Fundamentals of Materials Processing-2

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Module – 02
Lecture – 13
Chemical Vapor Deposition

Welcome to lecture 13 of thin film deposition module and in this will continue our discussion on chemical vapor deposition. In the previous lecture we had looked at how the reactor geometry and vapor placement place a role in a determining how the uniformity of the thin film on one vapor or across many vapors will look like. So, that gives us an idea how to design a word reactor. We also looked at how the reaction can be control into two different regimes or the deposition rates such that it controlled by either the reaction rate or the mass transfer. So, we have that one additional parameter to adjust by which we can ensure the uniformity of thin film deposition.

Now, we will look at the thermodynamics of the reaction and how that thermodynamics plays a vital role in remaining that what temperature and how to tune our reaction to have a good uniformity and control over thin film deposition.

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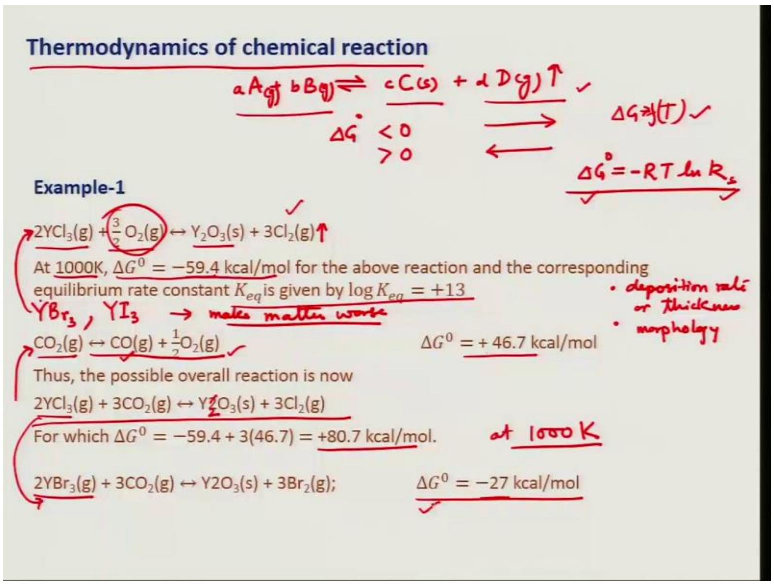

Thermodynamics of chemical reaction

$aA(g) + bB(g) \rightleftharpoons cC(s) + dD(g)\uparrow$ ✓

$\Delta G^{\circ} < 0 \longrightarrow$

$> 0 \longleftarrow$

$\Delta G \rightarrow f(T)$ ✓

$\Delta G^{\circ} = -RT \ln K_s$

Example-1

$2YCl_3(g) + \frac{3}{2}O_2(g) \leftrightarrow Y_2O_3(s) + 3Cl_2(g)\uparrow$

At 1000K, $\Delta G^0 = -59.4$ kcal/mol for the above reaction and the corresponding equilibrium rate constant K_{eq} is given by $\log K_{eq} = +13$

YBr_3, YI_3 → makes matter worse

- deposition rate or thickness
- morphology

$CO_2(g) \leftrightarrow CO(g) + \frac{1}{2}O_2(g)$ ✓ $\Delta G^0 = +46.7$ kcal/mol

Thus, the possible overall reaction is now

$2YCl_3(g) + 3CO_2(g) \leftrightarrow Y_2O_3(s) + 3Cl_2(g)$

For which $\Delta G^0 = -59.4 + 3(46.7) = +80.7$ kcal/mol. at 1000 K

$2YBr_3(g) + 3CO_2(g) \leftrightarrow Y2O_3(s) + 3Br_2(g)$; $\Delta G^0 = -27$ kcal/mol

So, in this lecture we will talk about mostly thermodynamics of the reaction. So, as you can see that thermodynamics of a chemical reaction is important for chemical vapor deposition, let say that we have a reaction were a molecules of A and b molecules of B react to give c molecules of C which is a solid, plus d molecules of D which is a byproduct and it goes into gas phase these both are gas phase.

