Biomedical Ultrasound: Fundamentals of Imaging and Micromachined Transducers

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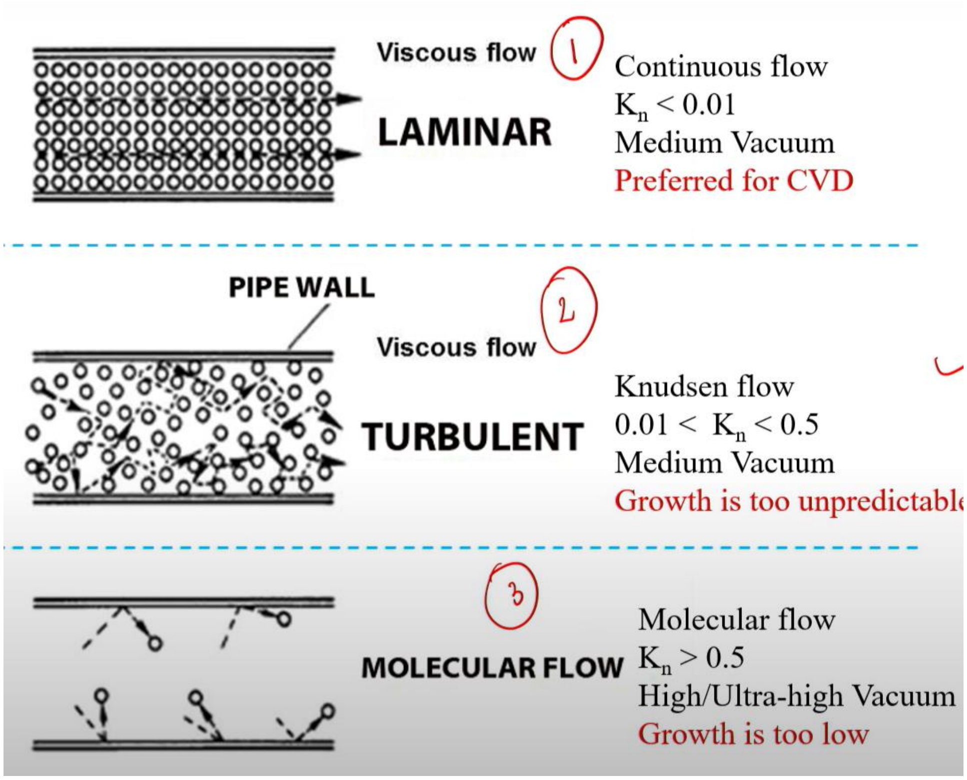
Lecture: 26

Chemical Vapor Deposition II

Hi everyone, welcome to this particular session on chemical vapor deposition. So, in the last class we have seen about the basics of a chemical vapor deposition process and what are the basic considerations that must be taken into account while choosing a particular source material, while choosing a particular substrate. So, in today's lecture we will begin with the type of gas flows that can happen in a CVD chamber. So, as a slide show there are three different types of gas flow mechanism.

The first one can be a laminar flow; the second one is a turbulent flow mechanism, and the third one is a molecular flow mechanism. So, in a laminar flow as you can see.



Continuous flow
$K_n < 0.01$
Medium Vacuum
Preferred for CVD

Knudsen flow
$0.01 < K_n < 0.5$
Medium Vacuum
Growth is too unpredictabl

Molecular flow
$K_n > 0.5$
High/Ultra-high Vacuum
Growth is too low

Laminar flow happens when the different layers in particular fluid flow parallel to each other. There is no intermixing between the fluid layers and there is very little turbulence existing in a laminar flow mechanism and the particles are consistently distributed and there is a uniform velocity throughout the flow process. So, laminar flow is also known as a continuous flow mechanism and to distinguish between the different types of gas flow, we have a mathematical quantity that is known as the Knudsen number. Knudsen number which is denoted by Kn and this Knudsen number is given by the ratio of the mean free path of the molecules divided by the characteristic length of the flow channel.

$$K_n = \frac{\lambda}{L}$$

So, characteristic length refers to the dimension which is a dimension of the physical scale of a system and this particular ratio is used to differentiate between different types of flow mechanisms. So, in case of a laminar flow the value of Knudsen number is very less for example, it is less than around 0.01 and the type of laminar flow is achieved in a medium vacuum condition. And this is a particular fluid flow regime that is preferred in a chemical vapor deposition mechanism because in this particular laminar flow the velocity at which the flow happens is uniform and there is very less turbulence as I already mentioned. So, we can have a uniform and predictable growth rate in a CVD reactor where the gas flow is maintained in the laminar regime.

