## Chemical Engineering Principle of CVD Processes Prof. R. Nagaranjan Department of Chemical Engineering Indian Institute of technology Madras Module-3 Lecture 22 CVD Applications: CVD of Silicon

Good morning and welcome to our next lecture in our course on chemical engineering principles of CVD process. We have been discussing some applications of CVD and some typical reactor and designs in the last couple of lectures. So today we will talk about CVD of silicon. Of all the materials that are deposited using CVD Silicon both in crystalline form as well as poly crystalline form is probably the most commonly deposited material.

It is essentially a multibillion-dollar industry around the world, so it is important to spend some time talking about this process. Silicon CVD reactors are essentially of 3 types, one is the horizontal flow low pressure CVD systems which are quite common.



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And the second most frequently used configuration is the stagnation point flow CVD reactors and the third most popular configuration is fluidized bed CVD reactor. Now as you know the difference between the system is in a horizontal flow CVD reactor essentially the wafers amount are mounted parallel to the flow of the fluid and deposition occurs by diffusion across the boundary layer that develops on top of the substrate or wafer. In the case of the stagnation point flow, the flow is vertical to the wafer and deposition occurs in the stagnation region adjacent to the vapor surface the fluidized bed CVD reactor is particularly useful when you trying to coat the silicon onto particles. So essentially you can imagine a bed consisting of particles to be coated and then you bubble gas through this bed where you are actually doing (()) (2:34) thermal pyrolysis to create the precursors of the silicon which then deposit on the outer surfaces of the particles which can be silicon particles in a epitaxial silicon film growth. So the film formation happens around the particles that are suspended in this bed.

Now if you look at these different configurations, as we have discussed early during the course each has its advantages and disadvantages in terms of the thermodynamics, kinetics and also the transport phenomena but one thing that is important to appreciate is the fact that when you talk about CVD reactor in general there are multiple timescales and also multiple link scales involved.

So when you are trying to develop a model to simulate CVD in a reactor you have to be able to deal with these multiple timescales which can be really different.



(Refer Slide Time: 3:49)

For example if you look at the CVD process itself, you know, we have previously broken it down into, you know the first part is essentially the fluid dynamics which on a length scale can be of the order of meters and on a scale could be of the order of seconds to minutes, it is essentially the time that the carrier gas that is introduced into the CVD reactor has available to traverse the reactor and also establish a steady-state conditions over the substrate on which the deposition is taking place.

(Refer Slide Time: 4:31)

The second process that happens of course is the boundary layer transport. Now when we talk about transport across the boundary layer that we are obviously talking about very thin dimensionless which are typically of the order of micro-meters to fractions of a millimetre, about the times, what is the typical diffusion time scale? How long will a molecule take 2 drivers, you know, let say 10 microns of boundary layer.

Will it be like milliseconds or microseconds or picoseconds? It is actually of the order of about 10 to the power minus 8 to 10 to the power minus 10 seconds because diffusion process remember is at a straight line process, it is a random moment and coalition process, right? So a molecule is just not going to be able to transport itself convectively. It is going to have to randomly walk around and then if it encounters another molecule it is going to bounce, so it is essentially a sequence of random events that result in net portion of the vapor of the particle. So the timescales are much slower.

Now there are also homogeneous chemical reactions happening and in the case of homogeneous chemical reaction and in the case of homogeneous chemical reaction what is the length scale? For a reaction to happen the molecules have to be closed on an atomic scale, right? So we are really talking about nanometres as a (()) (6:26) scale and about the reaction times, homogeneous reactions in general have a higher activation energy barrier compared to heterogeneous reactions.

So the timescales are roughly comparable to the diffusional timescales. As you have seen before the Damkohler number is the relevant number that measures the typical time constant for diffusion to the typical time constant for chemical reaction and it can vary from a very large value were very small value but on an average that say that these times are comparable and then you have the heterogeneous chemical reactions.

(Refer Slide Time: 7:14)

In the case of heterogeneous chemical reactions again the gas phase molecules have to get very close to the substrate or solid surface on an atomic scale, so here again in terms of length scales we are talking about nanometres. However heterogeneous reactions typically proceed much faster than homogeneous reactions because there is a lower activation energy barrier and so the timescales here can actually be of the order of, can happen very quickly compared to the homogeneous reactions or boundary layer transport.

