Fundamentals of Material Processing - 2

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Module - 02
Thin Film Deposition
Lecture - 12
Chemical Vapor Deposition

Welcome to lecture 12 of Thin Film Deposition module. In this lecture we will continue our discussion on chemical vapor deposition of thin film deposition process. If you recall in the previous lecture we had looked at that how the transport of gasses into a chemical vapor deposition chamber might affect the deposition uniformity. So, for any chemical vapor deposition process or it is based on the chemical reaction. So, we need to have two approaches or two very important aspects: one is the transport of the reactance and the reaction itself.

Now, most of these depositions are done in by gas phase reactions we could also use liquid phase reaction, but liquid phase reactions will be very uncontrolled for thin film deposition because in liquid phase the reaction rates are much faster and we cannot controlled the transport. In gas face phase we can control the transport of the reactance to the substrates were they form a thin film so that, our control growth rate or deposition rate is controlled and we can control the properties such as thickness and morphology of the thin film. So, 2 very important things, one is transport of reactance and second is the reaction thermodynamics of the reaction.

So, in the previous lecture we had seen that how boundary layer plays the role when the gases flowing on its surface, it forms the boundary layer and how that plays the role in the how the reactance are distributed in the chamber.

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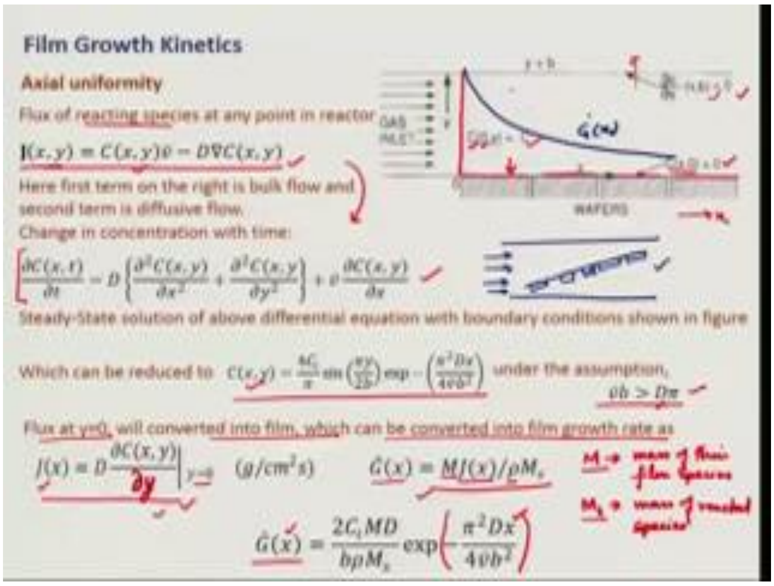

Film Growth Kinetics

Axial uniformity

Flux of reacting species at any point in reactor

$J(x,y) = C(x,y)v - D\nabla C(x,y)$ ✓

Here first term on the right is bulk flow and second term is diffusive flow.

Change in concentration with time:

$$\frac{\partial C(x,t)}{\partial t} = D\left\{\frac{\partial^2 C(x,y)}{\partial x^2} + \frac{\partial^2 C(x,y)}{\partial y^2}\right\} + v\frac{\partial C(x,y)}{\partial x}$$ ✓

Steady-State solution of above differential equation with boundary conditions shown in figure

Which can be reduced to $C(x,y) = \frac{4C_i}{\pi}\sin\left(\frac{\pi y}{2b}\right)\exp-\left(\frac{\pi^2 Dx}{4vb^2}\right)$ under the assumption, $vb > D\pi$ ✓

Flux at y=0, will converted into film, which can be converted into film growth rate as

$J(x) = D\frac{\partial C(x,y)}{\partial y}\Big|_{y=0}$ $(g/cm^2 s)$ $\hat{G}(x) = MJ(x)/\rho M_s$

M → mass of thin film species

M_s = mass of reacted species

$$\hat{G}(x) = \frac{2C_i MD}{b\rho M_s}\exp\left(-\frac{\pi^2 Dx}{4vb^2}\right)$$

In this lecture we will discuss how this affect this formation of boundary layer affects the uniformity of the thin films. So, as you see that in this figure here we have a tubular reactor, in which the gases the reacting gases are coming from the left and we have kept the vapors on which we want to the deposit thin film along one of the chamber walls in excel direction. Now the transport properties of the reactance will dictate how the thin films are growing so the equation that governs the flux.