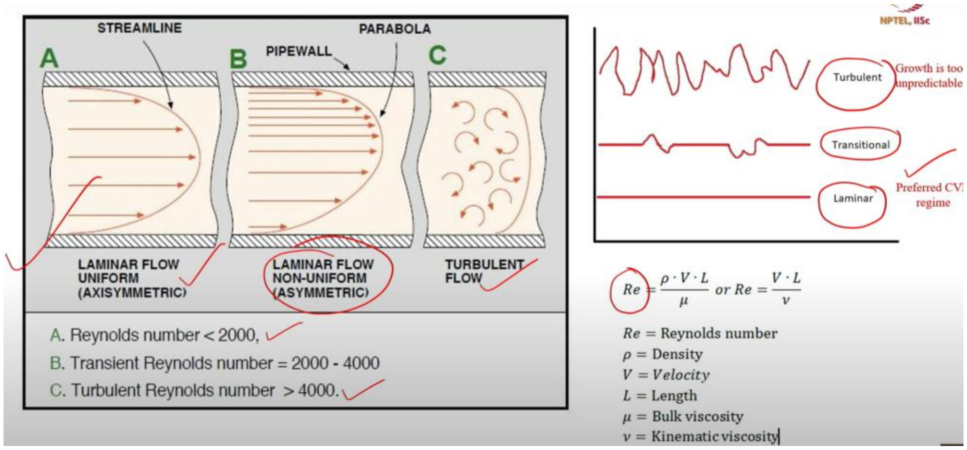
But coming to a turbulent flow mechanism here the different fluid constituents have a excessive kinetic energy. So, all the particles will be moving in a random direction. So, there will be a random shift in the pressure as well as the flow velocity. So, that will appear in the form of eddies and whirls in your particular flow mechanism. So, turbulent flow is the least preferred mechanism in a CVD reactor because the growth rate is very unpredictable if the fluid flows in a turbulent fashion because as we already mentioned due to this excessive kinetic energy, the fluid velocity and the pressure will also be in a random shifting manner.

So, turbulent flow mechanisms are least preferred. And for turbulent flow to happen we can say that the Knudsen number or that particular mathematical quantity lies between that of a laminar flow value and a molecular flow regime. That means it will be between 0.01 to 0.5 and due to a highly unpredictable growth rate turbulent flow is not that preferred.

And coming to the next mechanism that is a molecular flow mechanism, here the value of Knudsen number is greater than 0.5. This particular type of flow happens in a very high or ultra-high vacuum, but since the as we already know in very high vacuum the mean free path that is average distance that a molecule can travel without undergoing collision would be entirely different from a chamber where the vacuum conditions are different. And especially due to this ultra-high vacuum, the growth rate happening in a molecular flow regime or in a chamber where the molecular flow is maintained would be very low. So, comparing these three types of flow mechanism, we can say that laminar flow is preferred due to the uniform growth rate and uniform velocity maintained within the chamber, whereas turbulent and molecular flow, they are least preferred due to very unpredictable growth rate or due to a very less growth rate.

These particular flow mechanisms are the least preferred. Again, we have another quantity that is a Reynolds number it is again a dimensionless quantity that is used to predict the type of flow mechanism that is happening within our chamber. So, as we already mentioned in turbulent flow mechanism you have a unpredictable growth rate whereas, there in a laminar flow mechanism you have a uniform velocity and uniform pressure for the fluid flow happening in the chamber and that laminar flow is a preferred CVD regime. And you have a transitional flow between these 2 regimes as well that is again shown in the first figure. There is a laminar flow, then there is a turbulent flow, then there is a transitional region between the laminar and turbulent flow.

And again, using the value of Reynolds number, so similar to how we differentiate between the different flow mechanisms using a Knudsen number, we can use this Reynolds number quantity to differentiate between the different types of flow mechanisms. So, for a laminar flow process the value of Reynolds number would be less than 2000 and for a turbulent flow chamber the Reynolds number would be very high greater than around 4000 and in between 2000 to 4000 if the value of Reynolds number is in between these two 2000 and 4000 you can say that the flow is in a transitional region. So, the importance of these types of mathematical quantities comes into picture when you are trying to design a CVD chamber. So, the parameters associated with the design of a CVD chamber should be chosen such that the flow pattern that is maintained inside the chamber should be laminar in nature. So, the same concepts are described in this particular slide that is a Reynolds number it is a dimensionless quantity.

