

Chemical Engineering Principle of C V D Processes
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Lecture No 01
Introduction

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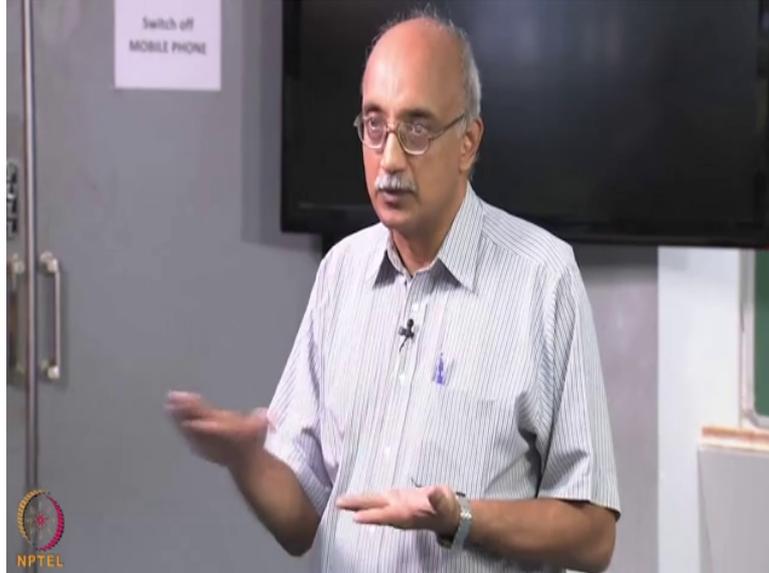
Good morning and welcome to the first lecture in our course on Chemical Engineering Principles of C V D processes. I think many of you told me that you have taken an introductory course on manufacturing of microelectronic devices and I am sure many of, all of you

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know that chemical vapor deposition is an essential step of this process in order to make a thin film

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on the substrate.

Now the reason that chemical vapor deposition is fascinating to study is because it really brings together the various disciplines of chemical engineering. It involves chemical reactions, it involves transport phenomena. And it involves heterogeneous equilibria, homogeneous equilibria, nucleation phenomena, so virtually everything that you have learnt in a good undergraduate chemical engineering curriculum, you will have an opportunity to apply when you study chemical vapor deposition as a process.

The definition of vapor deposition is that you actually deposit a, a layer or a film on a surface from a vapor phase. So essentially you have a gas phase that is in contact with the solid surface and you are condensing something from this gas phase which contains trace vapors as well on to the solid surface. So vapor deposition itself is essentially a conversion of material that is in vapor form to one that is in the solid form. When you think about it, there are obviously many circumstances we encounter in daily life that involve vapor deposition phenomena.

Now there are two ways in which you can classify vapor deposition that is physical vapor deposition and chemical vapor deposition. The difference between the two is really crucial to

understanding how C V D or chemical vapor deposition is unique when you compare it to physical vapor deposition or P V D.

In physical vapor deposition what happens is that there is a compound or a metal or an element that is suspended in a gas phase, which then gets realized as a solid or liquid film on a substrate. So the material that condenses is the same as the material that is present in the vapor phase. So some real life examples of physical vapor deposition, what is the simplest one you can think of?

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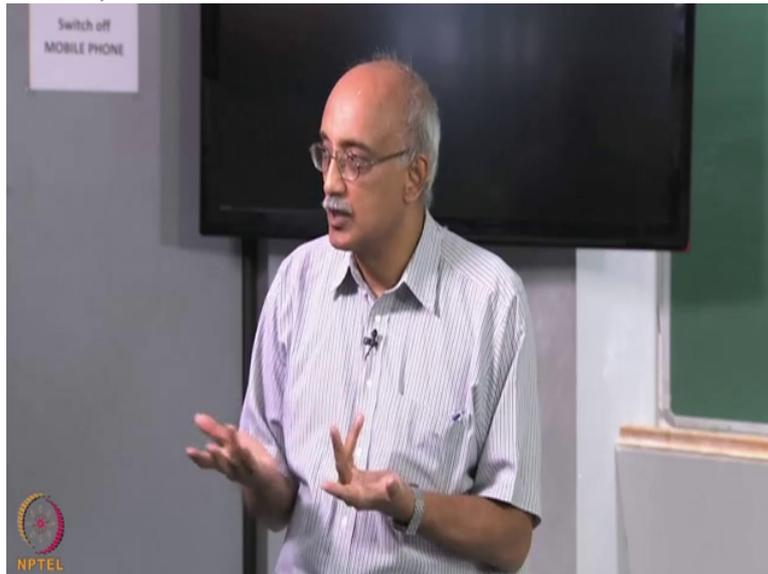


(Professor – student conversation starts)

