Chemical Engineering Principle of CVD Processes
Prof. R. Nagaranjan
Department of Chemical Engineering
Indian Institute of technology Madras
Module-3
Lecture 23
CVD applications: CVD in Free-Molecular Flow Regime

Good morning and welcome to this lecture in our course on chemical engineering principles of CVD processes. In the last few lectures we have been looking at various applications of CVD technologies, different reactor designs and some of the modelling and simulation challenges associated with these particular designs of reactors.

So we will continue the discussion today and we want to look at a reactor that is very different from what we have been looking at so far. The main difference is this reactor operates in such a way that the continuum assumption breaks down. As you know all the equations which we have been formulating are all based on the continuum approximation which basically says that the Knudsen number is very small which is the mean free path divided by characteristic dimension of the system is much smaller than 1. Under such conditions the Knudsen number is much smaller than 1 and therefore the continuum assumption is valid.

However as your characteristic dimensionless shrink and as the mean free path becomes larger you have to start questioning the validity of the continuum assumption. This can happen particularly in ultrahigh vacuum systems because as a pressure drops the distance between the molecules increases and the possibility that the molecules can travel fairly long distances before encountering each other is also high and therefore the mid feedback tends to become somewhat comparable to the dimensions of the reactor itself and that is called the free molecular regime.

And so when you make the transition from continuum modelling to free molecular regime modelling there are certain things that you have to be aware of. So a good example of this kind of a system is a, one of them is a pulse pressure CVD reactor for depositing oxides such as titanium oxide metal organic compounds. We had called this MOCVD if you remember metal organic CVD.

Typically the precursors are metal Alkoxides and they had reacted with an oxidation under fairly low-pressure conditions and the advantage of using the metal organics is that they tend to vaporize easily they have a high vapor pressure. Now this particular reactor the main design difference is that instead of injecting vapours into the system you actually do the vaporization (()) (3:20) and they way you do that is you take the liquid precursor send it to or spray it through a nozzle into the reactor.

The nozzle itself has an ultrasonic setting on it the addition of the ultrasonic feature to the nozzle breaks up the liquid into very very fine droplets and as they enter the reactor they vaporise immediately because the burning time of a droplet goes as droplet size squared roughly, so the finer the droplet the more rapidly it burns. So in the system you essentially inject this very very fine aerosols into the reactor and as soon as the experience the high temperature and low pressure conditions they burn very easily and thereby the vapor is created which then reacts with the substrate form the film and so on.

So in this particular case for the modelling of the reactor is more, we do not really look at the continuum flow but rather at what individual molecules are doing. So the model if you recall from the last lecture we had identified various timescales and length scales associated with various components of an overall model of a CVD reactor. Again in the case of free molecular regime the macroscopic modelling, you know, the conservation laws and even some of the constitutive relationships are actually not valid anymore.

So you essentially start focusing more on the substrate itself as the molecules arrive at the substrate what happens? Rest of the system you make certain simplifying assumptions, for example you can just assume that the entire reactor is well mixed, so that the concentration of the reactant is the same everywhere within the reactor.

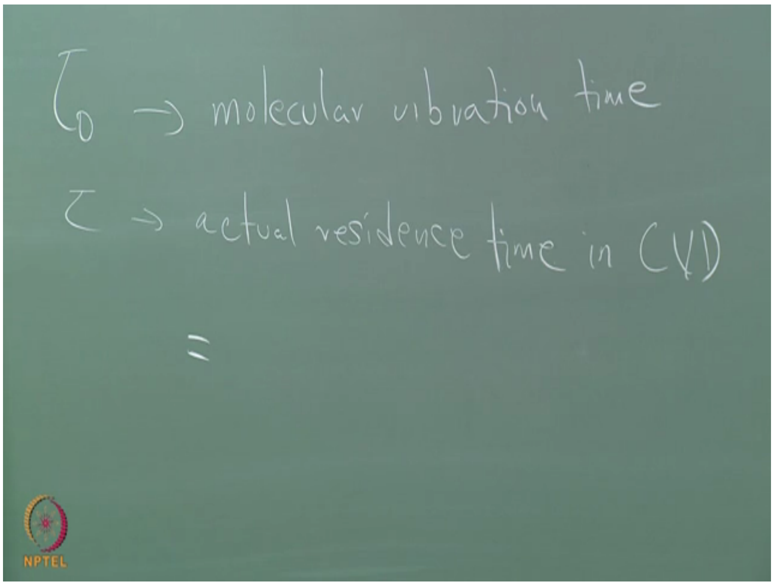
Now normally in continuum systems that is a very questionable assumption because we know that due to the viscosity effects that are present the fluid dynamics are very different at different locations in the reactor, for example a boundary layer develops near the substrate and mass transport occurs by diffusion across the boundary layer even if the rest of the reactor is nominated by the convective transport.

But in the case of a low-pressure system where you are getting close to the free molecular regime you do not really have to look at the macroscopic fluid dynamics in that much detail. You can essentially assume that molecules are flying around and assume that it is a well mixed reactor, so that the molecular concentration everywhere is the same and you tend to focus more on what happens when the molecules arrive at the substrate.

And in fact, you know, Monte Carlo simulations are used in order to vigorously calculate the deposition rates in the free molecular regime but if we look at a slightly simplified model of what is going on, now for example when a molecule arrives on a substrate one of the key factors that determines whether it sticks to the surface or not is the residents time on the substrate, how much time does the molecule actually stay in contact with the substrate.

And in the case of where there is no chemical attraction between the molecule and the substrate this simply is reflected by the molecular vibrations status of the specific molecule. Every molecule has its own vibrational mode and in the case of free molecular transport regime the molecule arrives at the substrate and sits there kind of vibrating for some period of time and then it leaves.

(Refer Slide Time: 7:40)



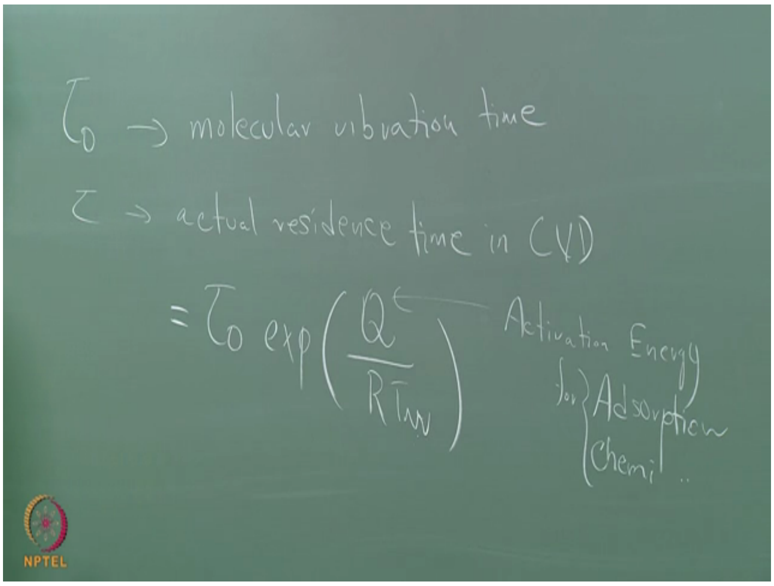
$\tau_0 \rightarrow$ molecular vibration time

