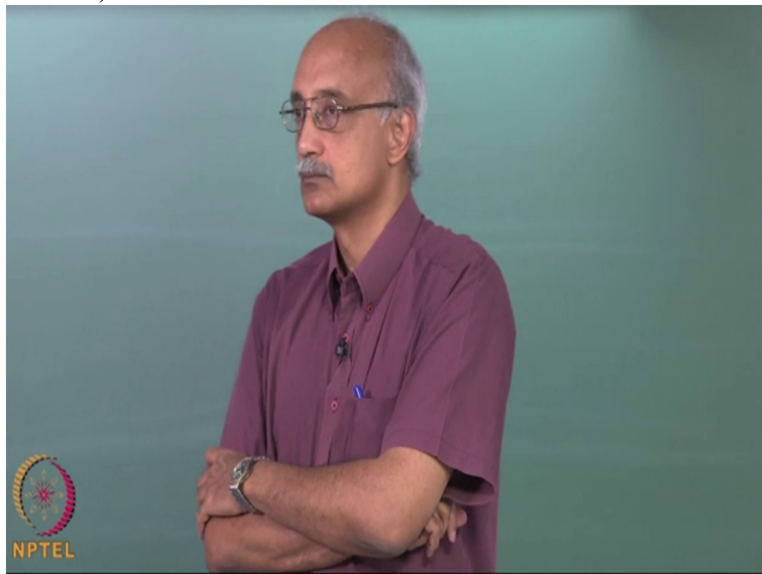
Chemical Engineering Principle of C V D Processes
Professor R. Nagrajan
Department of Chemical Engineering
Indian Institute of Technology Madras
Lecture No 08
C V D of Metals

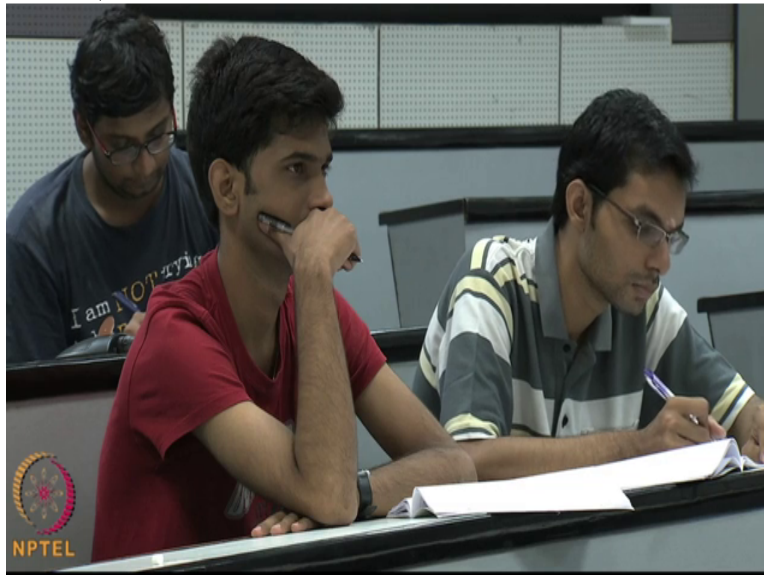
(Refer Slide Time 00:16)



Good morning. Welcome to the next lecture in our course on Chemical Engineering principles of C V D processes. In the last lecture we talked about methods of classifying C V D processes particularly based on the operating pressure. So we talked about the atmospheric pressure C V D, low pressure C V D and plasma enhanced C V D.

Today we are going to talk about another classification of C V D process that is based upon the film that you are depositing as well as the precursors that you are using to produce the reactive materials that result in the film formation. As I had mentioned briefly in one of the previous lectures metal films can also be deposited using a

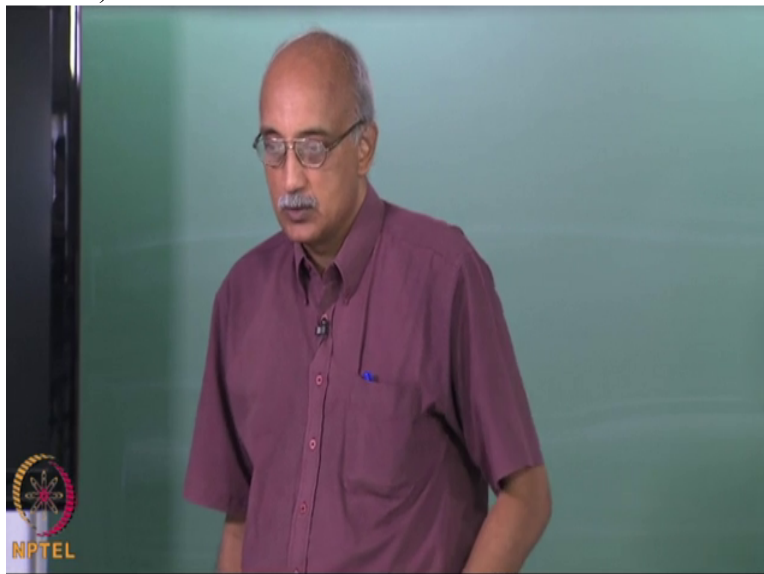
(Refer Slide Time 01:09)



C V D process.

The reason that you want

(Refer Slide Time 01:13)



to deposit a metal using C V D is that even though it is not the easiest or most convenient process, it again has the best step coverage. Now particularly in microelectronics as device geometries continue to shrink because you are trying to pack more and more circuits into smaller and smaller areas, you start having these fairly deep trenches where the aspect ratios are very high.

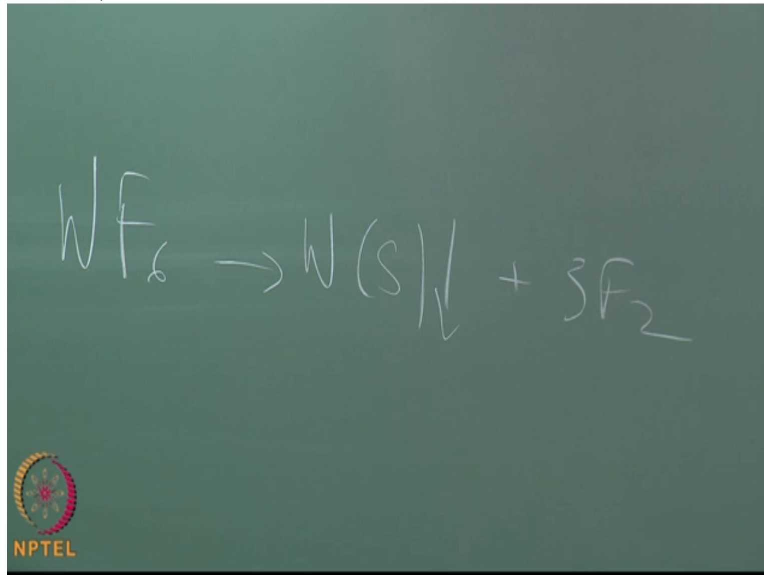
And if you are trying to get a metal layer into these, the deep features it is very difficult to do with virtually any process other than chemical vapor deposition. So the biggest advantage of C V D in this context, in the context of metal deposition is that it has very good what we call throwing power, throwing power essentially means the ability to coat uniformly over widely varying features of the surface.

And so metal C V D has been around for quite a while. The most common metal that is deposited using C V D is tungsten. We have mentioned that in one of the earlier lectures. Now tungsten is a reasonably reactive metal and in the past, tungsten C V D has essentially been done using the low pressure C V D process, horizontal flow L P C V D but one of the difficulties in that kind of, it was basically hot wall horizontal flow L P C V D that was being used but because tungsten was quite reactive the problem was that it would not only deposit on the substrate but also on the reactor walls and so forth.

So the one change that has happened over the years is people are now tending to use more of cold wall type of C V D process for tungsten deposition. In fact the wall temperatures must be kept less than 150 degrees Centigrade in order to prevent tungsten depositing on the walls, and the chamber itself. Now as far as the precursors that are used for tungsten, the most popular ones are W C l 6, W C O 6 and W F 6.

Now W C l 6 and W C O 6 are solids at room temperature but with high vapor pressure. W F 6 is a liquid at room temperature but tends to vaporize fairly easily once you exceed the room temperature. In fact the most common mode of depositing tungsten is to use a mix of W F 6 and H 2. Actually W F 6 itself can obviously give you tungsten solid plus 3 F 2 but

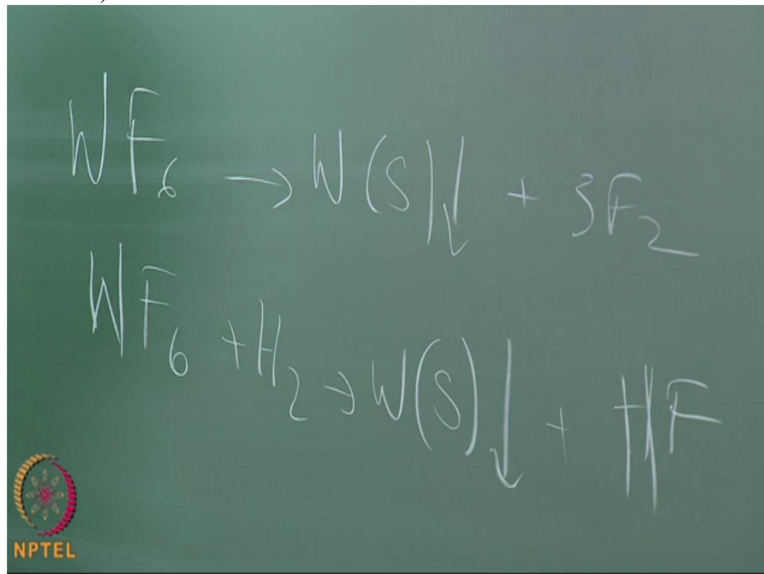
(Refer Slide Time 04:30)



the energy barrier in this case can be quite high.

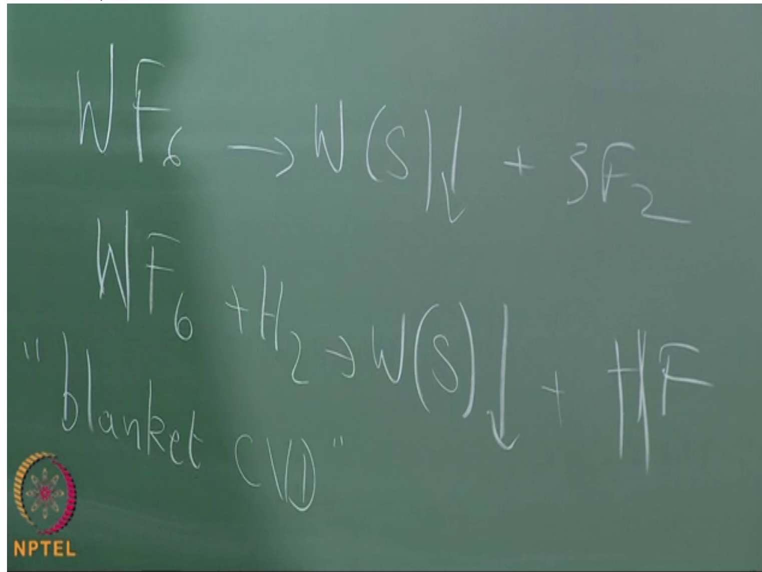
A preferred way of doing this is essentially to use H 2 as a carrier gas which will give you H F as a byproduct.