So it could be of the order of 10 to the power minus 12 to 10 to the power minus 15 seconds, especially as you drive towards the equilibrium the reaction is virtually instantaneous which means that the time constant is extremely small.

(Refer Slide Time: 8:13)

The next step is the adsorption part, you know, reaction occurs you have formed a solid film that is thermodynamically feasible but now it has to be accommodated by the surface. So the adsorption process involves time constant and here we are really talking about angstroms link scale because we are talking about essentially vacant sites on the surface that can present themselves to the molecule that is depositing and allow it to get fixed to the surface.

So very very small timescales I mean link scales, however the timescales depend on temperature and pressure, the adsorption process can become the rate-limiting process if the surface is not sufficiently energised. So the adsorption process itself can have time constants at can range from 10 to the power minus 15 to 10 to the power minus 8 essentially encompassing the time constant associated with the transport phenomena and the chemical reactions that are taking place.

(Refer Slide Time: 9:35)

Now 6th process in this is surface diffusion where once molecule is absorbed on the surface migrates on the surface and forms clusters and the clusters eventually grow into a continuous film. So there is a time constant associated with this process as well and again we are talking about length scales that are of the order of angstrom and timescales for molecule to move about on a surface find adjoining molecules form clusters then for the clusters to grow attached themselves and form a continuous film can take much longer compact to the diffusional or the adsorption processes.

(Refer Slide Time: 10:41)



So we are back to the timescales that can be as much as 10 to the power minus 3 to 10 to the power minus 4, it is the order of milliseconds, right? I think it is the summary of the complexity of trying to model a CVD reactor because if you look in the literature, you know, this talk about silicon CVD which as I said is the most researched and most published CVD process in literature.

(Refer Slide Time: 11:10)



You will see that the models are presented very few of them try to deal with all of these steps on the process there are CFD papers that essentially concentrate on the fluid dynamics. They are very good at modelling the microscopic flow behaviour in the system; they are very good at predicting velocity distribution, temperature distribution, pressure distributions and by extension also the mass fraction distribution of the reacting species. (Refer Slide Time: 11:33)



However the boundary layer transport path or in principle can also be covered by CFD. However they tend to be somewhat weak, they tend to use very basic definitions of mass transfer coefficients. Now in a few lectures we have discussed how your nominal mass transfer coefficients have to be corrected for the various phenomena that are taking place, virtually none of the CFD coats that are available will provide you these correction factors for thermophoresis or for Stefan flow or for the affect of homogeneous chemical reactions on transport rates or the affect of heterogeneous chemical reactions on transport rates for the combined effect of both. These are enhancement to the theory which are typically not included in the CFD type of papers.

However the papers that do deal with these types of phenomena tend to place less emphasis the CFD part. So firstly there is this segmentation of papers in this area.

(Refer Slide Time: 12:38)



So typically this part, the boundary layer transport part is the province of research groups that are very focused on diffusional phenomena and the various parameters that affect diffusive phenomena. If you look at the homogeneous and heterogeneous chemical reactions that are taking place, again that is entirely different set of research groups that are focused on that area.

This essentially specialized in characterizing the various chemical reactions that are taking place in measuring the rate constants, studying the kinetics, developing empirical and semiempirical models for these chemical reactions that are happening both in the gas phase as well as heterogeneous league. So that is again an area of literature that has sprung up and grown at it is not necessarily linked very well to these 2 components.

Something like adsorption and surface diffusion is actually more under the province of people that are working in things like Monte Carlo simulations and molecular dynamics because essentially what we are talking about there is what happens at the interface between a surface and a vapor molecule. How does the adsorption process happen? How do the adsorb molecules move, what are the driving forces for them to essentially jump from one interstitial site to the next one?

What provides the kinetic force? What provides the thermodynamic motivation? Why does not the molecule just stay where it is? What is it that makes it try to find the nearest neighbour and form agglomerate rather than staying single molecules and then the whole simulation of how it happens?

