Chemical Engineering Principle of C V D Processes
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Lecture No 07
Pressure Effects on C V D Processes

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Good morning and welcome to the next lecture in our course on Chemical Engineering principles of C V D processes. In the next few lectures, I want to spend time again talking about the various types of C V D processes and trying to differentiate between them. In particular one of the key variables in controlling the C V D process is the pressure.

As I have mentioned earlier in the course, the most C V D reactors are either at atmospheric pressure or at lower pressures and according to the pressure at which the C V D processes run, you can classify the C V D processes as atmospheric pressure C V D, low pressure C V D as well as plasma enhanced C V D which typically is done at pressures that are even lower.

So when we talk about low pressure C V D, we are typically talking about a tenth of atmosphere, where as in terms of plasma enhanced C V D we are talking about pressures that are hundredth of an atmosphere or even lower if you want to go to a ultra-high density plasma C V D. So when do we use what kind of process? I mean what is the factor that differentiates between these processes.

The simplest way to think about atmospheric pressure C V D is that it is the process that is used when you are looking for high rates of production and low costs of production. So it is typically used for components that do not have a high sale value essentially.

So for example if you are trying to make a dielectric film like S i O 2 then atmospheric pressure C V D is a very suitable process. But if you are trying to make crystalline silicon, probably isn't. And also we use atmospheric pressure C V D when the rates of deposition have to be quite high by which I mean that the rate of thickness growth is of the order of about 1000 Angstroms per minute.

So when you are looking for such large rates of deposition and film growth you tend to use atmospheric pressure C V D. The primary advantage of the atmospheric pressure C V D process is that it can be designed as a continuous flow process.

All the other type of C V D processes that we will talk about are essentially batch processes where you have to have a chamber which is depressurized, you know, vacuum is applied, process runs, and then you open up the chamber and take out the substrates.

In the case of the atmospheric pressure process, you can design it so that substrates are constantly being cycled through. Obviously that helps in terms of throughput we can do a lot more product when you run anything in a continuous mode compared to a batch mode and also it helps in the simplicity of the equipment.

You know any time you have to provide a vacuum in a process, it is very difficult. It is expensive and it is prone to leaks. Unless your vacuum chamber is perfectly designed, hermetically sealed, there are always going to molecular level leaks happening.

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And the C V D process is especially sensitive even to very, very minute quantities of leakage because all it takes is a few molecules of a
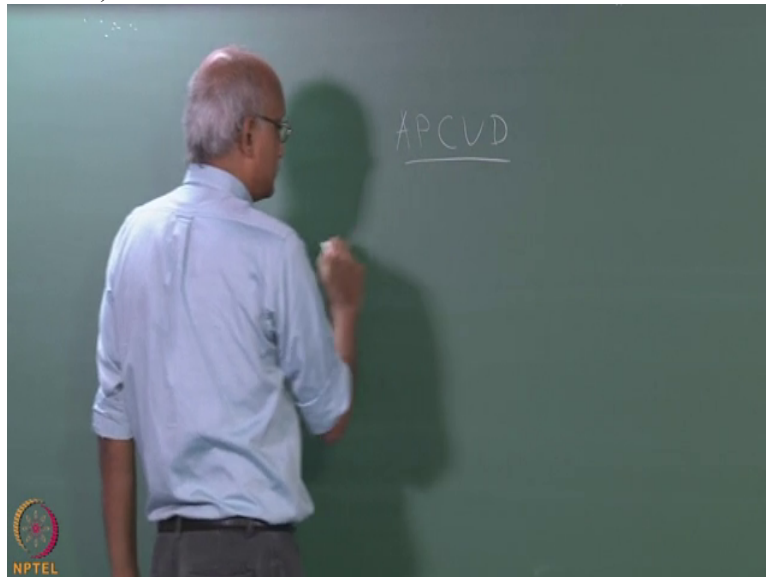
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particular impurity to, for it to react with the components inside the C V D reactor and thereby deposit on the film.

So in the case of A P C V D, atmospheric pressure C V D reactor

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you can conceivably have an entirely open chamber so that the reactants are coming in this way and the byproduct gases are going out that way and when we talk about a continuous throughput process, essentially you can have a belt drive mechanism where you are constantly taking the cassettes through on a conveyor belt which is
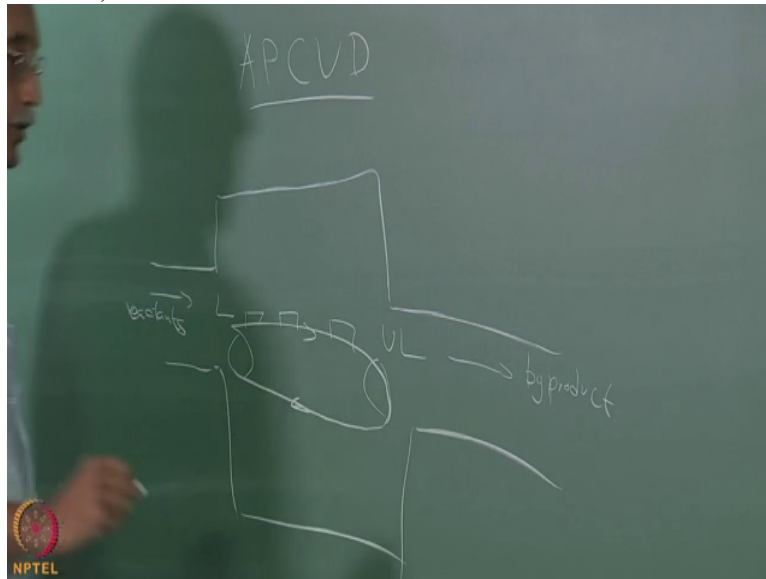
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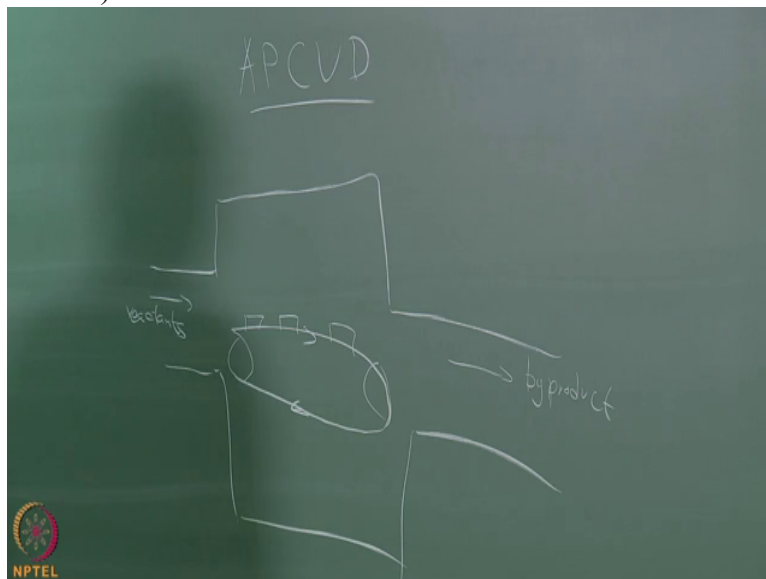
constantly rolling, right

So this then becomes the load station and this becomes the unload station.

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You will load your substrates to be coated on the upstream side and then it will go through the C V D process and then you will download the substrates with film on the downstream side and then the belt itself will typically go through a cleaning solution to remove any impurities that might have
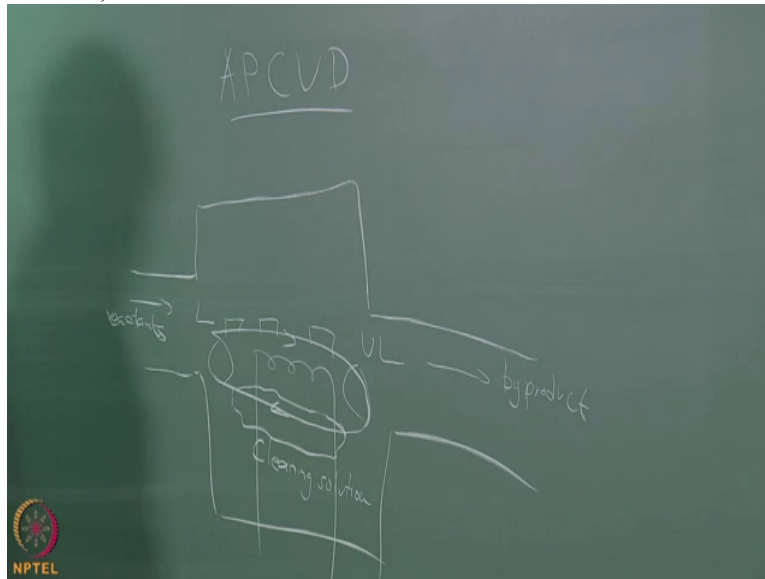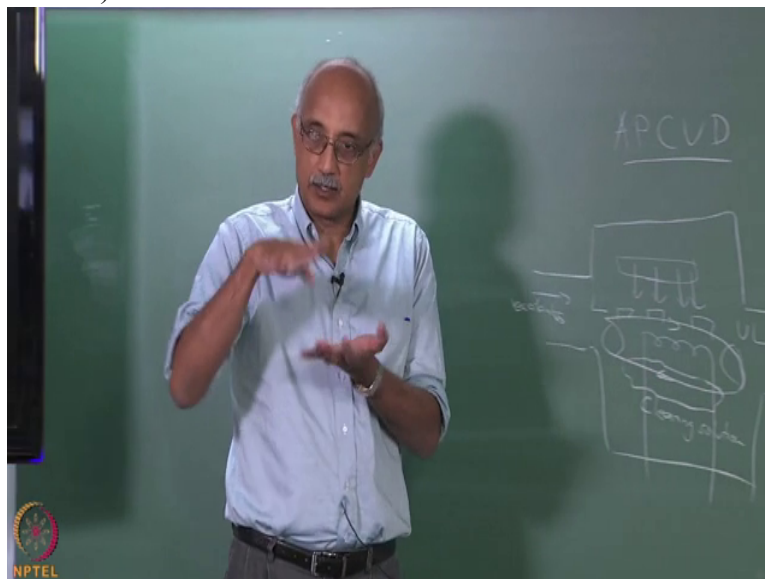
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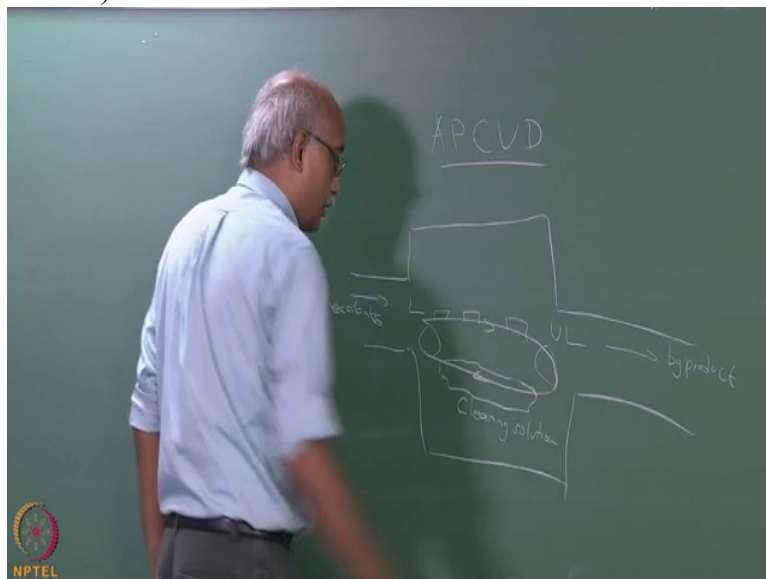
deposited on it.