Student: Water vapor

Professor: Yeah, dew, mist,

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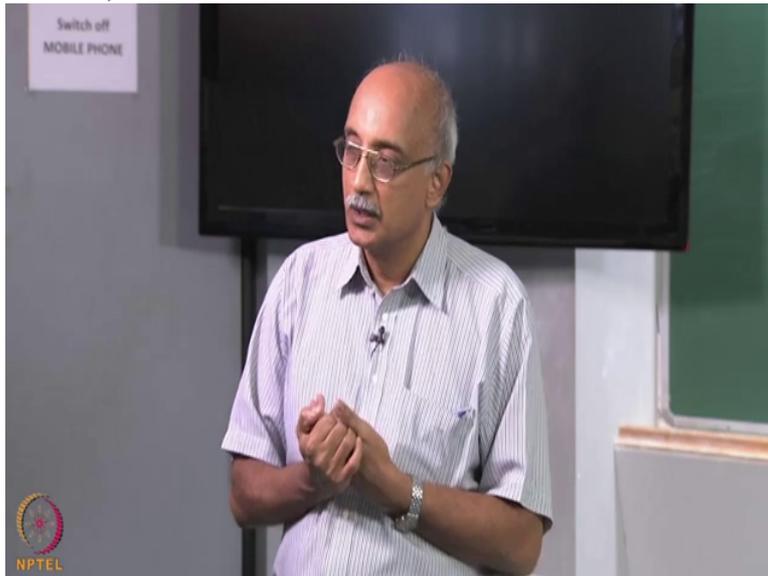
essentially what is happening is water vapor that is in the air is condensing on to surfaces in the form of a thin film of liquid, right? So that is a classic example of physical vapor deposition. Can you think of any others that that fall into that category?

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Student: soot deposition

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Professor: What is soot? Or chemical form.

Student: 0:03:30.2

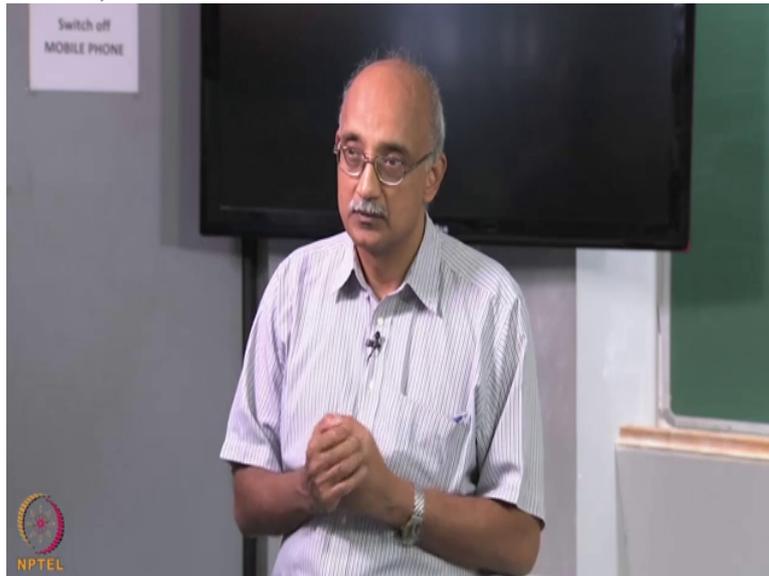
Professor: Right but where does the carbon come from? The carbon,

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that deposits as soot, where does it come from? Is it present as carbon in the gas phase?

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Student: Condenses from the gas phase

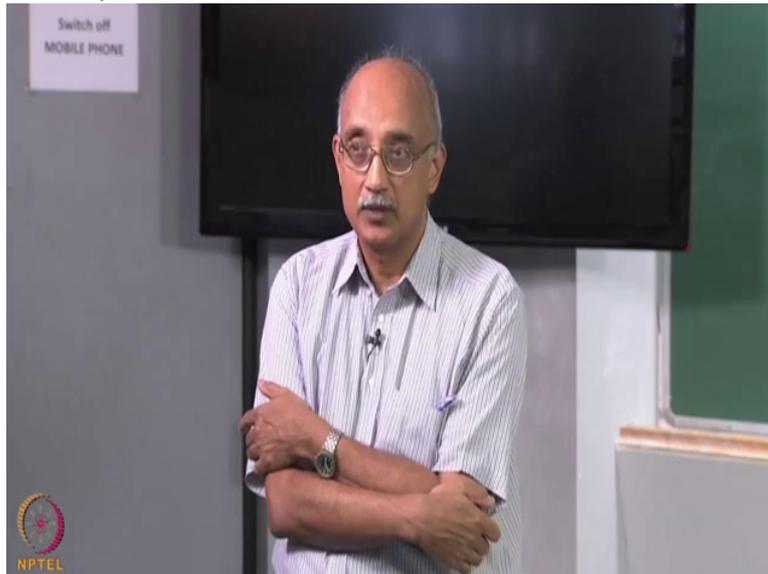
Professor: Right. It condenses as carbon and you call that soot but it is present as carbon

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in the gas phase, only as carbon. Now in fact soot deposition is a very good example

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of chemical vapor depositions. In physical vapor deposition again remember that the condensed species has to be the same as the species that has been present in the, in the gas phase. Not just one of the species but the only species in the gas phase that gives rise to this condensate on the substrate. About things like acid rain, is that physical vapor deposition or chemical vapor deposition?

Student: Chemical vapor deposition.

Professor: Right, I mean when you get for example, corrosive films on the surface like fluorides or sulphates or whatever; it is not always the case that the fluoride that precipitates is present in the same fluoride in the gas phase as well. There are some reactions that are taking place in the gas phase which dissociate the depositing molecule into various constituent molecules which come together at the surface to then form the film on the surface.

(Professor – student conversation ends)

So the definition of chemical vapor deposition by extension is where the chemical composition of the condensed phase is not necessarily the same as the composition of the, of the same condensing element that is present in the gas phase. And typically

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chemical vapor deposition will involve multiple gas phase species which

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get transported to the substrate and condensed in the form of a single film.

