Chemical Engineering Principle of CVD Processes

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Module-3
Lecture 20
CVD Applications: Hot Filament CVD (HFCVD)

Good morning and welcome to this lecture in our course on chemical engineering principles of CVD process. In the last few lectures we have been looking at the transport process involved in CVD systems particularly mass transport but at the same time recognising the influence of other types of transport phenomena on the mass transfer process that are taking place in a CVD system and earlier we have also looked at the thermodynamic aspects but before (()) (0:48) the last few lectures has been on, how to define control volumes and conservation equations for CVD reactors.

How to write the appropriate constitutive laws, how to calculate the relevant dimensionless mass transfer coefficient such as Nusselt number, Stanton number and capture efficiency and also how to apply correction factors appropriately when there are phenomena occurring that cost the process to deviate from its nominal values. So whenever you have a augmentation effect such as Phoretic affect or an inhibiting effect such as kinetically Limited homogeneous or heterogeneous reactions.

The affect of this phenomena have to be incorporated as suitable correction factors in the expressions for the Nusselt number and Stanton number, so we also looked at how we do that. For the remaining of the course we are going to be looking at some specific CVD reactor configurations that are commonly applied in the industry and as we do that we will try to also assess how thermodynamic and transport principles would apply in each of this cases.

We will start with CVD reactor configuration that is actually modelled on the tungsten filament bulb that we had discussed in one of the earlier lectures. If you remember we said that one of the causes for bulb to be thrown away is when there is substantial loss of tungsten material from the filament which deposits and coats the walls of the bulb causing a loss of light transmission.

So it is a process that is CVD because the bulb is filled with the reactive environment. It is not just filled with air or inert gases, it actually has a halogen filling and if you recall the reason for this halogen filling inside the bulb is to provide a reactive chemistry that will

continuously bring tungsten back to the filament even while depletion of tungsten is going on.

So if you can establish a steady-state between the 2 in theory a bulb can last for ever but it is clearly an undesirable process. In the case of an electric bulb you want to minimize the tension lost from the filament you want to minimize deposition on the bulb wall and so on but somebody had the bright idea why do not we use the same concept to actually intentionally deposit films on substrate.

So if you can actually design a CVD reactor that kind of looks like a bulb that you can use what is going on inside an electric bulb but in a positive and productive manner. So that is idea behind this type of CVD process. The basic concept here is quite simple you provide a very hot location within the reactor which causes dissociation of the reacting species that come to the vicinity of that hot material, whatever it is, it could be a simple wire, it could be a filament, it could be ribbons but some source of high heat which will cause dissociation to happen inside the CVD reactor and then the dissociated species will transfer to the substrate and deposit on the film as a substrate.

Now this concept was introduced first in 1979 and it was called thermal CVD, in 1985 the name was changed to catalytic CVD and for about another 6 years or so, people continue to refer to this mode of chemical vapor deposition as catalytic CVD and then in 1991 the name was again chained to hotwire or hot filament CVD. Now the reason for, you know, calling it a thermal CVD or hot filament CVD are obvious.

I mean basically you are introducing a hot zone inside the CVD reactor and causing the species, vapor species to be generated because of that hot source of heat but the reason for calling it catalytic CVD is not so obvious but what it refers to is the fact that if you want to take Silane and reduce it directly to silicon, you have to make the Silane molecule lose, you know, 4 hydrogen's simultaneously.

So it takes a lot of energy to make that happen whereas if you use this type of a hotwire or catalytic CVD essentially you set up a sequence of steps, you only have to do is really dissociate SiH4 to SiH3 plus H, SiH3 then dissociates to SiH2 plus H, SiH2 dissociates to SiH plus H and SiH finally dissociates to Si plus H. So when you set up the reaction sequence that way it turns out that energy barrier or the total energy input required to convert Silane to silicon is much smaller.

So essentially this hot filament has played the role of a catalyst by lowering the activation barrier for the conversion to happen and that is the idea behind calling it a catalytic CVD reactor. The advantages of this type of reactor are that it provides a very intense source of energy within the reactor geometry itself. So it obviates the need for example for introducing plasma into the reactor where plasma would be another source which can also help in the dissociation of the gas molecules.

But any time you use things like plasma in a reactor you add both to the cost as well as complexity of the equipment. So the hot filament CVD process substantially reduces the energy input to the system to make CVD possible. The other advantage of the hotwire type of CVD reactor is that deposition rates can be quite high. It all depends on how hot you can get the filament to without causing loss of material from the filament itself.

And so for example if you use tungsten or tantalum as your filament material, you can heat it up to close to 1800 degrees centigrade or even close to 2000 degrees centigrade. So those are very high temperatures and they can cause a complete molecular dissociation of the reactance that you are feeding into the CVD system. Another advantage of the hotwire type of CVD reactor is that the reactor configuration itself is quite simple.

