Chemical Engineering Principle of CVD Processes
Prof. R. Nagaranjan
Department of Chemical Engineering
Indian Institute of technology Madras
Module-4
Lecture 25
CVD Overview

Good morning and welcome to this lecture in our course on chemical engineering principles of CVD process. I thought we will use this lecture to just quickly summarize what we have covered in the course and if you have any questions you can ask some also today. So if you look at the material that we have covered, we started out by first discussing the fundamentals of chemical vapor deposition, what are its unique aspects compared to other methods for forming films on surfaces.

The particular advantages and disadvantages of CVD process and we also looked at the various types of CVD films particularly the crystalline, poly crystalline and amorphous films and we looked at the various process designs and reactor designs for making CVD films. Again focusing mostly on the temperature distribution the cold wall versus hot wall and also the pressure atmospheric pressure CVD, low-pressure CVD and ultrahigh vacuum CVD or plasma CVD.

Then we spent a few classes talking about the various properties of CVD films and how they are to be measured both quantitative analysis as well as qualitative analysis? And the middle portion of the course we primarily focused on the thermodynamics, chemical kinetics and transport phenomena associated with CVD reactors. So we looked at a method that will enable us to find the equilibrium composition of CVD products using a free energy minimization algorithm.

And then in terms of transport phenomena we primarily focused on the so-called microscopic model where we formulate conservation laws for mass momentum and energy and use constitutive relationships to provide closures to these conservation laws and again we focused on the mass transfer aspects and that is the most central transport phenomena in a CVD reactor and described the Fick diffusion that delivers material to the substrate on which the film is being formed.

And we also looked at various adjustments that we have to make to the diffusional deposition rate to account for what we call the analogy breaking mechanism such as thermal diffusion, homogeneous reactions and heterogeneous reactions. In particular we derive formulae for the correction factors that we need to apply when such Phoretic forces and other external factors are present.

In the last part of the course we looked at some very specific examples of CVD processes in CVD reactors such as we looked at Silicon CVD, CVD of coatings, CVD of oxides, hotwire or filament CVD to make metal films and finally nano materials as well. So overall that is the portion that we have covered as part of this course. Now for the exam I think as I have mentioned before I really want you to have a good understanding of the breath of the subject that we have covered and some knowledge in depth particularly about the chemical engineering aspects which is the thermodynamics, chemical kinetics both heterogeneous and homogeneous as well as transport phenomena.

And also spend some time talking about CVD processes that are not intentional but are actually undesirable such as born out of tungsten filament lamps and also hot corrosion of turbine blades and so I do not think we have covered those in any of the quizzes yet, so that is possible that maybe one or 2 questions in your term exam on those 2 and in one of the recent lectures actually couple of lectures we talked about multiscale model which is a very unique aspect again of CVD reactors because there are at least 4 major length scales and corresponding timescales that are present in any conventional CVD reactor.

And it is important to understand the differences between these scales and also how they are interlinked together. In the last lecture we talked about the hierarchical approach to multiscale modelling versus the concurrent approach. So for a given CVD film, you know the trick is how you relate something that is so surface specific. As a growth rate of a CVD film on a surface, there is something that is so macroscopic because all you really have control over is how much reactant you are feeding in?

What flow rate is? What the temperature is and what the pressure is? So that is something you are trying to control at a reactor level but on that basis you are trying to make a very very thin film or structure on a substrate. So you are trying to influence what happens at a nanoscale with parameters that you are only able to control at a much larger length scale. So that is really the challenge in a CVD reactor.

So unless you have a very precise understanding of how the phenomena are linked from the various length scales and timescales that are present in your system you can never achieve the kind of control over the nature of the deposit that you are forming on the substrate. The another question I think that is very relevant to ask in the term exam would be something around the multiscale modelling of CVD reactors and how you would apply that in order to make this linkage from the controllable parameters in your reactor to the functional parameters that you are trying to achieve with the reactor.

And you know at the largest length scale we have the macroscopic model or the conservation model which is where we spent quite a bit of time on. So here again I think I would expect you to be able to discuss essentially from first principles how you would form a mass transfer model for film formation happening in a CVD reactor and identify the appropriate correction factors to apply for various reactor of any conditions.

For example if you have a cold wall reactor I would expect that you should be aware that in a cold wall reactor natural convection is going to be dominant because the temperature difference between the hot substrate and the cold wall is going to drive natural convection phenomena and secondly I would expect you to be aware that the temperature gradient is again going to require you to include thermal diffusion as an influence in your deposition rate calculations.

So you have to be able to calculate the correction factor corresponding to thermal diffusion and apply it to your result. Similarly if I tell you that it is a hot wall reactor then I expect you to appreciate the fact that when you have a hot wall reactor the probability of heterogeneous nucleation is much higher and so the probability that some material condense in the gas phase and potentially be transported as aerosols to the surface is also higher.

So again I want you to demonstrate that level of understanding, when do homogeneous kinetic's becomes important? When do heterogeneous kinetic's becomes important? And again central to all this is a figure that we have drawn several times, so it relates the logarithm of the deposition rate to the inverse of the surface temperature. You really have to be able to identify the various regions that are present in that graph and ascribe you know reason for the behaviour that you see.