Again it could be a solid film or a liquid film although in the context of this course, we will be mostly dealing with solid films. The difference between the two is that, when you consider chemical vapor deposition to form a solid film, the, the only transport process you need to be concerned with is from the vapor phase to the substrate. You can assume that once the solid film forms on the substrate it remains in place. So you do not have to worry about the flow of the condensate.

However we will look at a couple of examples where chemical vapor deposition happens but the condenser itself is mobile. So it is actually able to move along the surface under the action of various hydrodynamic forces and so on. So it is certainly possible in general that C V D processes can lead to mobile condensates. But in most manufacturing industries where C V D is employed as a process, the whole idea is to produce the film which is very stable and which is well-adhered to the substrate on which you are making the film, Ok.

So let us talk about C V D. Can we think of some examples of chemical vapor deposition? We have already talked of a couple, you know soot, acid rain, any others that you can think of, that you encounter just about every day in your life? Although one of the examples I am going to talk about, we encounter less and less in, in day-to-day life than we used to but, and we still do, I mean I don't see any here but may be in some places. Anyway I will give...any examples that you can up with?

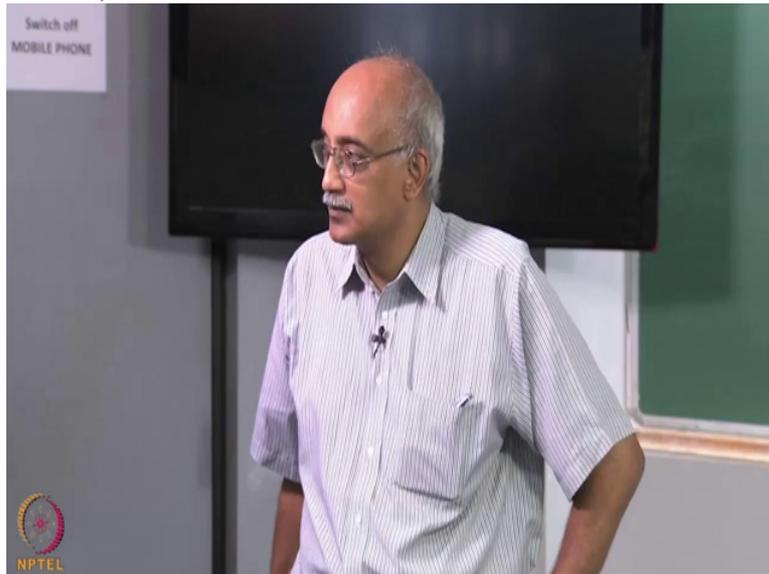
How many of you still remember bulbs, incandescent bulbs,

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filaments? They are still around, right, not so many but they are still around.

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So what happens to a bulb...when do you change a bulb?

(Professor – student conversation starts)

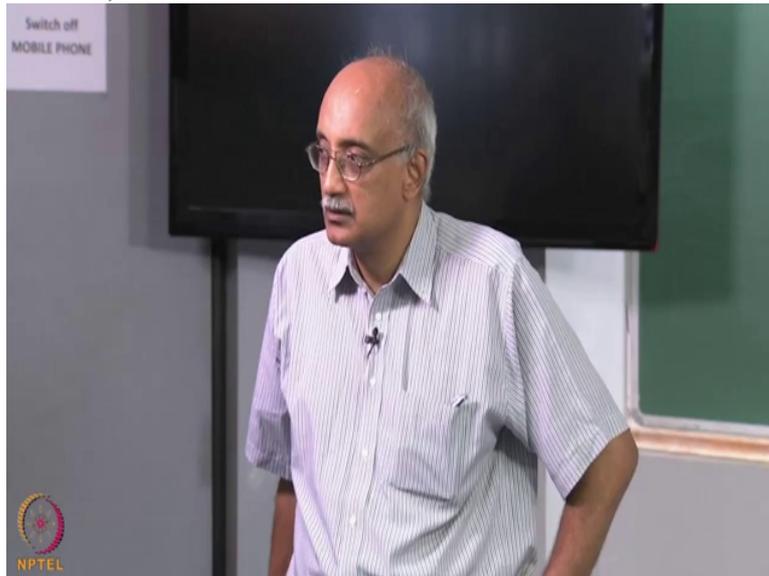
Student: When the filament breaks

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Professor: How do you know when the filament breaks?

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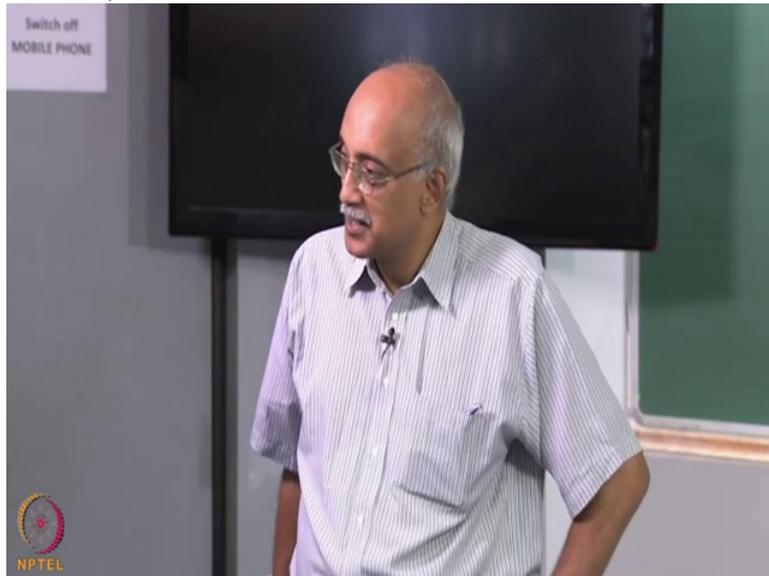
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Student: 0:07:50.8

Professor: It just does not turn on.