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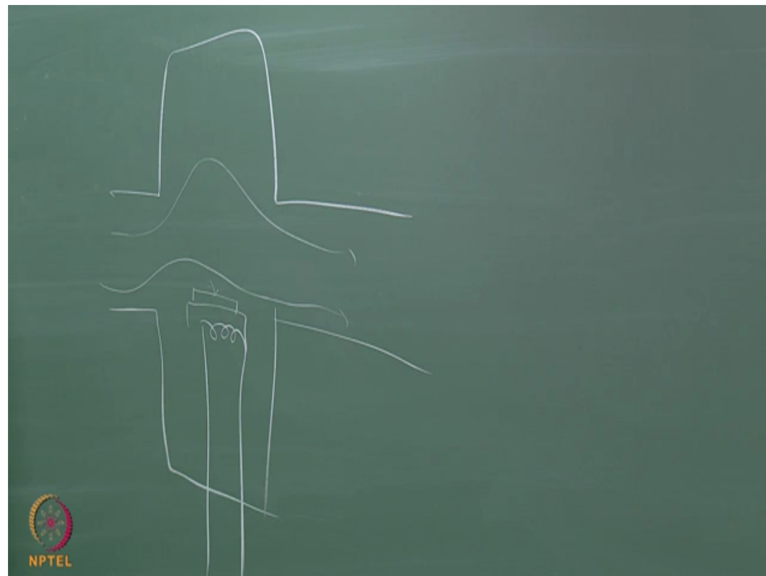

So again what we are really looking at is an extension of a bulb. So in the normal CVD reactor you would have a substrate to which you are providing some source of energy and so you have your vapor sitting here and the gases are flowing in some fashion over this reactor and the deposition process takes place over here. So the reactance's are preheated before they

enter the reactor and typically you use a cold wall configuration to ensure that the deposition only happens on the substrate.

So this is one variant of design of a CVD reactor and here of course the wafers can be horizontally oriented or they can be vertically oriented or they can be oriented at an angle you can do a single wafer at a time you can do a batch of wafer there are a lot of variations that you can build into the design of this type of a CVD system which is called HFCVD, you know, horizontal flow CVD reactor that is possibly the most commonly used, CVD reactor configuration primarily for bulk production of silicon wafers.

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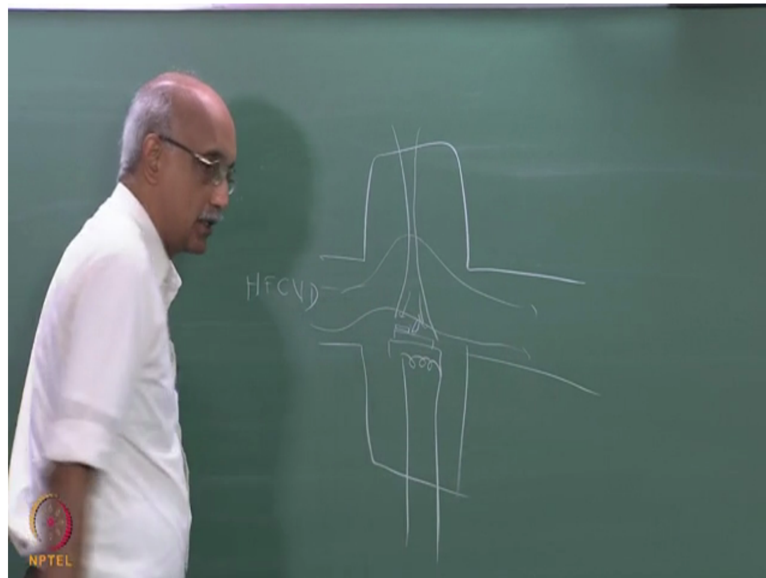

Another variant on this that we have discussed is a stagnation flow reactor where the reactance entered in a vertical flow setting up stagnation layer around the substrate which helps in terms of maximising the residents time of the reactance species and therefore maximising the deposition rate and the uniformity of the film on the surface as well and stagnation flow CVD systems are also used quite commonly in various applications.

Now one of the limitations of both these methods is that if you look at actual utilisation of the gases for example if you are feeding in hundred kilograms of Silane, how much of that really gets reduced to silicon and how much of it is essentially vented out as, you know, exhaust gas the utilisation is quite low particular in the horizontal flow system it is less than 20 to 30 percent.

Because it is only the layer of the silent molecules that come in direct contact with the substrate that are likely to deposit the silicon film. The utilisation is a little higher in the stagnation flow system although it depends on the molecular weight of the reacting species. The higher the molecule weight of the reacting species the greater is the probability that it will initially separate and impact on the substrate and cause film formation.

But if the molecules are lighter than they are more likely to follow the streamlines of flow of the carrier gas and it is quite simple that again the rate of incidence of the substrate and therefore the efficiency of conversion of the reactive species to product film and they are quite low. What are the major advantages of the catalytic CVD or hotwire CVD reactor? Is that the conversion is extremely high.

If you introduce Silane into a CVD reactor with a hot filament the likelihood that the SiH4 will bring down and form silicon atoms that actually impact on the substrate is quite high it can be as much as 40 to 50 percent I mean you are never going to get close to 100 percent however 40 to 50 percent is quite achievable. The disadvantages of the hot filament CVD reactor, the first one is controlling the temperature of the filament, filament temperature becomes one of the key variable here.

The filament material does not play a huge role as long as you know you make sure that its vapor pressure is low for example you do not want to use carbon or graphite as your hot filament because the carbon can evaporate from the filament and then be included in the film as a contaminant but tungsten, tantalum, platinum, Rhenium there are many materials that satisfy the requirement that you have to be able to heat it up to a very very high temperature without causing loss of material from the filament due to evaporation.