$\tau \rightarrow$ actual residence time in CVD

$=$

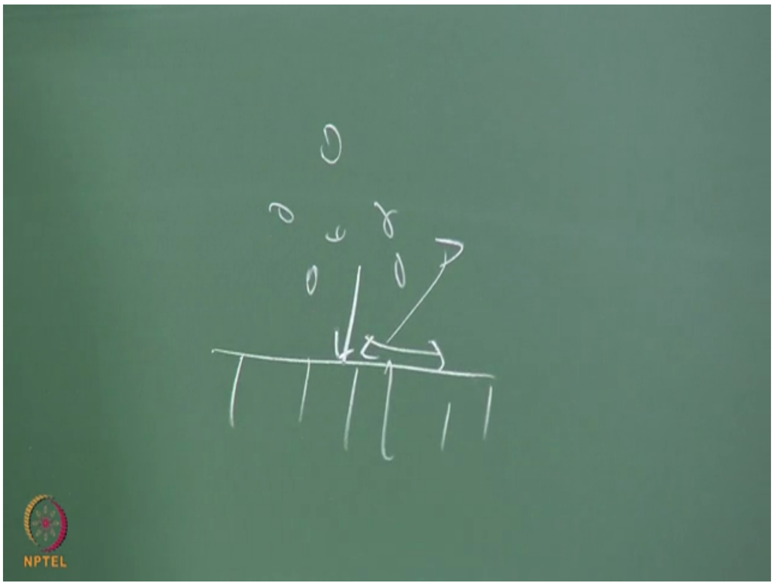
So if you call that time some Tau 0, this is the molecular vibration time on the substrate, a characteristic time for which the molecules sits and vibrates on the surface then the actual resident time which is essentially chemical enhanced. There is a heterogeneous chemical reaction there is going to bind the molecule to the surface which means it is not going to leave as quickly it is going to stay at the surface longer.

(Refer Slide Time: 8:30)



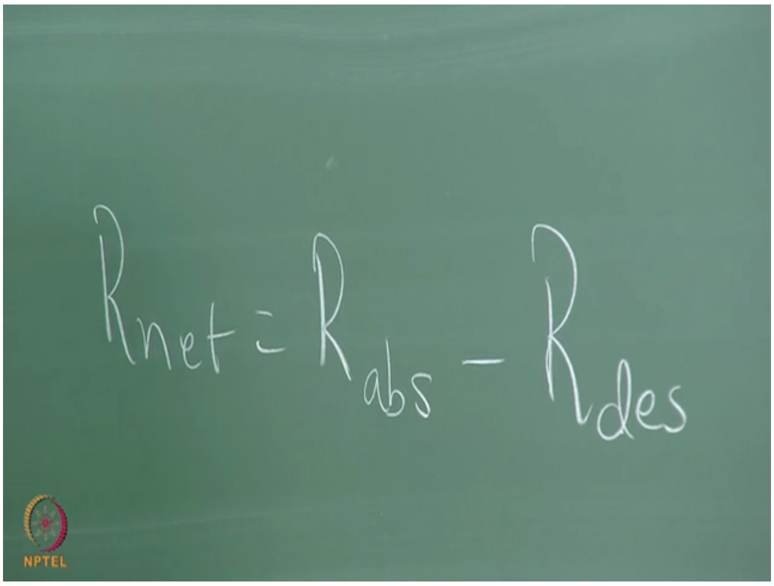
And that is given by Tau 0 times exponential of some Q over RTw where TW is the temperature of the substrate and Q is an activation energy for adsorption or chemisorptions. So this Tau 0 is going to be greater than Tau 0 by some value. Now as long as Tau over Tau 0 is significantly greater than 1 that is 5 to 10 times or 5 to 10, the probability of capture or the sticking coefficient starts to approach 1. In other words the longer the molecule spends on the surface the higher the likelihood that it will be incorporated into the surface. So the probability of capture, probability of incorporation increases as this value increases.

(Refer Slide Time: 9:58)



Now if you look at the dynamics of what is happening at the substrate, so you have these molecules that are arriving and some of them are rebounding and the remainder are actually getting distributed on the substrate. So if you look at the rate of processes that are going on here the rate that is relevant to build up of the CVD film is the net rate.

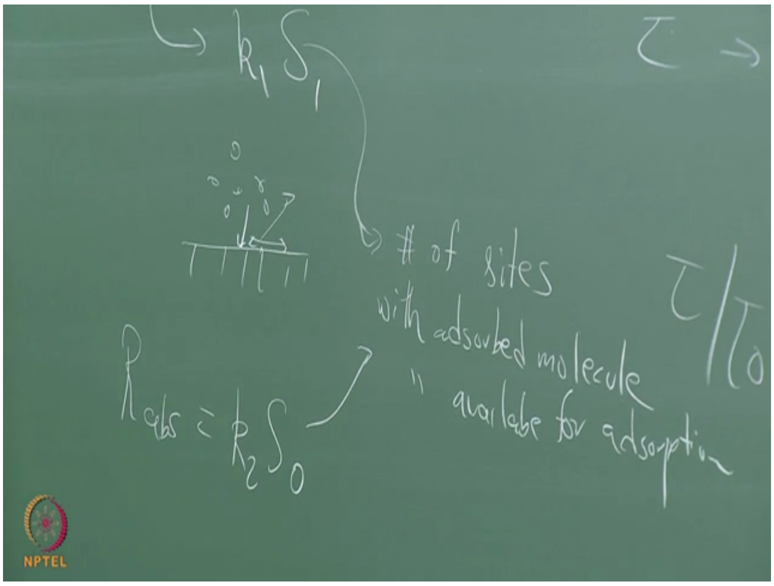
(Refer Slide Time: 10:43)



$$R_{net} = R_{abs} - R_{des}$$

So the R, let us call that R net is essentially equal to R adsorption minus R desorption where the rates can be of the order of number of molecules per unit time for example. So what you really have to do again this is particularly important in the case of low or high Knudsen number flows. You have to be able to describe the kinetics of each of these steps.

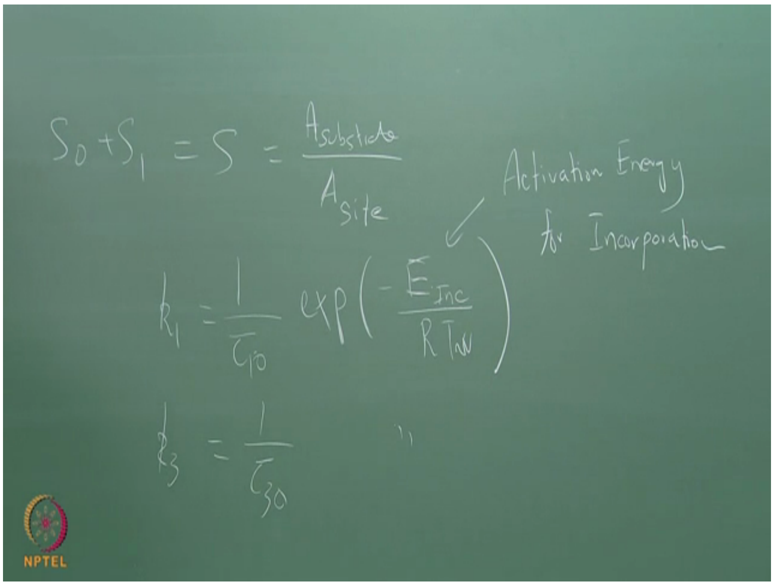
(Refer Slide Time: 11:09)



Now if you look at this step lets write that as some k1 times S 1 where k1 is let say your first order rate coefficient and that S1 is the number of sites with an absorbed molecule and similarly you can write the desorption candidates as let say some k3 times S1, so of course desorption is essentially the inverse of the adsorption process and again it depends on number of sites that have taken or absorbed a molecule.