Of course you would still need the heater arrangement so the substrates will be provide/provided

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energy source as they go through the C V D process. Now in this particular case, the gases are typically introduced through a tube that is sitting on top of the
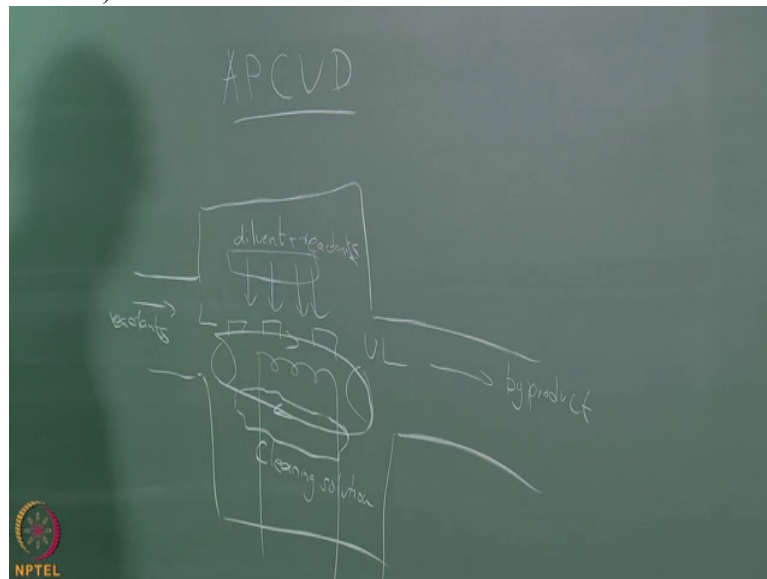
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film deposition location.

So this could consist of a diluant gas plus the reactants and

essentially this gas flow will be happening constantly, continuously even as the substrates are moving through continuously. So in principle it is a very simple flow-through process and has all the advantages.

What are some of the disadvantages of this kind of reactor? The first is it is open to the atmosphere, right? So there is really no way to prevent impurities from getting into the chamber. So your product, the film has to be robust enough to withstand impurities. So if you are looking for 99 point 9 9 9 9 percent purity, it is not going to happen. So you have to have a product that is a little more forgiving of impurities and other imperfections.

The second problem with this is that this type of a system is typically run as a cold wall reactor where only the substrate is heated. However the fact that the pressure is relative high, you know atmospheric pressure means that even locations that are further away from the substrate are susceptible to nucleation.

So a frequent problem in atmospheric pressure C V D reactors is that you have a tendency for particles to nucleate in the gas phase and then arrive on the substrate in particulate form which gives rise to again powdery or flaky deposits rather than a smooth and continuous film. So the way you try to address is really by controlling how the reactants are fed in. You try to keep them as much separated as possible until they actually get close to the substrate. So you try to play around a little bit with the gas delivery mechanism to ensure that the reactions do not take place far away from the substrate.

But essentially you pretty much have to live with it. In atmospheric pressure C V D reactor, the price you pay for the increased throughput and lower cost and simplicity and so on is that you really cannot expect a perfect film. You get what you pay for, actually.

So again that is the reason why this is primarily used for dielectric materials where the absolute purity or even the uniformity of the film is not a major issue. Now if you want to take this process and improve it in order to provide better controls, higher quality, more uniformity and so on, the first thing you need to do is make it into a batch process 0:09:22.6.

You have to provide an isolated and controlled environment for C V D to happen and that is done in an L P C V D process which is a low pressure C V D process
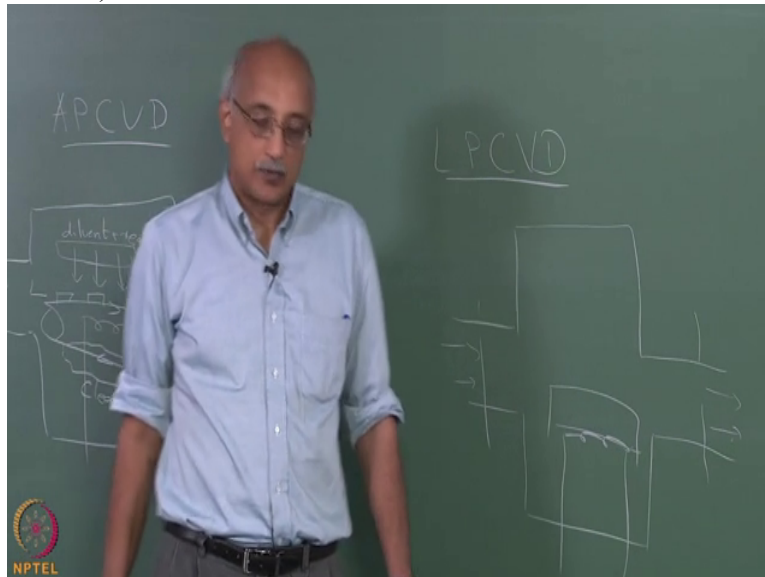
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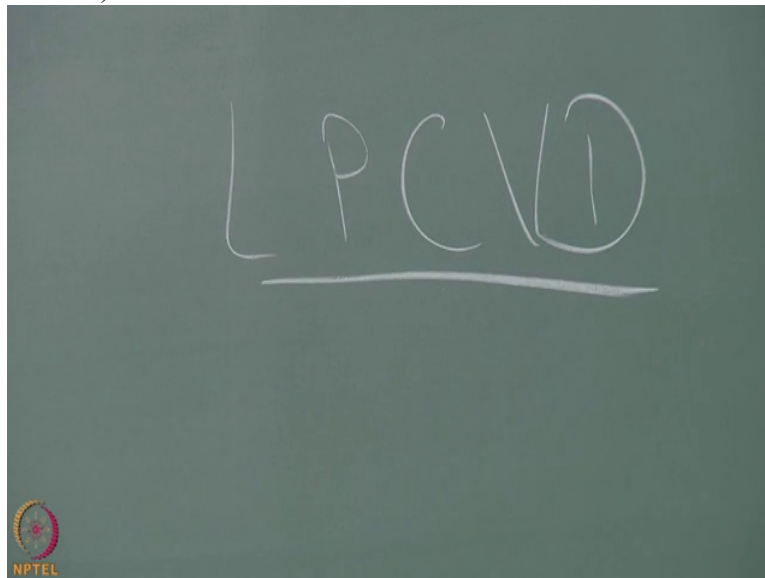
where the atmospheric conditions are kept at sub-atmospheric pressure.

So in this case you would have a reactor which is essentially a sealed reactor and the primary difference that you will see, you still have a substrate on
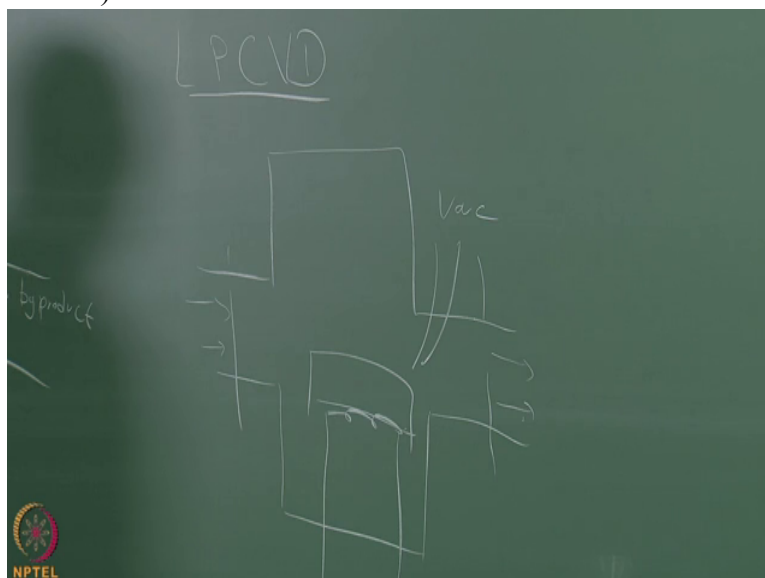
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which the C V D process is happening. But the primary difference is you will have an arrangement to pull vacuum from the system so that you can achieve a certain low pressure before you start depositing materials.
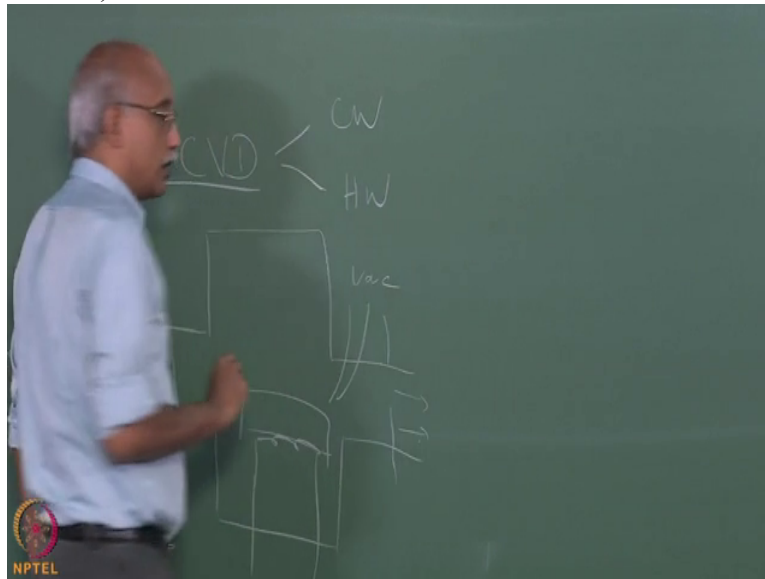
Now

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when we are doing low pressure C V D again there are two configurations in terms of the temperature distribution. There is the cold wall L P C V D and the hot wall

L P C V D where C W L P C V D implies that the substrate is kept much hotter than the reactor walls and pressure is kept low. And of course, hot wall L P C V D simply implies that the temperature distribution is fairly uniform within the reactor.

A cold wall reactor obviously has the advantage that nucleation is unlikely to happen in the gas phase and most of the condensation will happen at the substrate where as the hot wall reactor has the disadvantage that nucleation can happen anywhere in the gas phase. You can have substantial deposition on the walls of the reactor which can then flake off and so on.

The advantage of the hot wall reactor as we have seen before is that it makes the flow much more uniform. You do not have to deal with recirculation flows, natural convection and other effects that are associated with the steep temperature gradient in your reactor. And in fact, a majority, vast majority of L P C V D processes are run under hot wall conditions.

But

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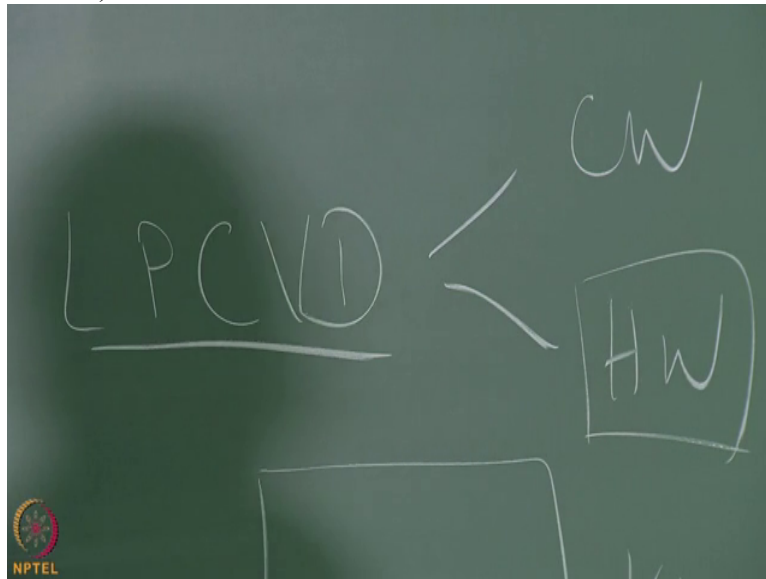
why would you do that when you know that reactor is susceptible to homogenous nucleation. Well there is one thing that helps. Can you think of why a hot wall L P C V D reactor would be better than a hot wall A P C V D reactor in terms of controlling homogenous nucleation?

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It is the fact that the pressure is low, right?

Chemical reactions are typically driven much faster under elevated pressure and elevated temperature conditions. So the fact that you are keeping the pressure low automatically implies that, to some extent chemical reactions are suppressed.

So by driving to a sufficiently low pressure, you can minimize the amount of homogenous nucleation that takes place in this reactor. A low pressure, by the way also helps in terms of reducing macroscopic induced flow such as buoyant flow or natural convection flow. So that is another reason why the low pressure C V D process typically gives you much better uniformity of the film compared to the atmospheric pressure C V D reactor.

Another way in which you can classify these reactors is that, they, like a low pressure C V D reactor is typically run under lower temperature conditions. What that means, if you recall the figure we drew relating deposition rate to temperature is that, at lower temperatures the kinetics become the controlling factor and not the transport.