So 1500 to 2000 degrees centigrade is, you know, easily achievable with the use of such materials. However control of the temperature can be quite important because the dissociation efficiency depends quite sensitively on the filament temperature. So that is one of the issues but the larger issue and the one that limits the efficiency of such reactors is the fact that, you know, you have to somehow control the flow of the dissociated species in such a way that close to 100 percent of the species and counter the substrate.

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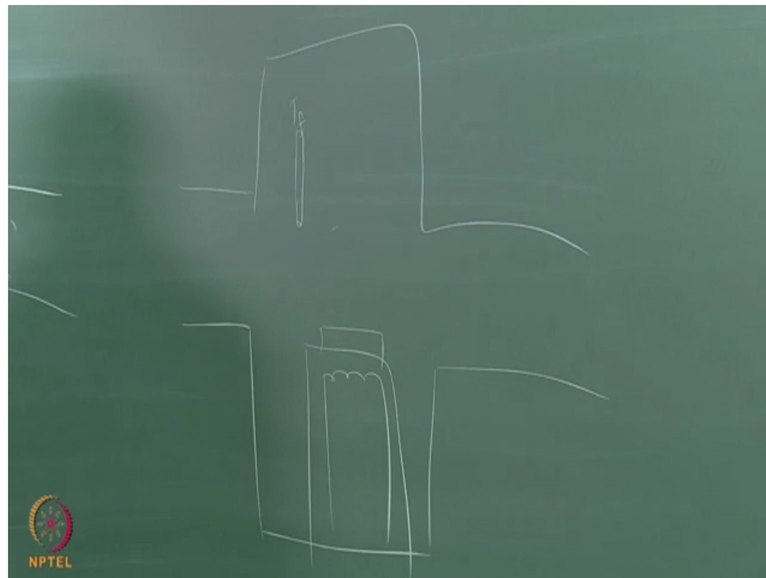

Now a normal hotwire CVD reactor the way that it is configured would be, so instead of this in a hotwire CVD reactor the way you would do your deposition is that you will still have a substrate holder on which you will be forming the film and it still requires some energy input but what you will do here is essentially have a hard filament somewhere inside the reactor it can be a single filament it can be an assembly of filaments that can look like fingers that can look like ribbons there are many configurations of this filaments that are possible.

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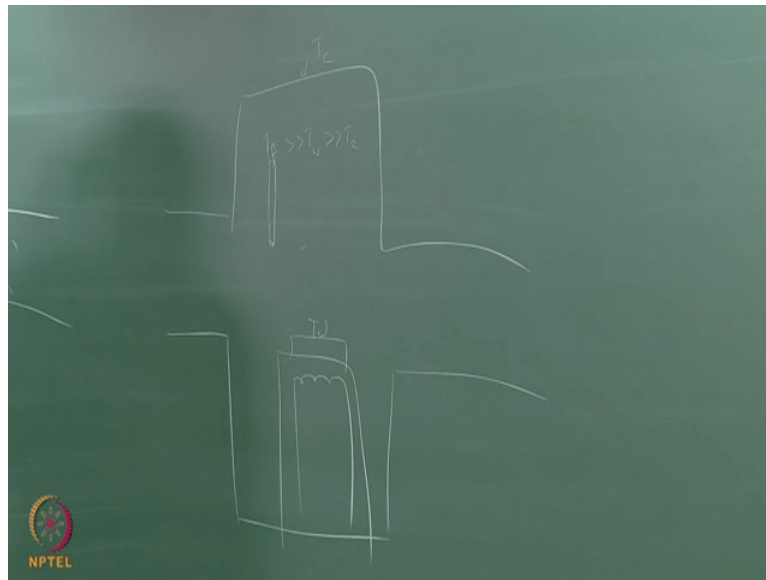

So this Tf would be kept, if this is Tw, Tf would be much greater than Tw and if this is your chamber walls again Tw will be much greater than Tc normally. So let say that, you know, we have Silane in this system, so Silane is impacting the filament and getting dissociated into Si and H, you can also have hydrogen as a carrier gas and even hydrogen will dissociate and form H radicals when it encounters the filament.

How do you ensure that all these dissociated molecules flow down and actually impact the substrate? So placement of the filament is one issue, the second is controlling the flow in the system. Now this type of reactor is naturally three-dimensional the flow will tend to go essentially the species that you are generating there is a preferential direction for them to go. So they will, it’s a diffusion control reactor typically.

Diffusion control means that, you know, diffusion is a random walk process, so the direction in which the dissociated molecules more is entirely random. So there is no preferred orientation of motion of these dissociated molecules which implies that you are not really directing them towards the substrate, you are allowing them to go wherever they want to go and then hoping that some of them will impact the substrate. So better way to do that is to introduce convective flow and use the convective flow to essentially turn this 3-D geometry into 1 D geometry.