(Refer Slide Time 04:52)



This process is traditionally known as blanket C V D for tungsten.

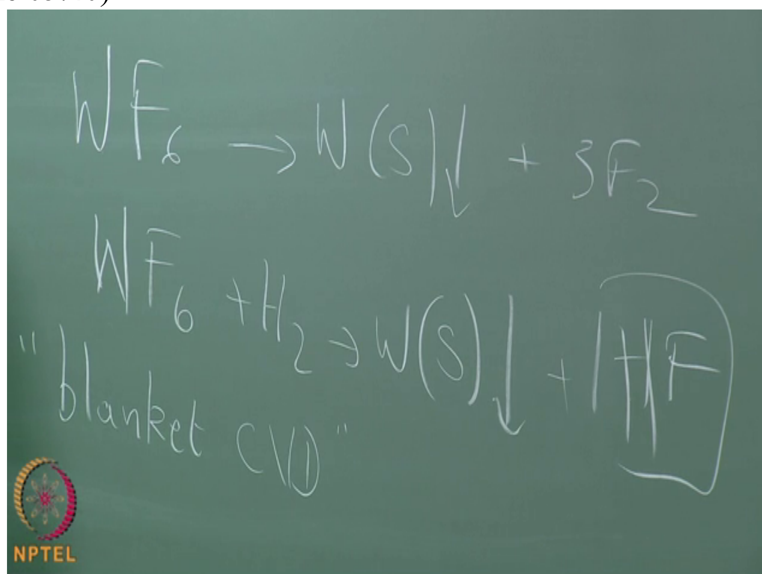
(Refer Slide Time 05:00)



It actually provides the most uniform film of tungsten on the surface. The only, there are couple of problems with this process.

The first one is that the deposition rate can be quite small. So it is not, it is not a hugely reactive system and so the film thickness tends to be quite small, so depending on your application, if you need thicker tungsten, it is probably not the way to go 0:05:33.6. The other problem is actually H F that is produced as a byproduct. Now this

(Refer Slide Time 05:40)



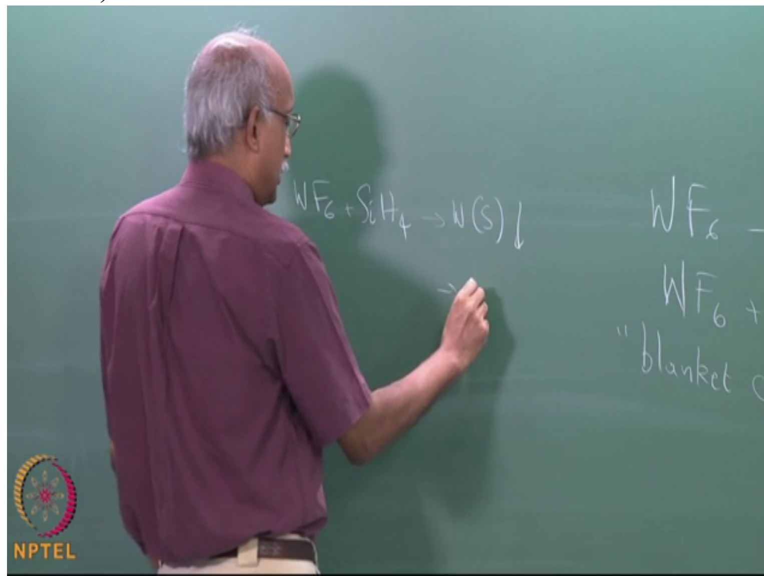
again introduces two problems.

One is H F is a kind of toxic chemical which needs to be treated before it is let out into the atmosphere. The second problem is H F also tends to adsorb quite easily on the substrate surface. So this reaction and deposition of tungsten quickly becomes limited by the rate of desorption of H F from the substrate on which it is adsorbing. And so this again can slow down the reaction as it proceeds.

As more and more H F is produced and starts occupying the interstitial locations on the substrate, it can actually delay the onset of tungsten film formation. So the alternative to this is to actually use S i H 4 silane along with W F 6 to get again tungsten solid.

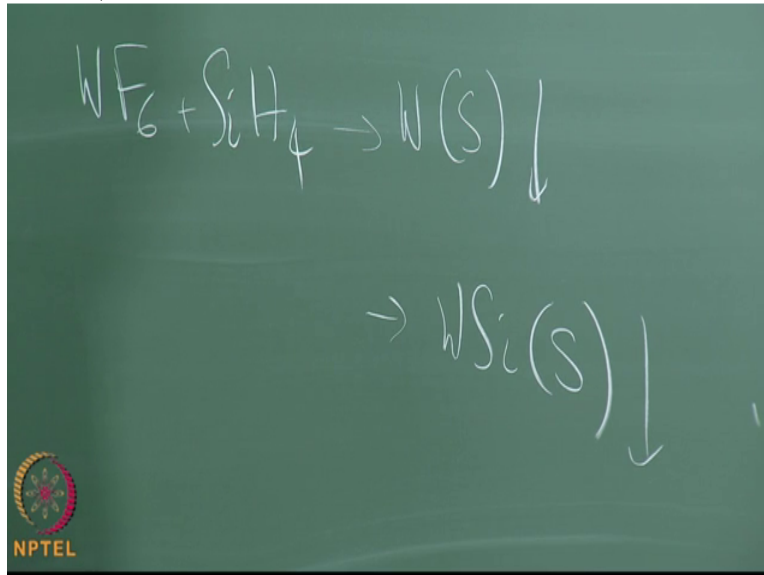
The advantage of

(Refer Slide Time 06:41)



this technique is that depending on whether the

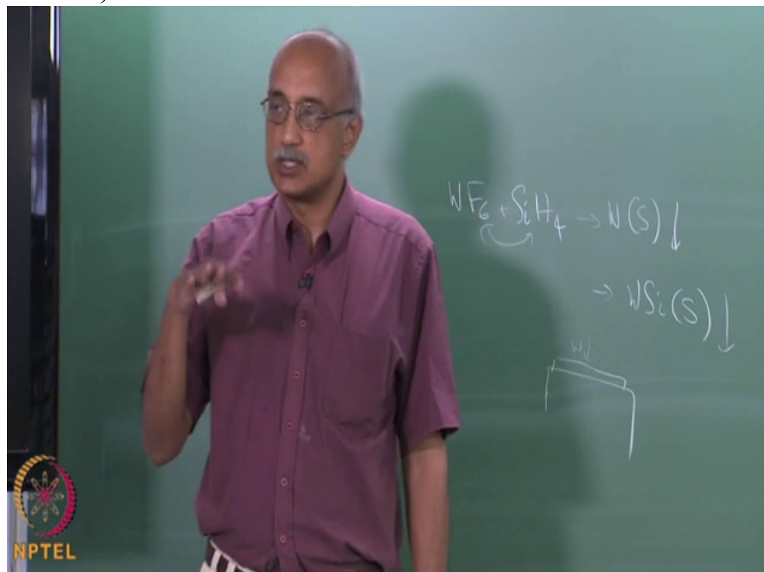
(Refer Slide Time 06:50)



reactant mixture is tungsten rich or silane rich you can actually get either tungsten or tungsten silicide depositing on the substrate. So you have a way of actually tweaking the composition of reacting gases to get the film that you are looking for, a layered deposit where you have tungsten, tungsten silicide, you can actually tune it fairly easily simply by controlling the flow rate ratio of W F 6 to silane.

The silane process has the advantage that it can; it has a lower energy barrier. The deposition rates can be significantly higher. However it does require that, instead of trying to deposit the tungsten directly onto the substrate, you actually put down a layer on top of the substrate which helps improve the adhesion

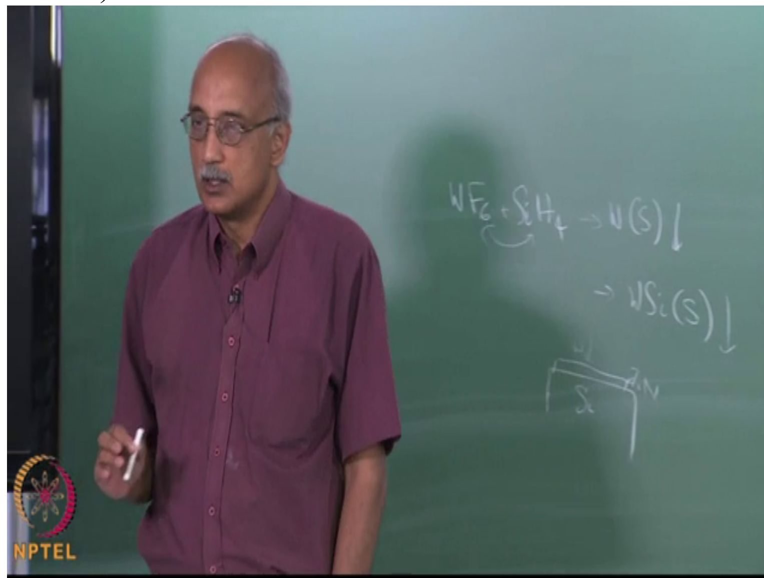
(Refer Slide Time 07:59)



of the tungsten to the substrate. So these are typically nitrides.

For example titanium nitride is frequently used as a underlayer to promote adhesion of tungsten to whichever substrate you are trying to put it down on. For example if you are trying to do particularly silicon, tungsten on silicon

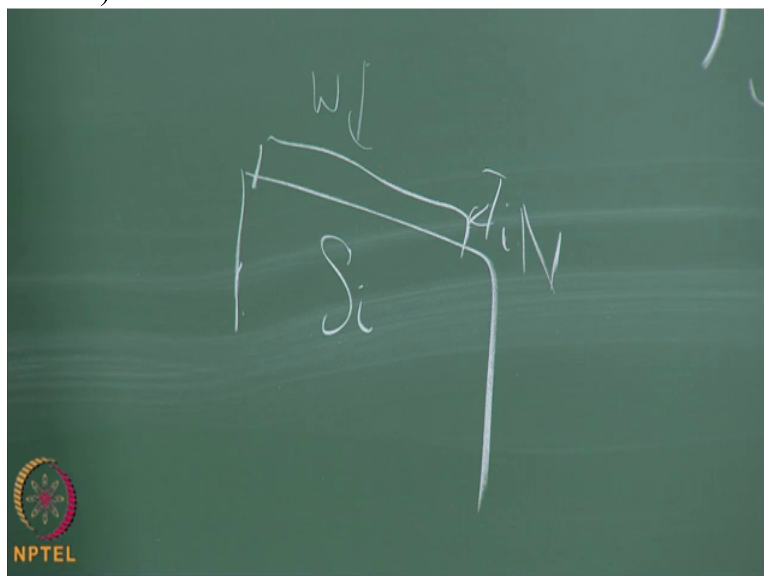
(Refer Slide Time 08:26)



the adhesion properties can be quite poor and so this intervening atomic layer helps improve the adhesion considerably.

