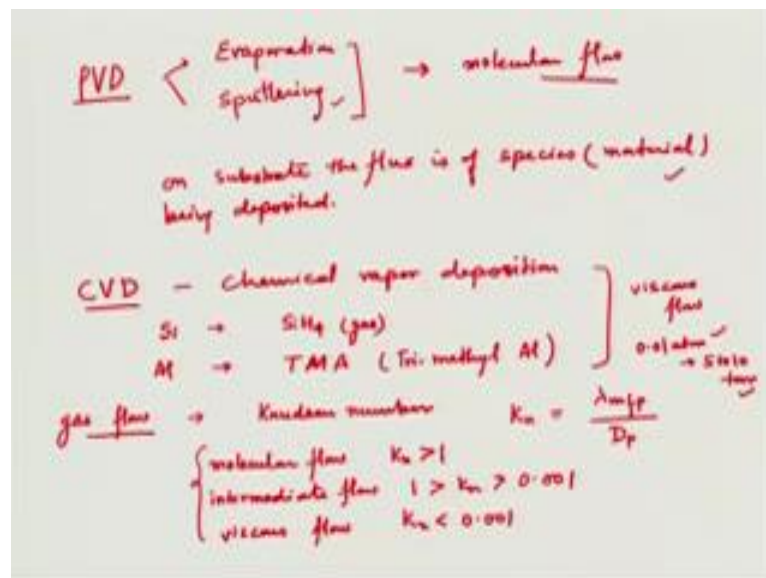


So various techniques that we have discussed so far under physical vapor deposition; these are evaporation and sputtering, broadly two classification for physical vapor deposition and in evaporation we saw that we would take our material heated by some means either resistive heating or through of some filaments or using electron beam and use that vaporized flux for deposition of thin films.

For sputtering, we had seen that we would take the help of plasma and using the high energy ions in the plasma, mechanically remove the material from a target and remove

the material from the target and deposit that on to our substrate where you want to deposit the thin film. In both these two processes one thing is common that we are using on substrate, the flux is of a species or a material being deposited. So, if you want to make thin film of gold; vaporized gold or evaporate gold and make a thin film of gold on our substrate. If you want to deposit aluminum oxide, we use sputtering to mechanically remove atoms or molecules of aluminum oxide and deposit on our film. Sometimes we also use reactive sputtering, so we have two fluxes coming in together on to the substrate, but the flux is in elemental form or molecular form of the species being deposited.

Now, by contrast in chemical vapor deposition or CVD; we have a flux of a material which as a part which you want to deposit. So, for example to deposit silicon we can use silane SiH 4 which is a gas, to deposit aluminum or any compound of aluminum we can use a liquid which is called TMA as a source of aluminum which is called tri methyl aluminum. So, in this way we are not using the elemental or molecular source of the material that you want to deposit and we want to have a reaction inside our reactor which will give me the required the machines that we want to deposit on our substrate.

So, chemical reaction is an important part and to get these constituents into our reaction chamber, we use gas phase. So, to distinguish a little bit more; we can use the flow or pressure because for p v d also we had used some pressure, but that pressure during sputtering was of an inert gas to create ions, here we are using the constituent gas and we are using its pressure for the flow of gases. Now if you recall the flows or gas flows can be classified based on number known as Knudsen number and this Knudsen number K n is defined as mean free path at the pressure of that gas is divided by the largest dimension of the system in which they are kept.

So, this is the definition of Knudsen number and based on Knudsen number these are defined in to three different flow regimes; one is called molecular flow where Knudsen number is more than 1. So, you can see if Knudsen number is more than 1 which means that mean free path is more than the dimension of the system, what it means that if the mean free path is larger than the atoms or molecules in the gas are interacting with the walls of the chamber or your pipe rather than among themselves and that flow is called molecular flow.

And on the other stream is viscous flow which as Knudsen number less than 0.001 very small which means that the gas pressure is high enough so that the lambda mean free path is very small. So, gas atoms are interacting with each other more than the walls and there is also an intermediate flow, which lies somewhere between 1 to 0.001; so this is how we can classify the gas flow and for PVD we mostly use molecular flow; molecular to intermediate and for CVD we use mostly viscous flow. So, at higher vest viscous flow in the pressure regime from 0.01 atmosphere to around 5 to 10 torr, so this is high to low.