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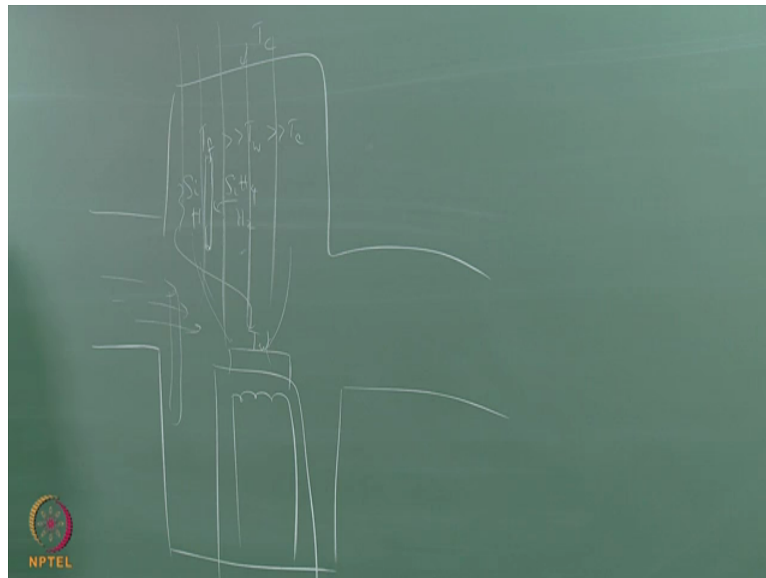

So if your filament is located here then you would want to provide a vertical flow, so that all the dissociated molecules are convected towards the substrate or if your filament is located upstream of the wafer and then you would want to direct your convective flow in this way, so that you kind of overcome the diffusional motion of the of the dissociated molecules and force them to encounter the substrate.

So you have to pay a lot of attention to the temperature control of the filament as well as the transport characteristics of the gas, the carrier gas to ensure that you are getting maximum dissociation efficiency at the filament and also the dissociated species or being made to encounter the substrate to the largest extent possible. So if I look at the design parameters in the system what are we trying to optimise?

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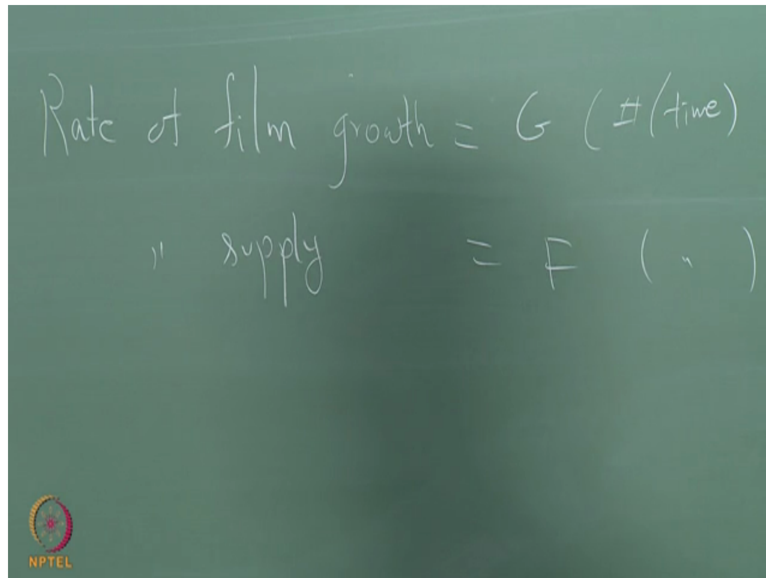

It is basically the rate of film growth let's call that some G which is number per it is basically the number of silicon atoms for example that are actually depositing on the substrate as a function of time. Now this is output parameter that you want to control, so what are the input parameters that are at your disposal. The rate of supply of the depositing molecules is another one, so you can call that let's say some F, so it's the rate at which you are feeding in the reactor molecules into the system to make the film.

So obviously G by F represents your deposition efficiency and it's this efficiency parameter that you want to try and optimise. So what you have at your control to try and optimise this when you look at what is going on F is your input feed and G is the rate at which the film is forming on the substrate but what is the link between the 2? It is what is happening at the filament. So you have to look at what is going on at the filament, so the first thing that you need to know is what is the dissociation efficiency?

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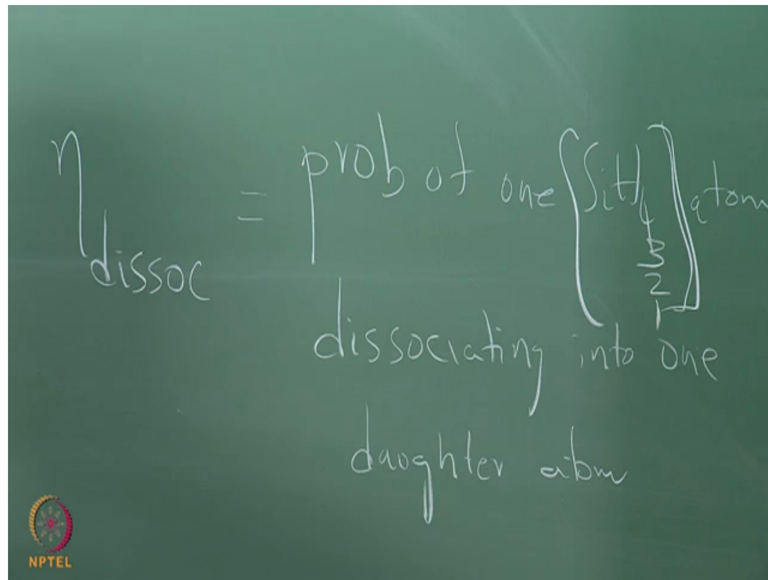

Where we define dissociation efficiency as the probability of 1 SiH4 atom dissociating into 1 let us call that daughter atom, so SiH4 would go to SiH3 and similarly SiH3, SiH2, SiH so on. So every item that strikes this filament you have to look at the probability of that getting dissociated into its next lower form and because that kind of leads you in the direction of forming silicon from SiH4.