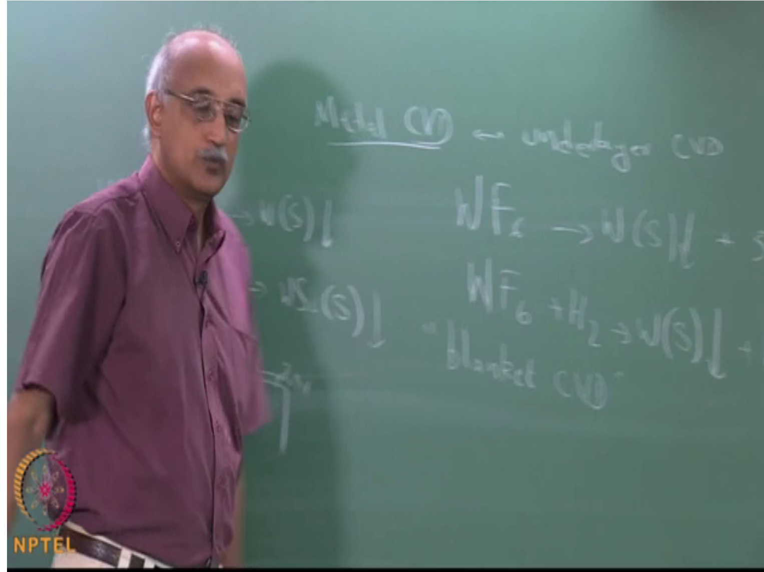
But of course, this itself,

(Refer Slide Time 08:40)



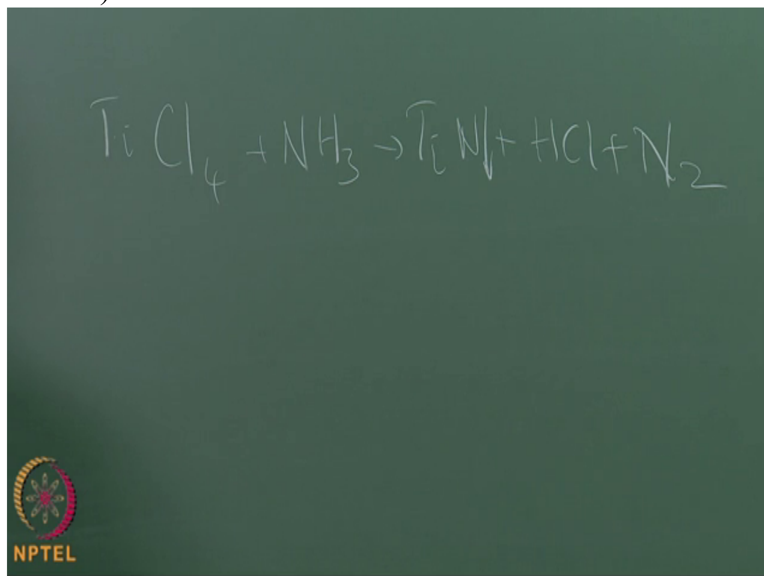
you know, how do you put down a nitride layer on the surface? That is another C V D process essentially. So metal C V D is typically preceded by growth of an underlayer

(Refer Slide Time 09:01)



which are typically nitrides that bond well to the silicon and also provide a good bonding surface to the tungsten and for that actually, many times the chloride precursor is preferred. So for example, if you want to put down a titanium nitrate underlayer and you want to do it using C V D you would set up a process like T i C l 4 plus N H 3 going to titanium nitride plus H C l plus N 2. So this would be the first step in your process to put on

(Refer Slide Time 09:45)



the underlayer and then you follow that up with your metal deposition process.

Again the downside of most C V D processes is the production of these byproducts that require some consideration and some treatment before they can be emitted. Exactly we will see later on that, you look at advantages versus disadvantages of C V D. The number 1 disadvantage of C V D is that the upfront investment can be quite high. It is not just a matter of building a reactor.

The reactor has to have many controls both on the input feed and on the operating conditions of the reactor and on treatment of the exhaust. So in terms of the complexity of the system the, the treatment facilities that are required as well as the controls that are required over the various processes, C V D reactors tend to be quite demanding. So what that means is it adds complexity to the design.

There are more things that can break down 0:10:51.9 essentially in a C V D reactor. Complexity equals cost. So any time we are saying we are adding complexity, what we are really saying is it can be more expensive. So the upfront capital investment can be quite high in a C V D reactor.

And also a C V D reactor cannot run in any kind of environment. It has to have excellent treating, treatment and venting facilities. And so you have to design the C V D facility keeping in mind what are going to be the potential byproducts. And here again the difficulty is, because it is a very reactive environment you cannot always predict the exact composition of the product species.

You could have variations depending on, I mean even a small change in your input conditions or your operating conditions can result in a significant change in the chemical equilibrium composition of byproducts. So you have to be, kind of constantly alert to that and make sure that whatever system you come up with for treatment and emission control is robust enough that you can actually handle small variations in the compositions of the products that are exiting the reactor.

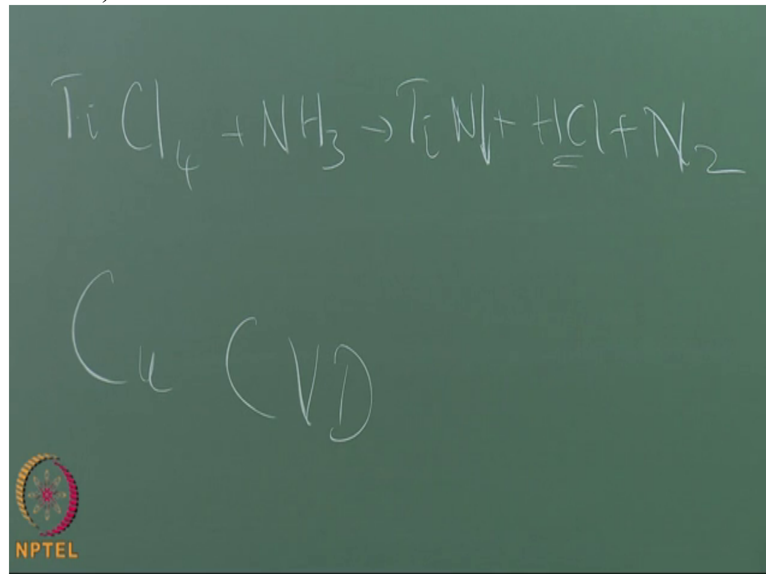
So this kind of becomes even more important when you treat, deal with things like metal C V D which is a very reactive system and you have to use reactive chemicals in order to make it

happen. Now silicon C V D is probably among the more benign C V D process. Typically you are using silane which breaks, thermally breaks down to silicon and hydrogen.

It is not a huge problem in terms of dealing here with the chemistries involved but as you get to more reactive C V D processes, you have to think harder about how you do it. The other materials, other metal that is frequently deposited using C V D is copper.

Copper is fairly reactive material also

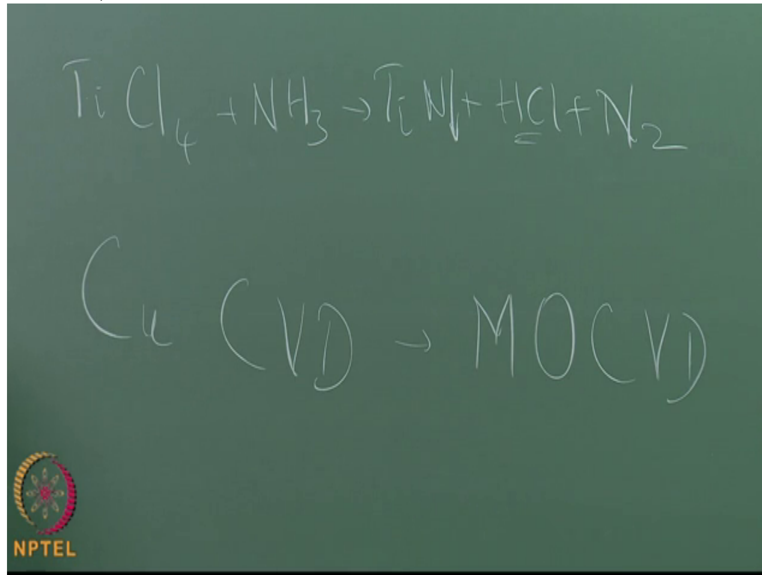
(Refer Slide Time 13:06)



but problem with putting down a copper layer using C V D is that it is not easy to find inorganic precursors from which copper can be deposited, unlike for example tungsten where there are both inorganic as well as organic vapor species that can be used to promote the deposition process.

So if you want to use C V D to make a layer of copper, you have use what is known as M O C V D which stands for metal organic C V D.

(Refer Slide Time 13:49)



It basically just means that the vapor precursor from which you are depositing the film is organic in nature. The reason you do this is again because there is no inorganic precursor.

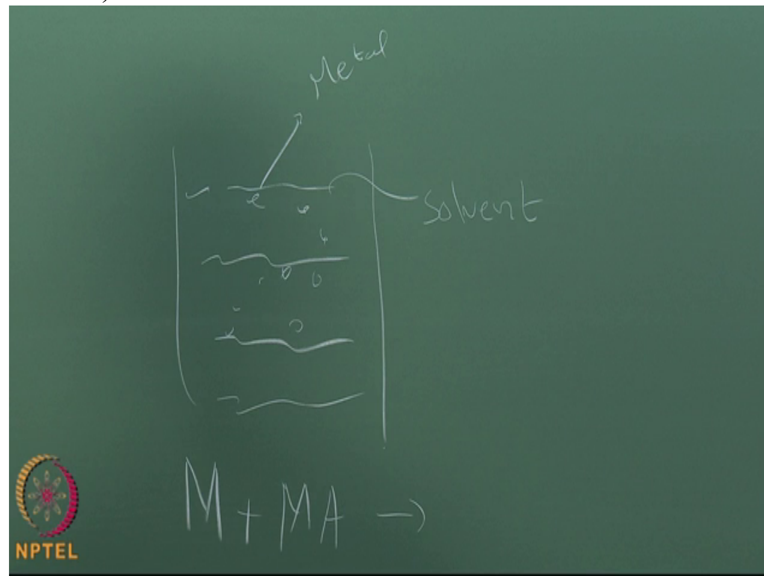
So M O C V D in many ways is the last resort. You only do it if there is no appropriate inorganic species that you can use in your C V D reactor. The reason again is that when you talk about metal organic C V D, the term organic implies the presence of carbon. Carbon frequently becomes the impurity in the film, very hard to keep it out.