Let us see this is a two dimensional state, we are going to ignore the third dimensional it is in perpendicular to the plain of paper. So, how the reactance are distributed in these two dimensions x and y? So, this is y axis and this is x axis. So, now, the flux of the species is of the reacting species at any point in reactor, will be governed by two things - one is the mass flow and second is the diffusion; mass flow with the bulk and diffusion across the boundary layer. Now we can use this expressions to end of affix second law to have the concentration with time, how the concentration is with time changing at different locations inside this reactor. So, this is a fix second law equation and we can solve this equation with these boundary conditions to get the distribution at any given time with x and y and this is a study state, now the boundary condition are such that any reactant which is the vapors reacts very immediately.

So, the reaction condition such as temperature and thermodynamic of the reaction are such that any reactance species which reaches the vapors reacts almost instantly. So, there is no buildup of the concentration of reactance at this boundary and also at this C is x equal to 0, the concentration is constant because the gasses are flowing coming in from the left, so at this x equal to 0 the concentration ration is constant and at this boundary there is no concentration gradient along this direction. So, these are my boundary conditions and if we solve this partial differential equation in these with this boundary conditions and under the assumption that my velocity and this b is more than diameter and pi or the diffusion constant into pi. So, under these assumptions which are valid, we get this distribution of concentration in x and y at any given point we knew how much concentration of the reactant is present.

Now, the flux at y is equal to 0 will be converted into thin film, which can be converted into film growth rate. So, any concentration at y is equal to 0 the flux in this direction will be converted into thin film. So, if you know this C x y, then we can. So, this is d y if we have we know the distribution of the flux of the concentration, we can calculate the flux coming on to the vapors at y is equal to 0. So, this is the flux and this flux which is number of atoms or of molecular of the reactant per unit area or per unit time, we can then convert using this expression into film growth rate; this is the film growth rate, this is the flux and is the molecular mass of the M is the mass of thin film species.

And M s is the mass of reactant species. So for example if we are using silent deposit silicon and would be if the atomic mass silicon, and M s molecular mass of silane, and this is the density of the thin film. So, using these two expressions, we can have growth rate or deposition rate thin film as a function of x, x is this direction and then you can see that it has an exponential dependences with a minus sign with x, which means that my deposition rate is decaying exponentially with x sorry this will be the. So, this my g of x right and since the deposition rate is decreasing exponentially with x, my deposition rate at various point or various vapors would be different and I will not have a uniformity.

Now, how do we counter this problem? For some reason we are bound to have a reactor like this, what we can do is that rather than keeping vapors at along the axis we can keep the vapors at an incline. So, this is my gas entered and these are my vapors at an incline such that the boundary layer thickness also decreases as you move along this axis along the vapors and you can achieve some kind of uniformity; this is one way of controlling the uniformity if you have large number of vapors, for the single vapor and small vapor it will not matter, but in production we want to deposit on large number and large area at one time to save the cost. So, you can use this.