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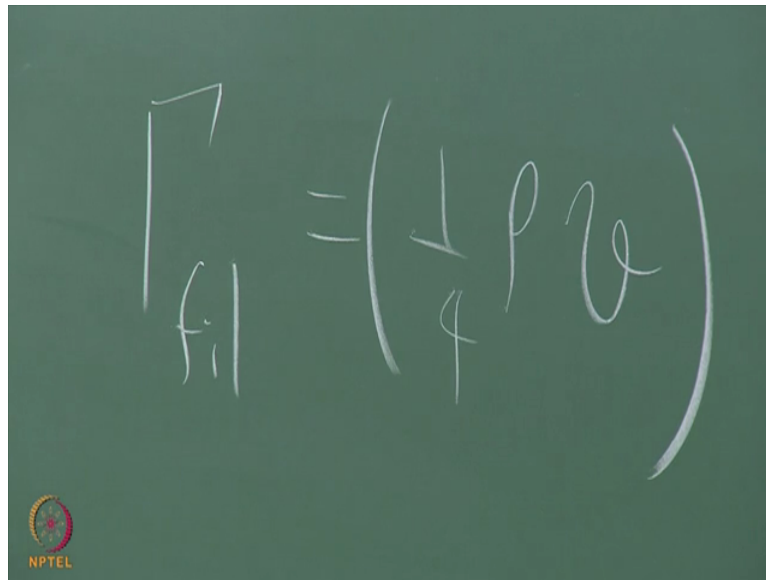

So that is one critical variable, the other critical variable would be the rate at which material is actually being supplied to the filament. So if you call that some gamma filament this refers to essentially the flux of Silane molecules that are striking the filament, the flux is given by 1 by 4 rho times V where rho is the density of the Silane molecules and v is the, essentially the thermal velocity at which the molecules are striking the filament, so this gives you essentially the number of molecules of Silane striking the filament per unit time per unit area.

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So if we take this and multiply it by the effective area of the filament, let us look at it as a cylinder modulate as a cylinder, so it is pi df times Lf, so this gives you the rate at which the Silane molecules are actually striking the surface. So this is the rate of incidence of SiH4 slash SiH3, SiH2, SiH at on the filament.

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So if I look at, if I take the ratio of this gamma parameter to F this gives you an efficiency of filament impact. It tells you what percentage or what fraction of feed molecules are actually striking the filament at any given point of time and then you take the dissociation efficiency

that tells you what is the probability that a molecule that strikes the filament will get dissociated into its next DOTA molecule.

So essentially this eta filament impact multiplied by eta dissociation gives you the efficiency with which the dissociated molecules are being supplied to the system. So in a sense this eta dissociation times the eta filament impact should determine the deposition efficiency.

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In fact there is an empirical relationship that has been obtained which relates the 2 as 1 minus eta deposition equals 1 minus eta d times to the power 4. So clearly there is a link between the 2 and some of these parameters themselves are also related to each other. So what we have presented here is a very simple kind of a mechanistic analysis of what is going on in the system.

And the fact that we have several efficiencies in the system there are linked to each other and each one must be separately optimised, right? If you are trying to optimise deposition efficiency you have to, A make sure that you are providing a path for the feed molecules to encounter the hot filament and B you have to make sure that you are operating the filament under conditions that cause as complete dissociation of the molecules as possible.

And finally you also have to make sure that you provide a transport path for the dissociate molecules to come and strike the substrate, right? So all of these kind of go together to establish the overall true efficiency of the system.

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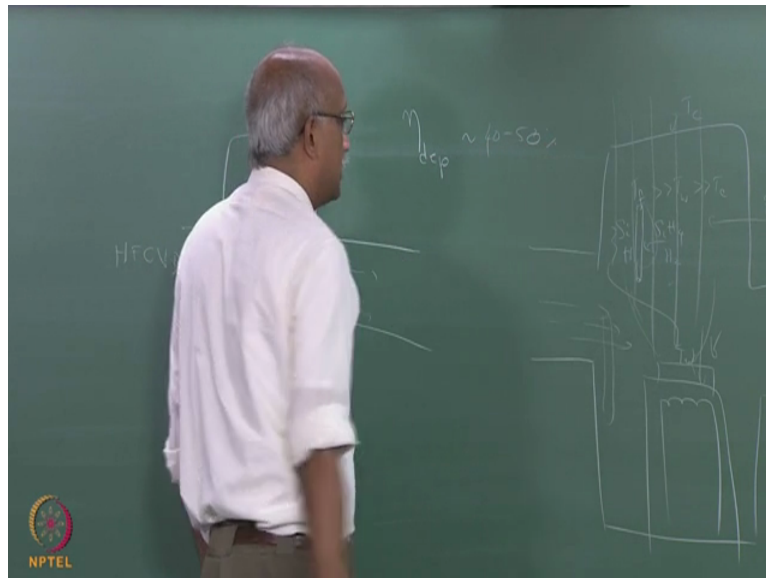

And as I said eta deposition of roughly 40 to 50 percent is achievable in a hotwire CVD system which is actually considered acceptable. So essentially there will be a recycle loop provided so that the feed Silane and hydrogen that escapes without being converted will essentially be captured and brought back into the CVD system, so that there is no wastage of the feed material because Silane is an expensive precursor to use in such systems.