So, this is the significant difference between the two methods let us go to CVD.

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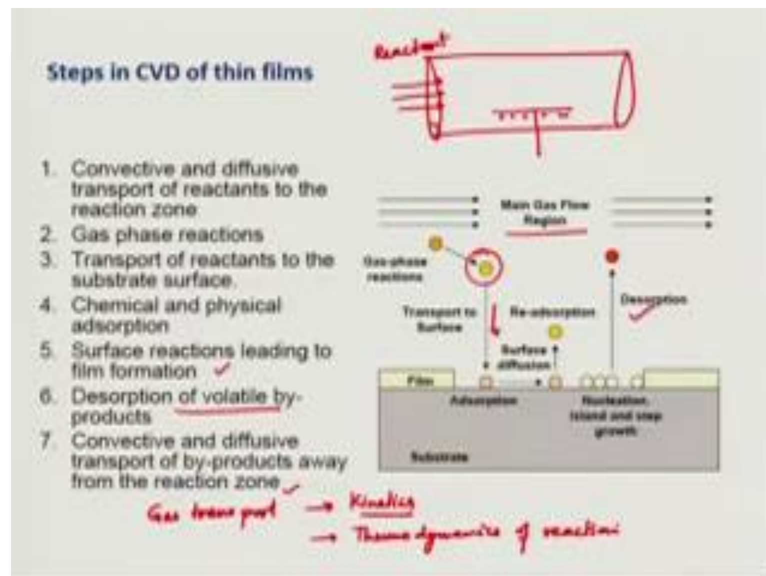


So, we have a reactor let us assume is a tubular reactor and in there we have kept a substrate which can be heated. So, through some filaments and my gases are coming in what are the different steps involved in the deposition of a thin films. So, far away from the substrate there will be again gas flow region and convective and diffusive transport of a reactant which is my gas reactant to the surface where they react is important.

So, far away from the surface it will be mostly convective flow and close to the surface, it would be diffusive flow. So, this is convective flow and diffusive flow there might be some gas phase reaction which are also important; transport of reactants to the substrate surface which is through diffusion, chemical and physical adsorption. So, these atoms or molecule from the gas phase will be either chemically absorbed or physically absorbed on to the surface, they will undergo reactions different constituents on the surface when

they come closer and if the temperature of the substrate is right correct for the reaction they will react together leaving something as the solid film behind and the desorption of volatile by products it is also important.

By product should not remain on the surface, they should go back to the gas phase there they are taking away by convection and which is important and the product which we need of the reaction forms a thin film. So, these are various steps involved, but if you look at it broadly there are two things; one is gas transport which we can call kinetics right because and it could be convection or diffusion or transport of constituents or reactants to the surface where they react. Second part is the reaction itself and which will involve knowledge of thermodynamics of reaction and both of these should be adjusted properly to get a clean uniform thin film that you want.

Now during chemical vapor deposition; remember most of this is in gas phase and in gas phase there are various type of reaction which can happen.

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Which are listed here, the gases may undergo thermal decomposition which is called pyrolysis such as this silane gas at 65 degree c when it goes pyrolysis, it results in silicon solid which is the thin film on the surface and the hydrogen gas which goes off as a byproduct and for deposition of nickel you can use this; nickel carbon monoxide gas and these there is an another reaction which can happen which is reduction of SiCl 4 with hydrogen or WF 6 by hydrogen resulting in one solid material which is the thin film and

the gaseous by product and you can see the temperature range is of for various reactions. Your gases may also undergo oxidation to deposit oxide films and you can also form compounds. So, if you have a source of silicon and carbon; you can form silicon carbide at (Refer Time: 12:00) temperatures, titanium carbide, silicon nitride sorry this is it should be 3 and also compound semiconductors such as gallium arsenide.

So these are formation of compounds; you can also have disproportionation reaction such that this reaction is goes in both ways, it is both backward and forward it depends on the temperature. If the substrate is lightly cooler then this reaction may go forward and from this gas you will get germanium and GeI 4 tetra iodide from diiodide or if your substrate temperature is higher; then you will get this reaction in the backward direction then these two will combined to give you diiodide and there is also another type of reaction which may happen which is called reversible transfer.