This one the R adsorption you can write as some k2 times S0 where S0 is in number of sites that are available for adsorption but it also depends on 2 other parameters, first is pressure and in a pulse pressure reactor the pressure is a function of time, it essentially scales between atmospheric pressure to extremely low pressures and also a concentration term. The concentration of the depositing species which is taken as a constant value in a well mixed reactor. So that is the overall kinetics of the adsorption process.

(Refer Slide Time: 13:04)



$$S_0 + S_1 = S = \frac{A_{substrate}}{A_{site}}$$

Activation Energy for Incorporation

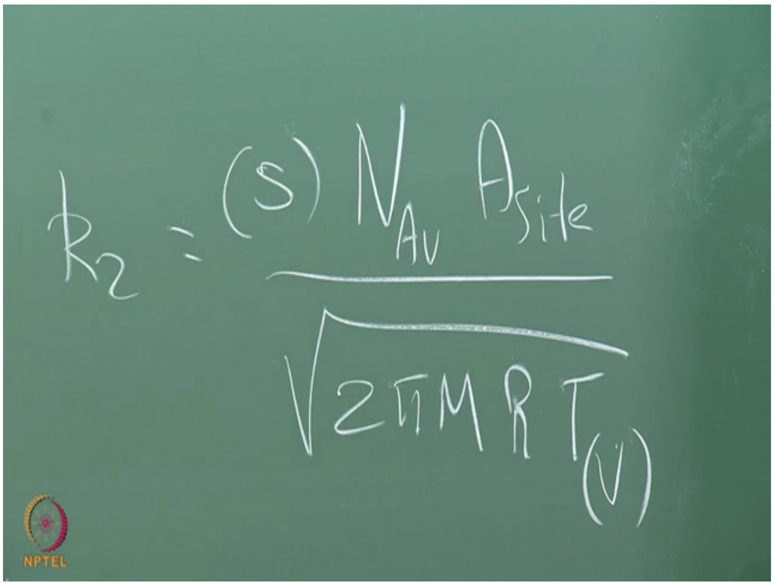
$$k_1 = \frac{1}{\tau_{10}} \exp\left(-\frac{E_{Inc}}{R T_W}\right)$$

$$k_3 = \frac{1}{\tau_{30}} \quad ''$$

If you look at S0 plus S1 of course that gives you the total area that is available and you can also write that as the area of the substrate divided by A site. So this S is total number of sites system both adsorbing sites as well as available sites and that is equal to the total substrate area divided by the area per site, right? So just a matter of representing the area. So if I look at for example classic one of these parameters k1, it can be written in terms of the residence time that we defined earlier.

And k1 is typically defined as 1 over del 1 0 times exponential of minus e incorporation over RTW where Tau 10 is a characteristic residence time corresponding to the adsorption process and this is the activation energy for incorporation, chemical reaction and incorporation of the adsorbed species into the substrate and again Tw is the temperature of the substrate and similarly we can take k3 as being equal to 1 over tau 30 times the same exponential parameter and where this down 30 is defined as a characteristic time for desorption of an ads of molecule on the surface.

(Refer Slide Time: 15:46)



$$k_2 = \frac{(S)\,N_{Av}\,A_{site}}{\sqrt{2\pi M R T_{(V)}}}$$

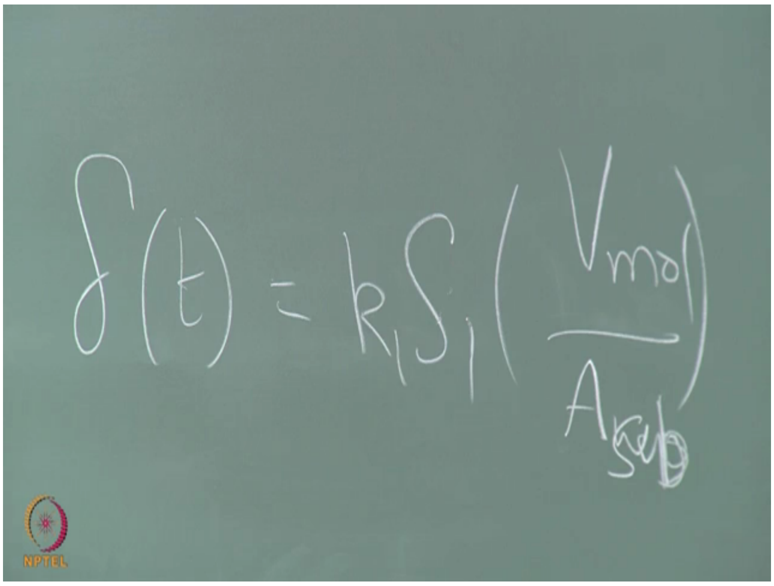
Now the third parameter k2 reflects the kinetic of adsorption. So it is something that must be calculate it essentially for the molecule theory of gases or it must be experimentally measured and recorded. So if you want to derive this from the molecular theory of gases then you have to go back to the Avogadro number, sticking coefficient and so on and it is actually written as S which is the sticking coefficient of the sticking probability times the Avogadro number and is the area of the adsorption site that is same parameter as this divided by square root of 2pi MR TV where this TV now is a temperature of the vapor zone by the way this model is called the Langmuir model.

And this expression for Tau is called the Henkel model and together they help us define the kinetics of thin film growth in the free molecular flow regime. The key assumption here is that adsorption of a molecule onto a substrate only occurs from a group of molecules that are present within one mean free path of the surface. So you take all the molecules that are present lambda away from the surface and you assume that surface adsorption can only happen when the molecules are within that layer.

It is basically based on the hypothesis that in order for adsorption to happen collision must happen and a molecule can only collide with a surface if it is present within one mean free path of the surface. So based on that assumption than the temperature TV is essentially the temperature of the vapor layer one mean free path away from the substrate, okay, whereas Tw is the temperature of the substrate itself.

Okay, so k1, k2 and k3 can therefore be obtained from the kinetic theory of gases as well as some experimental obtained constants the describe the rate processes. So once you have this you can then proceed to calculate essentially Rnet.

(Refer Slide Time: 19:00)

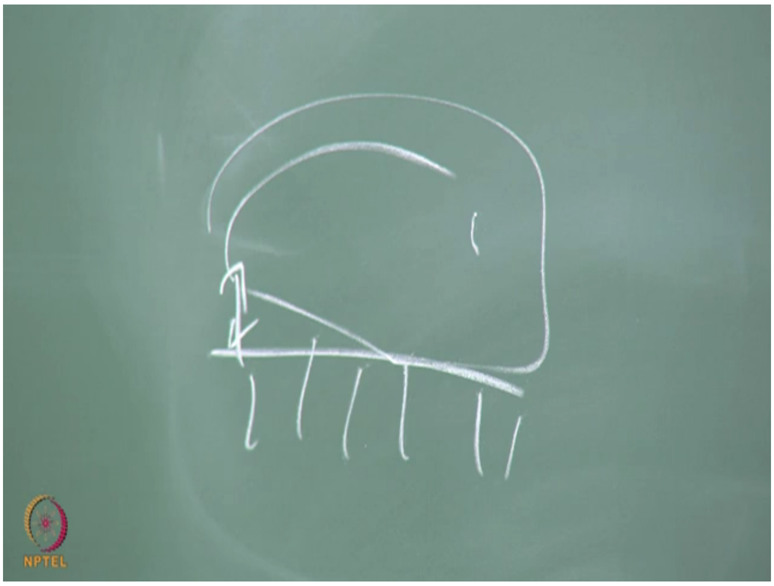


$$\delta(t) = k_1 S_1 \left(\frac{V_{mol}}{A_{sub}} \right)$$

So if we write an expression now for Rnet, right next question for delta that is the flim thickness as a function of time this will essentially be this Rnet which is equal to k1 times S1 and it will be multiplied by this is a number of molecules that are getting adsorbed on the surface. So this must be multiplied by the molecular volume of the molecule that is getting adsorbed divided by the total area of the substrate or A substrate as we have called it.