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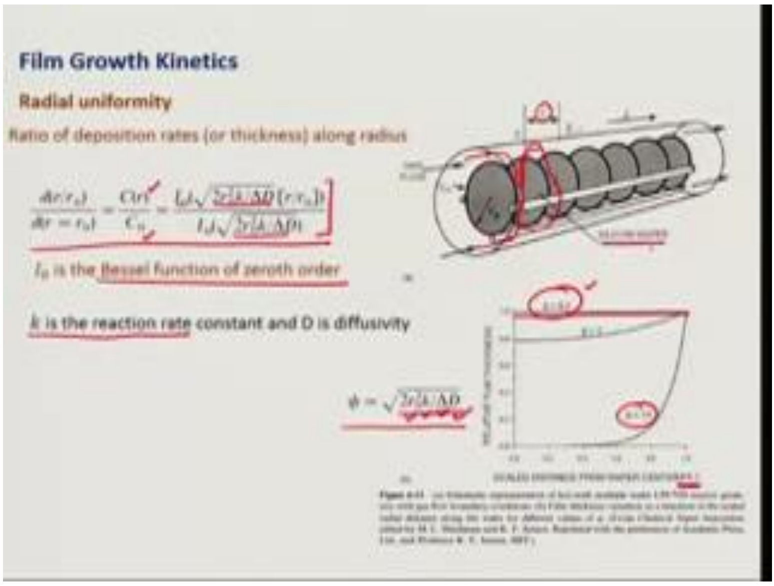

Film Growth Kinetics

Radial uniformity

Ratio of deposition rates (or thickness) along radius

$$\frac{d(r)}{d(r=r_0)} = \frac{C(r)}{C_0} = \frac{I_0[\sqrt{2r_0^2k/\Delta D}\,(r/r_0)]}{I_0[\sqrt{2r_0^2k/\Delta D}]}$$

I_0 is the Bessel function of zeroth order

k is the reaction rate constant and D is diffusivity

$$\phi = \sqrt{2r_0^2k/\Delta D}$$

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Now, let us look at another geometry of thin film deposition, many a times we use a tubular reactor and vertically stack our vapors to have thin film deposition.

So, such an arrangements shown in this figure here in which silicon vapors on which we want to deposit thin film are stacked vertically in a tubular reactor and so gas flow is from the left the concentration at the surface of the first vapor is C 0 and we want to know what is the radial distribution or the radial uniformity of the thin film of deposition on each vapor and there are certain parameters like delta which is separation between 2 vapors, and the radius. Now I will not going to into the details, but if you look here this gives you an expression that how the thickness or the deposition rates will vary along the radius and again if we say that my thickness is governed by mass transport not the reaction then it will be how the concentrations are distributed along the radius.

So, C 0 is at the outer surface of this vapor because gases are flowing outside and then they will move in right. So, the gases are mostly flow flowing here and then they will be go inside and spread and then go out and then go in right for reaction. So, C 0 is the concentration here and C r at any radius. So, C 0 is at r 0 at the periphery and this is the ratio between the two were I zero Bessel function of zeroth order we do not need to worry of this if you know this quality in the brackets which is given then you can find the what is the Bessel function of that quality in a standard mathematical table of Bessel functions.

What is important is this factor here, because it is here and here at both the places this depends on the radius, delta and the diffusivity of the reactance in the gas phase. Now if you look at here if phi is very small, if phi is very small you can see that deposition is very uniform. If phi is very large you have very worst differences in the deposition rate, relative thickness there is a lot along the radius this is the r over r 0 of the vapor. Now what does phi small mean? Phi small means that your radius is high and k reaction rate constant is high so that it does not depend on the reaction rate and your delta and sorry these are small r 0 k r small for that. So, that if the reaction rate is slow then it gives enough time for the gases to defuse and also diffusivity is high and also the separation between the vapors is high.

So, you can calculate using these quantities to some extends what would be your redial deposition rate uniformity in this kind of reactor and arrangement? And these are very often used to deposits a silicon oxide on a large number of vapors in one go. So, this is about the uniformity with the geometry reactor and number of vapors.