In this case some constituent gas these constituents in gas form, so what happens that you flow are seen through a bubbler of gallium or HCL through a bubbler of gallium and you carry this gas and where it reacts with arsenide to form gallium arsenide. So, in this case AsCL 3 gas carries molten gallium to the substrate in form of gallium chloride and at 800 degree c and at substrate it reacts with A s 4 to make the thin film of gallium arsenide. So, these are various type of reactions which might happen and there might be some more.

So, why we are discussing is because we have to keep the reaction thermo dynamics in our mind when we design our thin film deposition process and we should be to adjust the temperature according to reaction thermo dynamics. Now there is another aspect that we have to taken to account which is gas flow on surface.

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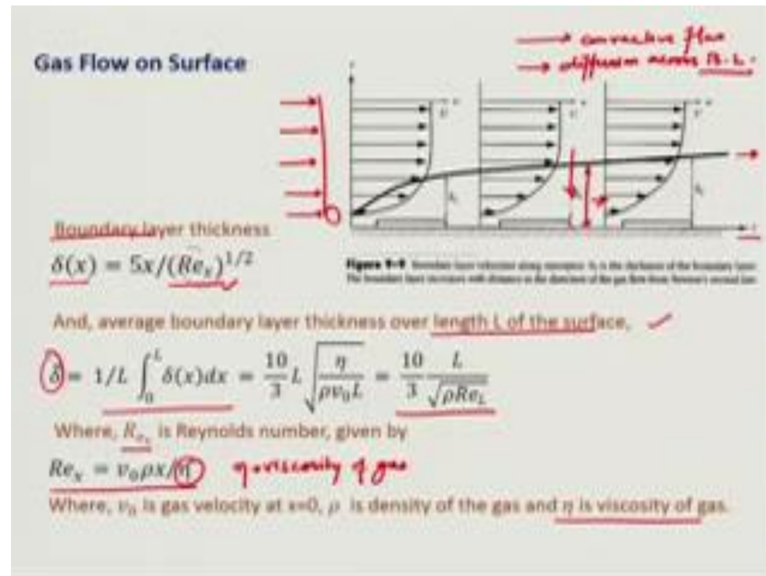


Now when there is a gas flow on surface; what happens is there is a boundary layer formation and this boundary layer formation is because of viscous flow and we know that viscosity is the force which resist the movement of the material. Important part is that when the gas is flowing, you would see that from here the gas has the uniform velocity outside the chamber.

But as soon as it is enters the chamber in this part of the gas comes in contact with a surface wall of the reactor and since the substrate or the wall of the chamber is at 0 speed the layers of gas in contact with this surface will come to a velocity of 0 and this develops a velocity gradient and as soon as you go further and further inside the chamber, this flow develops; this velocity gradient becomes more and more steep to a certain extent that after a certain distance of flow is fully developed then beyond this it does not change and since the layers which are very close to surface are moving very slow or not moving at all; they form a stagnant layer called boundary layer.

So, after certain distance this boundary layer fully develops and this. So, initially the thickness of this boundary layer changes, but deep inside it remains constant. So, this boundary layer thickness depends on the Reynolds number of the gas flow; gas flows can be described by many numbers. There are many numbers should describe gas flows in different regimes, here we are using Reynolds number. So, this is the thickness boundary layer thickness as a function of x, but if we have substrate of length L or and we want to

know what would be the thickness of the boundary layer, the average thickness we can just carry out this expression and we can find that this is the boundary layer thickness where R e x is a Reynolds number, which depends on viscosity of the gas.

So, if you have more viscous gas which resists the motion more severely then you will have higher Reynolds number; if you have higher Reynolds number you will have the smaller boundary thickness. So since these the boundary layer is the layer of stagnant gas right; the gas is not moving in that region. So, anything that has to come that is why the gases are flowing here but not in this region in the boundary layer, there is no lateral gas flow, no convective flow. So, the only possess through which the constituents; which are here can go to the reach the surface is by diffusion.