So what that really means is that this is the potential of doing multiple substrates at a time. You know that the drawback with an L P C V D process is that, compared to the atmospheric pressure process it is slower, right, because it has to be done in a batch mode. But what we do instead, you know, typically this process if you look at it; the coating is happening essentially one substrate at a time.

Whereas in the case of the L P C V D process you do not do one substrate at a time. You essentially take a cassette on which you mount multiple substrates and you coat all of them at the same time, right? So this is like a basket in which you can have number of wafers or substrates to be coated and it can happen simultaneously

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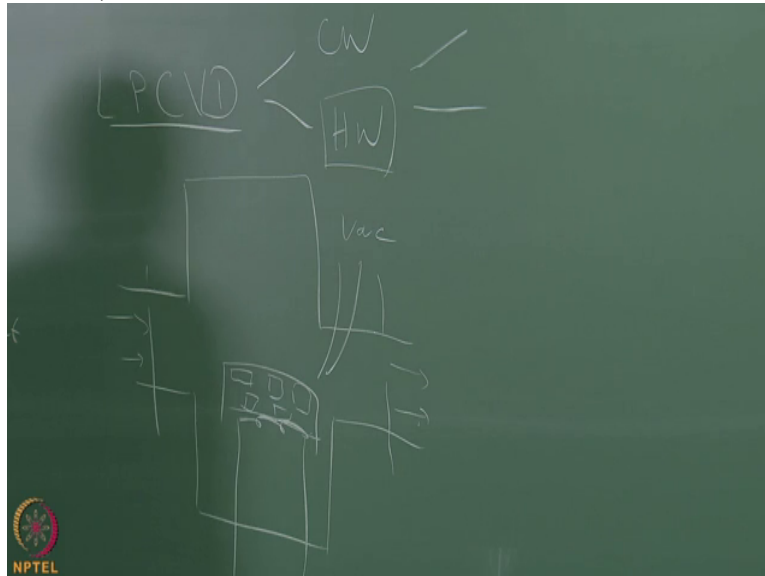
because the conditions are set so that the deposition processes is kinetically controlled. Which means that as long as you have a tight distribution over the, or control over temperature distribution, the uniformity should be fine.

Now in this case there are actually two different configurations as I mentioned. One is called horizontal flow reactor and the other is vertical flow reactor. This actually refers to how the vapors are positioned.
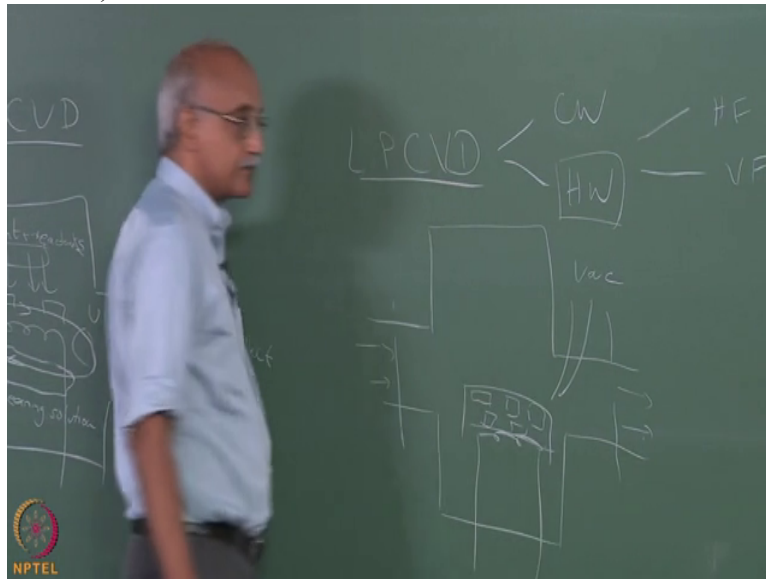
The vapors can be positioned so that they are parallel to the flow of gases and that is called as the H F C V D reactor.

Whereas the vapors can be positioned also so that instead of lying flat like this, they are actually standing up straight like this.
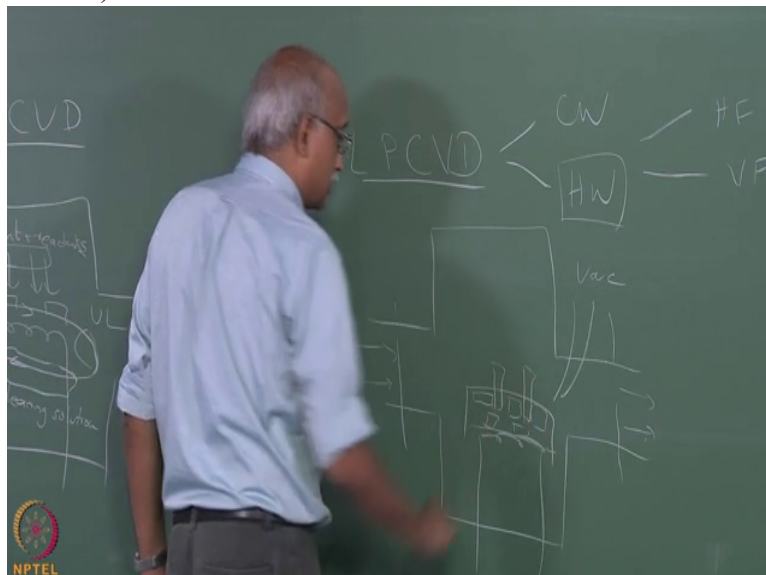
And that is called the vertical flow L P C V D reactor. The advantage of the vertical flow reactor over the horizontal flow is something that we have discussed in one of the earlier lectures that when you have a horizontal plate and you are flowing a gas through it, the uniformity is very, very difficult to achieve because the concentration depletion as well as boundary layer growth.

Whereas in vertical configuration where the wafers are actually, you know standing up, you can potentially direct the gases, and in fact what you would do in these cases, the gas inflow system will be designed so that there is a fresh flow of gas for every substrate. So that the flow is not going across them like this but rather there are multiple

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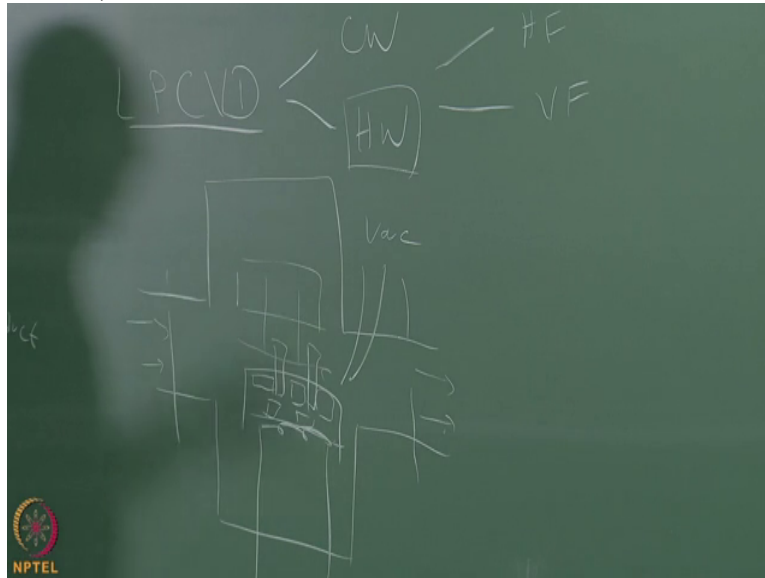
flow inlets so that each substrate that is vertically standing up sees the fresh feed of reactants and gas.

So it makes the uniformity much better. In fact with this configuration, vertical flow hot wall L P C V D it is possible to achieve better than 2 percent uniformity in the C V D film. That is if you measure
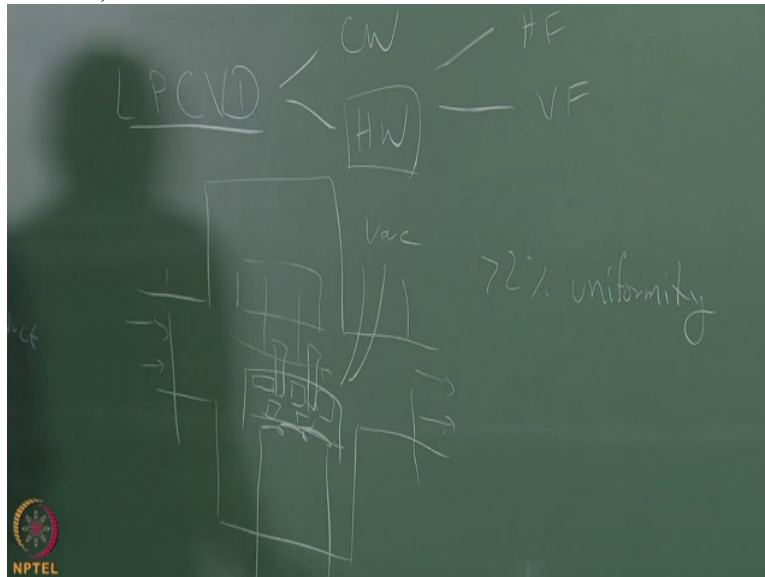
the C V D film across its length and you look at the variation in the thickness of the film, it can be controlled to be no more than 2 percent which by the way is very good in the C V D reactor.

And so the, this is again the preferred configuration.
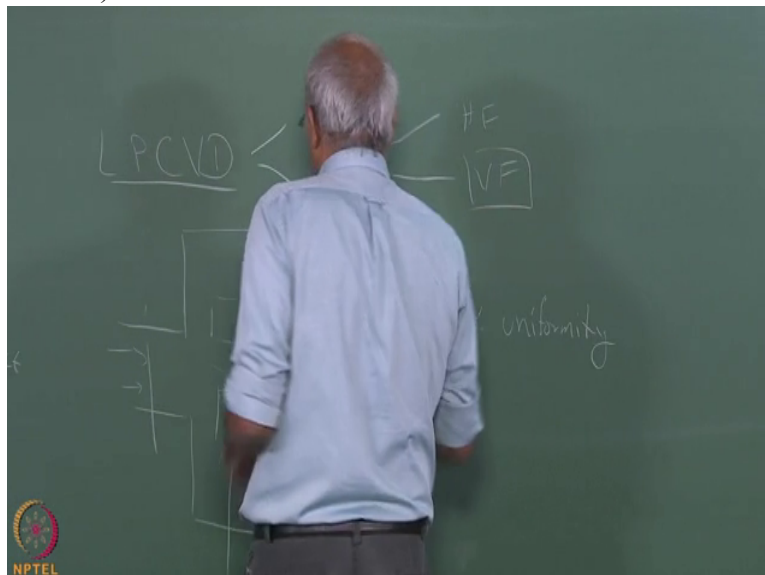
The cassettes or the wafers are mounted in a vertical configuration in the cassette and the walls are kept at about the same temperature as the substrate and the pressure is taken down to sub-atmospheric levels.
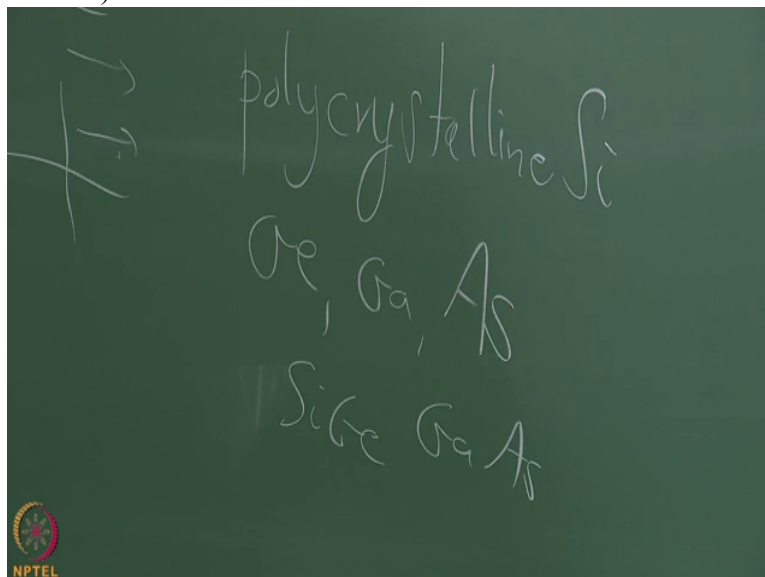
So it is obviously very good process and by the way this process is mostly used to make polycrystalline silicon. In fact this process is used to make many semiconductor devices, so

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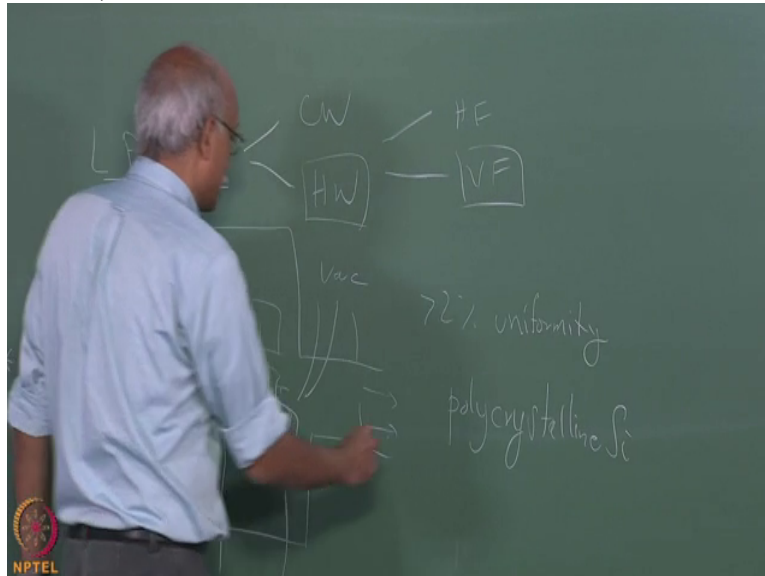
silicon, germanium, gallium, arsenic, S i G e, G a A s, there are many semiconductors and

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semiconductor compounds that are made using L P C V D process.