These are my reactants, this is my product and this is my buy product. So, this is what a chemical reaction would look like for a thin film deposition process. Now important part of this thin film deposition is delta G reaction the change in free energy for this reaction and we know if the delta G is less than 0 for this reaction, than this reaction will forward in the right direction towards right. So, more reactants will react to give you product. If delta G for this reaction is greater than 0 then a reversal reaction will happen. So, you will not get more reaction you will get less reaction and your reactants will remain as reactants they will not react to give you product.

Now, delta G is as very strong function of temperature that is why it is very important to understand how the temperature is going to play the role to adjust the reaction rates and how we can tune the chemistry of the reaction such that we have a control over the reaction rate. Now we also know that delta G is given as RT ln k. So, this is my on k is my reaction rate constant that we had encountered in the previous lecture when we were discussing reaction rate verses mass transport regime. So, this is my reaction rate constant and it depends upon on change in free energy.

Now, let us take an example of deposition of yttrium using these two gases; yttrium chloride and oxygen; if you react at on 1000 Kelvin you will get yttrium by 2 or 3 which is solid forms or thin film and chlorine is the byproduct.

So, you can use this reaction to design your thin film deposition process; however, the delta G for this reaction is very large and negative; negative very large which means that for this reaction it will proceed towards right very fast because K is K equilibrium is a positive 13. So, you will have very fast reaction; fast reaction means fast deposition of the thin film, once you have very fast deposition of thin film you are not able to control two things, you are not able to control deposition rate or thickness of the film and you are not able to control morphology. So, we do not want my reaction to happen very fast we want to it happen at a slow rate so that we can control and stop whenever we want. So, slow deposition rates are preferred.

Now we can also use substitute of these gases in terms of yttrium borate or yttrium iodide; we can replace this yttrium chloride gas by these two, but these make matter worse, they make this reaction rate go even faster, now what can be done that we can control this source of oxygen and how we can do that? We can use another reaction for supply of oxygen, we can use carbon dioxide gas and at that temperature around 1000 Kelvin this will dissociate into carbon monoxide and oxygen and this reaction has a delta G which is positive. Now the overall reaction if we combine these to reaction becomes this at 1000 Kelvin. This reaction be becomes this for this delta G is still very positive, which means the reaction will not proceed towards right resulting in yttrium .

So, now, we want the delta G to be negative, but very small number; what we can do is now we can replace this yttrium fluoride with yttrium bromide gas and use the same reaction such that we are again delta G is negative. Once delta G is negative again then we can and its and its smaller than this number, then we can you this to the designed our reaction for thin film deposition. So, this is an example of how you tune you the reaction chemistry in the thermodynamics to suite your purpose, this delta G should be small and negative that is my example 1.

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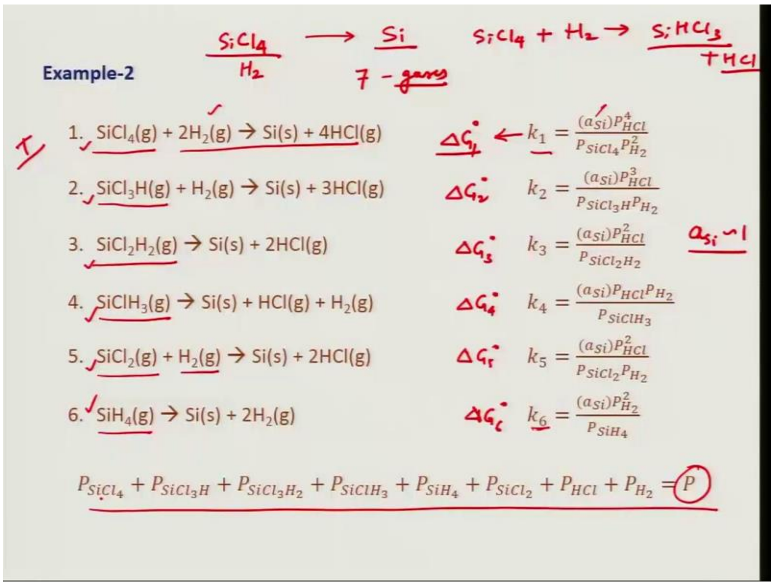