Because it is, you know at that level it is more of a probabilistic study it is not a deterministic study, you cannot look at a single molecule and try to predict its behaviour instead what you try to do is propose a multiplicity of possible behaviours and find the ones that gives you the highest probability of the re-occurring, right? So the type of simulation is very different what people are working in this areas are doing.

So essentially the point is that if you look at the literature during the silicon CVD there is none that really captures the entire phenomena, it is like a blind men and then elephant, right? They all look at different aspects of it and study in a great lot of depth but the linking of these various elements is not very strong and the reason again for that is because of the difference in the length scale on the timescale.

If all of these phenomena were going on roughly on that same timescale and same length scale it would not be so difficult for, you know one analysis in one aspect to be quickly extended to other aspects as well but because of the huge diversity in length and timescales is just not possible. For example again let us go back to silicon CVD, you know, when you look at fluid dynamics we have talked about it at length.

You start with the, you know, conservation equations start with mass conservation, and conservation, energy conservation, entropy conservation you apply the appropriate boundary conditions, initial conditions, you apply the appropriate constitutive relationships and you solve and that is essentially how you solve the fluid dynamic part of it, particularly the momentum conservation equations with the linear momentum as well as angular momentum enables you to do that more in the case where force convection is dominant as well as where natural convection is dominant we are using the appropriate dimensional numbers and so on.

When you talk about boundary layer transport, here again we have spent quite a bit of time talking about that aspect and we have dealt with not only the baseline process but possible corrections that you have to do to your model to account for it properly.

(Refer Slide Time: 16:53)



So in terms of what we have covered in this course, I would say most of our focus has been in actually in this area with a little bit of focus in this area and you know little bit focus on the other areas but primarily concentrated on this part which you know actually from a chemical engineering viewpoint it is the most unique for our discipline because there are other people can deal with the other aspects with the 2, 3 and 4 are really the span of control for chemical engineers, that is where we can do the most good that is where we have the most expertise and so primarily our focus in this course has also been on these aspects.

So if you look at silicon CVD, how would you describe the chemical reactions? We have said before in a CVD reactor the best way to model the homogeneous rate processes is by using a free energy minimization approach, right? But that assumes that you are driving every process to equilibrium and it also assumes that, you know, you have absolutely no insight into the processes that are going on but in the case of specific systems like silicon CVD there has been a lot of work done to diagnose what are the dominant chemical reactions taking place inside the reactor.

(Refer Slide Time: 18:19)



Particularly in the case of SiH4 Silane going to silicon solid there is quite a bit of literature that tries to describe exactly what the reaction sequence is. For example people would agree that the first step is that it decomposes into SiH2 plus H2 and then SiH4 combines with SiH2 to make Si2H6 and then SiH4 plus Si2H6 goes to make Si3H10.

SiH2 plus Si2H6 goes to make Si3H8 and so on. So there are these specific reactions have been identified people have also tried to characterize what is the longest chain length that is achieved before the molecules essentially become too unstable? So that they do not stay for very long and so this type of modelling is been done and the overall kinetics are obviously described bySnH4 going to SiS plus 2H2.

(Refer Slide Time: 20:06)



But if you look at the homogeneous chemical reactions for example SiH4 going to SiH2 plus H2 that reaction has also been studied in some detail and the reaction rate term corresponding to that has actually been written in the form of k1, k2 times CSiH4, so this is minus rS or SiH4 divided by k1 times CSiH4 plus k2 this is called the Lindemann's equation or Lindemann kinetics that k1 and k2 are constants and CSiH4 is a concentration of Silane.

It has the behaviour that when the pressure for concentration, actually this is written more in terms of partial pressure rather than concentration. So it is k1, k2 PSiH4 square divided by k1 times PSiH4 plus k2 when the partial pressures are high. In other words when the system pressure is close to atmospheric pressure then this behaves like a first-order reaction because k1 PSiH4 becomes much larger than P2 and then these 2 cancels, so essentially it becomes k1 times PSiH4 which is a first-order reaction.

However as you lower the pressure and you start using LPCVD this term becomes dominant combat the distance, so now it becomes a second-order reaction, so in the typical Lindemann kinetics depending on the value of the prevailing pressure the reaction can either run as a first-order reaction or as a second-order reaction. So this is the most conventionally accepted kinetic model.