The characteristics of the film will be different in the case of L P C V D compared to A P C V D. The fact that these L P C V D reactors are
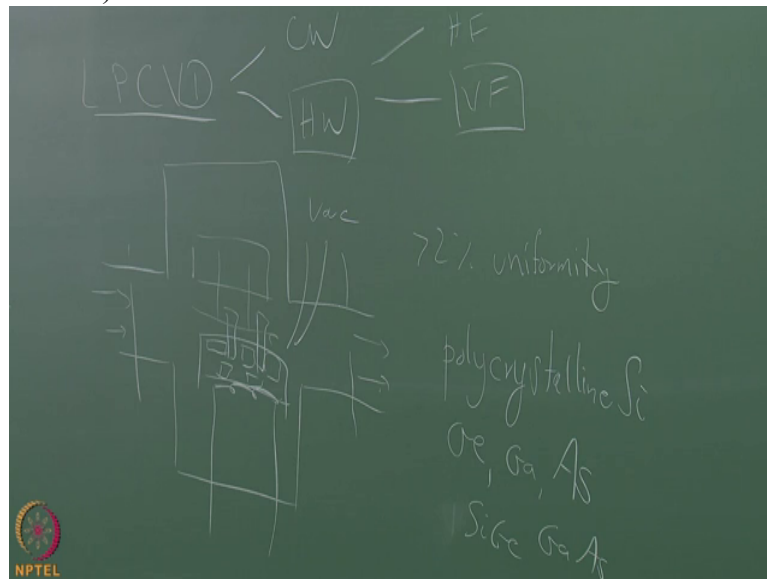
run at a lower temperature as we have discussed before essentially means that they won't be as crystalline in structure as the atmospheric pressure C V D reactors which are run at higher pressure and higher temperature.

So they are likely to be less dense, likely to be more porous and also there is a possibility that they can actually adsorb some of the product, byproduct gases and other impurities in the system. So typically the L P C V D process after its run, we do a high temperature annealing to bring
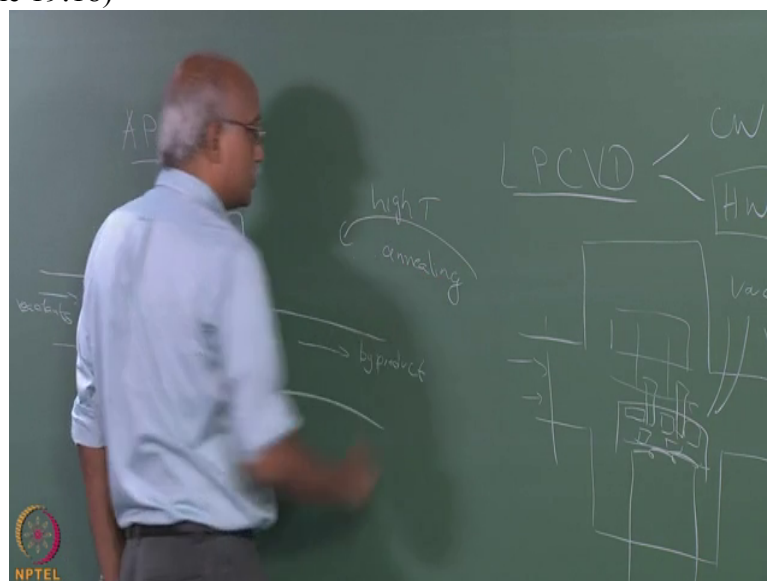
its properties, physical properties of the film to be more like the film properties that you get in an atmospheric pressure C V D reactor.

There are 2 important characteristics of the film that you try to measure and control. The first is the refractive index which is typically measured using

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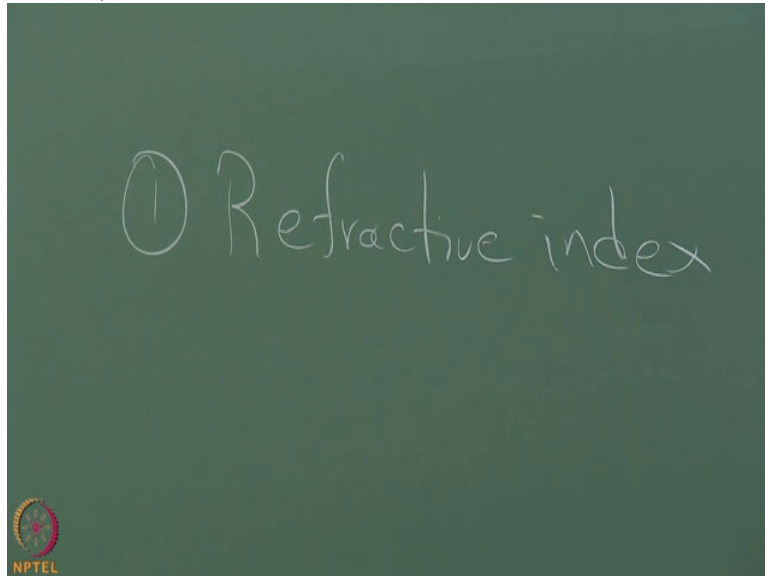
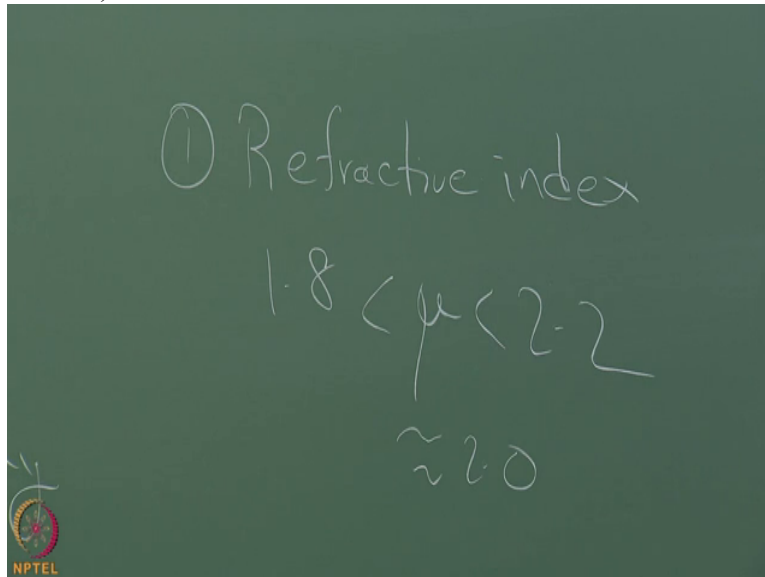ellipsometry and the specification for a poly silicon film is that

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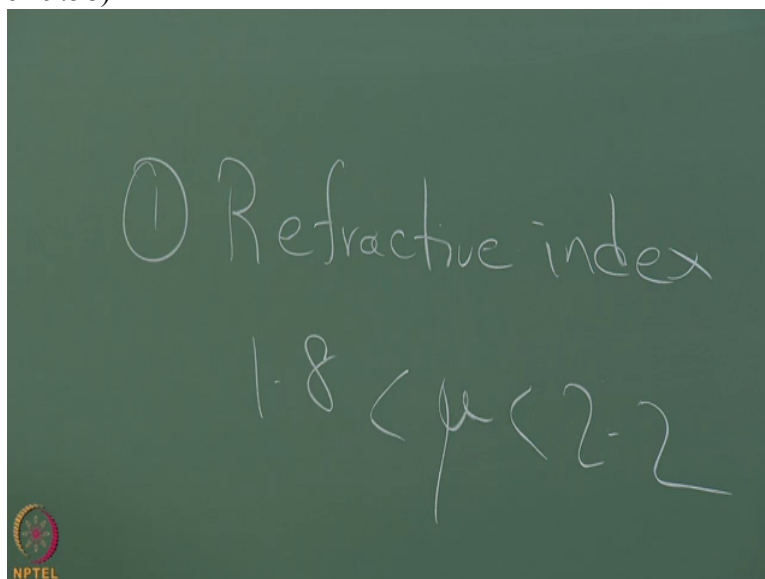
the refractive index must be in the range of 1 point 8 to 2 point 2. Nominally it should be 2 point O for a good film.

A high value of mu indicates that it is silicon rich

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and a lower volume of mu indicates that you have some impurities, typically oxygen in your system. And so as you measure the refractive index you constantly tweak the process so that you keep trying to bring it, bring it to the nominal value of 2 point O. So this is a, you know quantitative measure, fairly sensitive indicator of the composition of the film.

The second metric that is used frequently for quality control is the etch rate in 49 percent H F solution. Here the specification for a

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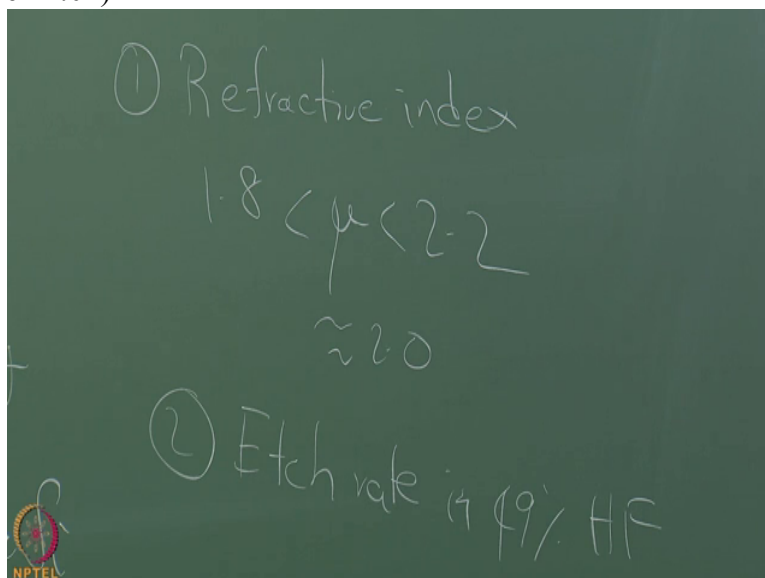
good C V D film is that this must be less than one nanometer per minute. So etch rates that are

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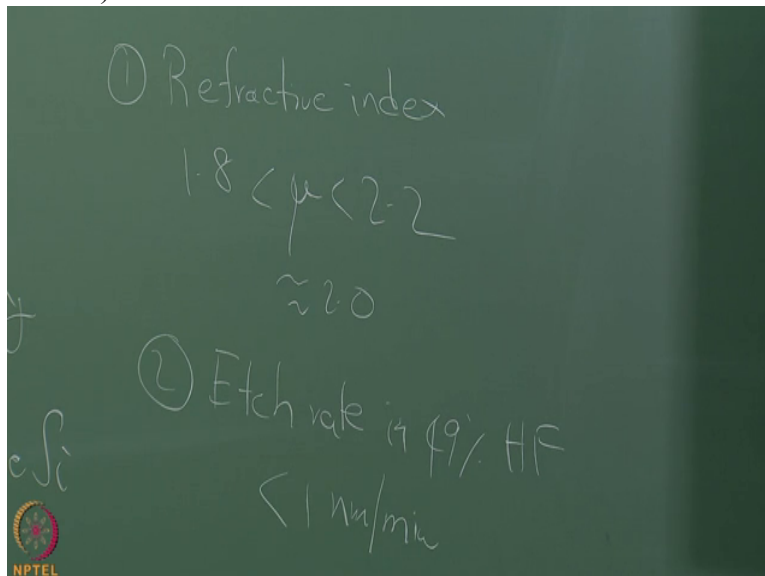
in excess of this basically imply that you have to do something to improve the solidity or integrity of the C V D film and again the most common process for doing that is to expose it to higher temperatures. And that will improve the etch rate as it is, as measured in 49 percent H F.