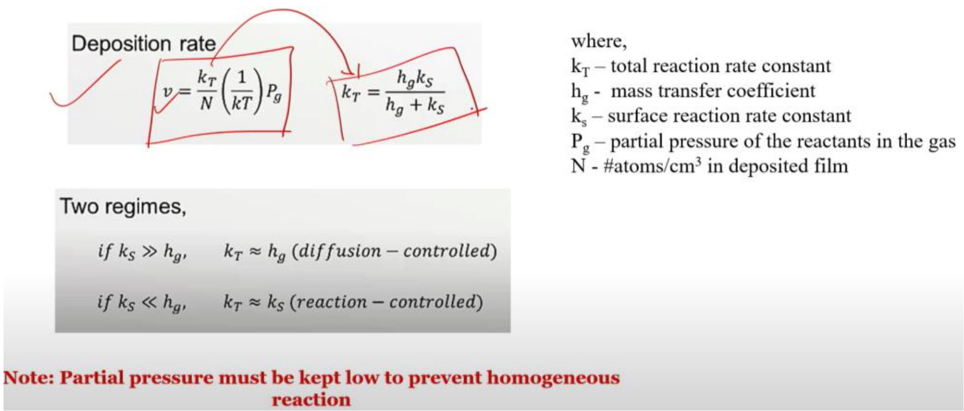


A. Reynolds number < 2000,
B. Transient Reynolds number = 2000 - 4000
C. Turbulent Reynolds number > 4000.

$$Re = \frac{\rho \cdot V \cdot L}{\mu} \text{ or } Re = \frac{V \cdot L}{\nu}$$

Re = Reynolds number
ρ = Density
V = $Velocity$
L = Length
μ = Bulk viscosity
ν = Kinematic viscosity

It is used to predict the flow pattern by measuring the ratio between the inertial and viscous forces and it is used in a wide variety of applications to predict the flow pattern from the liquid that is flowing in a pipe to over the passage of air in a aircraft wing as well. So, there is a wide range of applications where this Reynolds number quantity is used to predict the fluid flow pattern. So, moving on to the rate equation or the growth mechanism, we are not going into the particular mathematical derivation of this particular equations, so but we will just see what we can infer from these basic mathematical equations. So, the first equation as you can see it relates the deposition rate to the partial pressure in a CVD chamber. So, V is given by the deposition rate, and it is given by this particular equation where KT actually refers to the total reaction rate constant and it is again given by this particular expression where KT the total reaction rate would be given by Hg into Ks divided by Hg plus Ks.



Deposition rate

$$v = \frac{k_T}{N}\left(\frac{1}{kT}\right)P_g \qquad k_T = \frac{h_g k_S}{h_g + k_S}$$

where,
k_T – total reaction rate constant
h_g - mass transfer coefficient
k_s – surface reaction rate constant
P_g – partial pressure of the reactants in the gas
N - #atoms/cm^3 in deposited film

Two regimes,

$$if\ k_S \gg h_g, \qquad k_T \approx h_g\ (diffusion - controlled)$$

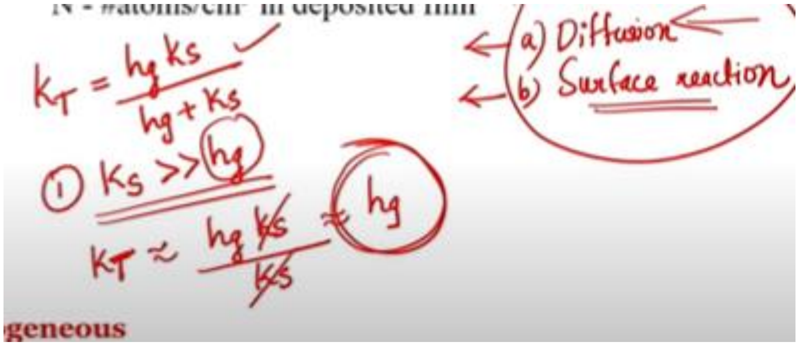
$$if\ k_S \ll h_g, \qquad k_T \approx k_S\ (reaction - controlled)$$

Note: Partial pressure must be kept low to prevent homogeneous reaction

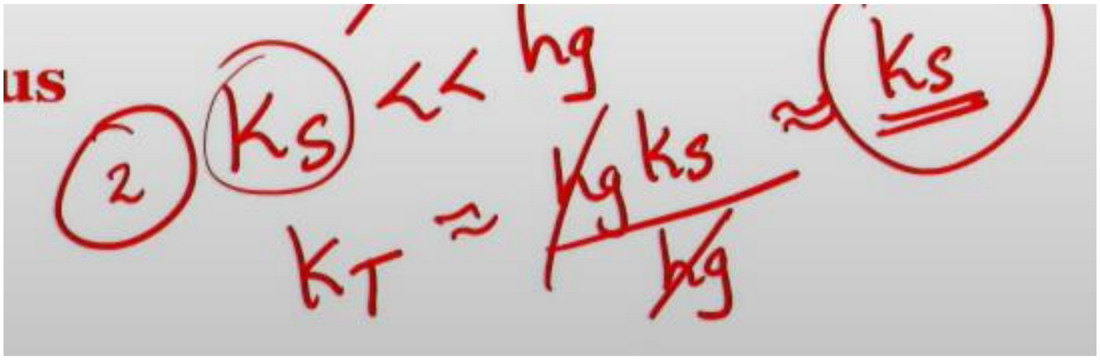
where Hg is a mass transfer coefficient. So, mass transfer coefficient is a quantity that describes the rate of mass transfer between two phases and Ks it refers to the surface reaction rate constant that actually refers to the rate at which a surface reaction happens. And when you refer to this particular equation KT is equal to Hg into Ks divided by Hg plus Ks. So, as mentioned here there can be 2 cases possible or 2 regimes you can divide the CVD process into 2 regimes based on this particular equation. So, the first case is when the surface reactions happen at a higher rate than the mass transfer coefficient.