So unless you are intentionally trying to incorporate carbon into your C V D film as a dopant you want to avoid using carbon containing precursors in your C V D process which is obviously impossible to do when you are doing M O C V D. So that is primary factor that discourages people from using M O C V D but it does have, you know, several advantages as well; because to prepare the vapor precursor is not too difficult.

So the way you do it is, you know, you would take the metal. You would grind it into fine particulate form. So these would be your metal particles and then you would either soak them in an organic solvent, could be ethyl alcohol, methyl alcohol, butanol and essentially let the particles react with the metal and produce the metal organic precursor or you would essentially use a bubbler where the liquid, essentially you would have a bed of particulate material and you would let the liquid essentially flow through the bed and react with the metals to form the vapors.

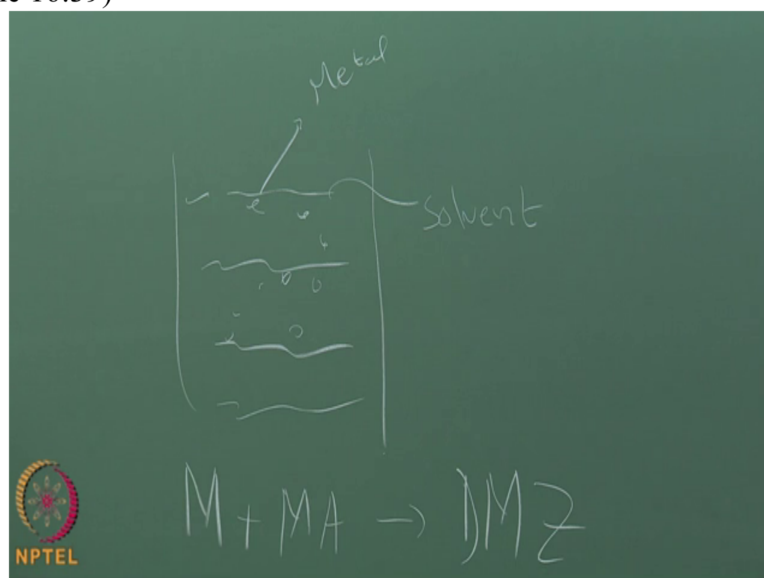
So when you do this, you can take basically any metal plus let us say that you are using methyl alcohol then you can make

(Refer Slide Time 16:28)



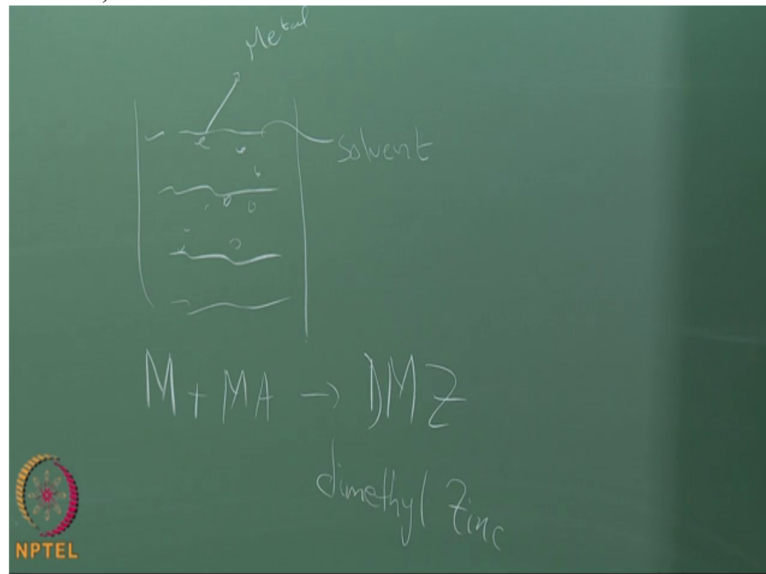
various components. For example D M Z is a compound that is used to

(Refer Slide Time 16:39)



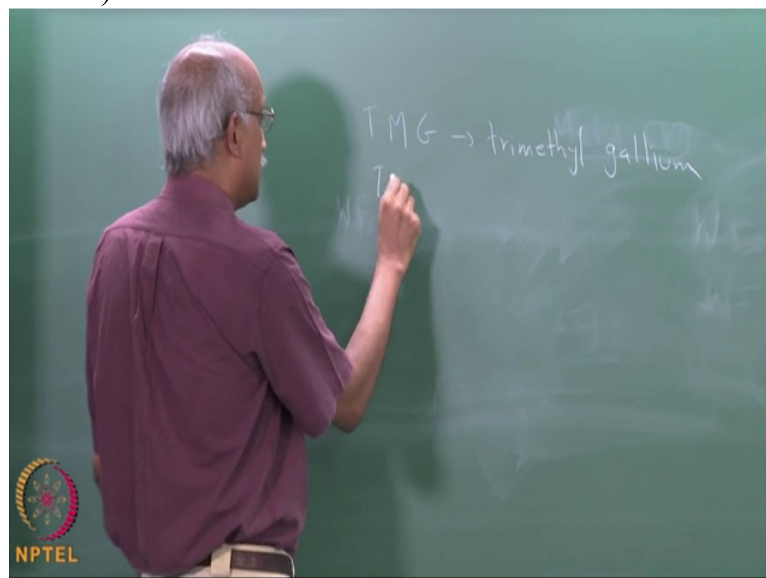
make zinc films. This stands for di methyl zinc.

(Refer Slide Time 16:51)



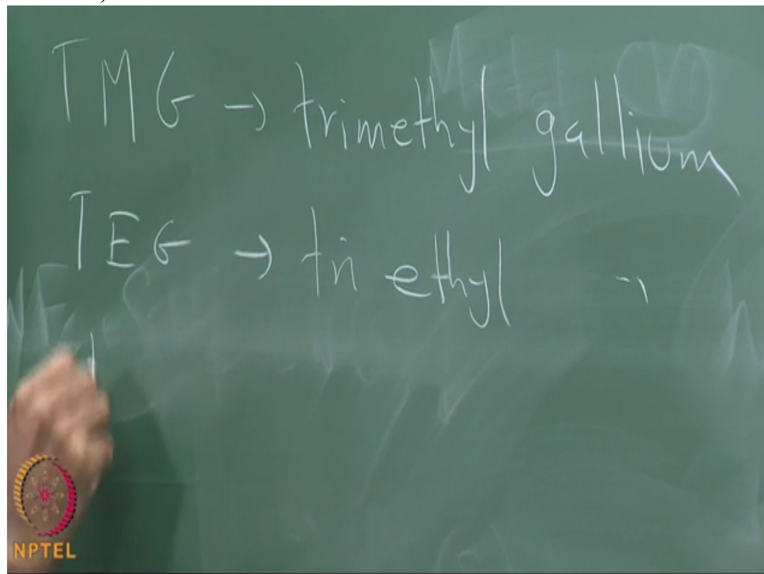
So similarly other popular precursors in M O C V D are T M G which is tri methyl gallium which is obviously used to make gallium films,

(Refer Slide Time 17:11)



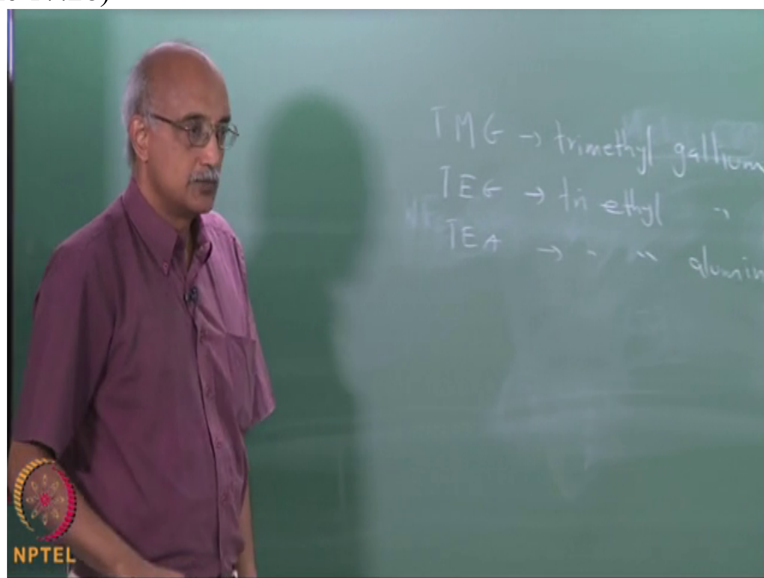
T E G stands for tri ethyl gallium,

(Refer Slide Time 17:18)



T E A which stands for tri ethyl aluminum,

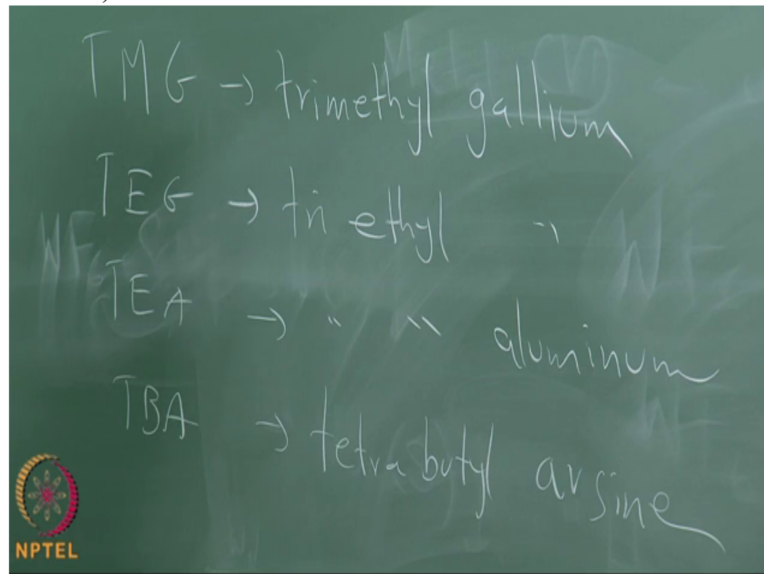
(Refer Slide Time 17:28)



T B A which is tetra butyl arsene.