In an L P C V D reactor, if you actually look at how the rate of deposition changes as a function of pressure and temperature, so if you plot film growth rate versus let us say, temperature of the substrate and you look at this dependence

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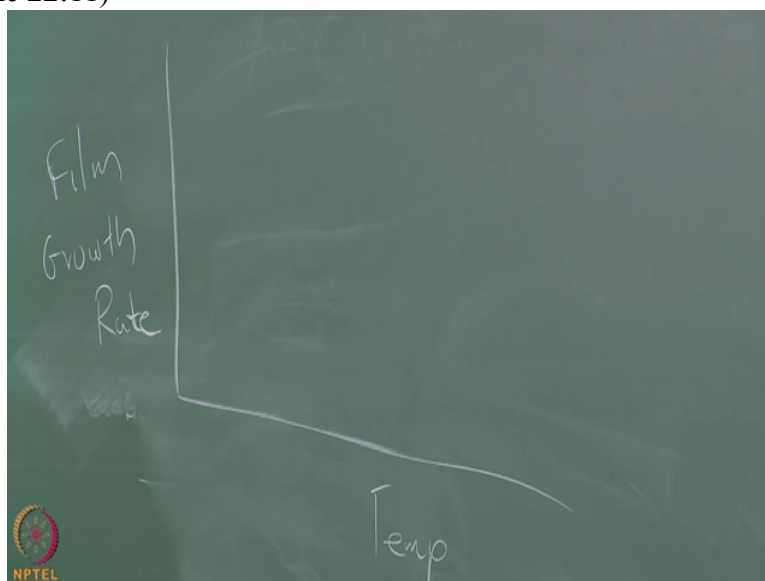
as a function of pressure, typically what you see is that you get a family of curves that look like that where the pressure, is it increasing or decreasing in this? Would the pressure be increasing in this direction or decreasing in the, in this direction?

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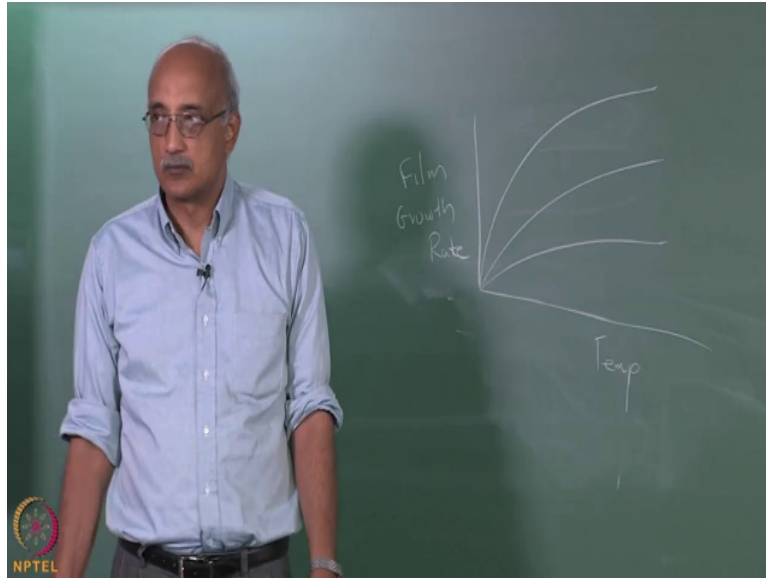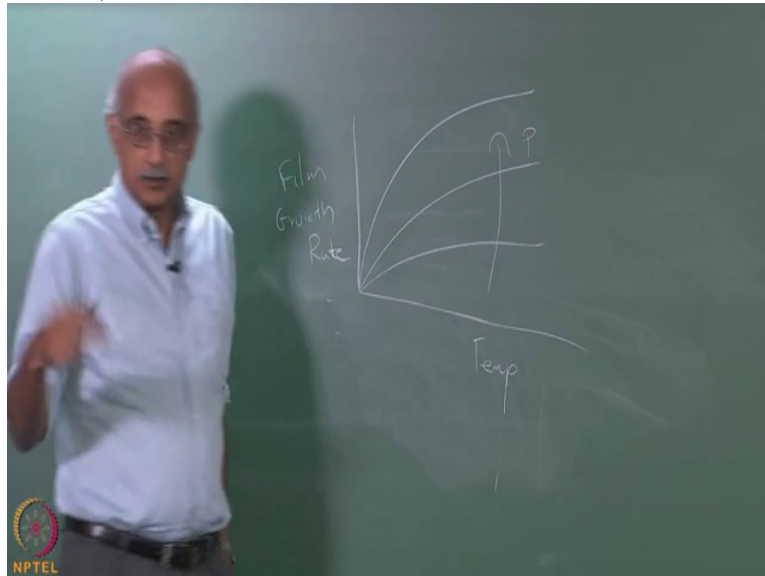

How many think increasing?

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(Professor – student conversation starts)

Student: 0:22:43.8 is decreasing. Some of 0:22:44.8

Professor: Again remember I said it is kinetically controlled. So as soon as say that it means higher pressure is good, right? If it is diffusion-controlled

the other will be true, the other way round will be true. If something is diffusion controlled, low pressure is better than high pressure but when process is kinetically controlled, higher pressure always helps.

(Professor – student conversation ends)

The reason being, higher pressure just very simplistically brings molecules closer together. So they are more likely to react compared to, if your pressures were lower. Ok, so we have looked at two categories of C V D. One is the atmospheric pressure and other is the low pressure C V D. Third kind of C V D process is what we call plasma enhanced C V D.
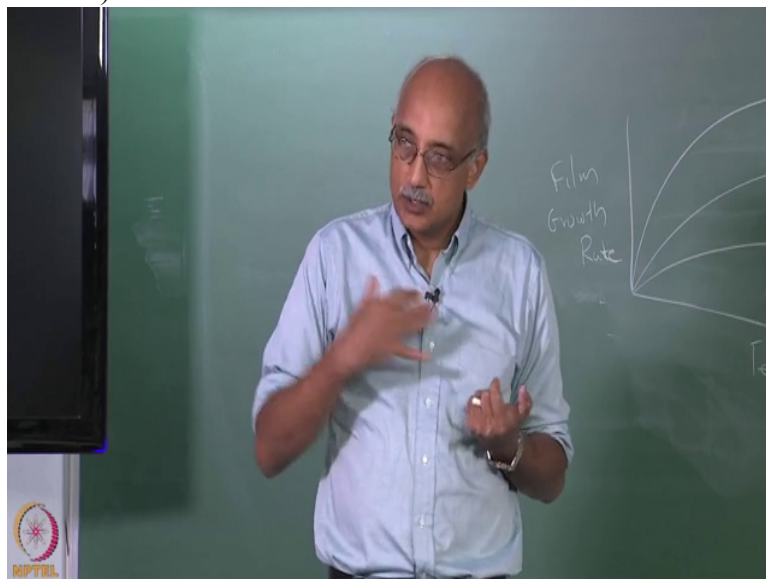
Plasma enhanced C V D is typically run at even lower temperatures than L P C V D and at lower pressures

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as well. The pressures in fact are kept so low that the, you either
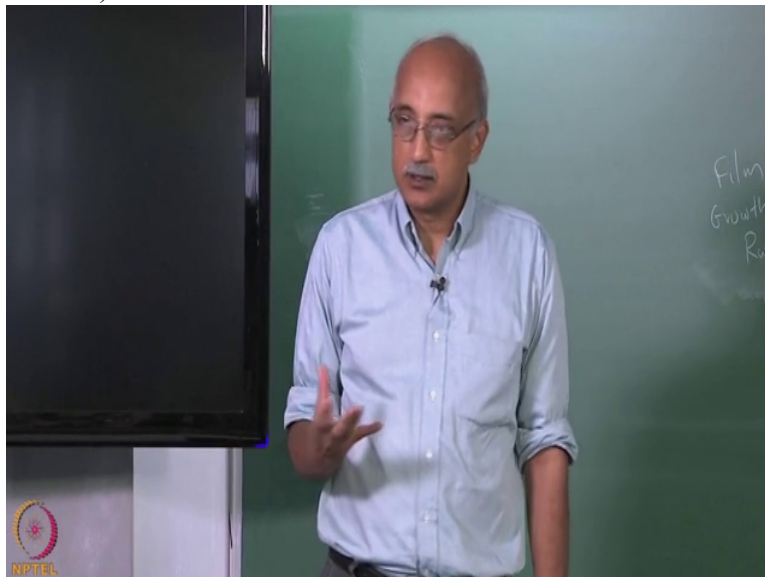
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introduce a source of ionization into your system or the pressures themselves are sufficiently low values can cause ionization to occur spontaneously as well.

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The advantage of a plasma enhanced C V D is when you have a temperature sensitive substrate
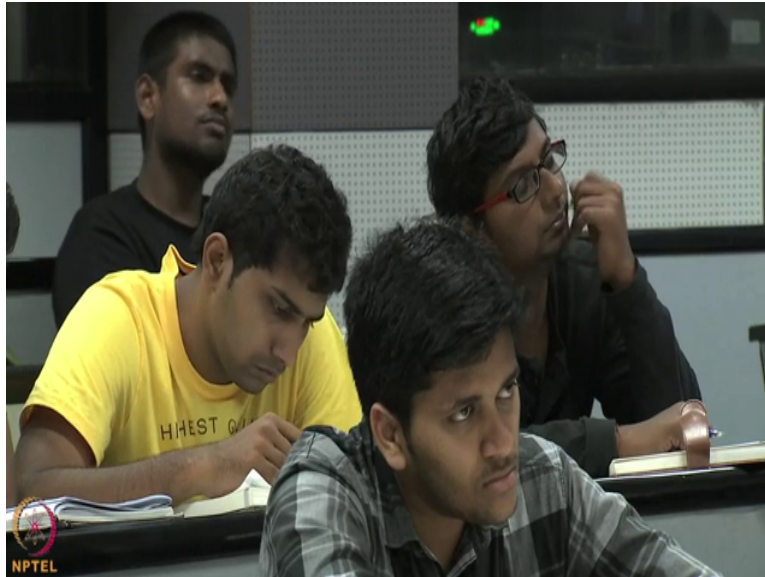
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and you cannot afford to heat it up much beyond room temperature, clearly you cannot rely on thermal source of energy to provide the energization to the substrate, so as an alternative means of energization of the substrate things like L A S E R C V D, photoelectric C V D and plasma enhanced C V D are resorted to.