Now the problem is there are models like this for each of these reactions and which have been developed over long period of time using extensive studies. So just describing the chemical kinetics of the system itself is like a lifetime research process, right? And that is the reason why for someone who is focused on the reactor as a whole is probably not worth it to try and describe the kinetics of each reaction separately by forming appropriate reaction rate laws and then measuring the constants and so on.

(Refer Slide Time: 22:42)



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Now if you look at for example what is happening inside a fluidised bed CVD reactor? As I said the fluidised bed CVD reactor is one where you have particles in a bed and you are flowing reactor gases over them and the silicon deposition occurs as a thin film around the particle surface. So if you look at this situation the modelling has been primarily looking at the overall behaviour of SiH4 going to silicon solid plus hydrogen gas and this has been

modelled as our SiH4 equals a kinetic rate constant times A by V times CSiH4 over 1 plus k1 times CSiH4 plus K2 times CH2.

Where A is the area of the particle the total surface area of the particle and V is the gas volume that is passing by. So it is basically the specific area of the particle, area per unit volume and definition of this parameter A by V is that it obviously depends on the porosity, it is actually written as 6 over dp times 1 minus Epsilon by Epsilon where DP is the diameter of the particle comprising the bed and Epsilon is the pore fraction of the bed.

So this is again what I would term more of an empirical relationship which has been observed to many measurements. So it is what we call a phenomenon logically observed reaction rather than 1 that is really based upon any fundamental modelling. So if you are trying to model the CVD process as a whole for a fluidised bed CVD reactor you would develop a first principle for the flow dynamics and for the diffusion process.

But then for the homogeneous kinetics as well as the heterogeneous kinetics that is presented here you would tend to use these kinetic rate expressions that are experimentally derived. So they have to be essentially fed in as a subroutine to the CFT model which is okay, you know it basically becomes a UDF, the problem with it is in terms of the rigour there is always a difference between the first principle model and a UDF that is provided strictly based on a criminal observation.

There is always a question Mark when you are providing a subroutine that is experimentally derived because there is no guarantee that if you extend your experimental conditions you will still get the same rate law all of, sorry.

"Professor -Student conversation starts"

Professor: User defined function, sorry, it is usually a subroutine that you feed to a code to incorporate certain specific behaviour which is not covered in the universal code. So the problem is when you try to integrate the 2 the amount of theoretical soundness is much greater in the first principles model compared to the one that you have provided based on actual mental observations.

So that leads to essentially a mismatch you have a model that is very good in terms of describing the flow dynamics and the diffusional behaviour but is kind of weak in terms of in

terms of describing the kinetic behaviour. Whereas on the other hand if you are working at it at the other hand you may have spent a lot of time in developing the best possible kinetic model but then you are essentially going to be taking in the flow dynamics and the diffusion or the transport phenomena as again a user supplied kind of a subroutine. It is very difficult for a single research group to have sufficient expertise to deal with all the 6 aspects in sufficient depth and so you tend to sacrifice one or the other.

"Professor-Student conversation ends"

Now the third aspect, so we are kind of, in the case of silicon CVD we have given some examples of homogeneous and heterogeneous behaviour and then there is this adsorption behaviour, right?

(Refer Slide Time: 27:42)



Now how do you model adsorption? So adsorption is modelled using Sigma which is a vacant site on the surface almost like a catalyst. So when you have SiH4 approaching a surface, approaching a vacancy what happens is SiH plus or SiH gets absorbed as a separate molecule H gets absorbed as a separate molecule and then H2 leaves as gas. So the asterisk here as initially indicates an adsorbed molecule. So it is the first step in adsorption.

The second step in the adsorption is Si2 SiH stars essentially combine through a process of clustering you get 2Si adsorbed plus again H2 leaving and similarly2 of the adsorbed each molecule is find each other and leave as H2 which frees up that we can cite for additional

adsorption. So this is a sequence that again has been observed specifically for silicon CVD systems and the modelling of adsorption usually follows some outline like this.

It is based upon very extensive investigations of the surface on a real-time basis; essentially you take the surface expose it to silicon Silane gas and observe what species get absorbed in what is a time-dependent behaviour? How stable are they? How do they migrate? How do they cluster and so on? So describing this as I said is a separate sign all on its own, you really have to have a very good understanding.