So we need to understand two kinds of flow; one is convective flow in the bulk of my reactor and diffusion across boundary layer; both of these are important for our reactants to reach the surface where they would react and form the thin film.

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Now, we had looked at what happens when the gases flowing on a surface, we can also look at what happens when the gas is flowing in a tubular reactor. We can approximate this tubular reactor as the two parallel if the gas flowing between two parallel plates to some extent and we can see that the radial distribution of velocities will be given by this expression and we understand that since there are two surfaces in two parallel plate, the gases flowing in two parallel plates there will be two boundary layers forming and at

some point these boundary layers from both sides will cross and form here in onwards, the flow which is developed will remain constant.

So, if you are designing our tubular reactor for chemical vapor deposition, we should make sure that this is not my reaction zone because the flows are not stable, they are different flows at different, the boundary layer thickness is different, but beyond the certain distance my boundary layer thickness will remain constant and we can use this region for uniform deposition of the film. Now for volumetric flow or bulk flow away from the boundary layer, the volumetric flow rate is given by Hagen-Poiseuille relationship which is shown here, which depends on the pressure gradient. So, the higher the pressure gradient because these gases are flowing in a pressure gradient; gases will only flow when you have two different pressures at two ends and the gases will flow from higher pressure to lower pressure and it depends on the radius of the reactor, the viscosity and also can be written in terms of velocity of the gas; average velocity and the flux of a gaseous species.

So, my gases are flowing at a certain velocity in the bulb, now what is the flux of my species. Suppose I have mixture of silane S i H 4 and hydrogen. So, the velocity; the other velocity would the pressure gradient would be the total pressure gradient, but if I want to know what is the flux of silane which is moving in that, we can use this expression where V i is the velocity of that is species silane how fast the sliane molecules are moving and we can relate it to pressure and using this expression and this is; so, we can relate the bulk flux of silane or my reacting species which depends on pressure and pressure gradient as well as temperature and we should also know that this viscosity is also function of temperature, so all these will change for bulk flow. Now bulk flow is one part, but we need to; these constituent should move across the boundary by deficit flow right.

So, we need to look at the gas phase diffusivity also of these constituents, gas phase diffusivity is given by this expression where and the temperature dependence is about n is or the of the order of 1.5 to 1.8, so it depends on temperature. Also the diffusive flux which we are more interested in can be converted to pressure gradient across the boundary layer. So, this is my convective flow or volumetric flow which is we had described on the right hand side and this is my diffusive flow and my substrate is here.

So, we must first come into the system by volumetric flow and then diffuse through the boundary layer to the substrate for reaction and thin film deposition and using the same expression we can convert concentration gradient to pressure gradient and where this is the partial pressure of constituent in gas or in bulk and this is on substrate. So, suppose I am if I take an example of reduction of silane as my thin film deposition process for deposition of silicon film.

So, I will have two gases in my bulk flow; both silane and hydrogen will be premixed and send inside the reactor and both of these should reach in proper amount on the surface of my substrate where they will react and form silicon, but if one of the constituents is not reaching the surface of my substrate in adequate amounts then my reaction will not proceed and it will not result in thin film deposition. So, for the case of deposition of silicon, we usually use hydrogen over pressure and silane and so the boundary layer mostly have hydrogen and silane diffuses through the boundary layer of silicon to reach the surface where they would react and form thin film..

So, we know that flow is very important; how the gas is coming and there are various reactor designs.