When we do plasma enhanced C V D, the surface temperatures can be as low as 300 Kelvin, not too far above room temperature. The advantage of plasma enhanced C V D is that
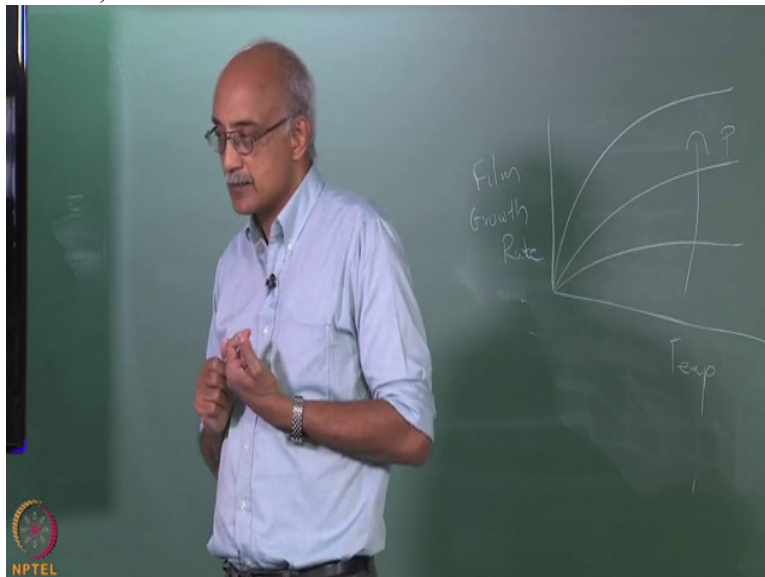
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it is again, from an energy viewpoint, from a substrate reactivity viewpoint, it is much better than A P C V D or L P C V D.

The downside of plasma enhanced C V D is that

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it is the most complex of all C V D reactors. The design of the reactor has to be paid a lot of attention to, in order to achieve the plasma conditions you are looking for and maintain them. The other disadvantage is, see the way a plasma enhanced C V D reactor works is you are energizing the substrate using a plasma. But at the same time you are also energizing the gas phase itself.

So the molecules that are present in the gas phase are also getting some of the energy transferred to them. So the same kind of problem as in hot wall C V D can happen. Your molecules, gas phase can become sufficiently energized that they start reacting in the gas phase and homogenously nucleating particles or aerosols and so on.
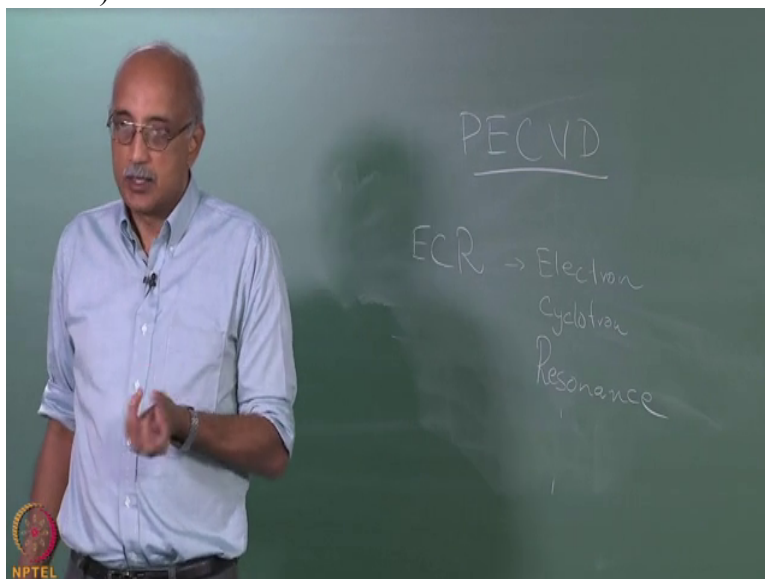
In fact there is a process called E C R

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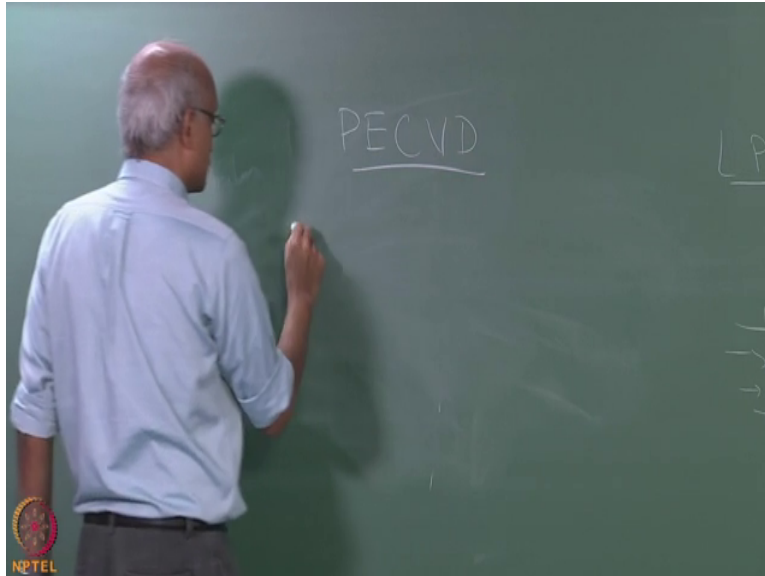
which stands for electron cyclotron resonance where what you really do is you provide sufficient plasma energy to take a radical or a species in the gas phase

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and turn it into a radical. For example, if you are trying to make, let us say silicon nitride by reacting S i O 2 plus N 2.

Not easy to happen, to make that happen, right? Or actually if I use SiH_4, sorry not SiO_2, while silane is a very reactive molecule, N_2 is not. So it is very difficult to use this process to make Si_3N_4. However if you can bombard this N_2 with high energy plasma and turn it into N, N is now very reactive with SiH_4 and it easily forms an SiN_3,

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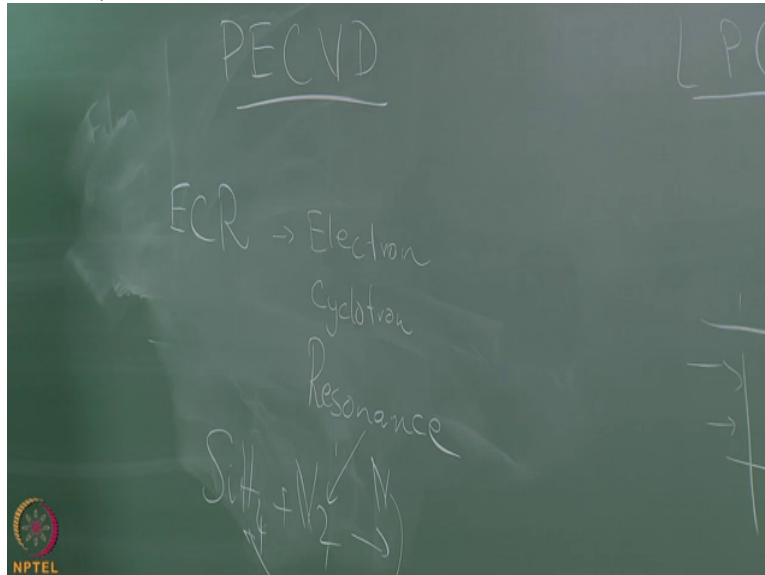
Si_3N_4 type of compound on the surface.

So electron cyclotron resonance is a technique by which you essentially convert neutral species in the gas phase to an ionized radical form which then reacts readily with the precursor vapors that you are introducing into the C V D reactor to get you the film that you want.

The variation of this is called the H D P C V D reactor which just stands for
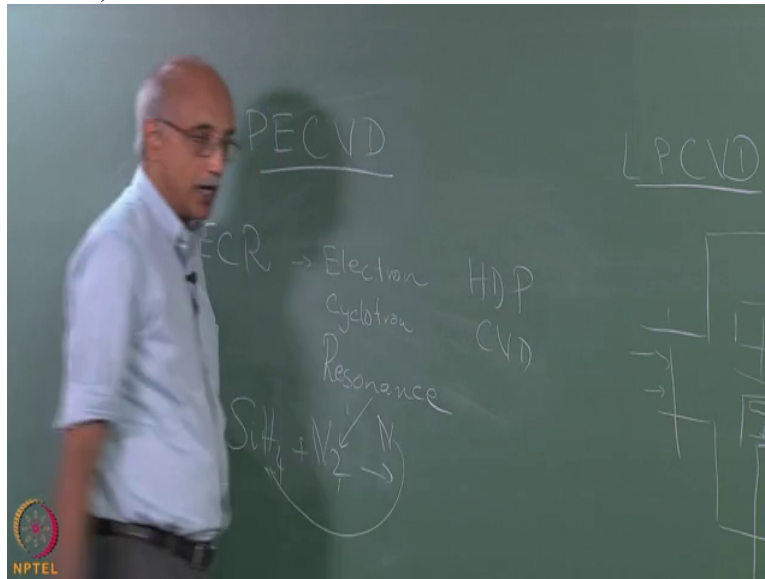
high density plasma which is an extension of the E C R to provide energization to not only the gas phase species and the substrate but in addition there is sufficient energy provided to start etching the surface. You know normally plasma enhanced C V D works in the simplest form by energizing the surface by providing an additional energy component to the surface. E C R C V D works by energizing the surface as well as the gas phase species.

High density plasma essentially goes one step further. It energizes the surface, it energizes the species in the gas phase and it actually etches the surface which is sometimes necessary if you are trying to simultaneously grow film on the surface as well as etch certain locations. So it is kind of dual purpose kind of a system where you are able to do both simultaneously.

The plasma enhanced C V D films are even more amorphous or less crystalline compared to the L P C V D films and certainly the A P C V D films which means that some of these thermal annealing or other processes are even more necessary in order to provide densification of the film and certain functional properties that you are looking for.

Now one of the advantages of the plasma enhanced C V D reactor is that it is a very tunable process. You can grow many different kinds of films in the same reactor with the same reactant species. For example, suppose I have a case where I want to build the multi-layer deposit. So that I want the film to have varying compositions across its thickness... How do you do that?

A C V D reactor in principle offers you the ability to do that because all you have to do is tweak the deposition conditions as a function of time to change the composition of the film. However that is easier said than done. It is very, very difficult to provide that kind of precision to the film formation process that you can have a graded composition that is tightly controlled. However in the case of plasma enhanced C V D that does become possible.

One of the common applications is multi layers of S i O 2 and S i 3 N 4.
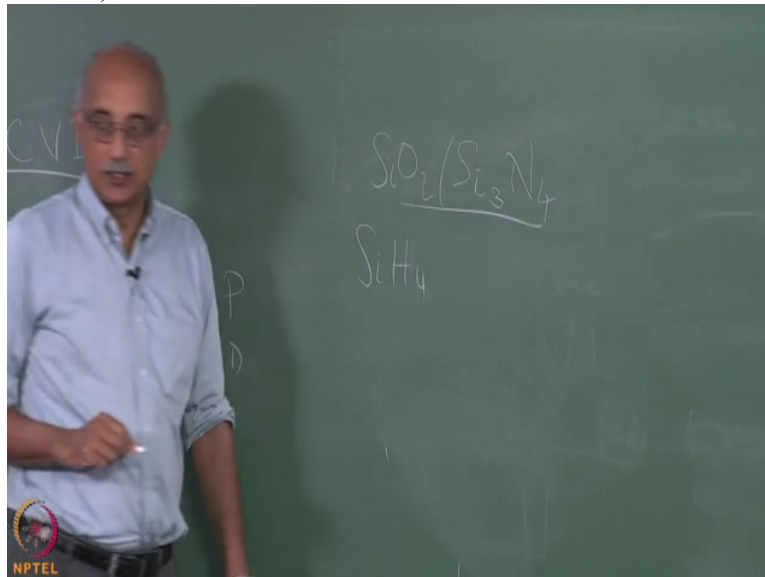
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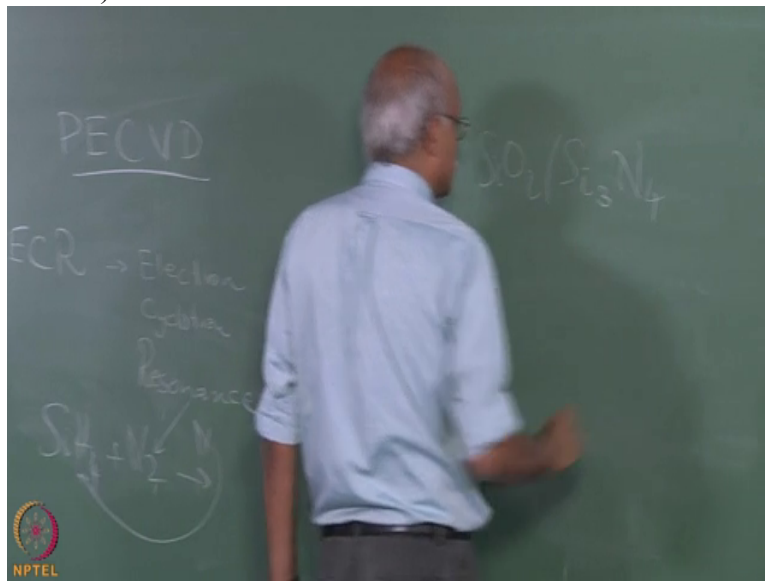
As we were discussing in the last class while they are both dielectric materials, silicon dioxide and silicon nitride have somewhat different properties in terms of hardness and moisture permeability and so on, so there may be cases when you want to put down these dielectric layers of varying composition.
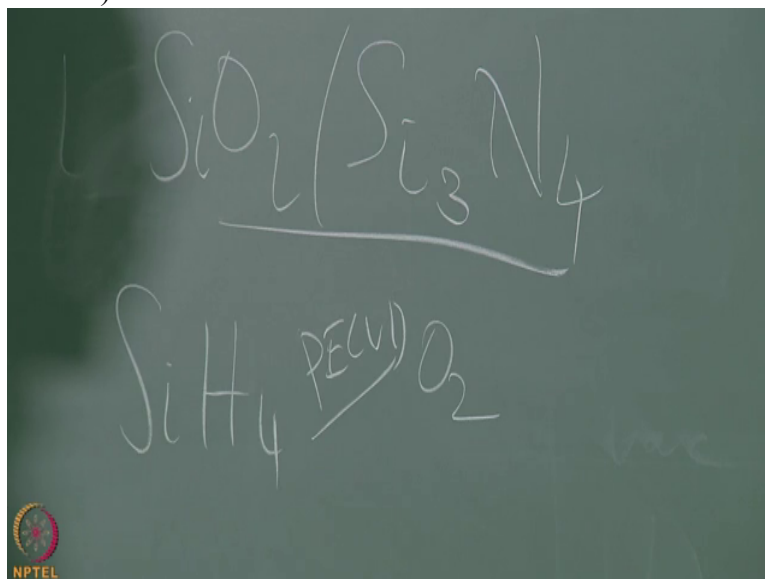
So in the case of, if you want to take, let us say silane