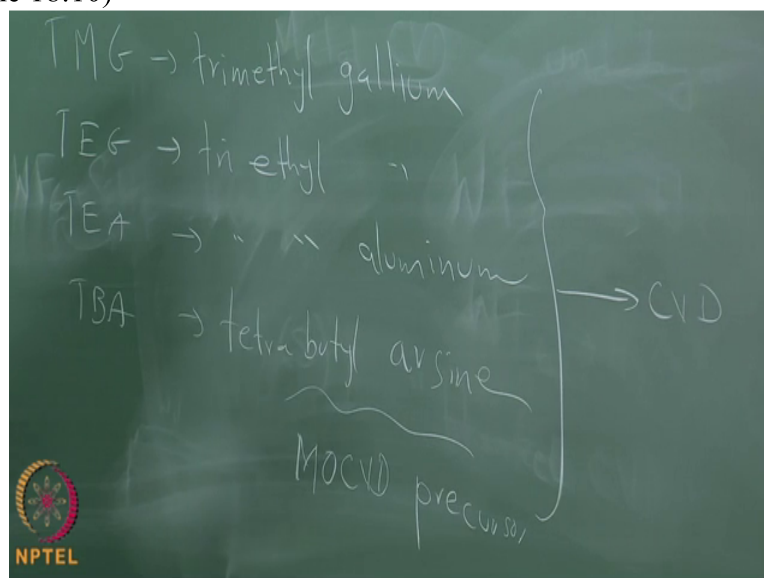
So in each case this is the

(Refer Slide Time 17:44)



M O C V D reactant or precursor. So these are in vapor form and they are fed into the C V D reactor in order to make the corresponding metal film.

(Refer Slide Time 18:10)



Of course what you are really trying to do is take the metal and turn it into vapor form, right? I mean that is basically what you are doing.

So another way you can think of doing this is simply by taking that metal piece and bombarding it with sufficient energy to directly vaporize the metal. So, for example you could take the metal and hit it with high energy ions, you can actually cause localized liquefaction of the metal and you can start evaporating the atoms of the metal so that they

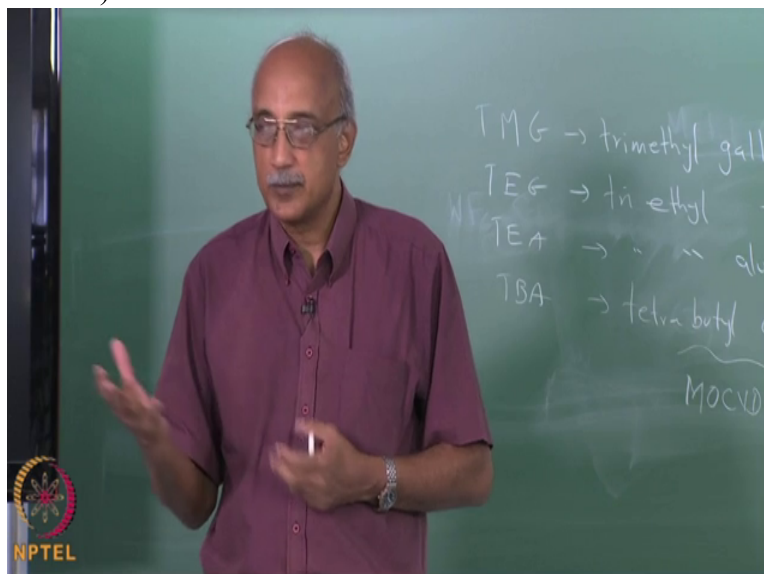
enter the gas phase. And this was actually the process that was used to make metal wafers long time ago.

Does anybody know the term for this when you actually use

(Refer Slide Time 18:57)

energy to

(Refer Slide Time 18:59)

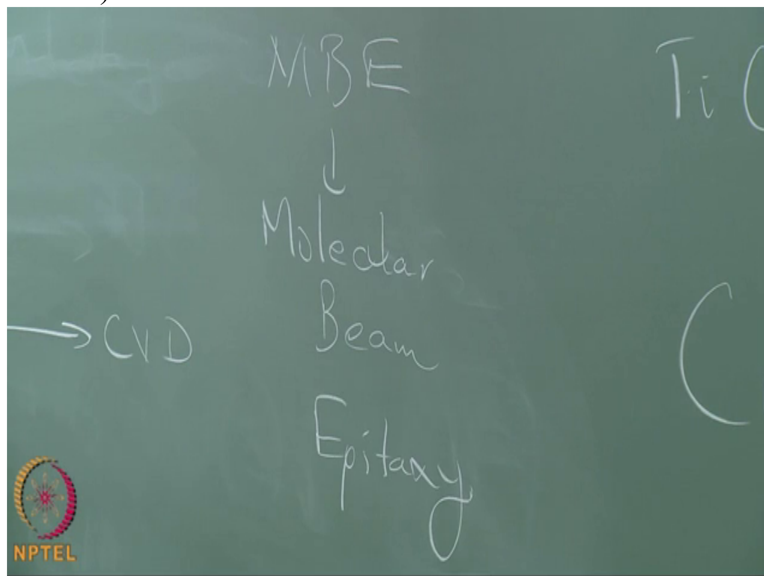


vaporize solid substrate into vapor form. You have heard of the term for that 0:19:06.0?

(Refer Slide Time 19:07)

It is called molecular beam epitaxy.

(Refer Slide Time 19:29)



This was the process that was in use before the1960s. So it was actually invented by professor at Yale University Professor John Fenn who won the Nobel Prize for this.

Molecular beam epitaxy simply implies that you are using a high energy beam to knock off solid molecules into a vapor phase. And so this M O C V D is kind of competitor to M B E 0:19:59.7 because it is essentially achieving the same thing, right? It is entraining 0:20:03.3 the metal molecules in the gas phase.

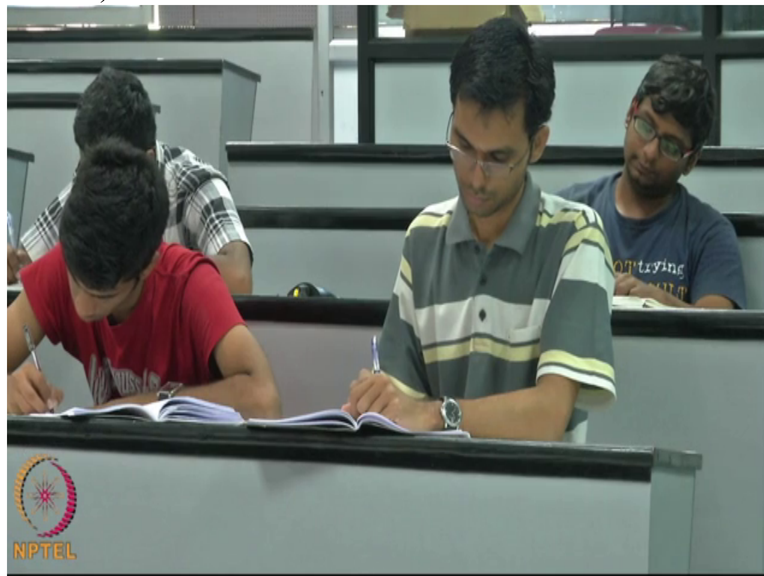
So the M O C V D process was invented in the 1960s and since then it has predominantly replaced M B E for C V D of metals because as you can imagine the energetics involved in this process are quite high and maintaining particularly the purity of the chamber is always a huge issue. And the other problem that happens in this particular case is that it does not, it does not etch the surface uniformly.

Essentially you are picking spots on the metal and entraining them where as in the case of M O C V D you are pretty much reacting the entire bulk material to make the metal wafers and so you get a much more uniform feel when you are doing metal organic C V D type of processes.

So this M O C V D process is now widely used also to make metal films. Now these processes again, the metal organic is highly reactive system. So you want to run M O C V D reactor under conditions where there is good control over the reactive nature of the system. In other words you do not want to run it at too high a temperature.

You want to run it at an intermediate temperature where the deposition process is kinetically controlled rather than purely controlled by transport phenomenon. If you recall the figure that we had drawn earlier relating deposition rates to

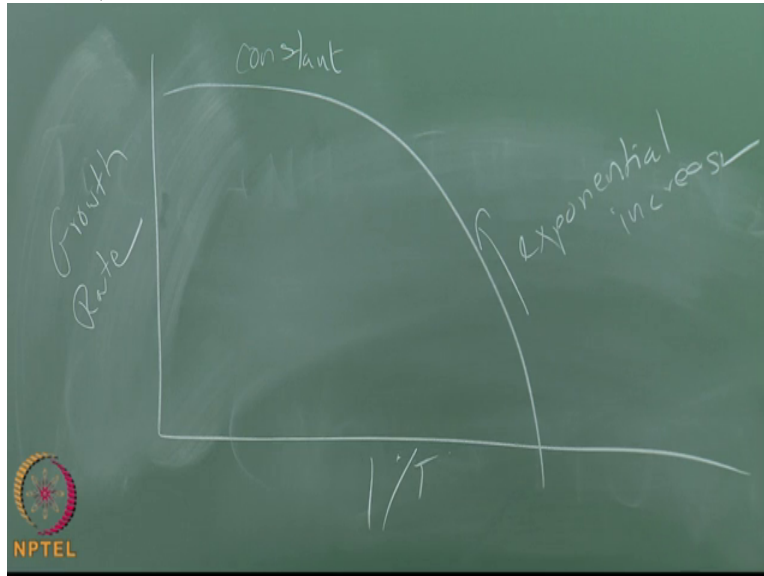
(Refer Slide Time 21:59)



substrate temperature 1 over T versus growth rate you recall that the general trend is like this, right?

There is a period, a low temperature period where actually as you increase the temperature there is an exponential increase in the rate of film formation. But then once you raise the temperature beyond a certain value it becomes constant. So this is the classic C V D signature.

(Refer Slide Time 22:47)



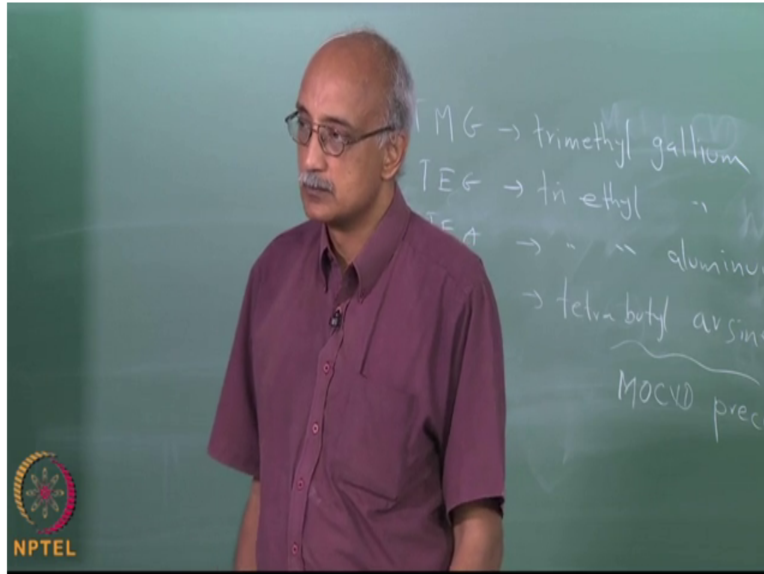
When we talk about metal organic C V D there is actually a small variation to this, which is that at sufficiently high temperatures you can actually start to see a reduction in the rate of film formation.