I mean basically you need a surface scientist or an interfacial scientist who understands how an approaching molecule interact with the surface which has a certain number of vacant sites that need to be filled and how the entire dynamics takes place? How does the initial adsorption happen? How does the later migration and clustering happen? And how does the desorption happens? Because all 3 steps are crucial for the steady state formation of an adsorbed film on the surface. (Refer Slide Time: 30:24)



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And then you have, you know surface diffusion as well. Now surface diffusion as I was saying plays a major role in how this happens because for this step, you know for Si H star going to 2SiH star requires diffusion to happen. The adsorbed molecules have to migrate find each other and cause the ejection of the H radicals or hatch ion as H2 molecule and similarly to adsorbed hydrogen radicals finding each other and becoming a gas phase hydrogen.

So this is essentially a surface diffusion step it as again being modelled but surface diffusion cannot be modelled from first principles, unlike gas phase diffusion particularly in the case of low-density gases and dilute species you can derive the diffusion coefficient from the kinetic

area of gases but when you are talking about surface diffusion, if you remember we wrote down an expression for it in one of the earlier lectures.

In involves things like frequency of jump attempts, it cannot be model from first principles or it is really a probabilistic phenomena again. All you can really try and calculate is what is the probability that a molecule that is absorbed down the surface will move to another location on the surface in a given amount of time and based on your estimated probabilities you can derive an average surface diffusion coefficient?

So on the surface; you know how do you bring this altogether? Is there a single model that can at least describe everything that is happening on the surface? The only way to really do that is through population balance modelling.



(Refer Slide Time: 32:35)

So the latest trend in CVD analysis particularly when it is focused on surface is to use a population balance approach. Population balance, you know as the name says to take it into account birth and death phenomena which cause the change in the population but also within the population, you know for example if you are looking at the human population and you want to do a model for number of humans between 10 and 20 years of age than your population balance model has to also include essentially terms that indicate growth into that age range and growth out of the age range, right? So you need those terms also.

Similarly when you talk about a population balance model or adsorbed molecules on a surface. You have to decide which molecule you are going to be modelling, so if you want to

look at the rate of SiH star then you have to clearly look at the rate at which these molecules are absorbing. So you have to look at d by dt of SiH star getting on the surface due to an adsorption process you also have to subtract from it the rate of loss of SiH star due to desorption.

Adsorption process itself can be reversible, so an adsorbed SiH molecule can also dissolve; so that you have to take into account minus we also have to look at how many of these SiH star molecules are you losing because of agglomeration with an adjacent SiH star molecule? And also you have to take into account the diffusional behaviour of the molecule separately because the analysis that you are doing this is typically at a particular x because you are treating time as the dependent variable.

So you are usually looking at how adsorbed molecule concentration is changing at a certain location the substrate. So you also have to look at simple migration of the molecule away from that location even if it does not result in agglomeration. So that is essentially a rate of change of SiH star due to surface diffusion which would depend on obviously the surface diffusivity of the molecule which again it would be dependent on the prevailing temperature and pressure conditions.

(Refer Slide Time: 36:05)



This term, the agglomeration term would be dependent again on temperature and pressure and the diffusivity term because all 3 will play a role in how the adsorbed molecules migrate and find each other but in addition you also have to look at properties like the cohesive behaviour of the molecules. Even if the 2 of them find each other how likely are they to agglomerate rather than bounce back, right? So that is essentially called cohesive behaviour and there is a parameter called cohesion coefficient which would depend on parameters like the surface energy of the vapours.

It also will depend to some extent on the viscosity of the fluid between them which can also affect how close the particles are molecules can absorb each other. It really depends on the intermolecular forces as well; you know one of the Van der waals forces between the molecules, what are the electrophoretic forces between the molecules? What are ionic forces between the molecules? What are the surface tension forces? What are the viscous forces? So this cohesion coefficient actually depends on all of these interactions. (Refer Slide Time: 37:30)



Now if you look at obviously the adsorption and desorption behaviour, they are predominantly concerned with the adsorption dynamics, what is for a given temperature and pressure? What is the rate at which the molecules can absorb and what is the rate at which molecules can desorb? And this again can be experimentally observed and incorporated into your model.