$\frac{SiCl_4}{H_2} \longrightarrow \underline{Si}$ $\quad SiCl_4 + H_2 \rightarrow \underline{SiHCl_3} + \underline{HCl}$

Example-2

7 - gases

1. $SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl(g)$ $\quad \Delta G_1^\circ \leftarrow k_1 = \frac{(a_{Si})P_{HCl}^4}{P_{SiCl_4}P_{H_2}^2}$
2. $SiCl_3H(g) + H_2(g) \rightarrow Si(s) + 3HCl(g)$ $\quad \Delta G_2^\circ \quad k_2 = \frac{(a_{Si})P_{HCl}^3}{P_{SiCl_3H}P_{H_2}}$
3. $SiCl_2H_2(g) \rightarrow Si(s) + 2HCl(g)$ $\quad \Delta G_3^\circ \quad k_3 = \frac{(a_{Si})P_{HCl}^2}{P_{SiCl_2H_2}}$ $\quad a_{Si} \sim 1$
4. $SiClH_3(g) \rightarrow Si(s) + HCl(g) + H_2(g)$ $\quad \Delta G_4^\circ \quad k_4 = \frac{(a_{Si})P_{HCl}P_{H_2}}{P_{SiClH_3}}$
5. $SiCl_2(g) + H_2(g) \rightarrow Si(s) + 2HCl(g)$ $\quad \Delta G_5^\circ \quad k_5 = \frac{(a_{Si})P_{HCl}^2}{P_{SiCl_2}P_{H_2}}$
6. $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$ $\quad \Delta G_6^\circ \quad k_6 = \frac{(a_{Si})P_{H_2}^2}{P_{SiH_4}}$

$$P_{SiCl_4} + P_{SiCl_3H} + P_{SiCl_3H_2} + P_{SiClH_3} + P_{SiH_4} + P_{SiCl_2} + P_{HCl} + P_{H_2} = \textcircled{P}$$

Now, have a look at another example, in which we are using Silane gas Si Cl or Tetrachlorosilane to deposit silicon. Now it is found then once you have this reduction of silane tetrachloride with hydrogen, you will not only forms silicon you will have many other species, this is experimentally observed we have many thing that will happen. This silicon tetrachloride will react with silicon, this is the straight forward reaction; however, you will also find that you have a Trichloro silane, Dichloro silane, Chloro silane, Dichloro silicon and this silane. So, all these 6 plus hydrogen 7 gases are found in the reactor when you start with just silicon tetrachloride; because in some reactions silicon tetrachloride with react with hydrogen to give you Si H Cl 3 plus hydrogen and chlorine.

So, this reaction will also happen inside the reactor in the gas phase. So, you will have all this gaseous species present and they have based on their reaction rate constants can be defined using these equations. Reaction rate constants are nothing but consecration or activities on the of the product divide by activities of the reactant. Activities of gaseous are in terms of their partial pressures and activity of solid as can be assumed to be 1, activity of silicon can be assumed to be 1. So, we have different reaction rate constant for this and which we will which are defined by the delta G of the reaction or change in free energy for that reaction at a given temperature T. So, we have the; this is delta G 1, delta G 2, delta G 3, G 4 delta G 5 and delta G 6. So, we have this change in free energy for these reactions and which we can convert into reaction rate constant. Reaction rate constants are depend on the partial pressures of these gases according to these expressions.

Now, we also know. So, we have 7 gases; 6 gases, 6 are listed here and seventh one would be hydrogen; we want to know how much of these gases are present at a given temperature T, we know how much silane we are flowing in at what pressure and how much hydrogen we have we know these two constants, but we do not know how the other gases the concentration of other gases will change with temperature. So, we can use this information to calculate that also since we have 7 unknowns we need 7 equations; we have these 6 equations and 7th equation is this that some of all partial pressure is the total pressure p within the reactor which is known.