in a plasma enhanced reactor and you want to make a silica film S i O 2, you have really three options as far as how you do that. The first is, let us say that all the processes are P E C V D

you can introduce oxygen into the system. So S i H 4 plus O 2 in a plasma enhanced C V D reactor will give you an S i O 2 film. But it is kind of an overkill.

It is a, what I call a brute force technique because oxygen is an extremely reactive species. And to try and do that in a plasma enhanced C V D reactor is not necessary. If you really want to make S i O 2 by mixing S i H 4 and O 2 you may as well do it in an atmospheric

pressure C V D reactor, right? The other possibility is to do this using C O 2 which actually works quite well
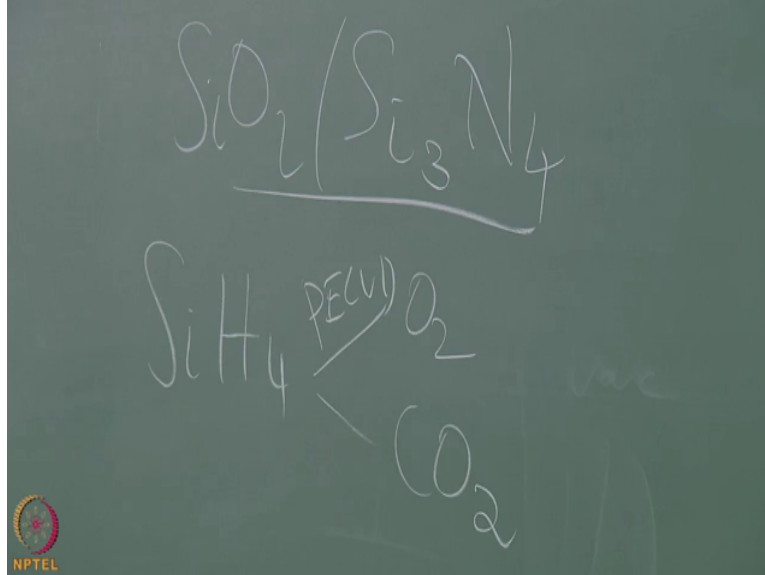
but what will be the concern?

Suppose you make S i 0 2 film using C O 2 as your reactant gas, do you have any issues with that? Do you see any issues? The carbon can be an impurity, right? Carbon can become part of the film and carbon is, you know, very difficult to get rid of once it gets absorbed. So the presence of carbon as an impurity is something that would worry some people depending on the process that you are running.
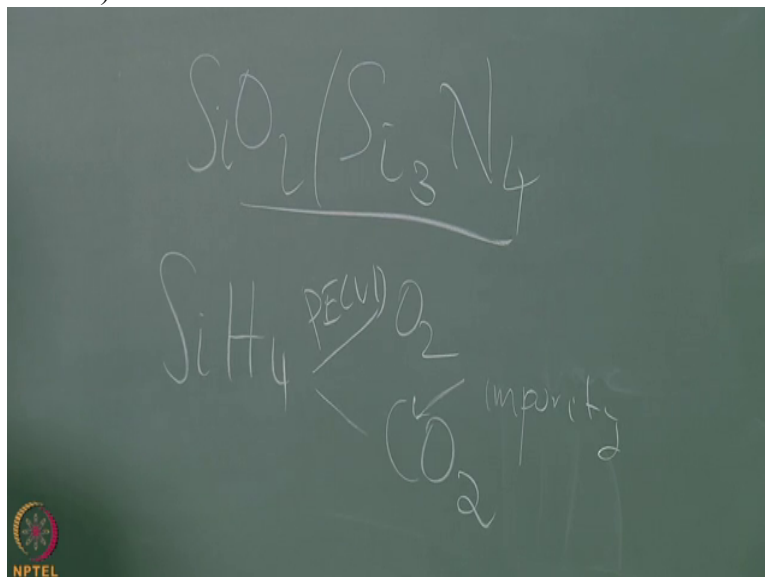
So in fact the preferred process for making S i O 2 is by using N 2 O as the

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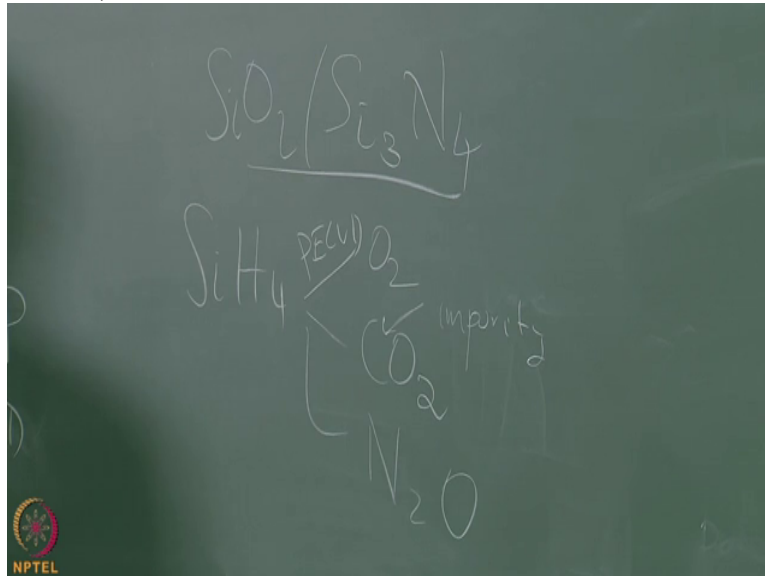

reactant gas. The other advantage of using N 2 O as the reacting species with silane is that by controlling the ratio of S i H 4 to N 2 O you can make either S i 3 N 4 or S i O 2. So simply by altering the ratio of this to this, you can have virtually a continuous transition from a film that is essentially S i O 2 rich to one that is S i 3 N 4 rich or any combinations there are.

So the plasma enhanced C V D process enables you to do that mainly because it is less reactive environment compared to atmospheric pressure C V D and low pressure C V D. So you potentially have the ability to, to control the process reasonably well. Another process that is similar to this is what we call a U H V process or ultra high vacuum plasma enhanced C V D.

So typically
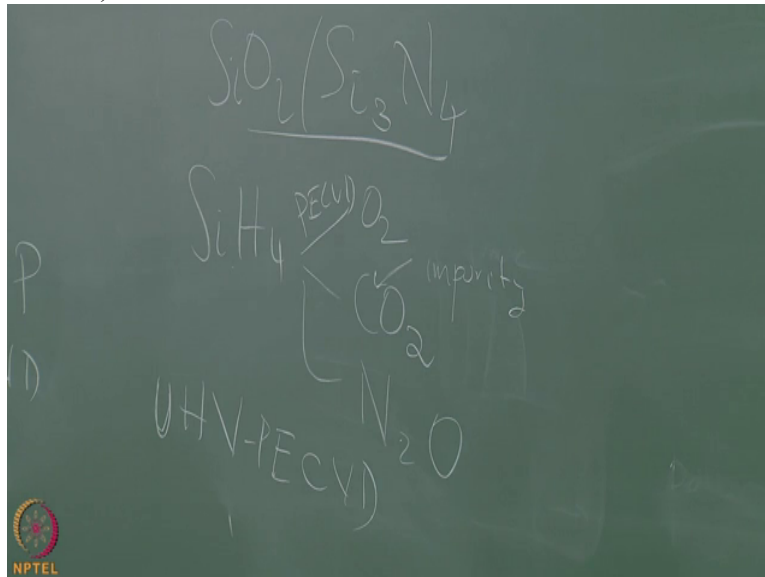
while, as I was mentioning earlier L P C V D may be run at one tenth of an atmosphere, and plasma enhanced C V D may be run at a hundredth of an atmosphere, ultra high vacuum plasma enhanced C V D typically runs at one thousandth of an atmosphere or lower pressures. The advantage here once again is that it can be done to keep the temperatures very low.

And when you talk about this type of ultra-high vacuum, you can almost start manipulating at atomic level. Now the problem with ultra high vacuum kind of plasma enhanced processes, there is actually two issues with it. The first is that when you pull the vacuum that low, the mean free path of the molecules becomes very large, right? So diffusion becomes very fast and you cannot dependably get uniform film thickness.

Essentially it becomes a process where the transport phenomenon starts to play a role. High mean free path essentially means that the probability of an encounter with another molecule is much lower. As the probability of encounter becomes lower, what that means is that you cannot repeatedly and reproducibly make the same film every time because it all depends on whether two vapor molecules are going to find each other or not. So that is one issue.

Particularly on the substrate, what we typically find is that uniformity starts to suffer as you lower the pressure. Of course the other parameter that you can control is the plasma intensity. If you increase the intensity of the plasma, you will get a higher deposition rate but it also

means that the uniformity will become poorer and in fact the deposit that you make is also less dense as you increase the power of your system. So there is a penalty to pay.

You get thicker deposits but they are less uniform and they are not as dense by increasing the, the power of your plasma. The other problem that becomes intensified when you go to very low pressures and plasma enhancement is that again, particles start forming in the gas phase. Under ultra high vacuum conditions or even under the high density plasma conditions, you know the heterogeneous nucleation process which happens sporadically in a low pressure C V D reactor, in a plasma enhanced C V D reactor it occurs to such an extent that particle formation is highly likely.