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Student: 0:07:56.9

Professor: But when you see the bulb, what do you see?

Student: Black

Professor: Black, so what is that black thing? Any idea, what is the chemical composition?

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What is the filament made of?

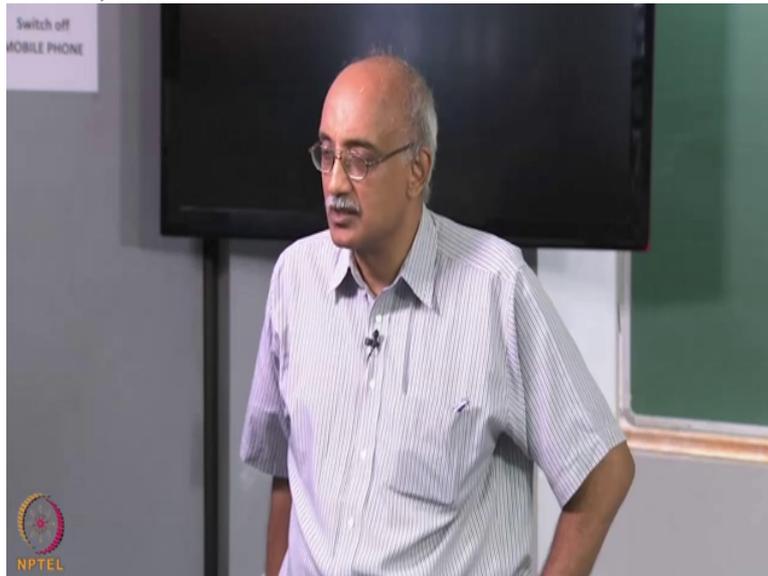
Student: Tungsten.

Professor: So what is the deposit?

Student: 0:08:12.9

Professor: So it is pretty much tungsten.

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So is that a physical vapor deposition process or a chemical vapor deposition?

Student: It must be oxides of...

Professor: Yeah, because the bulbs are not hermetically sealed or anything so yeah, the atmosphere inside does contain oxygen. See this is a case where we have a filament that is tungsten and the film or the deposit that is forming on the bulb wall is also tungsten. So you would conclude it is a physical vapor deposition process, right? Is that correct?

Student: It should be in the vapor.

Professor: Yeah remember the definition of physical vapor deposition is that the element that is depositing must be present in the gas phase in the same form. In other words, just because the filament is tungsten and the film is tungsten does not mean it is physical vapor deposition. What we need to look at is how is the tungsten present inside the bulb in the gas phase? Is it present only as tungsten or no?

(Professor – student conversation ends)

Well when you think about it, these bulbs do let in, as we were saying, some oxidizing species. In addition, all these bulbs are actually filled with some inert gases and sometimes some other additives as well. The filament burns at a very high temperature right, 2000 Kelvin whatever. So when that happens, as the filament is burning, it is emitting tungsten vapor. Tungsten is vaporizing, obviously.

But before it can get to the bulb surface which is basically at room temperature, it actually undergoes several chemical reactions. In fact the number of tungsten containing species

inside a tungsten filament lamp is of the order of close to a hundred. So even though the filament is tungsten, the film is tungsten, the tungsten element is getting transported from the filament to the bulb surface through the transport of many, many chemical species or compounds that contain tungsten as an element.

For example it could be, certainly tungsten itself is one of them. But it is not the only one. That is the key point to remember. The tungsten is also being transported in the form of tungsten oxide, tungsten nitrite, tungsten chloride, tungsten oxybromide, I mean there is just large number of chemical species

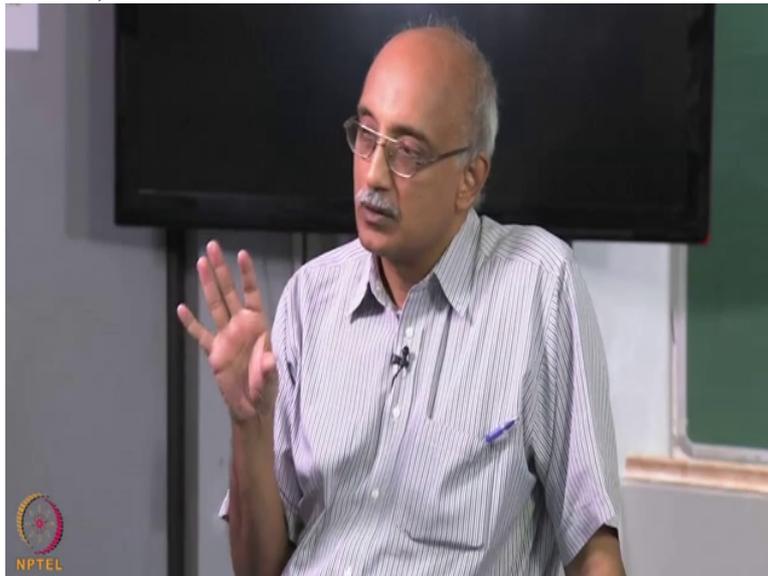
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that are present inside the bulb that are carrying the tungsten to the bulb, bulb wall.