So, we had two things: we know how much silane or silane tetrachloride we have flowing in and how much hydrogen we have flowing in we know that and we the total pressure inside the chamber. So, we can control these two, but we do not know how after reactions at a given temperature how the concentration profile for different gases or partial pressure profile will look like; to get that we can use calculations to solve this.

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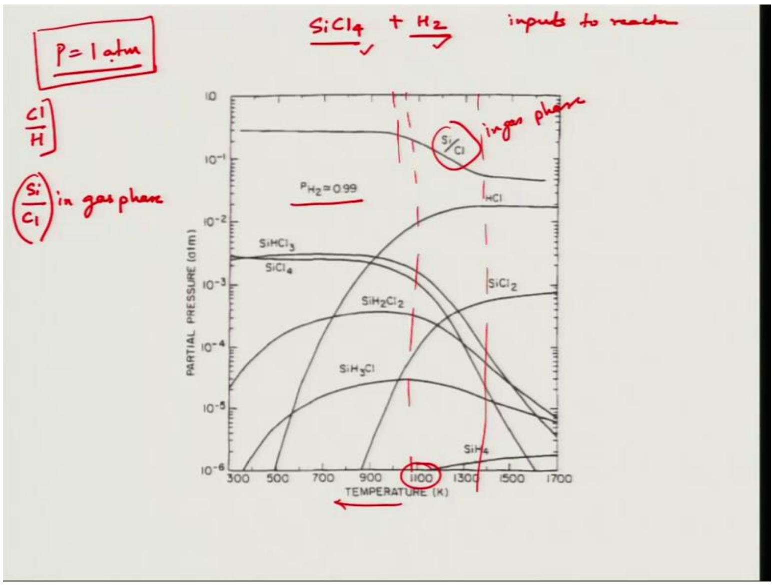

Now, in the next figure let us look at the implication of these calculations. So, first thing is to notice is that our partial pressure of hydrogen is very high. So, P is equal to 1 atmosphere, all most all the partial pressure inside the chamber is hydrogen and my reaction is described in that way. What we also know that is chlorine to hydrogen ratio right because we have silane silicon tetrachloride coming in my reactor and. So, Si C l 4 and hydrogen these are two inputs to reactor.

So, from this we can know that what is C l by H ratio; now after calculating what are the partial pressures of gases inside the chamber, we can convert that into silicon by C l ratio in gas phase because chlorine to hydrogen will remain constant, all the chlorine will be in gas phase all the hydrogen will remain in gas phase. Silicon however, will be in gas phase as different gases, but also will be in solid face has thin film. So, from partial pressure of gases we can calculate silicon to chlorine in the gas phase after we go through this calculations and we can calculate these partial pressures of different gases then we can calculate how much is the silicon to chlorine ratio in gas phase and from this we can judge what is happening inside the reactor.

Now, let us have a look at this at a very low temperatures my silicon to chlorine ratio in the gas phases very high right if the silicon is high in the gas phase, which means we are not getting deposition of the silicon right we want silicon to be in the solid phase not in the gas phase for deposition. So, if you see how these different pressures change with temperature so you can design your reaction around 1100 degree c, such that your silicon in the gas phase start to reduce. So, this is your lower boundary and then you can have this re region we have your reaction takes place.

So, silicon to chlorine in gas phase. So, as silicon content in gas phase goes down which means that you are getting more and more silicon deposition and if you lower the temperature then your silicon in gas phase goes up for the same silane to hydrogen ratio, which means you can also atch away the silicon which is deposited on the substrate. So, when your de depositing silicon you are this deposition and atching simultaneously and you can adjust your reactions by controlling at the temperature or the input which are two silicon chloride and hydrogen. So, this is how thermo dynamics plays a very important role in how to decide about your chemical vapor deposition process.

So, far we have been whatever process we are doing, we are doing at one atmosphere and may be at a slightly lower pressure.