Can anybody speculate why that might be happening? Why would you see

(Refer Slide Time 23:12)

a lowering of rate of deposition;

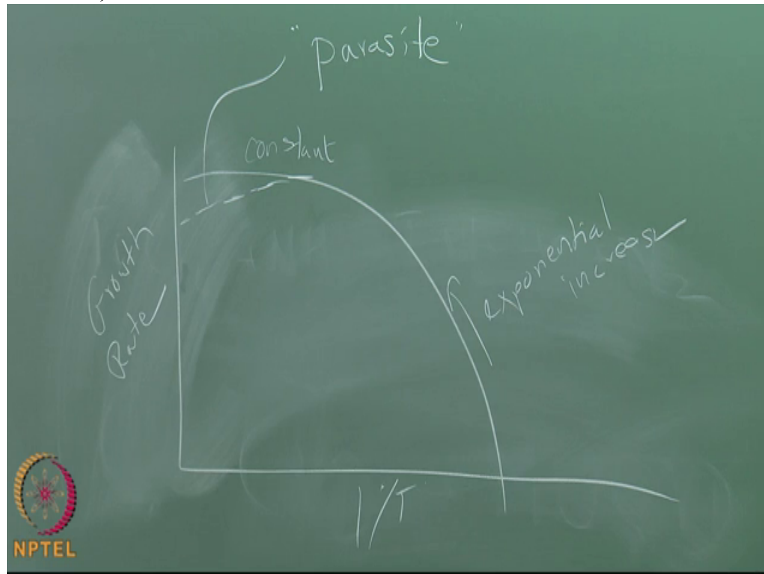
(Refer Slide Time 23:16)



any ideas? The primary reason is that it is a very reactive system. What that means is there can also be many parasite reactions that can be going on at the same time.

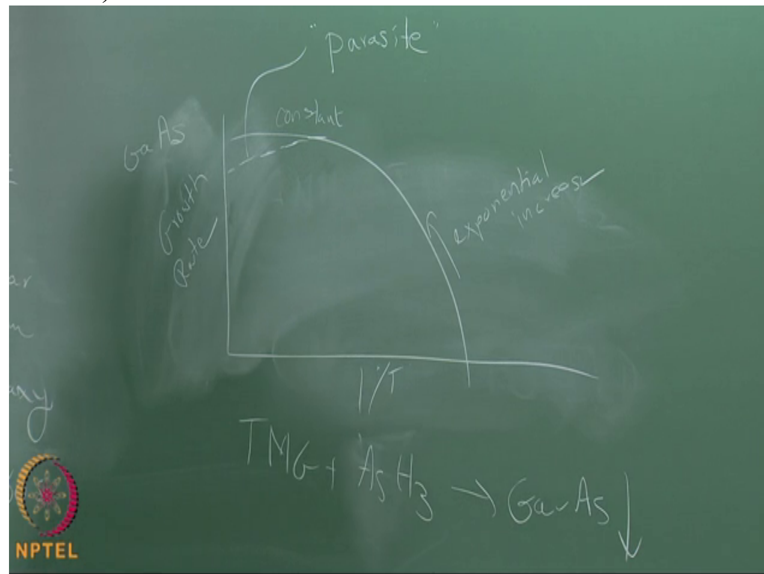
The parasite reaction is one that essentially scavenges the

(Refer Slide Time 23:42)



species that should be depositing as the film and instead causes it to form a different product so that, for example let us say that you have, you are trying to make gallium arsenide and what you are looking at here is the, the system itself is, you have like say T M G plus arsene which is giving you the gallium arsenide material.

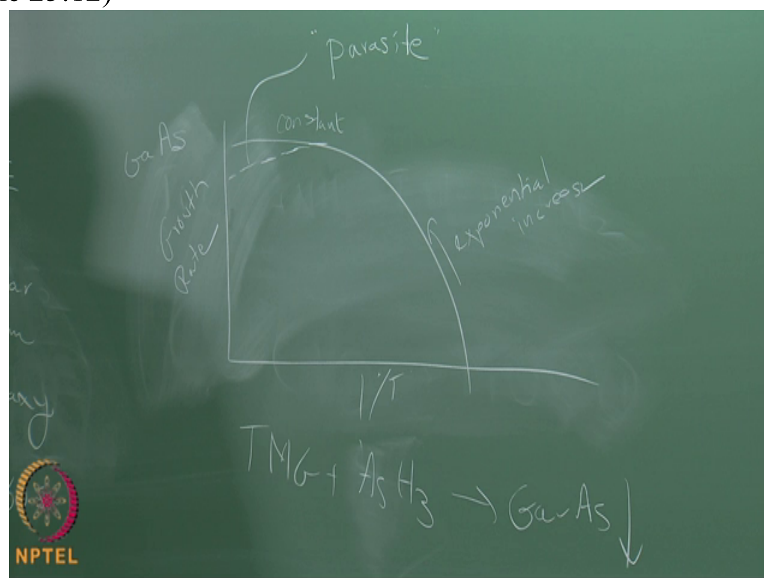
(Refer Slide Time 24:32)



Some of the parasitic reactions, there can be actually two kinds. The parasitic reaction can be such that it keeps the gallium and the arsenic from depositing on the surface. So it keeps them in the vapor phase. So they act like a 0:24:50.4 mechanism which prevents the formation of the film. Alternatively what happens is instead of forming gallium arsenide as your film, you can actually start forming gallium or arsenic as the film.

Then it becomes an impurity in the, in the C V D film. So when we look at the growth rate of the deposit

(Refer Slide Time 25:12)

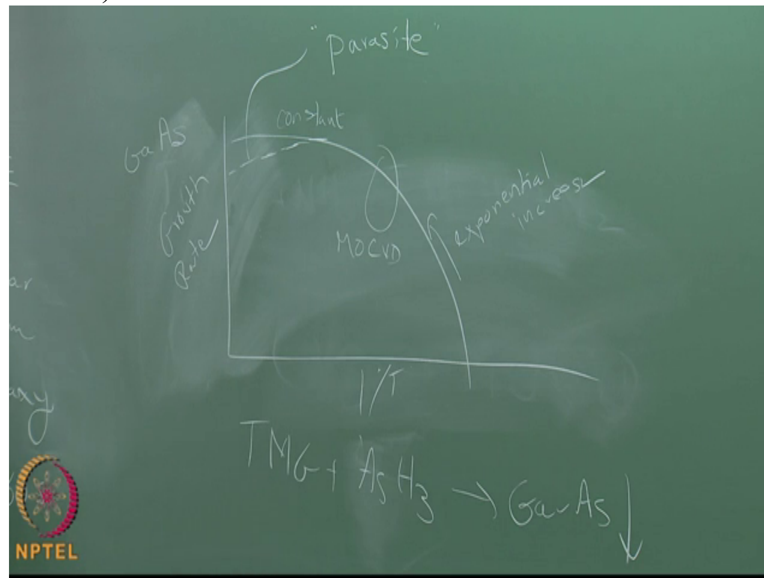


the overall thickness may actually be increasing as a function of time but the composition may be changing. But where as in the case where the depositing elements are actually

removed and kept in the vapor phase you will see a net reduction in the rate of film formation itself and when something like this happens, the, and that is one reason why you do not to operate in this range.

Typically M O C V D is operated in the intermediate range where

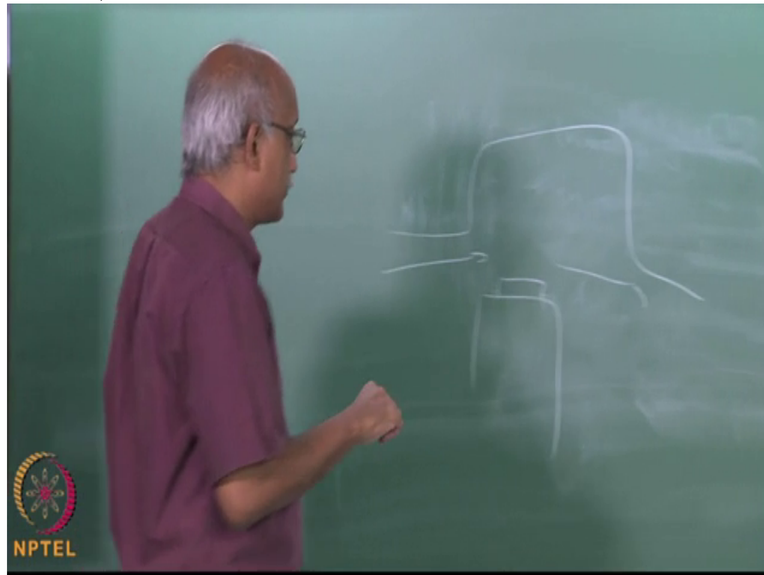
(Refer Slide Time 25:48)



there is still a significant effect of temperature and the conditions are not so reactive that you start forming all of these essentially unwanted or undesirable reactions either in the gas phase or on the surface. And for the same reason just like metal C V D, M O C V D is also done under conditions where the walls are essentially kept cold. That is a, again the downside you are using very reactive systems.

You get a very high film formation rates but at the same time your entire reactor is susceptible to formation of particles and so on. M O C V D reactors are run in two configurations usually. So the first is the classic horizontal cross-flow type of a reactor. But the other configuration

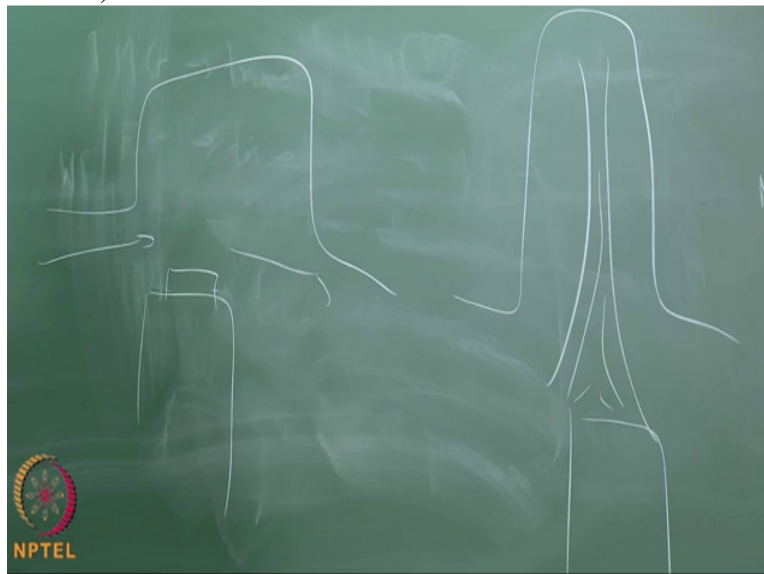
(Refer Slide Time 26:58)



that is widely used is the stagnation point flow reactor.