So that is a classical example of chemical vapor deposition. In fact in our next lecture we will talk a little bit

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about how do you model that, you know, what is actually going on inside a bulb and how can you design a bulb to maximize its lifetime. You know when the lamps were first, the bulbs were first designed, their lifetime was about a week. Now, you know it is virtually a very, very long time, right, 2 years, 3 years even longer.

So something was done to improve the reliability of these bulbs so, and it involves very interesting C V D principles. So we will talk about that as an example of a real life situation, it is not a commercial C V D application but it really illustrates the principle of C V D extremely well. So we will take some time to discuss that.

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Another real life example, which is not a commercial C V D process

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but one that again involves the formation of the condensate on a surface which is very different in composition from the gas phase is, you know, corrosion products. Combustion, you know, is a crucial process for energy generation and if you look at the energy scenario today, they are increasingly burning dirtier and dirtier fuels because we do not have a choice. And of course, in India, we burn a lot of coal but even when you are burning liquid fuels, all liquid fuels contain impurities. The most common impurity from the corrosion view point is actually sulphur. The liquid fuels are hydrocarbons but virtually all of them come with suspended sulphur as one of the impurities.

So in a combustor you are burning the fuel, so you are essentially mixing it with an oxidizer and the most common oxidizer that is used is air. But air itself has impurities as well. Particularly in marine environments the air that you inject into a combustor can have salts for example. So you can have sodium chloride so on.

So when you take these fuel with impurities and oxidizer with impurities and you burn it, again you reach very high temperatures, you know the adiabatic flame temperatures can be of the order of 2000 Kelvin or so. And so what happens then?

Basically everything dissociates, right? So in a typical combustor in the gas phase you have hundreds of chemical species that are present. So the sulphur which was originally in the fuel, after the combustion process, gets converted to many, many species that contain sulphur. For

example it could still be present as sulphur but SO_2 , SO_3 , H_2SO_4 , you know, huge number of compounds.

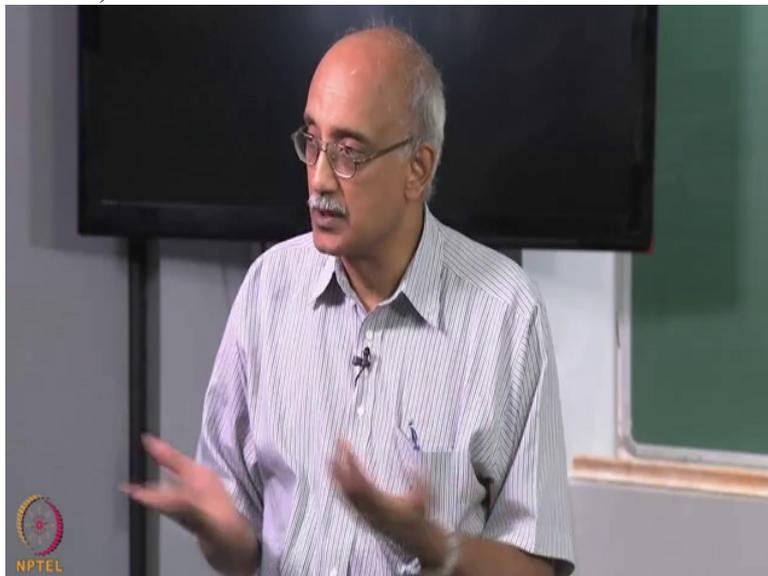
And similarly the air, the impurities in the air such as, say sodium chloride,

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many different forms and so what happens?

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Basically all these species are present in the gas phase and they react in a gas phase. But on a surface that is exposed to the flow of the combustion gases whether it is a boiler or whether it is a gas turbine, whatever surface you are using to extract either energy or momentum from the combustion gases now receives a condensate which is very different in composition from

the species that were present in the fuel and in the oxidizer and also very different from all the vapor species that were present in the combustion product gases.

For example when corrosion happens it is typically due to sulphates that condense. And in fact these sulphates are known as molten salts and the process by which they corrode the surface is known as hot corrosion. And if you look at the combustion industry, hot corrosion, corrosion in general and in particular, hot corrosion due to molten salts causes losses that mounts to billions of dollars a year. So it is a very critical phenomena again to try and understand, characterize, control and so on.

So if you look at the process by which for example, sodium sulphate liquid forms on the surface is another classical example of a C V D process involving again many principles. To do, to model the combustion process you have to apply kinetic theories as well as equilibrium thermodynamics to predict the temperature that is achieved when combustion happens and to predict the composition of combustion product gases.

And then to predict how these product gases that are, the product gases that are formed after the combustion you know, how does the composition of the gas change as the temperature changes. Because the mean stream of the combustion gases is at a very high temperature but the surfaces that the gas comes in contact with is at a much lower temperature. So there is a temperature gradient that, that gets established.

So at every location in the flow path, a new equilibrium is established corresponding to the local temperature and the local pressure. So the composition of this gas that is flowing constantly changes as it flows. So again you have to consider chemical kinetic phenomena as well as equilibrium phenomena to understand how the composition of the product gas changes.