So if you look at this from a thermodynamic and transport point of view, thermodynamically it is a very favourable system because you are able to achieve extremely high temperatures at the filament and as we have discussed it before the higher the temperature the closer to chemical equilibrium you can get which represents the maximum rate that you can achieve. So the thermodynamics are certainly very favourable in such systems.

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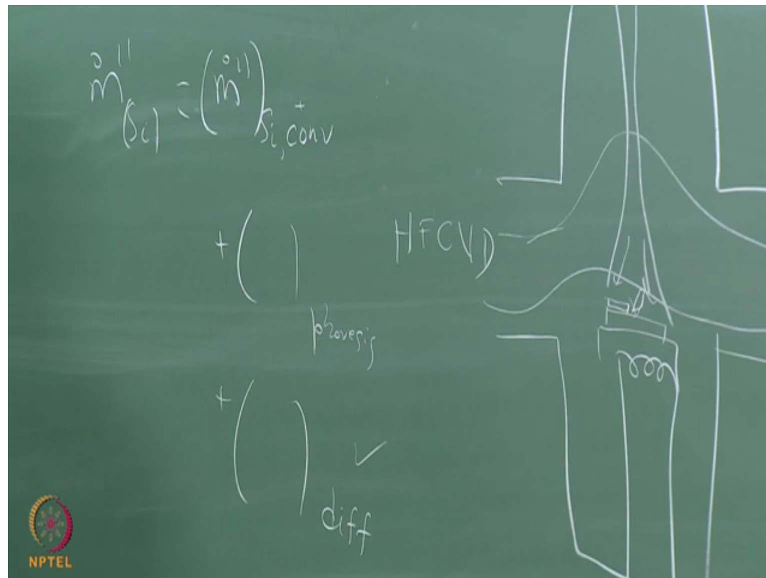

The transport aspects, you know, here is we have done before we have to break it into, you know, m dot in this case we are looking at the deposition of silicon element it is going to be a combination of m dot silicon convection plus Phoresis plus diffusion. So if you look at this what is favoured in such reactors? Diffusion is also favoured primarily because the hot filament enables you to dissociate the (()) (27:39) virtually into their elemental state and the lighter the molecule the greater will be its diffusion velocity.

So the typical diffusion fluxes, diffusion velocities that you see in a hot filament CVD reactor are substantially higher compared to the horizontal flow CVD systems or stagnation flow type of CVD systems, so that is good. Phoresis you know the major Phoretic affect in this case will be thermophoresis because the presence of the hot filament introduces a very steep temperature gradient.

So now whether that helps you or hurts you depend on the diffusing species as I said in one of the earlier lectures. If the diffusing species is lighter than a carrier gas then thermal diffusion occurs down the temperature gradient from hot to cold, so in that case it helps. Basically the thermal diffusion will be an additional factor that drives the diffusing species from the hot filament towards the substrate.

But at the other hand it can also drive diffusion towards the walls of the chamber. So that could be more losses due to unintended deposition around the chamber walls but you know in general as long as you are using the diffusing species that is lighter than a carrier gas you are

okay. Now in the case of other types of Phoretic phenomena that are present typically they are negligible compared to the thermal diffusion process that is going on.

Now when you look at convection that is where you have a lot of flexibility in terms of how you design the system to adjust that parameter you can essentially leave it as simply a hot filament with some nominal flow across the CVD reactor or you can play around with this convection process to maximize the rate at which species is delivered to the system. So in general I would say diffusion is favourable, Phoresis is favourable, convection is questionable unless you intentionally force the convection process to happen in such a way that the dissociated species are brought to the material I am into the substrate.

Now this is the rate at which deposition flux is happening towards the surface. However if you look at the rate of growth of the film while there is related to this it also depends upon the surface accommodation and surface diffusion characteristics of the substrate on which deposition is happening. So when you look at that part of it, you know the capacity of the substrate to absorb the species and build the continuous and uniform film with it.

The hot filament type of CVD reactor in some ways is not advantages because in order for the uniform film to form one of the things you look for us, you know, very uniform temperature of the surface because the surface temperature is the number 1 factor that drives surface diffusion and therefore has a significant influence on the uniformity of the film and also the surface temperature dictates the rate at which molecules are arriving and dissociating from the surface.

So that coverage at any location as well as the uniformity of the coverage on the substrate or both dictated by the temperature distribution on the substrate and the way that hot CVD reactor is (()) (31:41), you know, we have a fairly intense source of heat at one location and then the rest of the reactor is being driven at much lower temperatures it is not easy to achieve uniformity of temperature. So that can also be a negative factor in use of a hotwire CVD system.

The rates of deposition can be quite high because of the high utilisation efficiency but the uniformity is something that you have to kind of keep your eye on because it is quite easy for that to be adversely impacted because of the way that this type of CVD reactor is designed. In fact, you know, when thermal CVD was introduced like I said back in 1979 timeframe after

couple of years it completely vanished because people were experiencing all kinds of problems with it.

They were getting huge masses of material but it was arriving in a way which was not really conducive to use that film later in the process. So about 4 years people kind of said let us start using this process but others started working on it and try to kind of iron out some other problems associated with hotwire CVD I have now brought into a stage where it is again a commercially viable process but at the same time, you know, it is something that you have to use with caution and it does require more controls on both uniformity of temperature and uniformity of flow compared to the more conventional horizontal flow CVD reactors or stagnation flow CVD reactors.