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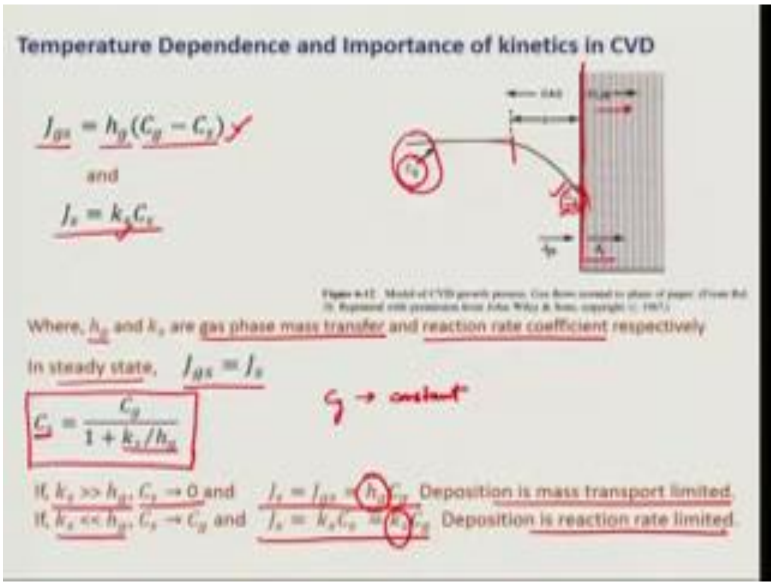

Temperature Dependence and Importance of kinetics in CVD

$J_{gs} = h_g(C_g - C_s)$ ✓

and

$J_s = k_s C_s$

Where, h_g and k_s are gas phase mass transfer and reaction rate coefficient respectively

In steady state, $J_{gs} = J_s$

$$\boxed{C_s = \frac{C_g}{1 + k_s/h_g}}$$

$C_g \rightarrow$ constant

If, $k_s >> h_g$, $C_s \rightarrow 0$ and $J_s = J_{gs} = h_g C_g$ Deposition is mass transport limited.

If, $k_s << h_g$, $C_s \rightarrow C_g$ and $J_s = k_s C_s = k_s C_g$ Deposition is reaction rate limited.

Now, let us have a look how this also depends on the temperature because we had said in the previous slide that is the reaction rate is slow then you will have the more uniformity.

Now let us look at that aspect how the temperature dependents help in uniformity and thickness uniformity.

So, in this picture if you see that my substrate is vertical like this and this is my film deposition. So, this is formation of film, my gases are flowing in the bulk perpendicular to paper or this plain of the screen, this is my boundary layer at the surface of the of the substrate were the film is growing right. So, you will have a boundary layer because the gases are flowing with form of boundary layer at the interface of substrate. Now from the gas phase transport from bulk to the substrate which is the substrate the concentration at the substrate will depend on the concentration differences because this is the through diffusion and we have used a term h g; h g are gas phase mass transfer which is also related to diffusivity of gas in gas phase.

So, this gas phase mass transfer across the boundary layer, we have assumed that this is constant flow. So, we can maintain the C g in the bulk flow always. Now at surface whatever is the flux we do not want the buildup of concentration here so that this concentration differences drops below certain level then it will stop diffusion. So, there will be. So, if there is a more concentration here then the reaction rate will be higher and it will try to keep the same flux from the gas phase. Now the flux which is being consumed to convert this gases into film will be depend on the film deposition rate. So, the film deposition rate will depend on the concentration at the surface and reaction rate.

So, how fast the thin film growing or the reactant is converting to thin film will dependent on the constriction at the surface and also reaction rate. Now in study state to avoid any buildup of concentration, both of these fluxes should be equal. So whatever coming in from the gas phase is reacting at the surface to give you thin film so that this C g minus C s will remain constant and that is your study state. In study state if you solve this using this equation, you will get and expression like this so, this C g is constant. Now the concentration at the surface will depend on the ratio of K s over h g means reaction rate over mass transfer rate.

Suppose if K s is very high; so the reaction rate is very fast and we can do that by having appropriate temperature, suppose a reaction happens very fast which means increase the temperature of the substrate then by increasing the temperature, we can increase the reaction rate coefficient such that if K s is very high compare to h g or the mass transfer then my concentration will drop to 0 at the surface, because reaction rate is very fast here. So, whatever is coming to the surface is reacting to give you thin film very fast ok.

Now, if that is happening then my thin film deposition rate will depend on mass transfer then this reaction holds if C s is 0 then it will depend on my mass transfer. If the reaction rate is very high then my deposition rate will depend on mass transfer rate; on the other side if my mass transfer is very high and reaction rate is very low then these two concentrations will become equal; because my mass transfer is very fast and I am not able to use the concentration at the surface to convert into thin film at higher rate so these two concentrations over time will become equal. If that happen my thin film growth rate or the flux which is being converted to thin film will depend on reaction rate.