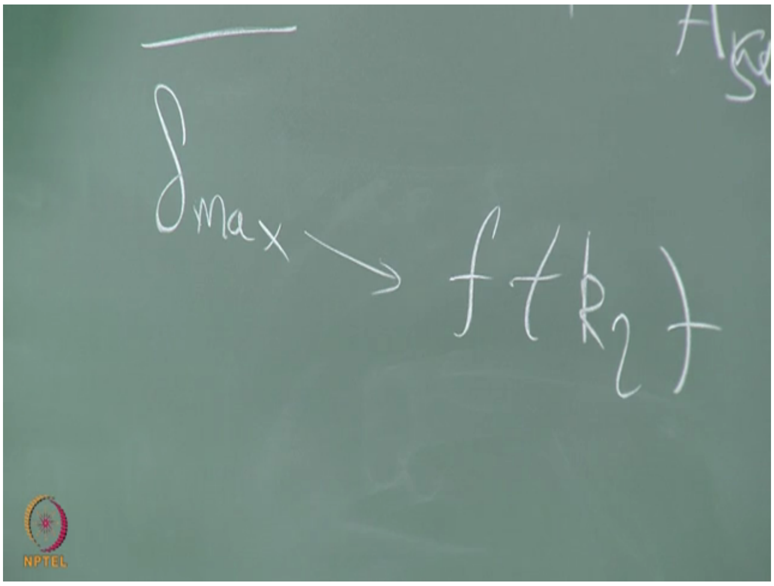
So what you are doing here is taking the total amount of material that is arriving in terms of volume dividing it by the area, so you are essentially looking at this whole area on which deposition is happening and you have a certain volume of material that is arriving.

(Refer Slide Time: 20:18)



So if you divide the volume by the surface area that gives you this end dimension of the thickness of the film where it is depositing. So this is the formula that is used to calculate the rate at which the film thickness builds up over time and what you can do is, you can non-dimensionalize this by taking delta Max which is the maximum rate of film growth which would assume that every molecule that impinges on the substrate sticks to the surface.

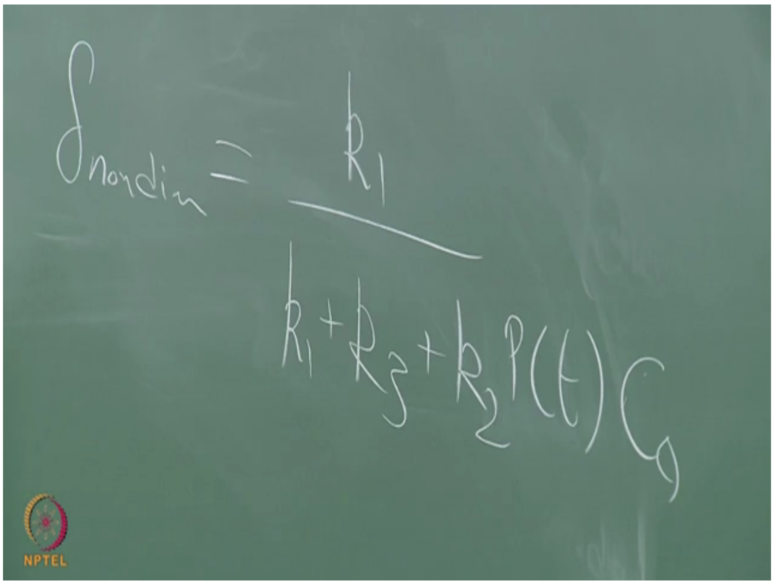
(Refer Slide Time: 21:05)



$$\delta_{max} \rightarrow f(k_2)$$

So this delta Max will essentially be only a function of k2. In other words you will assume that R adsorption equals R net, so that gives you the maximum value.

(Refer Slide Time: 21:22)



$$\delta_{nondim} = \frac{k_1}{k_1 + k_3 + k_2 P(t) C_0}$$

So if we take this parameter Delta T over delta Max that gives you a non-dimensional value for film thickness it is obviously dependent only on these 3 parameters k1, k2 and k3 and in fact the expression that is written is k1 over k1 plus k3 plus k2 times P of t times C0 which is the concentration of the depositing material in the gas phase. So this expression is normally used to model a growth of a thin film on a substrate then free molecular regime flow.

Now the interesting thing about this course is, that it is totally based upon the kinetic rate constants so for surface processes, the prevailing pressure and the prevailing concentration of the depositing species. If you recall I mean if you compare this with a film growth rates that you have calculated earlier in the continuum flow situation we were primarily looking at the mass transfer coefficients that govern diffusion for calculating the rate at which film is depositing.

So that is a big difference when you go from continuum approximation you forget about the Nusselt number, you forget about Schmidt number all of that does not make any sense because the implicit expectation is that you are in continuum flow range which is a good assumption most of the time but particularly in CVD systems in the kind of low-pressure CVD systems that we have talked about here, plasma enhanced CVD systems, the conditions can be such that the mean free path are quite large and then you have to be really really careful about applying the continuum approximation in those cases.

Instead you essentially revert to this type of molecular view of what is going on. You try to model how many molecules are contained within a certain volume of gas? How many of those molecules are likely to impinge on the substrate? When they do what is the probability that some of them will rebound? What is the probability that some of them will get incorporated into the substrate? And based on this kinetics you estimate the rate for growth of the thin film.

There is a very different type of modelling approach and it is not as I would say theoretically based as the continuum model because actually the theory of free molecular flow is not very well developed even now and by the way the challenge becomes especially critical when you start approaching this transition range. As the Knudsen number gets close to 1 it becomes increasingly difficult.

If very small Reynolds number we know how to deal with, you know, that is basically continuum extremely large Knudsen numbers we know how to deal with because you can essentially track molecules like particles, so that is basically what we are doing. We are following individual molecular dynamics and using that to calculate what happens but in the interim when the mean free path is comparable to the dimensions of the system when you kind of have a situation where you can have intermittently continuum and intermittently free molecular behaviour that there is virtually no theory yet to describe and most of the analysis is done purely on the basis of experimental data and empirical observations.

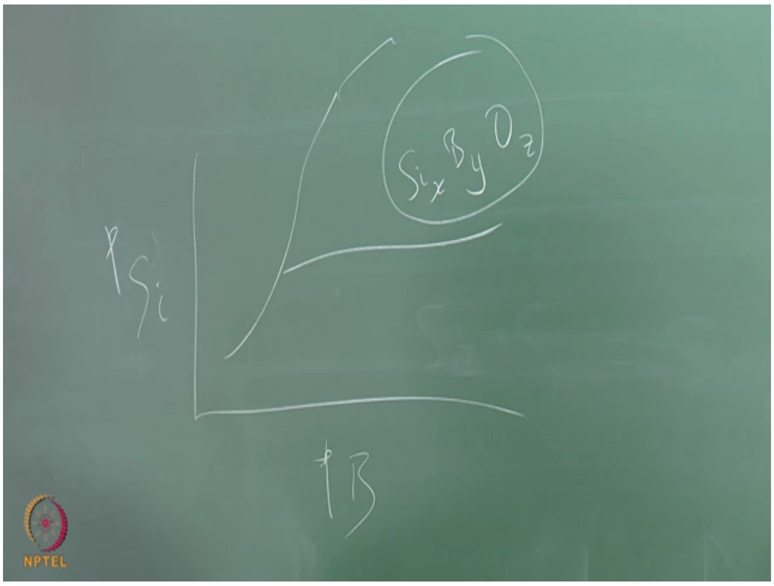
Okay, so that is an interesting extension of the CVD reactor design that brings the free molecular regime into play. Another aspect of CVD systems that we have touched upon in the past are that they can also be used as doping systems. Now the challenge when you use dopants is that, they are present in even smaller quantities than the CVD material, you know, CVD material itself you typically want to use at high dilution, so that its concentration is in trace amounts in a carrier gas.