So, in a CVD reactor you can say that there are basically two steps. The first one is either diffusion or second one is the surface reaction. So, these are the two predominant steps that are controlling the entire CVD process. So, in order to take into account, the diffusion process as well as the surface reaction you have different mathematical terms in the expression for the total reaction rate constant. So, first case when your surface reaction rate is much higher than your mass transfer coefficient that means in your particular CVD chamber.

Surface reaction happens at a faster rate than the diffusion concept. Diffusion concept means the rate at which the mass transfer happens. So, if this is a particular case you can simplify the equation of KT as Hg into Ks divided by in the denominator you can neglect Hg, and it will be Ks alone because Hg value is very less. So, in such a case when you simplify the mathematical equation it will be approximately equal to Hg as a as it is mentioned here. So, that means whenever in a particular CVD chamber surface reaction rate exceeds the rate at which mass transfer happens you can call that particular process as diffusion controlled.



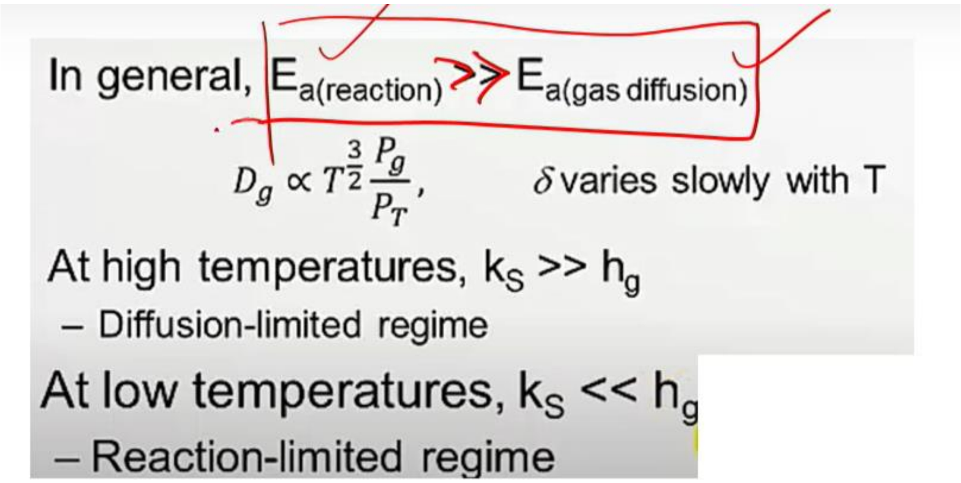
That means out of these two steps whichever is a slower step would be the rate determining step in a CVD reactor. So when your total reaction rate constant entirely depends on the mass transfer coefficient, you can call that particular process as a diffusion controlled regime. When you move to the second case where the surface reaction happens at a very less rate than your mass transfer coefficient, again when you substitute it in the equation for the total reaction rate constant, what you would be getting is Hg into Ks divided by the denominator you can approximate as Hg alone because the value of Ks is very small. So, when you simplify this particular equation what you get would be KT is approximately equal to KS. So that means in this particular case the diffusion of the say chemical vapor deposition process is said to be operating in the reaction-controlled regime.



So, these are the two basic regimes at which a CVD reactor can operate either in the diffusion control regime or in the reaction control regime and the main take away point from this particular slide is that, so these there are two mechanisms particularly that plays a major role in a CVD chamber that is a diffusion process and a surface reaction process and which of the process is happening at a slower rate that would be the rate limiting step of a particular CVD reactor and if the diffusion process is slower than the surface rate reaction you can call it as a diffusion limited regime. And if the surface reaction rate is lower than the diffusion process you can call it a reaction-controlled regime. And as I have also mentioned the partial pressure within the chamber should be maintained such that heterogeneous reactions are preferred because otherwise the film that is deposited will be of poor uniformity and poor quality. But at the same time from this first equation, you can see that to have a higher deposition rate you should have a higher partial pressure. But if the partial pressure is very high then homogeneous reactions or gas phase reactions may happen at a faster rate which would result in a poor uniformity of the film that is deposited.

So, this is actually a tradeoff between the partial pressure and the growth rate and the film quality. So, always we try to maintain the partial pressure, so that we can have a acceptable deposition rate as well as you can have a heterogeneous reactions being preferred in your CVD chamber.