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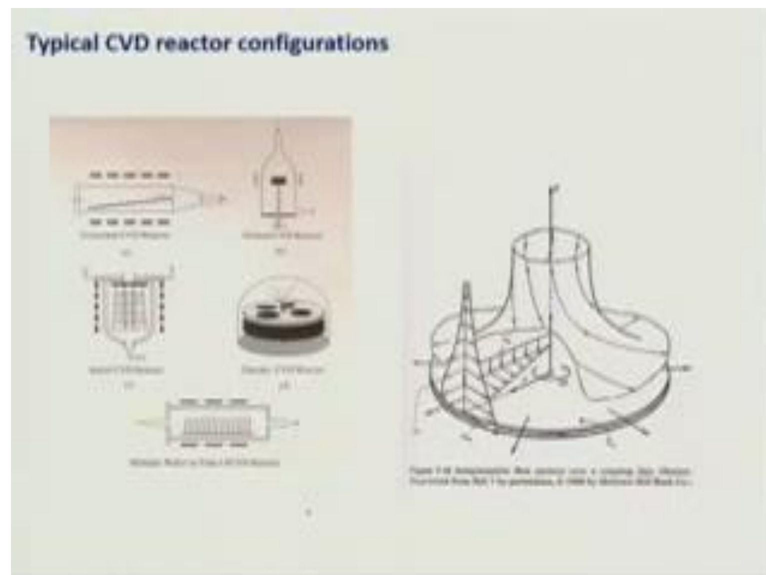


So, you can have a horizontal CVD reactor where the filament is outside to heat the substrate and you have a tilted substrate holder and you passing your gas, the gases react to form the thin film. You can also have a vertical CVD reactor, where your substrate is

kept here and it is heated inductively to raise a temperature and the gases come from that all, you can also have a barrel type CVD reactor for where you have barrel and these substrate are kept one of the another; gases come from top and they will react. You can also have a pancake CVD reactor, where your substrate holder is horizontal and it may also rotate and the gases come from the bottom and flow evenly across.

You can also have a multiple vapor in tube reactor which is horizontal and you can stack your substrates one after another and this is a horizontal reactor. This figure also shows because of uniformity you sometimes need to have a rotation of the substrate or substrate holder and this substrate holder will also rotate the boundary layer along with it because there is no relative motion between boundary layer and the substrate. So, when the substrate is moving, their boundary layer also will move and how this will develop into a flow pattern which will help in increasing the uniformity of that thin film.

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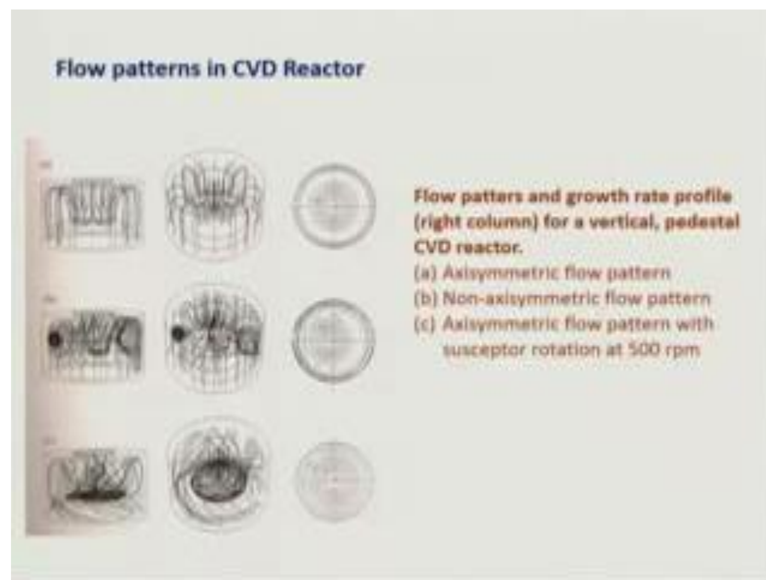


Let us have look at different flow patterns in CVD reactor and which are also influenced by where you put your inlet and outlet of the gas. In this case so the gases come from top, the substrate is here which is heated. So, then they go uniformly out from this reactor, so this flow results in the thin film uniformity which is shown here; you see that there is two large extent there is some uniformity was there is no deposition here because once the gases come in, they bounce of the substrate and then they go (Refer Time: 27:50) this is the case where your vacuum pump is on one side.

So, there is if the gases are coming straight down, but their flow is non symmetric and you get non symmetric deposition profile. In this case, the gases are coming straight down and substrate holder is rotating. So, you have both vertical and peripheral flow of the gases which results in more uniform deposition of the thin films. So, all these parameters are important from the (Refer Time: 28:30) designer CVD reactor from the point of view of flow of gases.

We will stop here and in the next lecture, we will look at how the gas flow is defined the uniformity of the thin film being deposited.

Thank you.