But one you have done that then next phase is you have to then calculate the associated transport rates, at what rate does the depositing species get transported to the surface? And that of course requires, first you have to do a momentum conservation exercise to understand the velocity distributions. Then you have to do, you know, heat transfer calculations to establish the temperature distribution.

And then using the velocity distribution you have obtained through momentum conservation and the temperature distribution that you have obtained through energy conservation, you establish your mass transport rates and phenomena. And this all has to be done in a very self-consistent manner. So it is an iterative process where you are constantly solving the 3 conservation equations, mass, energy and momentum together with the thermodynamic constraints to obtain self-consistent values for the composition distribution of the product gas as well as the associated rates of transport of the depositing species.

So to do something as simple as estimating for example, at any location of a turbine blade what is the thickness of the molten salt layer that is depositing, you have to go through this very, very complex calculation to obtain that local thickness. Because that local thickness of the molten salt depends on the rate at which the salt is arriving from the gas phase.

But in the case of, particularly the rotor blades, you are also constantly, the condensate is also moving on the surface. So you have to establish the balance not only between the arrival rate from the gas phase but also the flow along the turbine blade. And why is that important, because the local corrosion rate depends on the thickness of the local molten salt layer, right? So in order to do a corrosion map of a surface you have to do all these calculations upfront to obtain that and based on your corrosion mapping you can actually come up with a protection scheme, you know. If you can identify which areas of the surface are particularly susceptible to high rates of corrosion, you can actually provide additional protection there in terms of protective coating and so on. So this is another classic example of how chemical vapor deposition in a non-commercial process becomes a process that is very, very critical for you to understand and, and control.

So these are two examples that we will look at initially, you know the bulb blackening problem and the hot corrosion problem as two examples of unconventional applications of C V D. And then we will look at some more conventional applications of C V D such as formation of, you know, semiconducting films which is, I believe the application that you have some familiarity with.

In commercial manufacturing the primary use of chemical vapor deposition is to make very, very thin films on the surface which have certain characteristics that you cannot obtain

through other means. For example, a chemically vapor deposited film not only is very thin but it is also very uniform. It can follow contours. It can even follow steps. I think many of the microelectronic devices that you are familiar with have a configuration which has fairly steep features.

In a conventional coating process it is very difficult to follow these patterns and obtain a uniform film thickness. However the advantage of chemical vapor deposition is that, because it is based primarily on vapor diffusion to the surface it can provide a uniform thickness pretty much on every exposed surface. There is no corner effect, there is no edge effect, there is no end effect. You get a perfectly uniform film on whatever surface that you want to coat. The other advantages are that in the C V D process is that the film that you get, the structure of the film can be controlled by controlling the vapor deposition conditions.

For example if you want a highly crystalline film, you can set your process conditions so that the film that you contain can even be a single crystal. It means that you have to adjust your operating conditions particularly temperature, pressure and your reacting species in order to obtain a crystalline material on the surface.

On the other hand, you may be interested in more of a amorphous film which has less structure to it. And again with a C V D process it is fairly easy to tune the conditions so that you go from a condition of depositing crystalline materials to a condition of depositing amorphous materials without having to essentially redo the entire reactor. All it takes is a few small changes in the operating conditions.

So on one hand you have a crystalline film which has a very, very clear structure to it. On the other side you have the amorphous film which has very little structure to it. And what is in-between? Do you know the term for it?

(Professor – student conversation starts)

Student: Plasma

Professor: Yes

Student: Plasma

Professor: No, no. Plasma is the gas phase. The film itself, the intermediate structure is known as polycrystalline.

(Professor – student conversation ends)

So you go from crystalline to polycrystalline to amorphous and it is very interesting that in a C V D reactor you can essentially just turn a knob and get whatever type of film you want and also the other advantage is if you make an amorphous film and then you decide later that you want a crystalline film, you can actually do some post treatments to the amorphous film to make it into a crystalline film.

So you can control not only the rate at which you are depositing the film and thereby the thickness of the film but you can also control the structure of the film. Because the other important aspect is the composition of the film. You want to have very tight control over the chemical composition of the film.

Here again the advantage of the chemical vapor deposition process is that the whole thing occurs in a very well-controlled environment. You control the reactant species that you are feeding into the reactor and you control the temperature and pressure and the velocity distribution inside the reactor. So you can predict and achieve exactly the composition that you are looking for. The possibility of impurities getting integrated into the film is considerably lower than in other deposition processes that you could think of.

When you talk of physical vapor deposition for example, mostly what is done is you take a solid material which is of the same composition of the film that you are trying to achieve and then you entrain material from that solid specimen into a gas phase and then make it deposit on to the substrate. For example if you are trying to make a silicon film, you would take a silicon ingot and essentially vaporize silicon from it and try to make it deposit on a surface, you know. That is a physical vapor deposition process.