Then moving on to the effect of temperature, so we all know that the activation energy required for a particular reaction to happen is always greater than the activation energy for a particular diffusion process to happen. So, activation energy it is a minimum energy required for a chemical reaction to happen and the activation energy for a diffusion process it is actually equal to the value of potential barrier that needs to be overcome by an atom to get transferred to a new position. So, always the activation energy for the reaction will be higher than the energy activation energy required for a diffusion process to happen.



In general, $E_{a(reaction)} >> E_{a(gas\ diffusion)}$

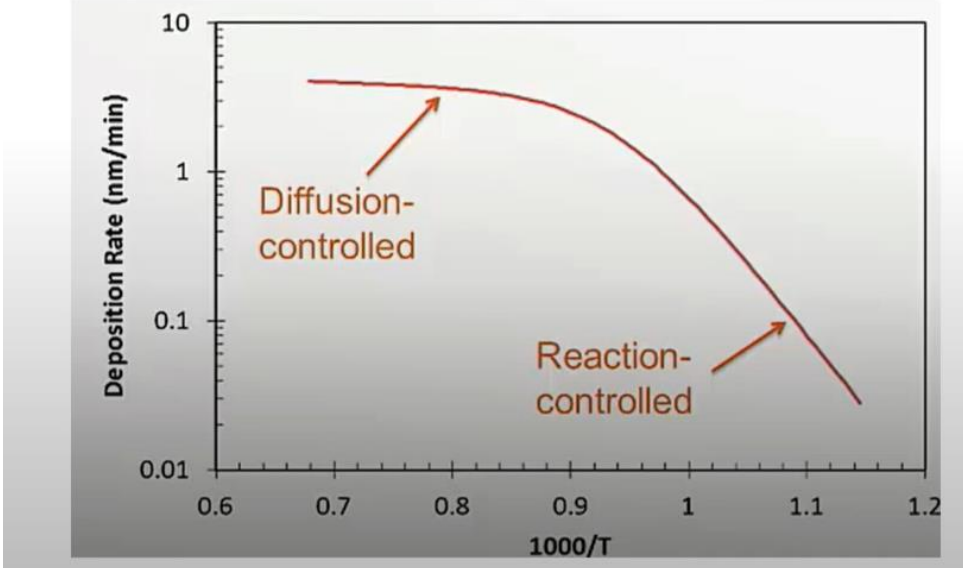
$D_g \propto T^{\frac{3}{2}} \frac{P_g}{P_T}$, δ varies slowly with T

At high temperatures, $k_S >> h_g$

– Diffusion-limited regime

At low temperatures, $k_S << h_g$

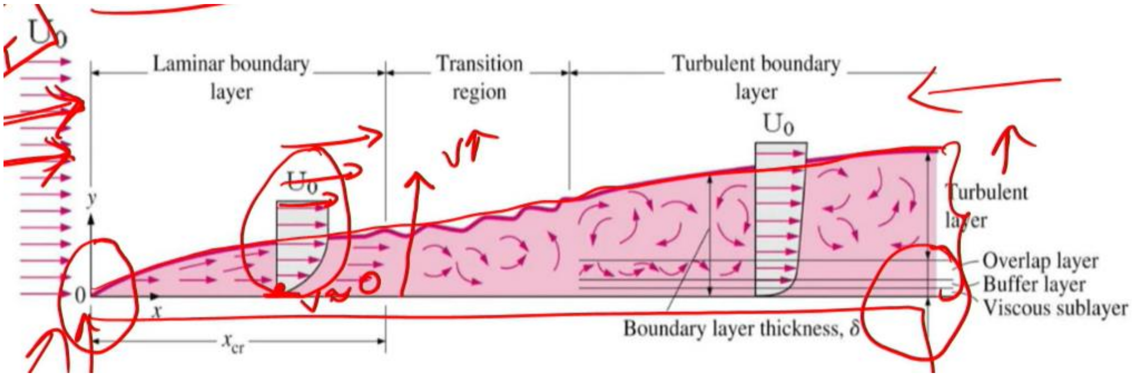
– Reaction-limited regime



And this particular equation shows the relation of diffusivity with that of partial pressure. So, you can see that diffusion technique, or the diffusivity is always proportional to T raise to 3 by 2 into the ratio of partial pressures. This is a total pressure and Pg is a partial pressure of the reactant molecules. This is the relation between diffusivity and temperature and partial pressure. So, we can see that diffusivity always follows always varies very slowly with that of temperature whereas when you think of a surface reaction it varies a large extent with respect to temperature.