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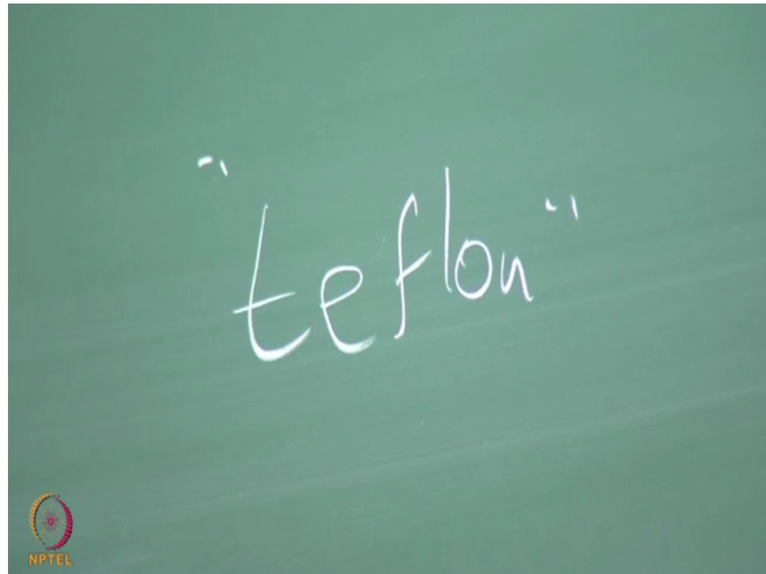

Now the type of materials that are deposited in such reactors can be again a wide variety. Silicon is probably the most commonly deposited film using hotwire CVD but another one which is kind of interesting is Teflon. Now Teflon as we know is basically a barrier material it is a polymer, it is a very inert material, chemically inert it provides excellent protection against corrosion, erosion many kinds of phenomena.

Teflon is essentially a non-sticky surface, so Teflon coating for example is used even in cooking vessels, right? So Teflon is a commercially very important product and the deposition of Teflon has always been a challenge again from the uniformity viewpoint and also the adhesion and cohesion viewpoint. You know when we say adhesion is basically the sticking of the Teflon film the substrate that you are trying to coat and cohesion is essentially

the interlayer adhesion in the Teflon film itself. Both are very crucial for the deposited Teflon film to be usable and to be useful. So CVD, particularly the hotwire CVD process has gained favour as a method for depositing Teflon because it offers certain advantages.

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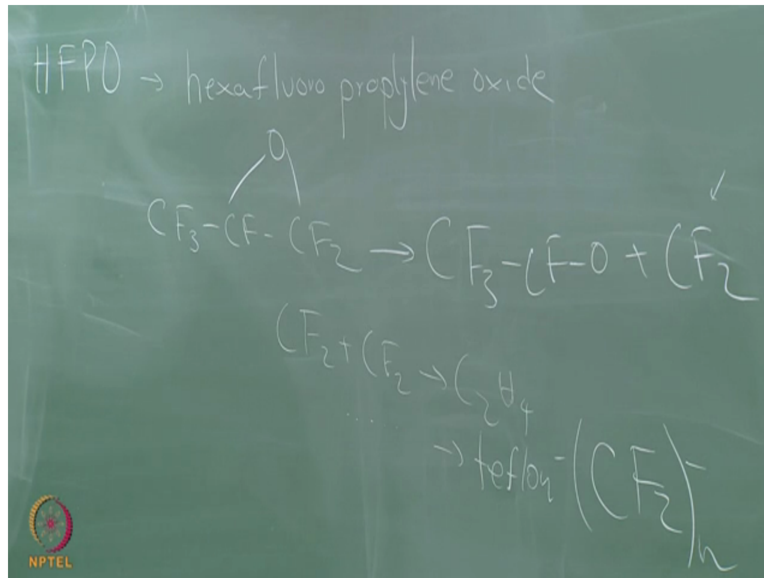

In hotwire CVD reactor to make Teflon film you use something called HFPO as your precursor which stands for hexafluoro propylene oxide which has a configuration of CF3, CF, CF2 OO. So what you try to do is break this down into CH3 or CF3, CFo plus CF2, so the CF2 is your monomer that is essentially use to build the Teflon Polymer. So CF2 will combine with another CF2 to form C2H4 and you continue this process until you make Teflon which is basically a CF2n type of Polymer.

So clearly when you are trying to make Teflon as a film the most important part of it is the dissociation part, you have to be able to dissociate the HFPO molecule into CH3 CFo and thereby releasing CF2 and the CF2 there has to be transported to the substrate and made to deposit. So clearly what you do here is use the filament as your heat source to cause the dissociation to happen.

Once the CF2 forms you still need to provide a reactive environment, so that the CFt molecules can keep associating with each other and ultimately forming a fully assembled polymer film on the substrate which is Teflon. So if you look at some of the challenges of making Teflon coatings and the reason that the hotwire CVD reactor is quite advantages for this process, is that the presence of the hotwire provides your dissociation mechanism, right? That part is obvious.

Now how do you again get the CF2 to link to other CF 2 molecules? You have to provide a chemically reactive environment again with high-temperatures being present and provide also sufficient energy, so that the homogeneous kinetic barriers are overcome because (()) (37:46) CF 2 molecule to combine with CFt molecule in the gas phase and form C2H4 takes energy and so in a system where for example let say that you are just using a heat source to do this initial dissociation, how do you go from there to form a Teflon film? You really cannot.