So how do you deal with that? I mean you do not want those particles to fall on your C V D films and damage its properties. So what people use what are known as particle traps. There are like scavenging type of devices where you use usually a thermal gradient so that you know if you have a reactor and this is your substrate on which you are trying to make the film but instead your particles are forming over here,
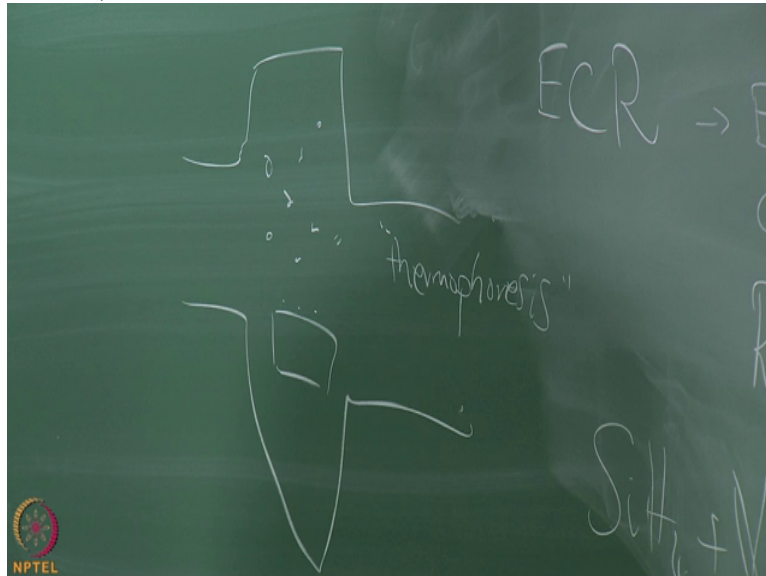
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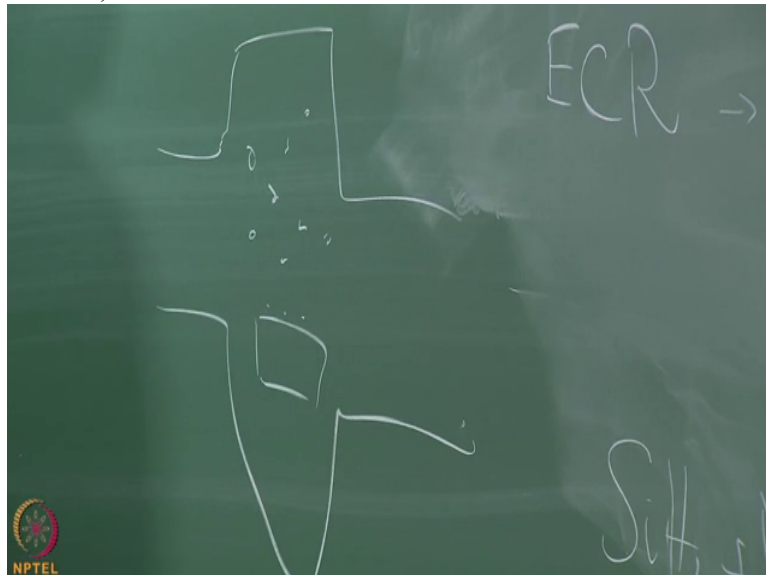
you provide essentially a temperature gradient in a certain direction.

For example the temperature gradient should be such that the particles in the gas phase are pulled away from the substrate and towards the exhaust. You do that by making use of a property called thermophoresis.

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Thermophoresis refers to the diffusion of particles down a temperature gradient.

As you know diffusion is typically associated with the concentration gradient, right? That is called Fick diffusion in the case of vapors. It is called Brownian diffusion in the case of particles. But the movement of vapor molecules due to the temperature gradient by the way is known as Soret diffusion and the movement of particles from high temperature to low temperature is called thermophoresis.

So what you do is you apply a temperature gradient so that the exhaust

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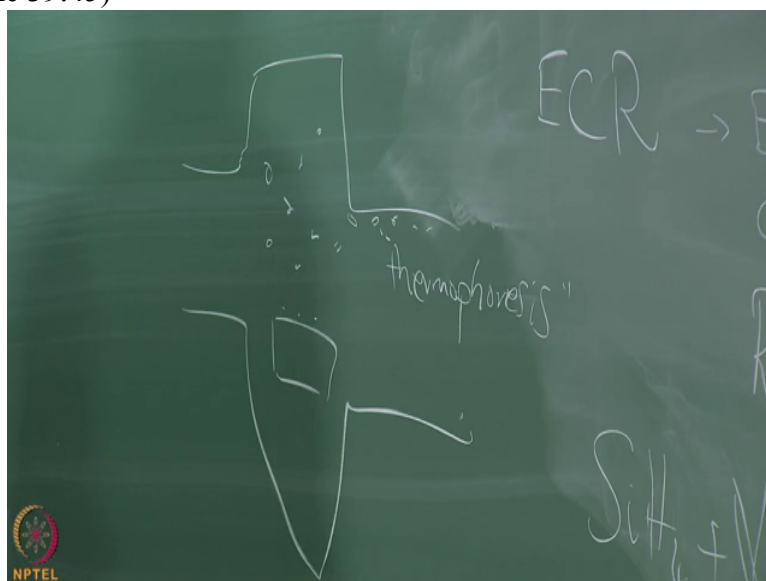
system is kept at a lower temperature compared to the bulk of the C V D reactor. So automatically any fine particles that are formed in the gas phase due nucleation in the gas phase will be automatically sucked towards this exhaust by using this temperature gradient.

The application of thermophoresis as a particle trap is widely used in these plasma enhanced C V D reactors and by the way thermophoresis or thermal diffusion can actually have an adverse effect on C V D film formation. We will talk about this later when we talk about transport processes and their effect on C V D phenomena because as you can imagine, by the same token if you are keeping a substrate hotter than the surrounding gases, then vapor molecules that are trying to deposit on the substrate can be essentially transported away from the substrate because of a temperature gradient.

So though the concentration gradient may be helping you in terms of pulling molecules towards the surface, the thermal gradient particularly in the cold wall reactor can be quite a significant effect in driving diffusion away from the surface and that is another reason why hot wall reactors are typically favored over cold wall reactors.
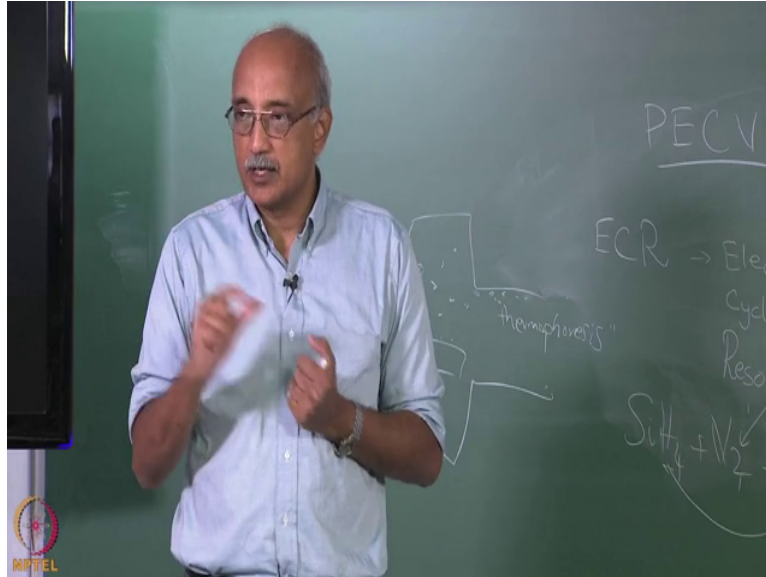
Because thermal diffusion when thus set in can be an order of magnitude greater than the molecular diffusion or Fick diffusion that we are familiar with.

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So it can significantly counteract the effect of the diffusional deposition mechanism, particularly in the boundary layer region

where convection is absent, thermal diffusion can play a huge role.

So you try to design the reactor in such a way that you do not have to deal with thermal effects and that is again done by having a fairly uniform temperature distribution inside the C V D reactor. Ok, so we have talked about atmospheric pressure C V D, low pressure C V D and plasma enhanced C V D today. In the next lecture we will talk a little more about metal C V D as well as metal organic C V D reactors which are two other important classifications of C V D reactors.

So with the discussion of those two, we would have covered the five most widely used C V D reactors in the world and after we do that we will start looking into some of the process parameters in a little more detail. Any questions on what we have talked about today?

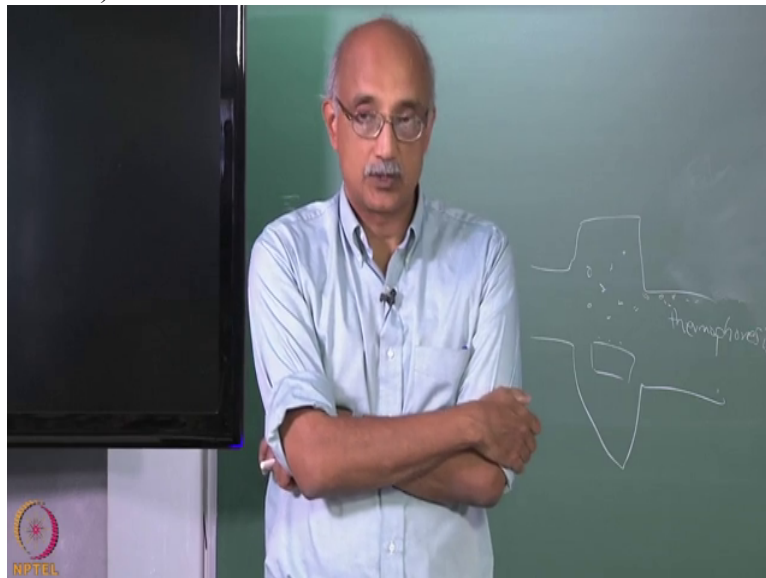(Professor – student conversation starts)
Student: Sir, generally

atmospheric and low pressure C V D we have homogenous nucleation because the pressure is higher, yeah. So how are particles forming in...?

Professor: That is because in P E C V D even though the temperature

is low and pressure is low, the plasma itself is providing the energy, right, I mean two neutral species are unlikely to react but if you bombard them both with plasma you energize them, you turn them into ionized radicals, they are very, very, very keen to interact
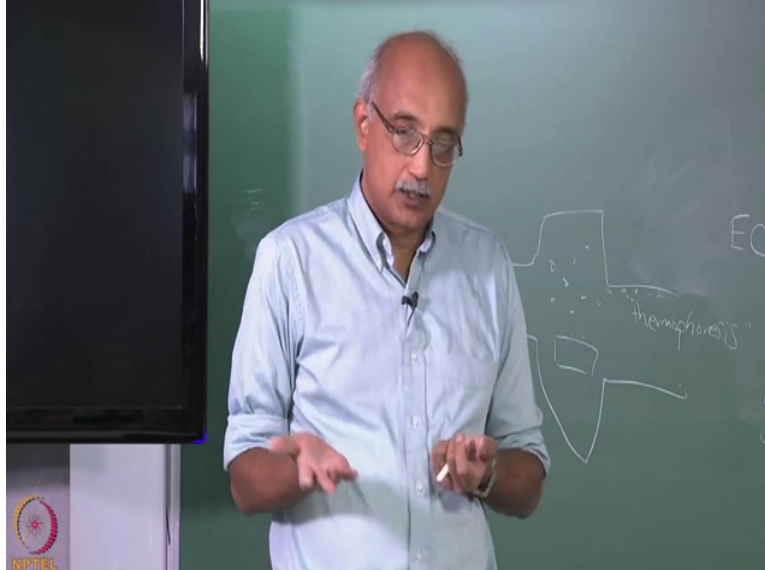
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and react with each other.

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So it is the fact that, you know the same reason why
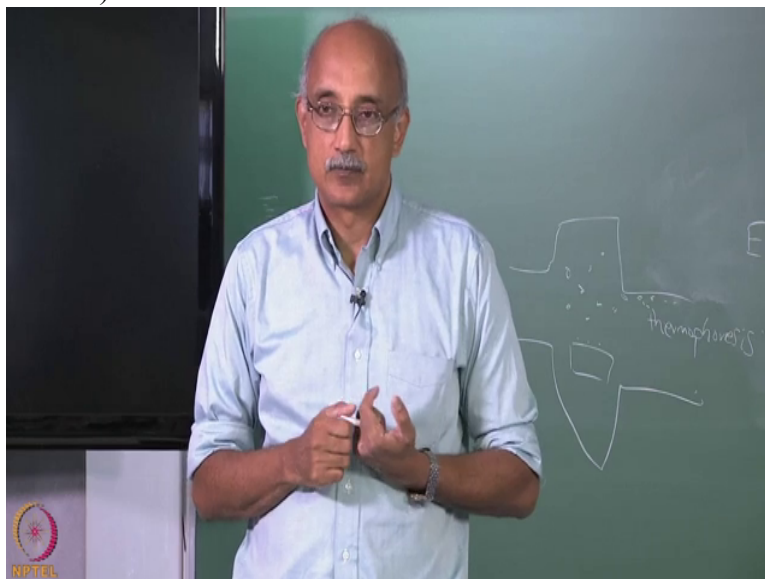
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the deposition happens on the surface. You are energizing the surface using a plasma, similarly the gas phase molecules are also energized because of the presence of the plasma. And in fact I would say that the effect on the gas phase energization

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is more immediate and more direct than the effect on surface energization.

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Ok, see you at the next lecture.