So when you think from that perspective you can say that at very high temperature surface reaction would be more happening at a more faster rate than the diffusion mechanism and so whenever you have a very high temperature in you chamber, the technique that is rate limiting would be the diffusion mechanism. So, at high temperature you can say that the CVD process would be in a diffusion limited regime. And at low temperatures so when the temperature is low surface reaction would significantly reduce compared to the diffusion process. So the Ks would be lower than Hg and as I told whichever is a slower process would be the rate limiting step and here the reaction rate will be the rate limiting step in the CVD process and so at low temperature you can call that the CVD technique operates in the reaction limited regime. So, this particular graph it is a pseudo-Arrhenius plot that shows the relation between the deposition rate and temperature in fact it is 1000 by T.

So as just now as we discussed the regions between the switching of the reaction regimes between high temperature and low temperature, we can see that at high temperature that means since X axis it is 1000 by T in the pseudo-Rhenius plot. This is a high temperature regime and at high temperature regime the reaction would be operate the CVD process would be operating in a diffusion limited regime and at a low temperature region the CVD process would be operating in a reaction limited regime that is the dependence of CVD process upon temperature. Then there is another concept that is so for example when you consider this particular figure say for example this is a CVD chamber and this is a figure shows how the gas flows across your substrate that is placed in your CVD chamber. This is a point at which the precursor molecules are taken inside your CVD chamber. So, this is a point x equal to 0 where the precursors are taken inside, and this is a point x equal to L where L is the length of your CVD reactor or length of the chamber over which in which you have kept your substrates. So, whenever the precursor molecule flows above your wafer surface what happens is similar to that of the friction mechanism you have shear forces that will reduce the velocity of these gas molecules. So, as the gas molecules travel along your substrate surface throughout the length of the chamber, there would be a velocity gradient existing throughout the length of the chamber due to this shear forces acting on the gas molecules. So, you can say that at points close to the substrate surface the velocity would be almost equal to 0 and as you move away from your substrate in the vertical direction the velocity would keep on increasing. So, this is the velocity profile of the gas molecule above your substrate surface.



At the points close to the substrate surface you have almost zero velocity because the effect of the shear forces would be more and as you move away the velocity will keep on increasing because the effect of shear forces would be less at a distance far away from your substrate. So due to the existence of this velocity gradient for the gas molecule above your substrate you can say that a boundary layer is formed above your substrate surface. So this is not a physical kind of layer existing in the chamber but it is actually a concept existing in the chamber due to the velocity gradient and again this velocity gradient is happening due to the shear force that acts on the gas molecule when it flows above a substrate. So, as you move from x equal to 0 to x equal to L, you can say that the thickness of the boundary layer keeps on increasing. So the boundary layer which is rising due to the shear force increases along the length of your substrate and also as I told you, you are inputting or inserting the precursor molecules at the starting of the chamber in the CVD process.

That means at x equal to 0, you have an influx of CVD precursor molecules and along the length of the chamber, the precursor molecules will be consumed. So, when you think of the precursors available in the reactor for reaction, you can say that at the particular point x equal to 0, you have large number of precursor molecules available. But at x equal to L, the amount of precursor molecules available for the reaction would be less and this is due to the sources being depleted due to consumption. So, due to these two reasons, the growth rate will be decreasing along the length of the chamber. And to compensate for the reduction in growth rate throughout the length of the chamber, you can use various techniques.

For example, in your CVD reactor, you can use a tilted substrate. That means a substrate can be placed in a tilted manner. to account for the reduction in growth rate due to these two reasons. These two reasons is the increased boundary layer thickness throughout the length of the chamber and the depletion of the precursor molecules throughout the length of the chamber. Due to these two reasons the growth rate is reduced and to account for this reduction in growth rate along the length of the chamber you can use a tilted substrate as well as you can inject the precursor molecules at different points along the length of the reactor.

Instead of injecting the precursors only at the beginning point. So, these are the few steps that we can take into consideration while designing a CVD chamber where you can take into consideration the boundary layer thickness and the depletion of the source gas molecules as well. Coming to designing a CVD chamber as we mentioned there are two types of regimes that is a reaction control regime and a diffusion control regime. In a reaction control regime, as we already discussed, the rate of deposition is very sensitive to variations in temperature. So, whenever you are designing a chamber to operate in a reaction control regime, the chamber must be ensured to have the best possible temperature uniformity