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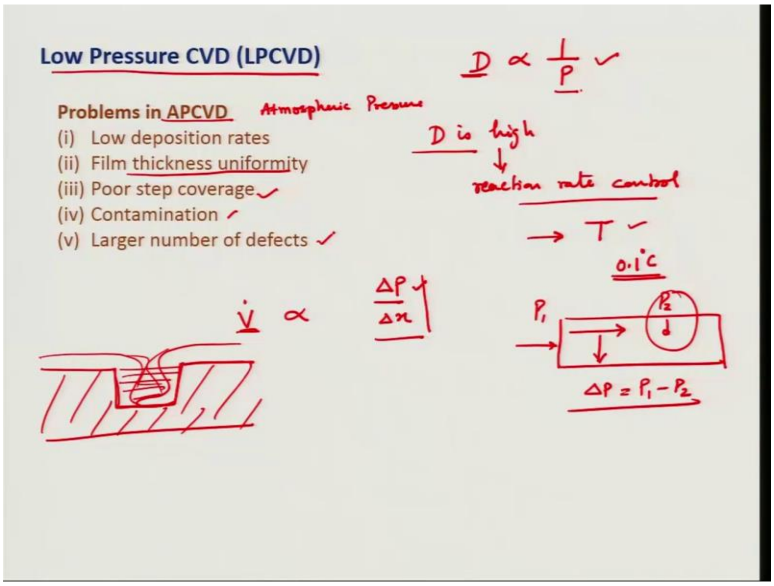

Low Pressure CVD (LPCVD)

Problems in APCVD

(i) Low deposition rates
(ii) Film thickness uniformity
(iii) Poor step coverage
(iv) Contamination
(v) Larger number of defects

So, the total pressure in this case was 1 atmosphere; however, we can also use low pressure CVD; now how does low pressure CVD help? Remember that our diffusion coefficient was proportional to 1 over P. Diffusivity in gas phase was proportional to 1 over P right and if the diffusivity is higher, then we are working in the reaction rate control. D is high or mass transfer is high then we are into reaction rate control, if we have reaction rate control which is a (Refer Time: 17:47) by temperature prime in the we can control temperature to very uniformly to a very large accuracy, we can control the temperature up to the 0.1 degree c accuracy. So, temperature control we have you can design our system with very high efficient temperature control, but mass transfer it is another thing. So, we need want to keep high diffusivity and for high diffusivity we need to lower the pressure.

So, some of the problems with APCVD which is atmospheric pressure, CVD chemical vapor deposition are low deposition rates remember that when we were discussing again Poiseuille equation in the volumetric flow rate was proportional to pressure gradient. If we have lower pressures then in inside the chamber, so this pressure gradient is from the inlet inside the. So, this is inlet pressure P 1 and P 2 inside the chamber. So, P 1 minus P 2 is your delta P right. So, by decreasing P 2, you can increase the pressure gradient. So, more volumetric flow rate inside the chamber, you have a more volumetric flow rate and simultaneously you have higher diffusivity. So, both you have bulk flow and your diffusivity is has increased. So, your mass transfer has increased which will result in film thickness uniformity if you control temperature uniformity.

Now this atmospheric pressure CVD also has poor step coverage, which means suppose if you have a feature like this on your substrate. So, atmospheric pressure will not result in the portion like this, it will not cover the entire this recess in the substrate because your mass transfer is not higher, now reaction rate is faster, but we your mass transfer is high then you will have uniform deposition. So, this is the problem which is over come in LPCVD, with high pressure or atmospheric pressure CVD you are also flowing in lot of gases because to maintain the same deposition rate and when your flow rates are high not the volumetric flow rate, but the flow rates are high for the same deposition rate then you will have large contamination because you had not pump down or removed residual gases and large number of defects. So, in this way your LPCVD process is an improvement over atmospheric pressure CVD and it results in better uniformity and better purity of thin films.