So, in this case deposition mass transfer limited and deposition is reaction rate limited. So, there are two process: mass transfer and reaction and they are happening in series one after another. So, the slowest of these rates will control your deposition rate.

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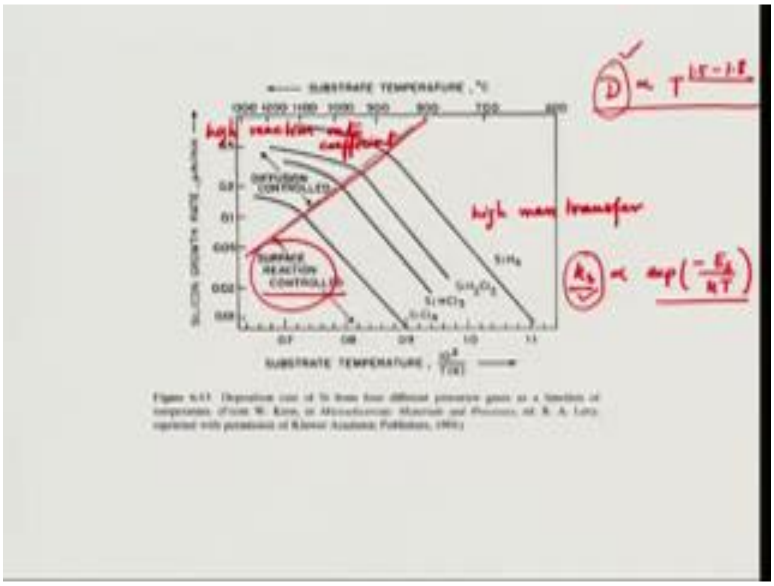

Let us have a look at this in how we can use this information to adjust our deposition parameters. If you look at in this graph, the substrates temperature and for deposition of silicon from silane gas using different gases is shown. Now if you see in this region so this is a demarcation line of two different regimes, in this regime it is surface reaction control means mass transfer rate is very high so, this is high mass transfer rate, if mass transfer rate is high then it is controlled by surface reaction rate and in on the other side it is diffusion control which means reaction rate is very high.

So, these are different regimes we can find demarcation between them following the thermodynamics and kinetics of your reactor or by some experimentation. Now what is important that we want to have uniform deposition, for uniform deposition my mass transfer should be very high so that we can control the deposition rate by the; and my mass also should be high and reaction rate is should be slow. So, that my concentration is distributed very evenly across the large area or all the weepers. So, that is one thing. However, if you see that if you are not able to control the temperature very effectively, if your temperature is wearing different places then this reaction rate is dependent on temperature as minus E s over k T. So, the reaction rate is a heinous type expression. So, it depends on temperature exponentially. So, if this small in non uniformity in temperature, it will affect your reaction rate to a large extend.

Since your deposition rate is controlled by reaction rate then you will have difference in reaction rate or the deposition rate at different points, because you are temperature is not uniform. On the other side when you have a high reaction rate. So, temperature is high enough, that you do not worry about the reaction rate at all. So, whatever is transferred is being converted into your thin film. So, you are not dependent on mass transfer; mass transfer does not depend on temperature to that extent not exponentially, it has a week dependence of T to power D that the diffusivity or mass transfer had a temperature dependence of about 1.5, 1.8 in that regime.

So, once you have that diffusivity not the exponential dependence then you can work with small non uniformity temperature, but then your diffusivity should be very high. So, now, depending on what you want you can control your reaction such that either is in diffusion control or mass transfer control or surface reaction control. If you can control that temperature very uniformly across all the substrate, it is always good to be surface reaction control, but if you cannot do this then you have to make sure that your diffusivity is very high and you work in diffusion control.

So, with this will stop here in this lecture and we will continue our discussion using some of example we will go into thermodynamic of the reaction in the next lecture.

Thank you very much.