Why is it that at very high temperatures you actually start to see a drop in the deposition rate? Why is it that at low-temperatures you start seeing more of an exponential behaviour with respect to temperature? In other words when does surface kinetics become important? When does gas phase kinetics become important? And when is said that diffusional phenomena dominate over either (()) (10:09) and how you express it?

You have to be able to express the relative importance of the various factors affecting CVD rates in terms of non-dimensional parameters. So you have to be able to define a Damkohler numbers, Nusselt number, Stanton number, Peclet number, so if you look through your notes these are dimensionless quantities we have defined which essentially represent the ratios of characteristic times.

So it could be the characteristic time of diffusion process chemical reaction or it could be the characteristic time for homogeneous reactions versus heterogeneous reaction. It is important that you should be able to express the relative importance of the various terms influencing CVD rates on the basis of the relevant dimensionless quantities. Again that is a contribution of chemical engineering makes.

Anybody can do experiments in a CVD reactor and look at the data and react to it but in order to be able to interpolate those results or extrapolate those results have to be able to define these so-called dimensionless parameters which enables you to do this kind of scaling and extend the region of validity of your experimental data. Otherwise you can never be sure that now whatever data you have collected for a certain set of conditions, if you develop a model based on those experimental data now those are called empirical models.

The problem with an empirical models is as soon as you go outside the range in which the data was obtained you can never be sure that the same model is valid and that is where the non-dimensional analysis becomes very important because we can then take the results that we get in one system and be able to apply it for multiple systems, so that is another value add that chemical engineers can bring to the study of chemical vapor deposition.

So I think, you know the point I made in one of the very early lectures is that a CVD reactor is like a microcosm of the chemical process industry. You know everything is happening inside a CVD reactor, everything that you have studied in chemical engineering and I hope that as we come to the end of the course you have a good appreciation for that. You should be able to assess how you know obviously the 3 transport phenomena that you have studied have relevance in the study of CVD systems?

How chemical reactions in equilibrium thermodynamics have a relevance in the study of CVD systems and also be controlled methodologies which is another importance of which is another important subject that chemical engineers learn also has applications in CVD reactors because the most important thing in a CVD reactor is to control the product which is the film and in order to be able to do that you need to be able to control all the different parameters that affect the operation of the CVD system.

So controlled methodologies are extremely important also in the investigation and optimization of CVD systems. So I hope that you have kind of been able to extract from both the lectures notes as well as the papers that I have been circulating. If you have any questions go ahead? Is there anything that has been bothering you from day one about CVD or everything that has come up in the last couple of days or is there anything that you think should have been covered which we did not cover in class or something which we covered in class which we should have not covered in class?

If any questions, feedback, anything is welcome?

“Professor -Student conversation starts”

Student: Regarding nano materials we have started very I mean we have gone through little bit more…

Professor: Yes.

Student: How to make that carbon powder in nano material.

Professor: Okay.

Student: Or any other how this …

Professor: By the way I have sent some papers in the morning, so I sent a bunch of papers on basically synthesis of nano materials. I do know that there is lot to be gained by teaching that in class I mean there is nothing very fundamental about it and so I have sent you some papers take a look at them and if you have any questions you can always get back to me.

See synthesis of nano materials I do not really believe that CVD is the best method for doing it, it is one of the methods and it is something you use when you are not able to use other methods but I do not think it has optimal use for CVD. CVD is really good when you are trying to make, you know coatings over surfaces that have, you know complex contours and stuff like that and also very very fine clearances. So it is well suited for you know microelectronics but when you are get in to the nano range I do not think CVD works as well as some of the molecular techniques that are now being used but yes it is certainly something interesting to look at.

Student: Chemical sensors that we usually use for fixed amount of…

Professor: Right.

Student: Nano materials are being coated on some surfaces than those materials are being used in for actual purpose.

Professor: Yes.

Student: In that case this CVD I think is much more…

Professor: Certainly. Anything else? Let me ask you what did you think was the most interesting part of the course?

Student: Application of various conservation equations which we learn separately, combination of (()) (16:05) and CVD.

Professor: You also have a course in transport phenomena, right?

Student: Yes.

Professor: Do not you try to do that thing in that course? In fact that is where you try to combine the various…

Student: We did not try to do that but I think we would…

Student: Maybe practically it was a scenario where we had a, like we have a CVD system and like you mentioned, if it's a diffusion dominant or thermal diffusion dominant…

Professor: Yes.

Student: Maybe practical scenario is in that case.

Professor: Okay. Yes one thing we did not really do a lot of solving numerical problems maybe that is something that can be done as well.

What was the least interesting part of the course?

Student: (()) (16:54) where it got very theoretical…

Professor: Yes.

Student: Spectroscopy and microscopy and all that.

Professor: So you would want to see some practical demonstrations, so that will make it more interesting because it is important to understand how CVD films are measured whether we like it or not it is something that we have to know.

I mean ellipsometry accounts was probably 90 percent of CVD film thickness measurements, so if you are only going to learn one technique ellipsometry we would be the right one to learn. Okay, you have any comments or…

Okay, fine, so let us take a little earlier today and if there are any numerical problems I think there will be designs such that you do not need a calculator but just bring one just in case, okay, alright.