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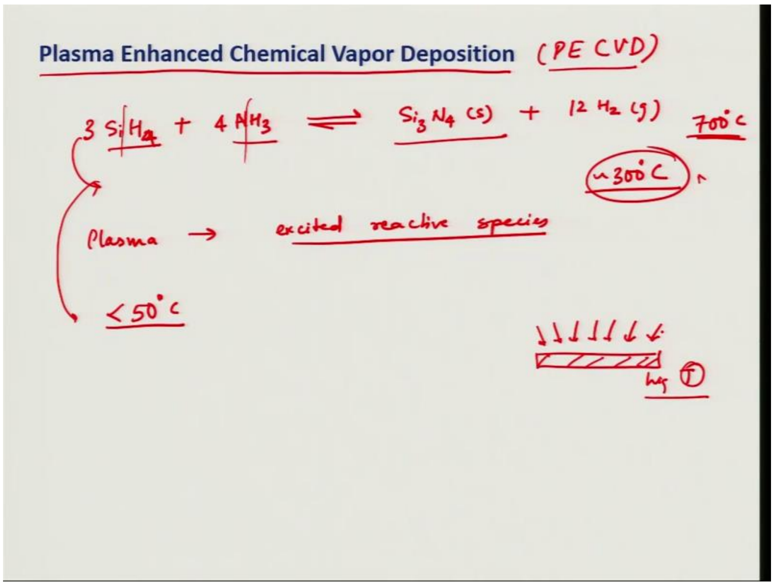

Plasma Enhanced Chemical Vapor Deposition (PE CVD)

$3SiH_4 + 4NH_3 \rightleftharpoons Si_3N_4(s) + 12H_2(g)$ 700°C

~300°C

Plasma → excited reactive species

< 50°C

Now, let us also look at another variant of CVD which is called PECVD plasma enhanced chemical vapor deposition. Remember that when we were discussing sputtering process we had described plasma and plasma was consisting of irons, electrons, neutral species and these irons also provide an excited species of the reactants. So, how does this help suppose we are using reaction for deposition of let us take an example of nitride. So, if you are depositing silicon nitride Si using Si H 4 sorry plus yes 4 NH 3, this is 3 silane 4 NH 3 both are gases and you are doing this reaction to deposit silicon Si 3 N 4 which is the electric film on your silicon substrate and you will get 12 hydrogen. Now this reaction happens at around 700 degree C. Now suppose you want to deposit this silicon nitride on glass, glass has a melting temperature or transaction glassension temperature around 400 to 500 degree C. So, you cannot go beyond that temperature with the glass substrate.

So, what do we do? We can use the PCVD process, in which this the same reaction can happen at a much lower a temperature around 300 degree C. Now why would that happened? Because in plasma you have excited reactive species, mainly namely the molecules of silane and ammonia, which will react at much lower temperature because the energy to break the bonds of these and keep this nitrogen and silicon in exigencies excited state where they react more readily is happened by plasma. So, in this way we can use plasma enhanced chemical vapor deposition to lower the temperature of for many many reactions and we can even do some of these deposition down to 50 degree C, the process is have been developed to deposit silicon nitrate down to below 50 degree C less than 50 degree C temperatures.

So, by using this PECVD process we can load the reaction temperature because the energy that was supposed to be coming from the temperature is now coming from plasma. This has one added benefit we do not need to keep our substrate at high temperature; this is my substrate at high temperature. If I substrate this high temperature for the reaction then we also have temperature related modifications in the surface or in the growing film; suppose I have something some pervious processes or thin films which I do not want to expose to high temperature. So, if we can lower the temperature we can also use benefit from that.

Secondly, we can also use this bombardment of ions right ions are present so they will be constantly bombarding the growing film, we can adjust the parameters of deposition such that these bombardment of the ions on the growing film will make the film more denser and more uniform. So, these are some added benefits of plasma enhanced chemical vapor deposition process.

So, with this we will stop here for this lecture; in the next lecture we will also look at another variant of chemical vapor deposition process and then from there we will discuss how we can use a these process for a process called epitaxial growth.

Thank you very much.