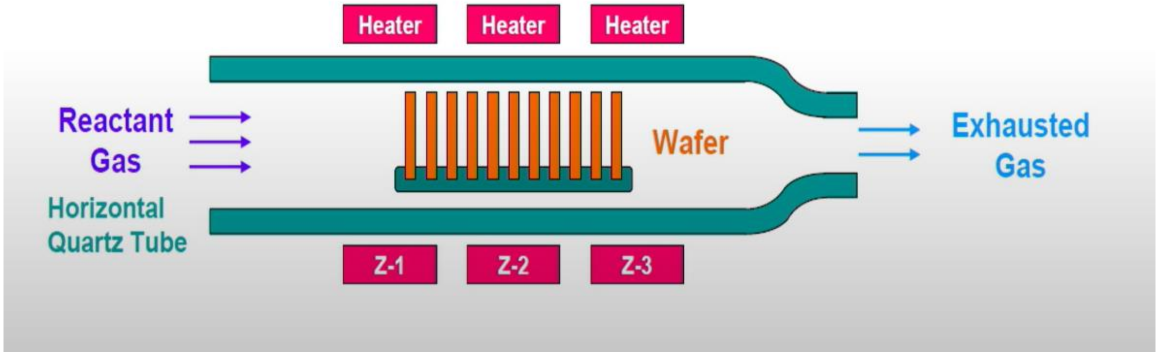
Whereas moving on to a diffusion control regime, whenever you are designing a chamber that needs to be operated in the diffusion control regime. The main control factor or the key point would be the variation in the gas flow. So, at that particular regime when you design the chamber you have to design it such that you have the best possible flow control and uniformity in the chamber. So, these are the two types of reactor the CVD chambers or reactors a Hot wall reactor and a cold wall reactor and hot wall reactor is used to hot-walled reactor is maintained, so that the temperature control after about 1 plus or minus 1 degree Celsius is possible in the hot-walled reactor. Whereas in a cold-walled reactor, the main concern will be to ensure uniformity in the flow of precursor molecules.

So, based upon the requirement of the rate limiting step, the chambers would be designed in a manner so as to achieve uniformity. In a hot-walled reactor, the concern will be to have a good uniform temperature control and in a hot cold-walled reactor, the main concern will be to ensure uniformity in the diffusion process or uniformity in the precursor flow. So, these are the different types of surface reactions that can happen in a CVD chamber. It can be a decomposition reaction where a molecule decomposes to its constituents at a particular temperature. Example is a decomposition of silane at a high temperature of around 650 degrees Celsius to form silicon.

Then you can also have a reduction process happening in your chamber in presence of hydrogen that is a tungsten hexafluoride it can undergo a reduction reaction in the presence of hydrogen to form a tungsten film. Then there can be oxidation process taking place in the presence of oxygen, also you can have the formation of compounds as well. So, these are just a few examples of the different types of chemical reactions that can happen in your chamber based upon the choice of your precursor molecule, the temperature and the pressure. Then moving on to the different types of CVD as I mentioned in the beginning, we have different types of CVD and few of them are listed here. One is the atmospheric pressure CVD, next is the low-pressure CVD or LPCVD, then we have plasma enhanced CVD or PECVD.

So, in atmospheric pressure CVD we know that we already discussed that diffusivity is proportional raised to 3 by 2 into the ratio of partial pressures. So based upon the pressure in the chamber the reaction rate or diffusivity will be the rate limiting step in the particular CVD process. So for example if you consider a low pressure CVD process in that the pressure that is maintained in the chamber will be very low. So, the amount of diffusion process happening would be high. So, in that case the rate limiting step would be surface reaction.