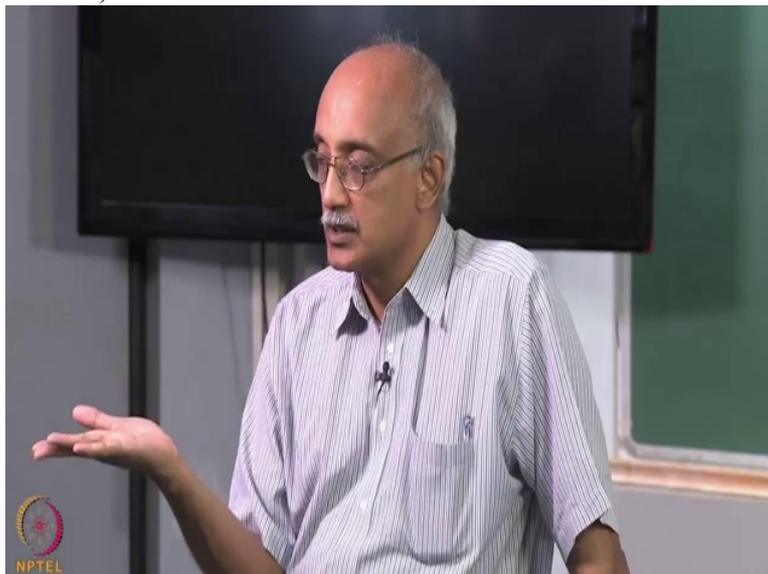
The vaporization of silicon from that solid silicon is, can be done thermally. Mostly it is done using high temperatures to get the vapor pressure up or it can be done by actually bombarding that silicon surface with some high energy materials. It could be high energy ions, it could be plasma, it could be laser, something that provides

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sufficient energy input to the surface to actually knock off molecules and get them entering into the gas

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phase and then you deposit on to the film.

Now the problem with physical vapor deposition is that a, it requires very high energies, you know, how do you get silicon to vaporize? You have to go to extremely high temperatures, right? Or you have to use a substantial energy source to make it happen. So physical vapor deposition has the potential to be even purer than C V D because there is only species that is present, the source and the final product are the same. However it is not an easy process to design, it is not an easy process to control. And the deposition rates can be

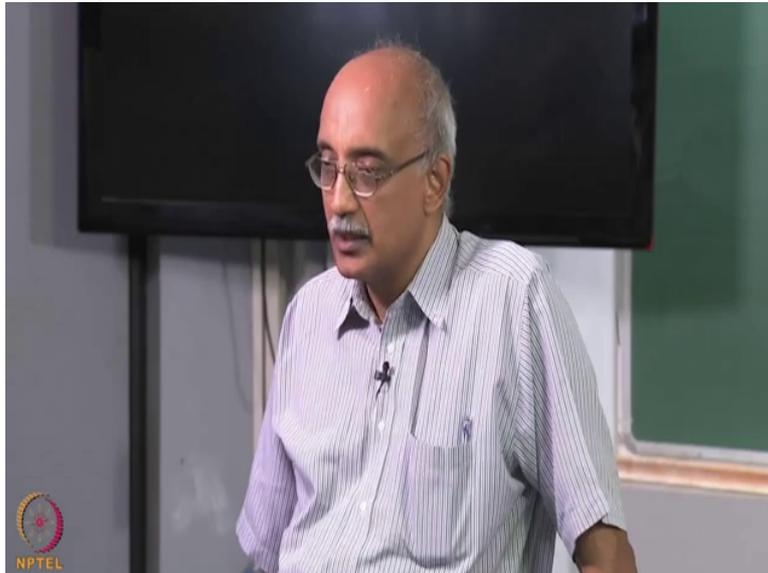
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very slow also.

And therefore chemical vapor deposition is a very elegant solution. It basically

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tells you that your source or your, the reacting materials do not have to be of the same composition as your product material, gives you a lot of flexibility. And you can actually achieve the, the film using various methods. For example C V D is conventionally classified into 4 methods.

The first is pyrolysis where you essentially take the species that is containing the element you want to deposit and just thermally dissociate it. For example silane is a very widely used

precursor for depositing silicon, right? Silane is what? SiH_4 . So a typical, a simple pyrolysis reaction will simply be SiH_4 going to Si plus 2H_2 . Is that a CVD process? Yeah.

Because in the gas phase silicon is present as silane but in the condensed phase it is present as silicon, right? So very clear and easy example of CVD and it is a very widely used process in industry as well, when people are trying to make silicon films using CVD, thermal dissociation of silane is certainly a process that is used. It is particularly suited for making crystalline silicon. So if you are trying to make pure, single-crystal silicon pyrolysis is widely used.

The other process, the second one that is widely used in CVD is reduction. For example you can take Silicon tetrachloride SiCl_4 and react it with hydrogen in a CVD reactor. Again you will get silicon and HCl . So this process of SiCl_4 plus H_2 going to Si plus 4HCl or whatever, another example of CVD right? You are making silicon but the silicon in the gas phase is not present as silicon. The advantage of this process over pyrolysis is that you can do it at a lower temperature. And lower the temperature that you use in your CVD, the more polycrystalline or amorphous the, the film becomes.

So the higher the temperature you use, the more crystalline the structure. And in fact the process that is used to turn an amorphous film into a crystalline film is called annealing and it is basically just, you know, baking it at high temperature for a long period of time and it changes that structure from amorphous structure to a crystalline structure.

So we have talked about pyrolysis and reduction. The third CVD process is oxidation. This is particularly used to make oxide films. So, for example you could take silane again SiH_4 and react it with let us say O_2 and you will get SiO_2 plus H_2 . So that is a CVD reactor in which you are making a silicon oxide film using oxidation as your primary reaction method.

And the fourth one which is used to make nitride films is nitridation. So you can take a compound like silane which is SiH_4 , react it with NH_3 and you will get Si_3N_4 plus HCl plus H_2 . So nitridation and also another film is usually made using such techniques is carbides. For example if you want to make silicon carbide you can do that using CVD reactor as well.