When you use a Dopant that is typically another order of magnitude smaller in concentration. Now the challenge that presents is that, when you have such small concentrations the limiting factor for incorporating the Dopant into your film becomes the thermodynamics of the system. You have to start with the thermodynamic phase diagram because the amount of material that is going to be available to form the Dopant in the film is going to be very very small.

And so unless you are operating well within the thermodynamic constraints the film may never form and so when you start analyzing some doping systems, you first start with a good thermodynamic phase diagram of the system and you try to operate your system, so that it is not anywhere close to the phase boundaries want to be right in the centre, so that even if there are small changes in the concentration of the Dopants.

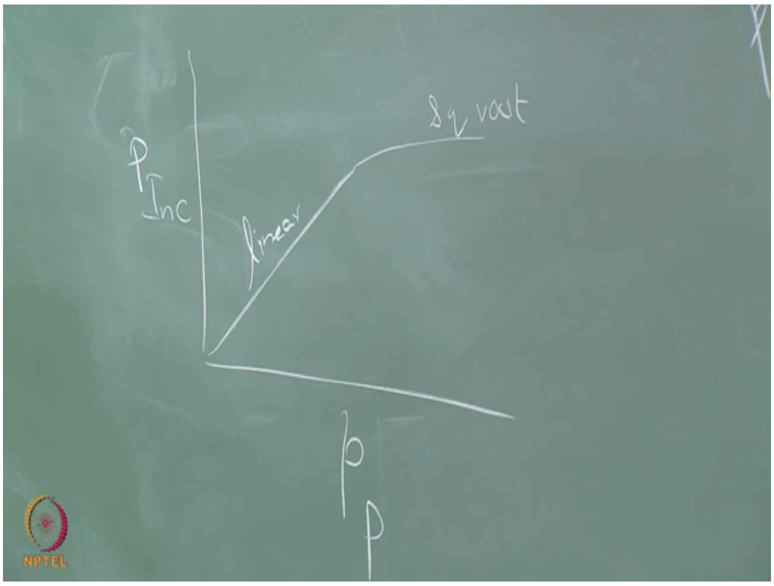
It is not going to prevent the Dopant from being incorporated into the film. Classic example would be if you have a silicon film and you want to incorporate phosphorus as a Dopant or another case we looked at earlier all these silicate and borosilicate glasses and phosphosilicate glasses where you try to incorporate boron and phosphorus into silicon dioxide.

(Refer Slide Time: 27:36)



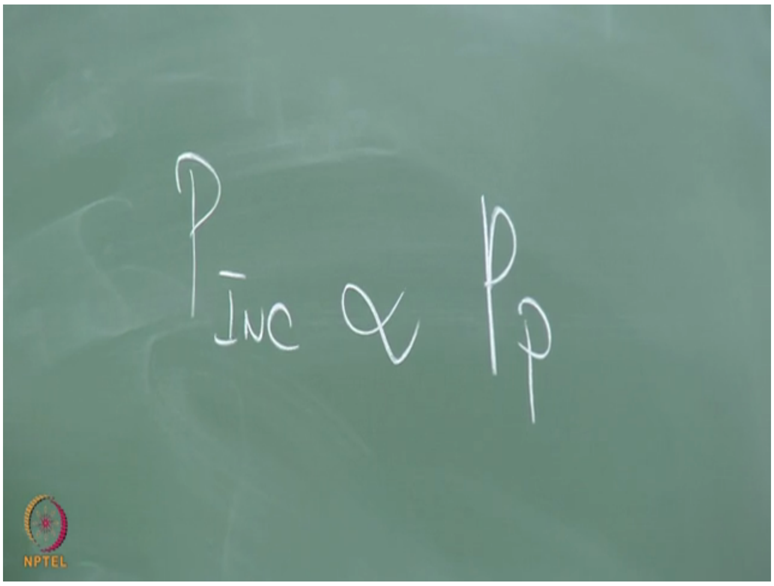
In all the system again you start with the analysis of the phase diagram, so once you have some idea about, you know, for example if you are incorporating boron in silicon, you know, you should have some picture of what the phase diagram is going to look like and supposing you are trying to form a borosilicate Six D3 or By Oz you have to know what concentration range is a partial pressure range is of B an Si. You have to be at the form for this film to be even thermodynamically viable and then you try to set your thermodynamics of the system, so that you operate at the viability range.

(Refer Slide Time: 28:24)



Another example as we are trying to incorporate phosphorus into silicon people have done studies of how the partial pressure of phosphorus influences the phosphorus incorporated into the silicon and what you find is you get a linear relationship for a while but then the slope drops and it becomes more of a square root relationship. Now this is actually difficult to predict because normally you would expect that this should be essentially a linear dependence.

(Refer Slide Time: 29:15)

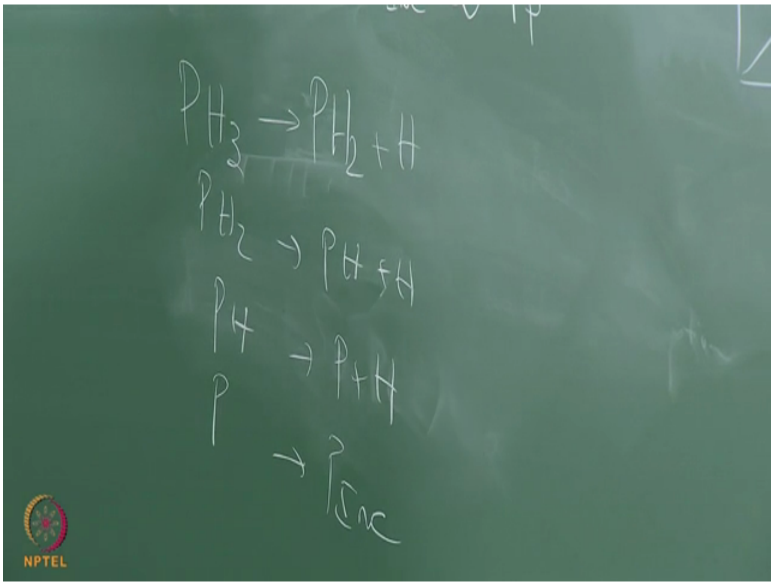


$$P_{INC} \propto P_p$$

The reason being that this P incorporated is obviously proportional to the partial pressure of phosphorus that is in contact with the substrate and unless it saturates you know you would not expect this type of behaviour and by the way this is not related to saturation there are plenty of available sites in your silicon to accommodate more phosphorus molecules it is not due to saturation.