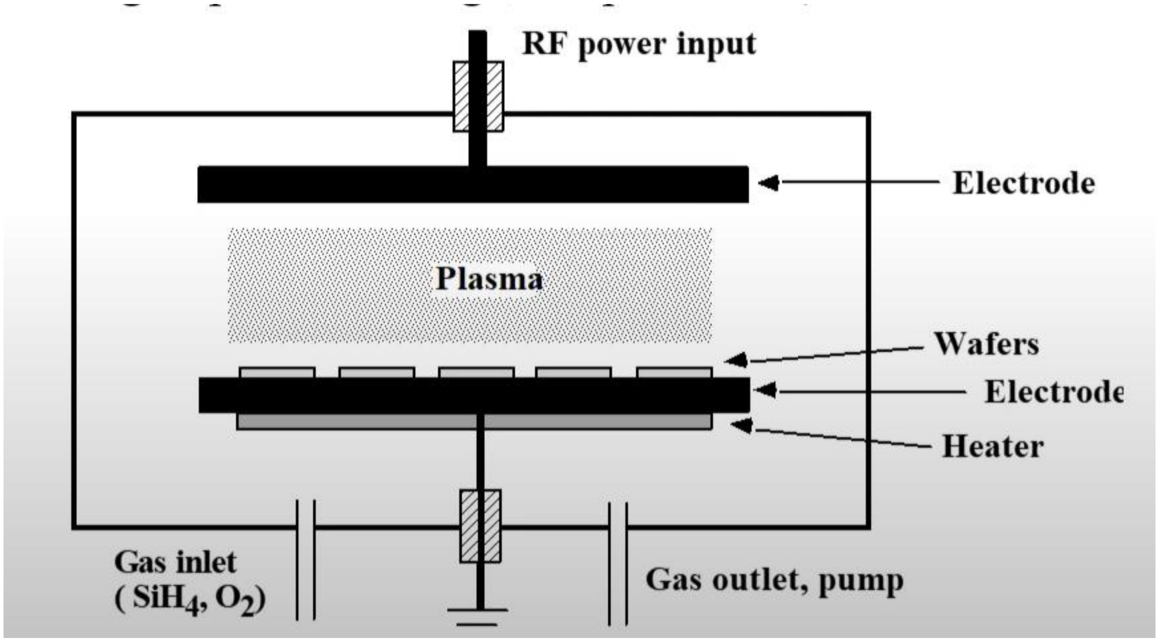
So, that is why in a low-pressure CVD or LPCVD we call it as a reaction limited regime process because diffusion happening at a very high rate and surface reaction is the one that is happening at a low rate. So, LPCVD where the pressure is maintained at a very low level it always reaction rate limited regime is the one in which LPCVD reactor operates. but the film formed will have excellent uniformity and purity, but compared to the deposition mechanism and atmospheric pressure the deposition rate would be a bit low. Whereas in atmospheric pressure CVD which based on this particular equation you can arrive upon the conclusion when the pressure is high then whatever is the rate limiting step it would be in that particular regime at which the CVD process operates. So, if the pressure is high diffusivity will be low so it will be a diffusion limited process, but we can have a high deposition rate due to a high pressure existing within the CVD chamber. But compared to LP-CVD the film uniformity or purity would be less. And entirely different from this we have plasma enhanced CVD whereas instead of thermal energy or in addition to thermal energy we would say plasma is used to initiate the accelerate the chemical reactions that would not have taken place at a low temperature if plasma is not generated. That means the main point of using plasma enhanced CVD is that we are further lowering the reaction temperature and so instead of thermal energy we are using plasma to force the reactions to happen. So, the main advantage of PECVD would be low temperatures.



Now the figure just shows the basics of an LP-CVD process. So, as we mentioned in LP-CVD or low-pressure CVD, the pressure would be kept very low, and the temperature would be sufficiently high about 500 to 800 degrees Celsius. And as we mentioned in the previous slide, surface reaction rate is a rate limiting step and so LP-CVD operates in a reaction limited regime. So, to enhance the reaction rate or to increase reaction rate you have to increase the temperature and since temperature sensitivity is very high the entire chamber should be designed such that we should have a plus or minus 1-degree Celsius control over the reaction temperature. Then also I have told about the existence of a boundary layer as well as the depletion of source or precursor molecules throughout the length of the chamber.

So, you can see that you can see that in a LP-CVD reactor throughout the length of the reactor you have a temperature gradient for example around 5 to 25 degrees Celsius of temperature gradient is maintained that is to compensate for the source gas depletion effect. Or we can say that instead of maintaining this temperature gradient we can use a distributed feeding. That means other than in letting the reactant gas only at the inlet point of the chamber you can insert the gas molecules at different points throughout the chamber. So either this distributed feeding can be used or you can maintain a temperature gradient throughout the chamber. In order to take into consideration about the source gas or precursor depletion effect.

So, this is a particular horizontal quartz tube reactor where it is heated through using different heaters. So that we can have a very precise control over the temperature, and you have the substrate holder where your wafers are arranged vertically or stacked vertically to have a higher deposition rate and uniformity. So, the next type of CVD reactor would be plasma enhanced CVD reactor. So, as I mentioned, instead of thermal energy in a PE-CVD reactor you have plasma to make the reaction happen better at a low temperature. So, RF energy is used to transfer the energy to the reactants that so that we can form radicals that are very reactive, and the reaction temperature is further reduced to say for example, less than 300 degrees Celsius because thermal energy would be very less critical when you already have RF energy existing in your chamber.



Then it is a surface reaction rate limited process and also since it is a reaction rate limited process, temperature control over the entire chamber is important to ensure uniformity. The main disadvantage of using a PECVD technique is that the film may not be pure also there can be damage to your substrate due to the formation of plasma. The plasma can damage your substrate, and the film also may not be pure, but the main advantage would be a very low temperature operation. So, these are just a few examples of CVD process. There are many more types of CVD techniques as well which you can go through and understand further based on the concepts that we have already discussed.

So, I hope you have got a basic idea of what is chemical vapor deposition, what are the different types of chemical vapor deposition, then how the CVD regimes are divided based upon the temperature of operation or based upon what is the rate limiting step in that particular CVD reaction. Then we have seen the basics of a design of a CVD chamber like how hot wall reactors are designed, how a cold wall reactor is designed and also, we have seen few basic concepts of the types of CVD like APCVD, LPCVD and PECVD. And furthermore, concepts on CVD you can explore further and that is all for the session on chemical vapor deposition. Feel free to get back to us if you have any doubts.

Thank you.