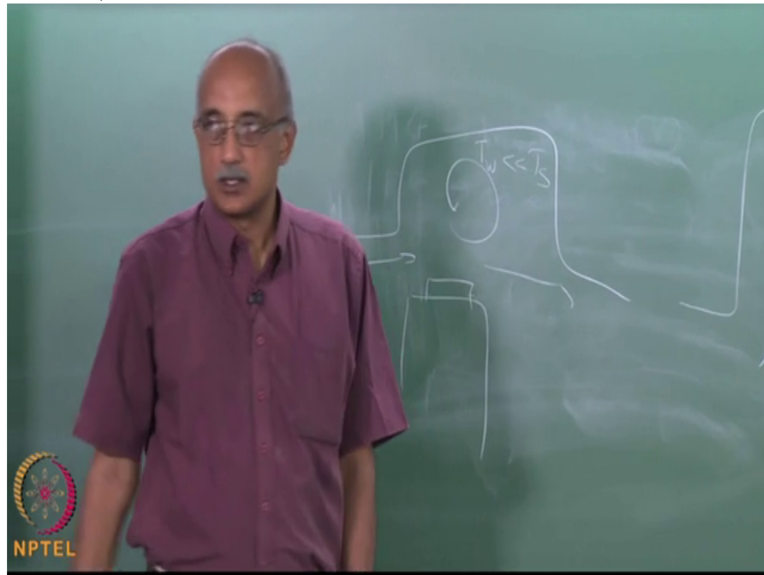
Now the reason that people prefer

(Refer Slide Time 27:13)



the stagnation flow reactor for M O C V D is that when you have the horizontal flow and you have a cold wall so that T w is much less than T s, as we have said before you can start setting up these recirculation cells

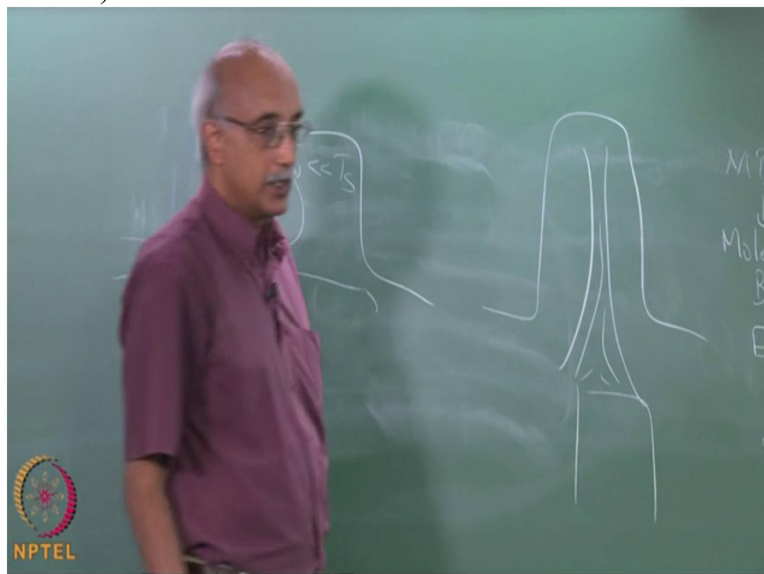
(Refer Slide Time 27:33)



which can introduce turbulence into your system and prevent the formation of the uniform film.

Lot of those problems can be overcome essentially by

(Refer Slide Time 27:46)



using a stagnation point flow reactor because here the flow is dominantly directed towards the surface. So even if your wall temperatures are much lower than your substrate temperatures the, essentially the downward flow of the reactant gases is sufficient to prevent significant recirculation cells forming and taking the material away from the substrate.

Of course in stagnation point flow also you can have localized recirculation cells but they are contained to the region that is very adjacent to the surface. So the effect of these convection roles are not felt through the entire reactor, they are kind of localized and their influence can therefore can be kept to a minimum. Whereas in the case of horizontal flow C V D reactor once natural convection effects start to show up it is very difficult to contain it.

By the way, the other way the turbulence can happen in a C V D reactor is that even if you have good controls over everything you know, your inflow, your temperature distribution and so on; if the geometry of the flow has certain sharp features, you know corners or turning radii that can sometimes be sufficient to induce turbulence. So it is not only the flow dynamics that result in turbulence.

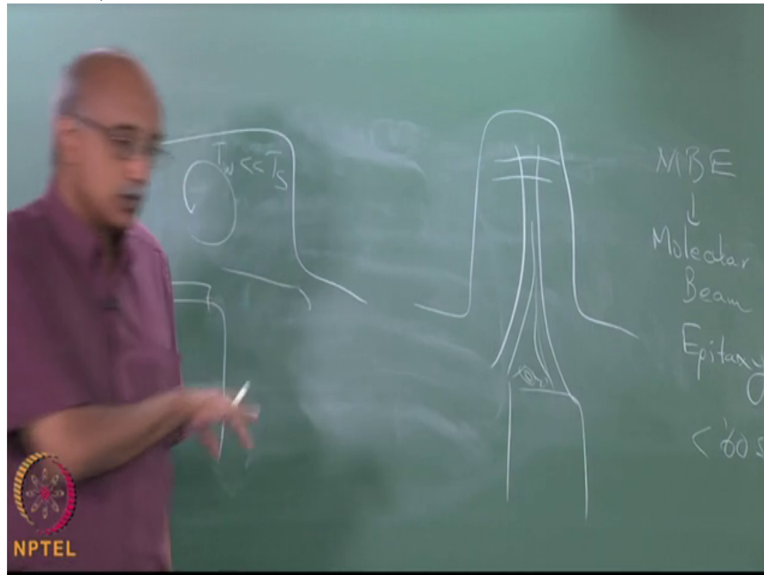
It can also simply be the physical design of the C V D reactor that can result in unintended turbulence effects; now that again, the horizontal flow design is much more susceptible to, compared to the stagnation flow design because the path from the inlet to the substrate is essentially a straight line in a stagnation flow reactor.

So the geometry of the reactor itself does not play a significant role in controlling the

(Refer Slide Time 29:47)

deposition on the film. If you are going to use

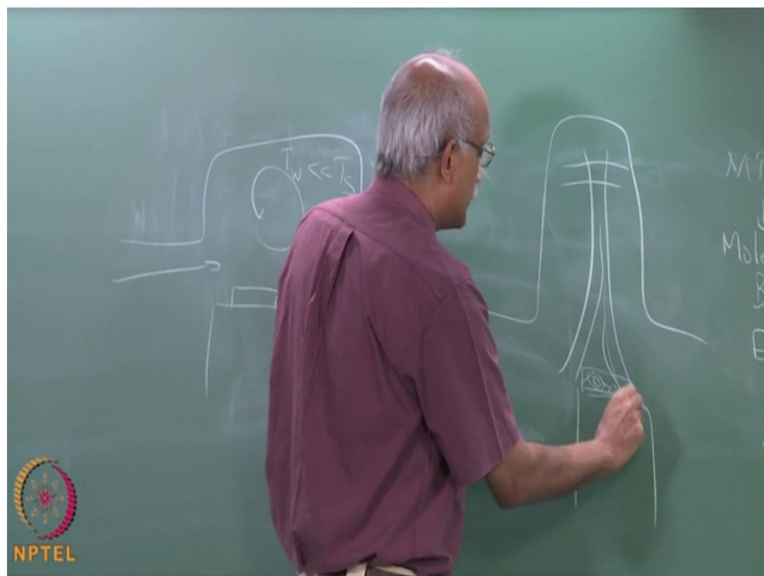
(Refer Slide Time 29:51)



a horizontal flow reactor many of the things that we talked about earlier in terms of the flow dynamics controlling the velocity profile so that you enter with a uniform or plug flow which then turns into a parabolic flow. That becomes very, very important to achieve in the case of M O C V D reactor.

In the case of the stagnation point flow reactor the primary thing that you would want to look at is what is happening

(Refer Slide Time 30:23)

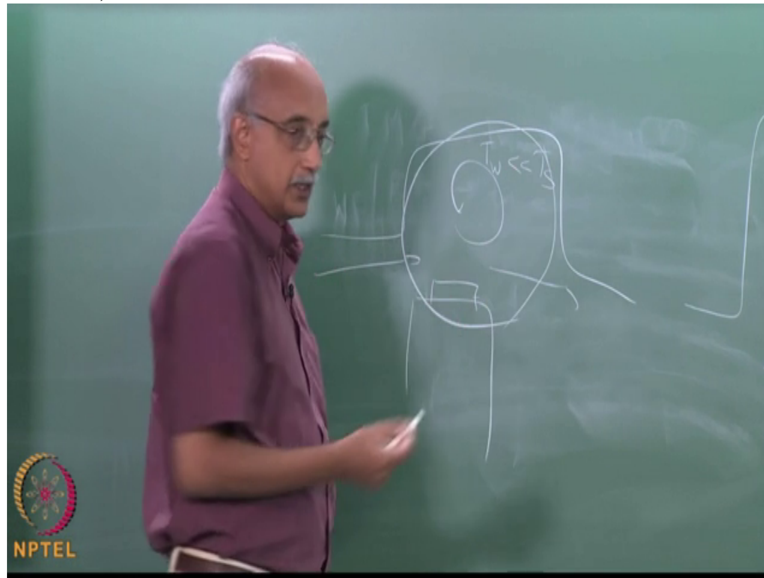


in the vicinity of the substrate. The thing that we want to ensure is that the residence time of the reacting species adjacent to the substrate is kept uniform along the length of the substrate.

And so you have to do some C F D modeling to understand how flow is going to happen in the vicinity of the substrate.

So again in terms of analysis and controls the focus in the stagnant point reactor is only around this region. So that reduces the complexity of the design and therefore the complexity of the cost. If are trying to do this in a horizontal flow reactor, you really have to do the C F D model

(Refer Slide Time 31:07)



over the entire reactor and you have to control not only what happens in the vicinity of the substrate but essentially everywhere within the reactor.

So the complexity goes up. Cost goes up. Alright so in terms of metal organic C V Ds these are some of the considerations you have to keep in mind given the high reactivity of the, the precursors. The other thing as I mentioned earlier is carbon. When you are trying to deal with systems that contain a lot of carbon; what you can try and do is either make the film itself sort of forgiving of carbon so that the properties of the film are not unduly affected even if there are some traces of carbon adsorbed into the film.