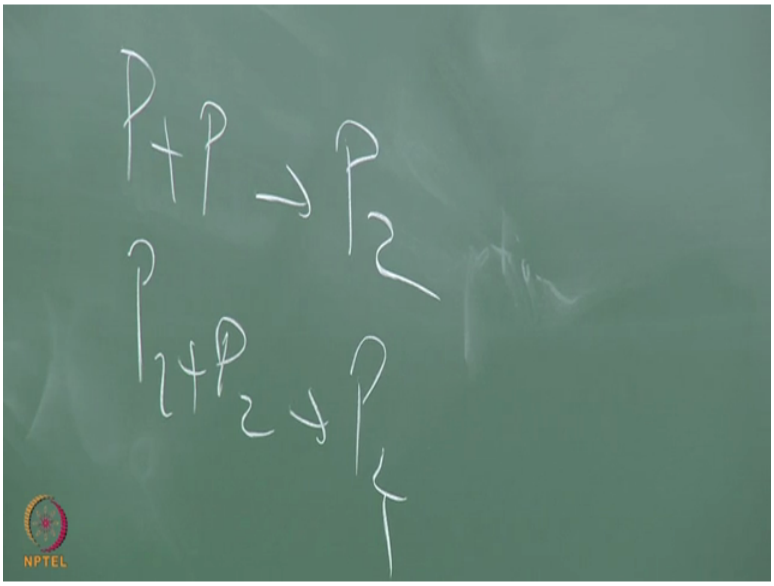
The reason that this happens is that the thermodynamics of the system changes as you change partial pressure because basically what is happening here is, the way you increase partial pressure is by increasing pressure and by increasing the concentration of the reacting species and as you do that, your thermodynamics itself shifts and some reactions are now favored which were not favored before.

(Refer Slide Time: 30:14)



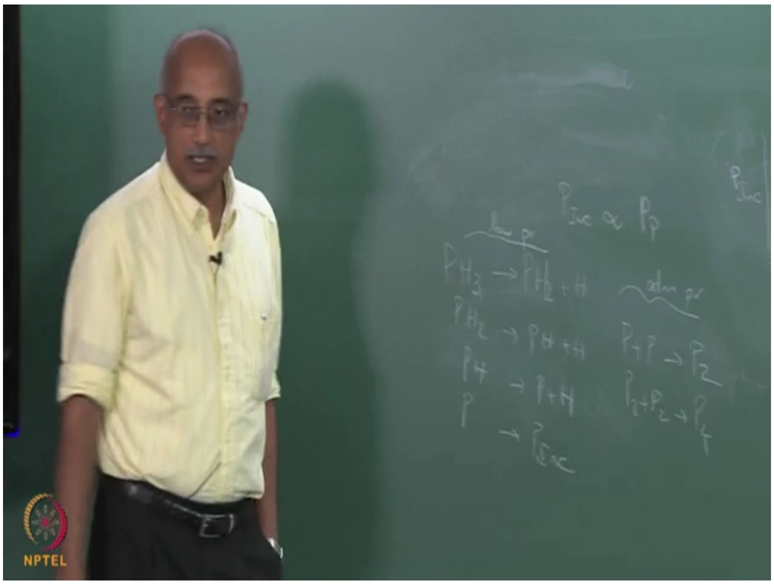
I mean if you look at really how phosphene which is the usual additive that is using this doping systems, how does phosphene incorporate phosphorus into the film? Basically you can, look at the sequence of steps PH3 goes to PH2 plus H, PH 2 goes to PH plus H, PH goes to P plus H and P then gets included or adsorbed into the substrate. Now as we know this is not necessarily the full range of reactions there can be many many more reactions taking place. This is somewhat of a simplistic representation of the sequence of reactions that can break down phosphene molecule and provide phosphorus molecule to get adsorbed and incorporated into the silicon film.

(Refer Slide Time: 31:16)



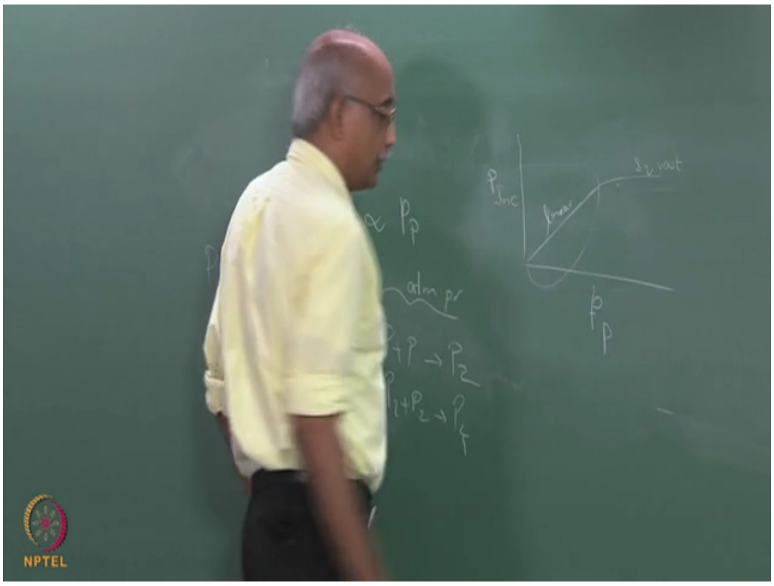
By the way there can also be secondary reactions for example P plus T can go to P2, P2 plus P2 can go to P4 etc these reactions can also potentially happen.

(Refer Slide Time: 31:36)



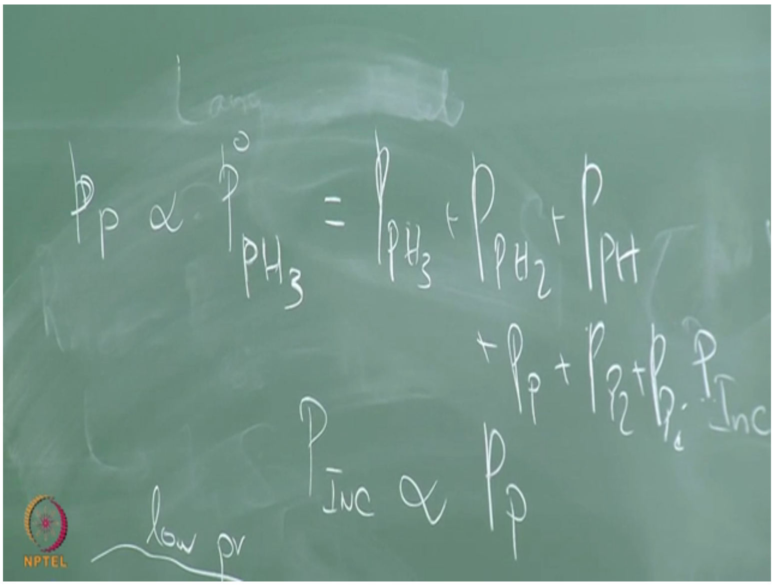
Now the interesting thing is that if you look at the effect of total pressure these reactions are more likely to happen closer to atmospheric pressure, essentially as you keep increasing the pressure the molecules get force together and start combining in forms that normally they would not. So in the low-pressure case these are the more likely that of reactions.