Now the advantage of doing this in a CVD reactor is, between the time that this dissociation happens and the time that you have to form this molecule you are providing sufficient residence time as well as a flow path inside the reactor where this association reactions can continue and you can keep forming higher-order molecules to the point where at the substrate where you now have a heterogeneous equilibrium it becomes thermodynamically favourable to form Teflon solid.

So the solid Teflon coating only forms at the substrate by controlling again the temperature of the substrate and by taking advantage fact that in order for the CF2 molecules to combine in sufficient density and close spacing to form a solid material you need a heterogeneous equilibrium. In other words it is very unlikely that you will form Teflon particles and the gas phase.

The homogeneous reaction barriers, the kinetic barriers are just are just essentially too large to allow the formation of Teflon particles in the gas phase but as soon as you introduce the substrate and you introduce heterogeneous chemistry the energy barrier for formation of a solid Teflon film is instantly lowered, so the probability of forming solid Teflon suddenly essentially goes from 0 to 1 it is a binary process.

Now again in reality what may happen is, in the gas phase you may start seeing some nuclei of Teflon forming but these are typically going to be smaller numbers and they will also be deposited onto the CVD film by particle transport or aerosol transport. So they may show of as (()) (40:20) when you inspect your Teflon film after the CVD process one of the things you would look for is the presence of any of this little, you know, protrusions on the film which may suggest that some material has deposited in particulate form.

Typically then what you would do is essentially a scrubbing or polishing or cleaning process that will dislodge any particular material that has deposited on the film and leave behind a smooth Teflon film. So that the Post deposition inspection and if necessary treatment every

required in order for you to opt in a nice smooth CVD film. In one of the later lectures we will talk about what are called aerosol CVD reactors.

The formation of aerosol in the gas phase while it is normally something to be avoided and sometimes be actually used purposefully to make certain types of CVD films and CVD coatings especially. So there are special types of CVD reactors that are called aerosol CVD reactors or CVS reactors chemical vapor synthesis reactor that we will talk about later which actually promote homogeneous nucleation and the transport of particles in addition to password of vapours to form films on substrates.

So I mean the use of the hotwire CVD reactors to form Polymeric films is also widespread because polymer CVD films are quite sensitive to substrate temperature. So it really cannot increase the substrate temperature too much but the filament temperature you have much more control over you can make the filament as hot as simple. Normally you may recall that in order to make polymer films you have to use low temperatures and typically plasma, you know, plasma enhanced CVD particularly in ultrahigh vacuum conditions is normally what is used to make polymeric films by CVD.

But that again introduces a cost and the equipment design can be quite complicated if you have to go that way. So the hotwire CVD process in the case of Polymeric films provides a commercially viable alternative to the use of high-density plasma for making polymer films and again the advantage of this is typically when you use the Teflon coating you are not looking for angstroms of thickness are not even nanometre, you are typically looking for microns of thickness.

And it is very difficult to get microns of film material on a substrate using plasma enhanced CVD or any of those other techniques because they have more for molecular level self-assembly type of film formation. So if you want to get Teflon film or any polymer film that has sufficient thickness then you are much better of using some kind of hot filament type of CVD process rather than one that uses plasma as a way of dissociating the molecules and also energising the substrate.

The only other thing you have to keep in mind is when you are doing polymer deposition on a substrate, the substrate preparation prior to CVD is also very critical. The surface has to be extremely clean at a molecular level and it has to be at sufficient energy to be able to capture

the molecules that are depositing. So usually the substrate does get pre-treated with some kind of an energization process it may be using heat or it may be using plasma.

In fact a plasma treatment instead of applying it to the entire CVD system and trying to dissociate the gas phase species in the case of hotwire CVD regularly for deposition of polymeric films the use of plasma irradiation is usually confined to the substrate only in order to increase its surface energy. Any time you take a substrate and you expose it to the impingement of plasma it causes as a surface energy to increase.

And as a surface energy increases the force of adhesion between the film and the substrate increases as well. So some either pre-treatment of the substrate or post-treatment such as baking or (()) (45:09) of the film may be required in order to increase the hardness of the film and also the adhesion of the film to the substrate on which you are depositing at. Alright, so the reactors that we have discussed today are the hotwire CVD reactor.

In the next few lectures we will look at a few other configurations of CVD reactors and we will try to highlight what are the advantages and disadvantages of the various types of systems and you know, what type of reactor configuration you would like to choose for the different products that you are trying to make. Any questions on what we have covered today?

“Professor -Student conversation starts”

Student: (()) (45:49) using the…

Professor: It is basically unidirectional flow for example Finola filament is on the top of the substrate essentially you will introduce vertical downward flow, right? And there are systems that are available, you know, you can essentially use a shower head type of configuration, you will have multiple nozzles through which you can introduce your carrier gas but do it all in such a way that it is essentially a vertical laminar unidirectional flow that will force all the vapours to then get transported.

Is the same way that (()) (46:21) rooms are designed for example, it prevents turbulence, it prevents mixing and it causes the flow to be in one direction and similarly if the filament is upstream of the substrate you will use horizontal laminar flow, so same purpose. Key things are unidirectional and lack of turbulence, okay.