The other thing you can try and do is use sufficient excess of the carrier gas to make sure that the excess carbon is flushed away as soon as possible. Adsorption is a time-dependent process. So the longer the time that you allow for vapor species to be adjacent to a solid substrate the higher the probability that it will get adsorbed. So by ensuring that there is a

strong flow maintained you can essentially keep removing the carbon from the vicinity of the substrate as quickly as possible. So providing horizontal flow actually helps in that case.

So the primary advantage and the reason that people still look at horizontal flow C V D as an option is the potential for carbon adsorption and in general, impurity adsorption is lower in horizontal flow of C V D setting compared to a stagnation flow. The same thing that worked to your advantage in terms of improving the deposition characteristics worked to your disadvantage of worsening the impurity deposition characteristics.

Any system that is more efficient in promoting deposition is also going to be more efficient in promoting the deposition of species that you do not want. So there is just a fine balance. A lot depends on what is your purity requirement. If for example, your film has to be more than 99 percent pure then you have to make absolutely sure that you cannot have impurities present then you may choose to pay a penalty in terms of some of the other characteristics of the system but ensure that you have minimal impurities captured in your film.

On the other hand if your film is something that you sell in the mass market, you do not care so much about whether it is pristine then you are probably better off using the stagnation flow type of reactor which will ensure that your reaction rates are very high, your deposition rates are very high and you know, the only thing it cannot ensure is the impurity-free deposit film.

So these are some considerations to keep in mind when you are trying to design these various reactors, you know, atmospheric pressure A P C V D, L P C V D, P E C V D, M C V D, M O C V D they all have different purposes and there is no one design that fits all. You essentially have to look at each of your applications and see what type of process is best suited for that particular film. And I think it is fair to say that C V D is the process that you invest in only if it is worth it, you know.

If you are trying to make a very thick film or you do not care how good the film is, you just want the film to be there and so on, you are probably better off not even looking at C V D as a process. C V D as a process requires chemical engineers to run, essentially. You need chemical engineers to design it; you need chemical engineers to run it, chemical engineers to control it and to optimize it and so on.

Whereas there are many other coating processes that can be done essentially as a turnkey operation which do not require such a, you know good understanding of what is going on inside the system; for example, coatings. So we will talk a little bit about C V D of coatings in the remaining time in this lecture and in the next lecture.

There are many ways to put down coatings from surfaces. You can spray them on, you can do dip coatings, you can do, you know, thermal coating processes, there are so many, there is electrophoretic coating, there is electroless coating, all of these methods work perfectly well in terms of making a coating on a substrate.

So why would you want to look at C V D if you want to simply have a coating on the surface? What are the advantages of C V D coatings? The primary advantage of course is that you can make very thin films. C V D is an atom-by-atom or molecule-by-molecule process. So it is essentially what we term as a molecular self-assembly process.

You are putting the film down a molecule at a time. The molecules find each other and they assemble themselves in such a fashion as to give you a continuous film which certainly offers you the attraction of being able to manipulate the coating also at atomic or molecular level. So if you are very keen on providing particularly a layered deposit, a layered film that there is a variation in composition as a function of sectional depth then C V D may be the only process that you can use.

The C V D is the only process that can give you that atomic layer definition. So in principle you can make a coating where the first molecular layer, let us say silicon oxide, the second molecular layer silicon nitride, the third layer is again silicon oxide, the fourth layer is titanium oxide, in principle it is possible to do it and each of these can be of the order of Angstroms thick. There is no other process that can really give you that level of control.

So if you have an application that requires that level of granularity then you have to use C V D. The other advantage of C V D is that it can pretty much coat any substrate, you know, no matter what its physical features. Particularly when you have these sharp changes in the geometry of the substrate, when you have deep trenches or when you have bumps and blisters

on the surface. These features are typically very, very difficult to coat with any process other than C V D.

So the more complex the geometry of the substrate the more attractive the C V D becomes because of its step coverage and throwing ability. These are the two terms that are normally used to describe the ability of any coating process to follow the contours of the substrate. The other advantage of C V D is it is fine grained coating. And grain size plays a huge role in determining ultimately the functional properties of the coating. And normally a finer grain is usually advantageous.

And here again, because C V D is a molecular level manipulation process the grain sizes tend to be also very, very small of molecular scale. And so it is very easy to get a fine grained structure using C V D as your deposition process.

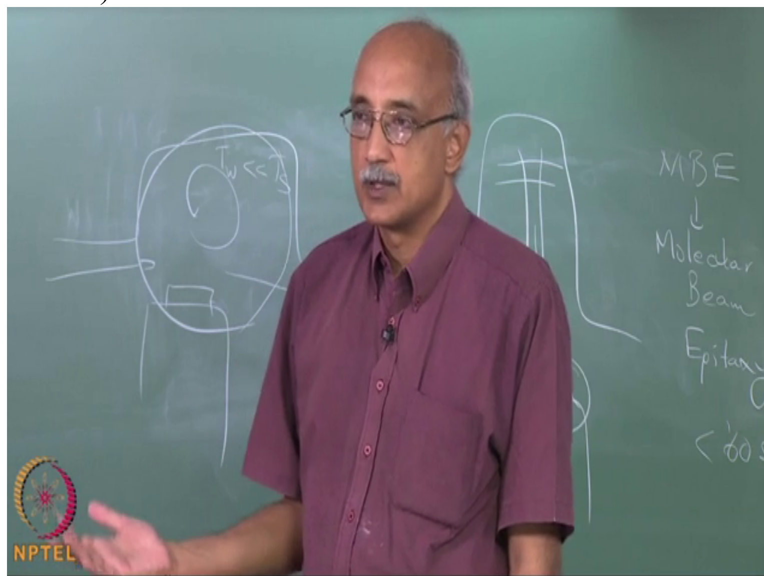
The other advantage with C V D is that you can minimize impurities because it is a well-controlled environment you really again have molecular level control on the composition of the film. So you can very, very precisely control the stoichometry of the deposit. I mean you just do not make S i 3 and 4, you can make S i x and y and have x and y change continuously as a function of depth. There is no other process that really can give you that kind of ability, right.

So the other advantage is that, typically C V D films tend to have good strength, good durability characteristics because you are relying upon interlocking layer to layer. The biggest advantage of C V D process is that thermodynamically, they are favored. Equilibrium thermodynamics favors

(Refer Slide Time 40:07)

the formation of the coating. So you do not have to force it to happen.

(Refer Slide Time 40:10)



As long as you have the right ingredients in place and you have devised the operating conditions appropriately, C V D will happen organically or naturally when the film will start growing.

Now that is always good in terms of, you know, having confidence in your ability to grow a good film on the surface. Now the disadvantages. As I mentioned before, the investment cost. To first set up the C V D reactor is more, significantly more expensive than virtually any other type of system you can imagine particularly for doing something like a coating on a surface.

The second problem, C V D films are not particularly well-adhered to the substrate and the reason for that is that typically adhesion is being achieved by chemical interlocking. You are relying upon the species that wind up on the substrate to chemically react with the, the surface and form a film. Now in principle, chemisorption forces are much stronger than physisorption forces. However that only applies when you can guarantee chemisorption to happen.

But if you have impurities on the surface or contaminants on the surface or byproducts that are getting adsorbed on the surface, they can compete with the reactant molecules and prevent this chemical interlocking from taking place and when that happens there is no backup, you know, there is no physical mechanism to lock the film to the surface. Adsorption is something that you always have to; I mean adhesion is something that you have to always watch out for.

The density of the film is also lower in C V D compared to thermal coating process. So typically C V D films need to go through a densification process which is a post C V D baking or annealing process to improve the quality of the film and get the properties that you are looking for.

But the primary problems of the C V D are the cost and the complexity. Because there are so many factors involved, I mean it is not enough to just control the flow dynamics; you also have to control the composition of the reacting species. You have to control the temperature distribution in the reactor. And you have to control what is happening in the vicinity of the substrate as well as what is happening downstream of the substrate because many of the byproducts of C V D processes whether for coatings or for other substrates are toxic in nature or corrosive in nature or have other types of environmental effects that must be prevented from happening.

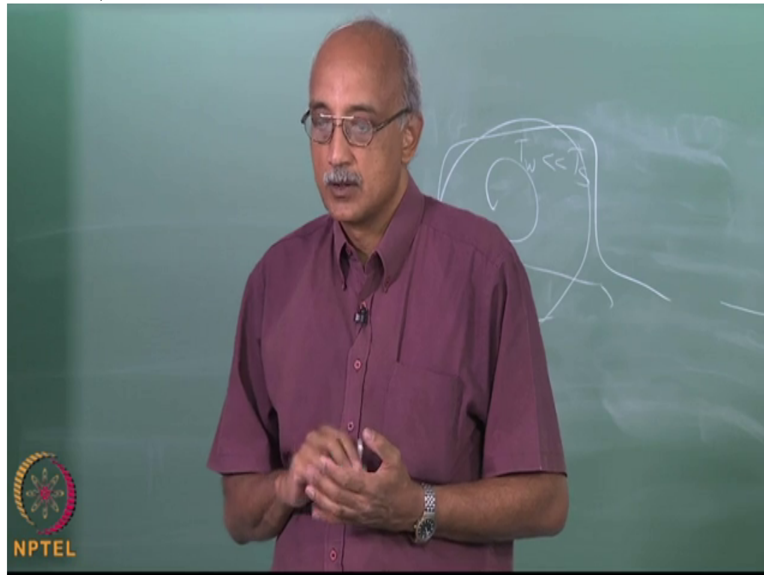
And so in the case of, for example, many coating processes tend to be liquid based where you essentially expose the substrate to the liquid and let the liquid dry on the surface. Or they can even be solid, for example powder coating is essentially a solid phase process where you turn the coating materials into very fine aerosols and spray them onto a surface in the form of a very fine powder.

In situations like that, you know the discharge that you have to deal with is somewhat easier to deal with than the case of C V D where the byproducts tend to be primarily vaporous in nature. The downside of that is they are very reactive. So if they do get into the atmosphere you know they are going to cause carcinogenous effects, toxic effects and so on. So it becomes very, very important to treat them at the outlet of the C V D reactor and ensure that they do not have any harmful effects downstream where as liquid and solid discharges are fairly, I mean there are fairly well-established processes to be able to deal with them. You can do it physically; you do not have to do it chemically.

So there are pluses and minuses to the use of C V D process in the application but C V D of coatings is a huge industry. It is a multi-billion dollar industry so there must be a reason why people want to do that. So in the next lecture we will talk specifically about C V D of coatings and what are some of the unique features of this process. Any questions on what we covered today?

(Refer Slide Time 44:41)

(Refer Slide Time 44:42)



Ok, see you tomorrow; see you at the next lecture.