(Refer Slide Time: 32:05)



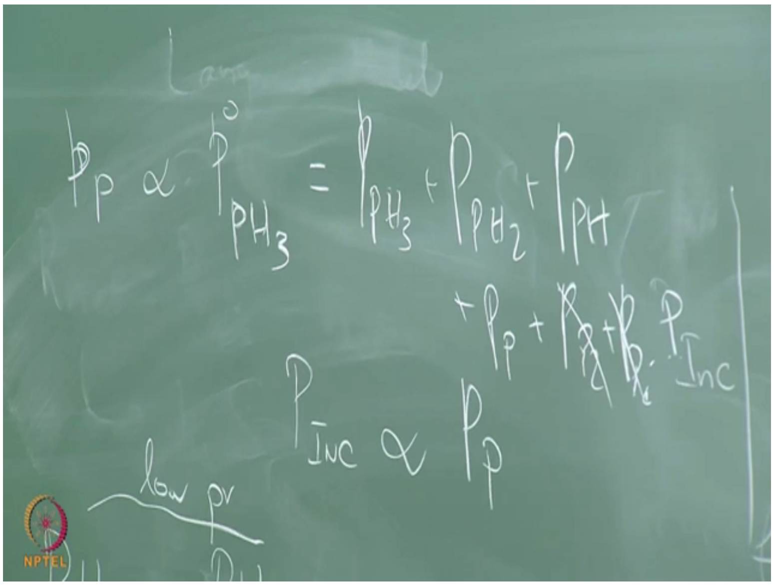
So what it implies is in the case of, you know, in this range the low-pressure range.

(Refer Slide Time: 32:12)



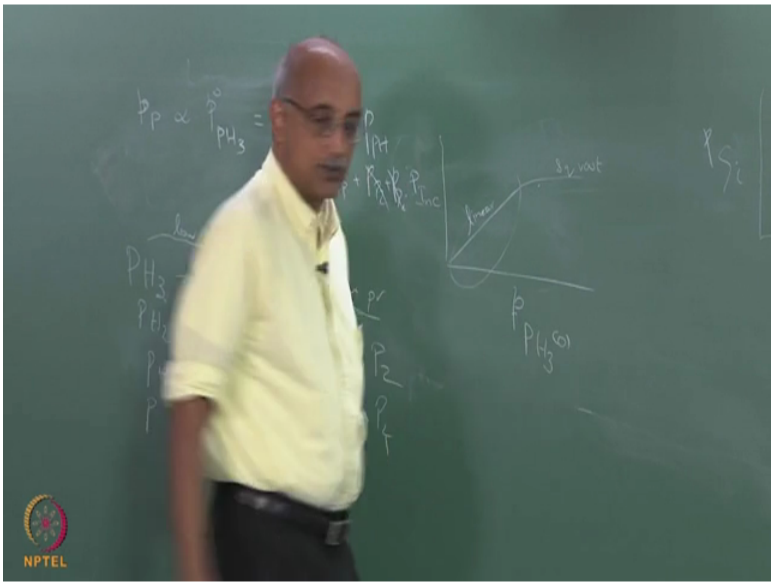
If I look at partial pressure of P that is proportional to the total pressure of phosphorus that was fed into the system P0 of PH3 which is essentially, you know, by mass conservation must be equal to P of PH3 plus P of PH2 plus P of PH plus P of P plus P of P2 plus P of P4 and so on.

(Refer Slide Time: 32:59)



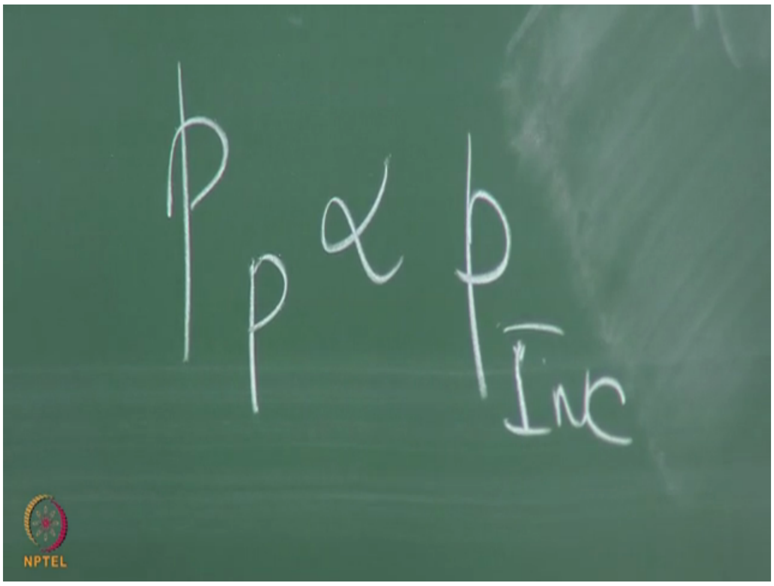
Now in the high-pressure case or in the low-pressure case P2 before etc can be neglected and actually it turns out that the dominant species for PH3 and PH2 in terms of the actual vapor pressure that are present in the system. So basically then in this particular case there is a linearly relationship between the Fick concentration of PH3 and the partial pressure of phosphorus near the substrate.

(Refer Slide Time: 33:34)



And that is why if you plot this initial concentration of phosphene in the system against incorporated amount of phosphorus into the CVD film you get a linear behaviour but as you keep increasing the pressure start forming these dimers.

(Refer Slide Time: 34:07)



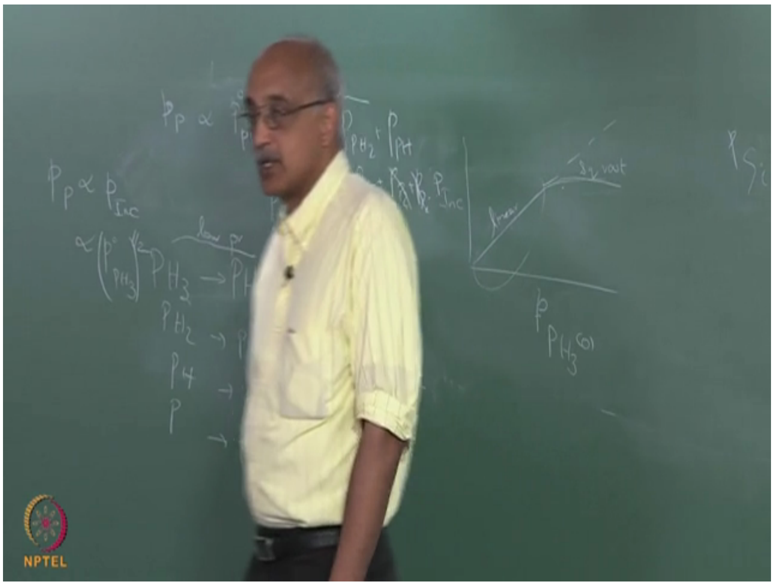
And when that happens PP which is really what is proportional to P incorporated is now not linearly proportional to the incoming for (()) (34:11) concentration but it is actually now proportional to P0 of PH3 to the power half because of the dimerization reaction that is the reason why you see this levelling of behaviour, the equilibrium has shifted from PH3 and PH2 being the dominant chemical species to P2 being the dominant chemical species and if you keep increasing the pressure further you will essentially see, you know, a levelling off or asymptotic behaviour because the dependence will become 1 4th and so on.

So the higher-order phosphorus molecules that you start forming the less will be the influence of initial feed pressure or feel pressure of phosphene on the amount of phosphorus that gets included in the substrate. So the key message here, you know, in the previous case we saw that as you keep reducing pressures to very low levels the interactions of individual molecules with the substrate becomes important.

The key focus really has to be on molecular dynamics in the gas phase as well as the kinetics of molecule adsorption and release and migration in the solid phase. Whereas in the case of CVD systems with doping chemicals as far as the Dopant is concerned the primary focus has to be on properly describing and capturing the chemistry or the thermodynamics of the various species that can form in the gas phase.

If you are thermodynamic database for example is not good enough, you know, for example if you do not have data in your database on P2 and P 4 and so on, you may never capture this effect.