So if you are trying to do a simulation of how of a thin film grows on a surface, you really have a choice to make I mean you try to model all this phenomena in full detail for you try to focus on a few of these and essentially take a simplified view of the other processes that are going on. Another way to look at it is the 6 dimensional problem essentially but you have a choice to make you can either try to deal with it as 60 problem in which case the numerical complexity and the computational effort that is involved can be quite large because of the different timescales.

You know, try to imagine building a computer core to deal with this entire process, certain steps have to be taken in 10 to the power minus, you know 12 or 10 to the power minus 15 second timescales time steps whereas some of the regions of the reactor we have to use much larger time steps of the order of second or meter. So coming up with a core that can really deal with that, you know as people that have done lot of programming will tell you it is very very hard. It is very difficult to get such course to converge because this huge range in the either to take a macroscopic view or microscopic view.

(Refer Slide Time: 39:33)



So the macroscopic investigators will deal with, you know the first 4 aspects in some details but they will tend to take a very simplistic view of the last 2, whereas a microscopic analysis of the CVD problem would tend to focus a lot more on the last 2 steps and take the others as essentially being given, they will use the simplest possible (()) (39:51) dynamic model, simplest possible kinetic model, simplest possible Thermo transport model and so what they assume...

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You know another way to look at CVD is, if you have a substrate there are 2 things that determines how the film grows, one is how does the material gets to the surface? The other is one but a real gas to the surface how does it interacts with the surface and start to grow as a film. So steps 1 to 4, well 1 to 4 deals with this part, how is material delivered to the surface and steps 5 to 6, actually I would say 4 to 6, so 4 is kind of overlapping step because it involves heterogeneous reactions or it does have some microscopic relevance but it also has a macroscopic relevance since you are also interacting with the fluid the other side.

So, 1 to 4 in this table or in this list deal with the macroscopic view of the CVD and steps 4 to 6 deal with the microscopic view of the CVD system. The challenge is how do you fit the 2 together, right? The issue there is not so much that we do not know how to do it? I mean it is certainly doable it is just that the computational effort involved, is that always justified on the basis of what you are trying to do?

For example if you are simply trying to develop a model for how the film thickness changes as a function of time then the model that is most relevant to you is probably the macroscopic model. On the other hand if you really care about not just the rate of growth of the film but also all of its morphological characteristics, all of its metallurgical characteristics, all of its crystallographic characteristics, all the things that material scientist, metallurgist would be interested in then you tend to focus a lot more on steps you know 5 and 6.

(Refer Slide Time: 42:01)



So again a way to think about this is chemical engineers would tend to focus on the steps, material engineers, surface scientist would try to concentrate on these steps, there are only very few people who are really working in what I would call the interfacial area, who try to kind of take both of these into consideration when trying to develop a model for the CVD process.

And by the way all the discussions we have had have been with one system silicon CVD. You can imagine that given the multiplicity of materials it can be deposited using CVD, all of these same considerations will apply for each of these systems and essentially as someone who is involved in modelling of CVD systems you have to make a choice, you have these 6 different aspects to deal with which ones are going to give importance to and which ones are you not?

And your selection should match your application, if you are trying to make high purity silicon with very precisely controlled structural characteristics for a semiconductor or microelectronic application then you cannot afford to neglect the last 2 steps, the molecular structure becomes extremely important. Another reason is my you know if you look at semiconductor devices, the features on a semiconductor device are now of the order of nanometres.

And so unless your model has nanometre resolution, you are not going to be able to predict what is going to happen again if you cannot predict you cannot control, you cannot optimise and so depending on certainly the characteristic feature sizes in your product you select the length scale that you want to focus on and based on your selection of length scale that decides your timescale.

Ideally that is the approach you should not make the decision of which aspects to focus on based on your capabilities but rather on what the product requirements are? What is a functionality that is expected of the CVD film? And how am I going to be able to capture that in my model? That should drive your analytical methodologies, okay.

Okay, so let us stop at this point, in the next class we will take up another system of CVD and try to illustrate some of these principles as well, any questions that you have? Okay, so I will see you at the next class.