So there are essentially these four types of C V D processes that can take place for making various types of films and as I said, the lower the temperature and pressure that you can operate the reactor at, the more amorphous will be the structure of the film that you make, which is in some cases advantageous and in some cases it is not.

So depending on the type of film, that you are trying to achieve you will design the reactor appropriately and choose the reactants appropriately and so on. The C V D reactor itself, there is really two major types; there is what is known as a hot wall reactor and what is known as a cold wall reactor. Since we are out of time on this lecture, we will start the discussion of these two reactor configurations in the next class. Any questions on what we have discussed so far?

(Professor – student conversation starts)

Professor: Yeah

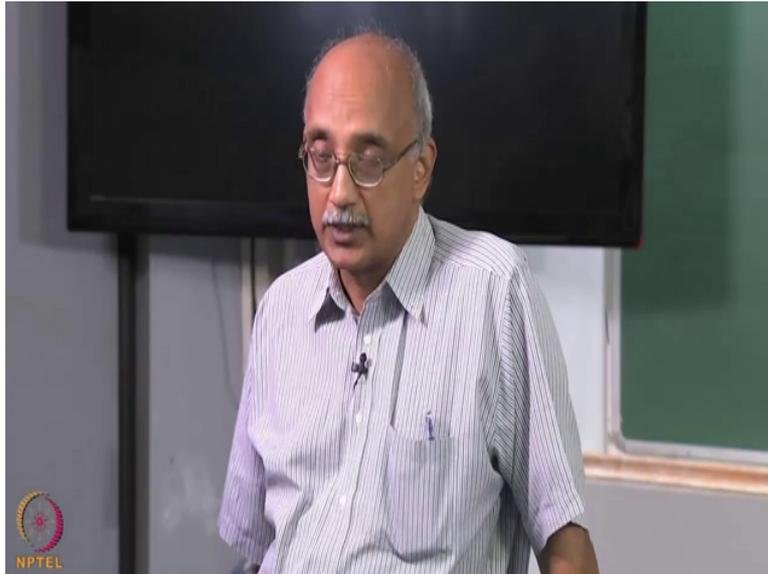
Student: Sir, in the main process, can the metal be reacting with the component in the vapor
0:31:22.6. The metal should not be touched, isn't it?

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Professor: No it is. It is definitely reacting.

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For example if you are trying to deposit silicon, right, the silicon in the gas phase is reacting with the other species that are in the gas phase and getting converted to, for example you have introduced silicon in the form of silane SiH_4 , the silicon does not stay as SiH_4 . It, silicon is the element, right and SiH_4 is the species or the compound.

(Professor – student conversation ends)

Silicon element is not going to get transformed, it is going to remain as silicon unless it is a nuclear reactor which CVD reactors are not. But it is going to change partners. So the Si in SiH_4 , once it gets into the CVD reactor will be present not only in SiH_4 , it will be present in SiH_2Cl_2 , it will be present as just Si, it will be present in silicon oxide, so that, that silicon element can be present in dozens of species inside the chemical reactor.

So that is the whole point, I mean we have to separate the element from the species.

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The element is what is depositing. But that chemical element is being transported to that surface as part of many, many

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chemical species that are present in the reactor. That is what we call multi-component transport, you know. The transport phenomena is not restricted to a single compound that transports the element but the element is distributed among various compounds which are all getting transported to the surface.

(Professor – student conversation starts)

Student: But in

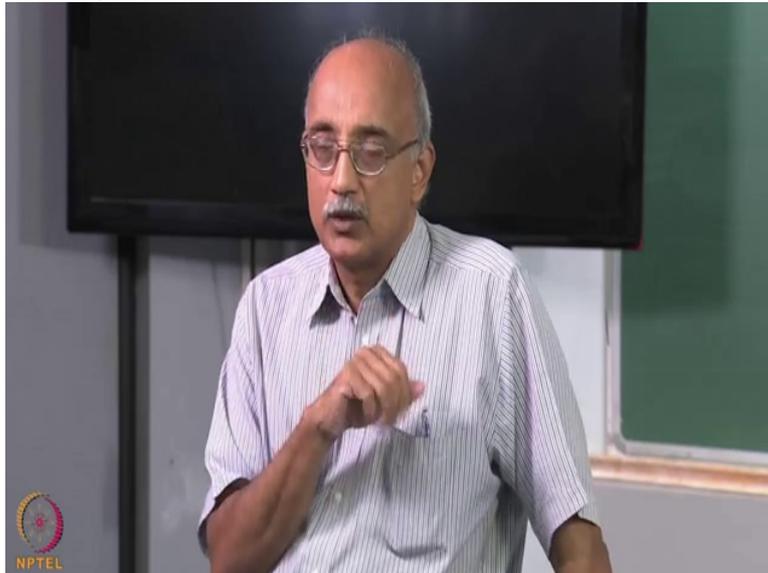
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case of sulfur corrosion the metal on which the coating is going on, but that will be disturbed no, sir?

Professor: Ok,

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now you are talking about the substrate itself on which the deposition is happening. No the substrate is typically inert. I mean it should be an inert surface. It cannot participate in the reaction. What we are talking

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about is the deposit that is forming on top of the substrate. That

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is participating in the chemical reactions also. Anything else?

(Professor – student conversation ends)

Ok so I will see you tomorrow then.