(Refer Slide Time: 36:18)



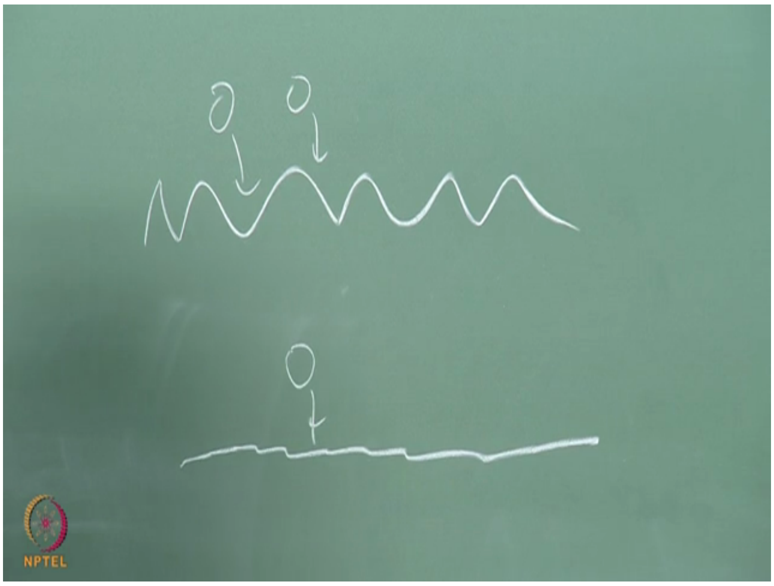
So your prediction will still be saying that, you know, will be going like this. Well I am sure when you measure the actual Dopant level in the film, you will see this levelling of effect and you will never know why. So it is very critical in such cases to be able to capture the thermodynamics and when you say capture the thermodynamics that has 2 aspects to it, one is how do you actually simulate the thermodynamics whether you use individual reaction sequences or whether use of free energy, minimization algorithm.

But the second part of it is do you have the relevant thermochemical data from these species in your database? And for many of the species that have encountered in CVD systems, thermodynamic database itself may not be adequate in which case, you know, you have to rely a lot on its experimentation and generating your own data to populate your database. The other interesting aspect about using of Dopant is that their effect on the surface is also reflected in the morphology.

The primary reason you use dopants is to give a certain character to the CVD film that did not exist before. For example as we describe in one of the earlier lectures, the reason you use boron and phosphor additives to silicate is to make it more flowable, so that you get a much smoother finish. In other words the dopants have a strong influence on the roughness of the CVD film and that is important to capture because the surface characteristic of a CVD film also has an influence on the sticking coefficient.

In other words as a CVD film becomes smoother and smoother, it is capture efficiency or sticking coefficient for arriving molecules will change and the change is not always positive or negative.

(Refer Slide Time: 38:35)



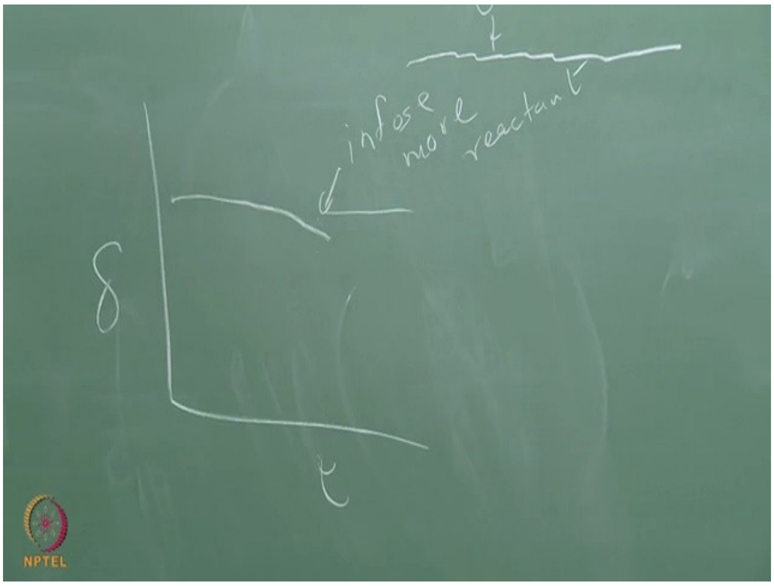
For example if you have a glass surface that looks like this and let say that by putting in some additives and flowing it at high-temperature you have been able to make it look much smoother on a microscopic scale, when an arriving molecule sees this surface versus this surface the effect of surface roughness on capture efficiency or sticking probability is different depending on the scale of the roughness that is present on the surface.

For example if the roughness asperities are larger than the arriving molecule diameter than it is fairly easy for arriving molecules to get captured on the surface. So surface will actually increase the sticking probability in such cases. Well, primarily because it now provides a larger surface area for capturing the oncoming molecules compared to the smooth surface. On the other hand if the arriving molecule is larger than the surface roughness then as you can imagine its contact is actually going to be reduced.

It is going to be now sitting on just 2 points instead of sitting on the entire surface. So the implication for that is, as you make the surface smoother and smoother by adding dopants the probability of capturing an arriving molecule actually decreases. So normally what we see is in doping reactors, as the doping process proceeds the CVD rate itself tends to drop and it is an interesting effect which is not really connected to the gas phase chemistry but simply related to the surface morphology.

The effect of Dopant in transforming the look and feel of the surface of the CVD film and so the design of a CVD reactor that uses dopants, clearly must be done differently compared to one-way you do not use a Dopant.

(Refer Slide Time: 41:06)



For example if you want to maintain a constant film thickness what you have to do is, that with time in a doping reactor if you plot of film thickness you may see an effect that has, you know, slide reduction overtime as the deposition proceeds. So you have to essentially correct for it by infusing more reactants at this stage. So you have to constantly be monitoring the thickness of the CVD film and providing the necessary adjustments to the operating conditions.

You can do this either changing the amount of reactant or you can do it by adjusting surface temperature for example, you can just raise it by degrees to get higher deposition rate and equalise it that way. The other interesting thing when we talk about the use of dopants into a CVD film is that, you know, it is kind of a layer by layer effect which you can use to your advantage for the most part.

You can essentially turn on the Dopant for some period of time, so that the Dopant is incorporated in a certain thickness and then turn off the Dopant supply. So you can have a CVD film that has various different types of dopants, different concentration of the dopants across its thickness.

But at the same time the fact that your Dopant is present only on the surface essentially means that if you want a CVD film that has a uniform Dopant concentration throughout its depth than either the Dopant has to be turned on from time 0 or you have to provide sufficient pathways in your CVD film for the Dopant material to diffuse through an equilibrate in terms of concentration.

So the microstructure of the CVD film is also an important when you are trying to design a CVD reactor grade in a Dopant as a constituent in the CVD film. So these are some testing aspects of designing CVD reactors with dopants and by the way the CVD reactor is considered to be the most convenient way to incorporate dopants because as long as they are the price able it is very easy to mix them in with a CVD reactants and have the deposition of the Dopant happen correctly with the deposition of the CVD film and so you get a fairly uniform distribution of Dopant material in the CVD film which is a huge advantage because there is virtually no other doping method that can really get the type of characteristic.

Okay, another application of CVD that is worth discussing in some details because it is an emerging field is CVD of nano dimensional materials, nano structured materials there are many types of nano films, nano particles that are now being synthesised using CVD. It is particularly advantages when you are trying to make nano composite materials where you are trying to incorporate many different elements into the same nano feature or nano product.

So that is worth discussing in some detail, so in the next lecture we will cover aspects of CVD as they apply to formation of nano dimensional films. So any questions on what we have covered today? Okay so I will see you at the next lecture then.