Chemical Reaction Engineering - II

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Module - 3
Lecture - 12
Case Study: Chemical Vapor Deposition

So, let us next look at a specific case study.

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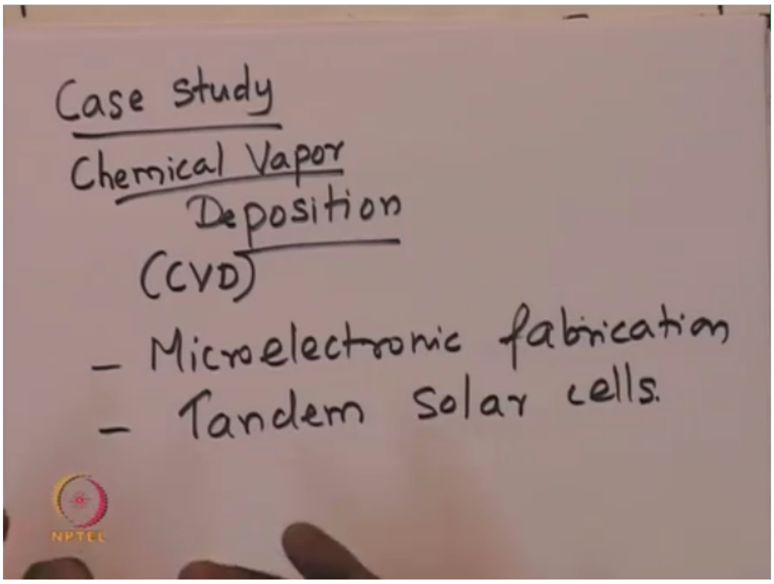

Case Study

Chemical Vapor Deposition (CVD)

- Microelectronic fabrication
- Tandem solar cells.

So, we will look at the chemical vapor deposition process. Take the example of chemical vapor deposition process, which here after I will refer to as CVD. So, chemical vapor deposition is actually an important process in the microelectronic fabrication. And it actually plays a strong role in manufacturing the tandem or the multilayer solar cells. So, the chemical vapor deposition is essentially depositing a particular material on a given substrate.

So, it is very similar to the heterogeneous catalysis process. And it has several applications in microelectronic fabrication. And it has applications in manufacturing of tandem solar cells. So, we will take a specific case of a chemical vapor deposition which is applicable to microelectronic fabrication and see how it can be viewed as a heterogeneous catalytic system. And how it can be modelled in order to obtain certain design parameters. An interesting example of that is growth of a germanium epitaxial film.

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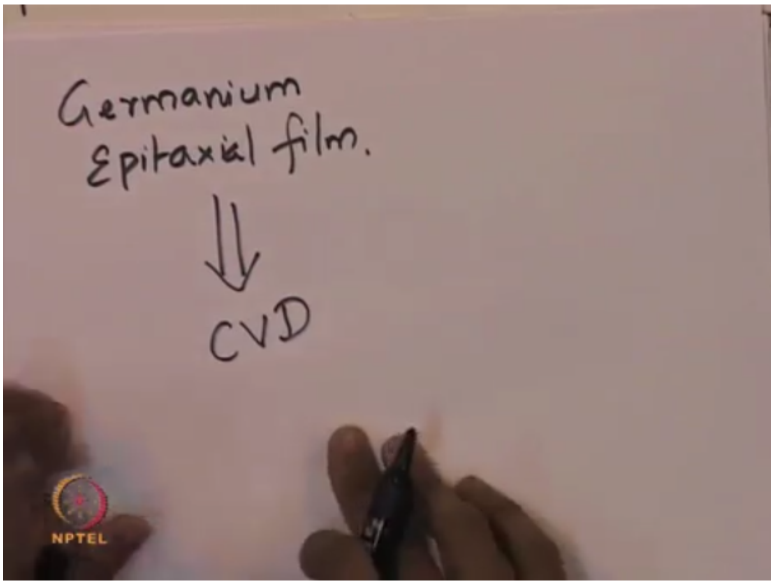

Germanium
Epitaxial film.
⇓
CVD

Germanium epitaxial film is actually an interesting example of; so, while manufacturing in microelectronic fabrication it is important to have different layers between the gallium arsenides and silicon. And so, germanium epitaxial film is a, serves a very good purpose of acting as an inter-layer between the silicon layer which is present and on top of it will be the gallium arsenide. It also acts as a good contact layer.

So, the growth of this epitaxial film is actually obtained by using this process called the chemical vapor deposition. So, the mechanism that actually governs such a deposition process is actually very similar to that of the heterogeneous catalytic reaction.

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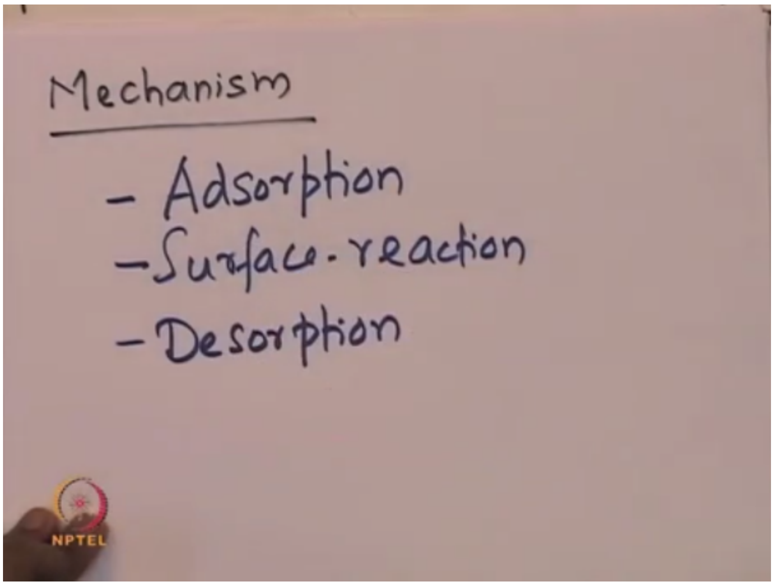

Mechanism

- Adsorption
- Surface-reaction
- Desorption

So, if we look at the mechanism, it is very similar to that of the heterogeneous catalytic systems. So, it involves the classical 3 processes. One is the adsorption, the adsorption of the reactants onto the surface of a substrate and followed by a surface reaction and then followed by a desorption. In addition to this there may be gas phase reactions. So, it is the adsorption of reactants onto a substrate surface followed by a surface reaction.

And then followed by a desorption depending upon the nature of the reaction. In some cases, there may not be a desorption. And in some cases, there may be a desorption step. So, it is very similar to the catalytic heterogeneous catalysis processes that we have learnt so far. And so, we will use those principles in order to model this chemotax, epitaxial film growth process. So, the mechanism, it involves 3 steps the first step is the, actually 4 steps.

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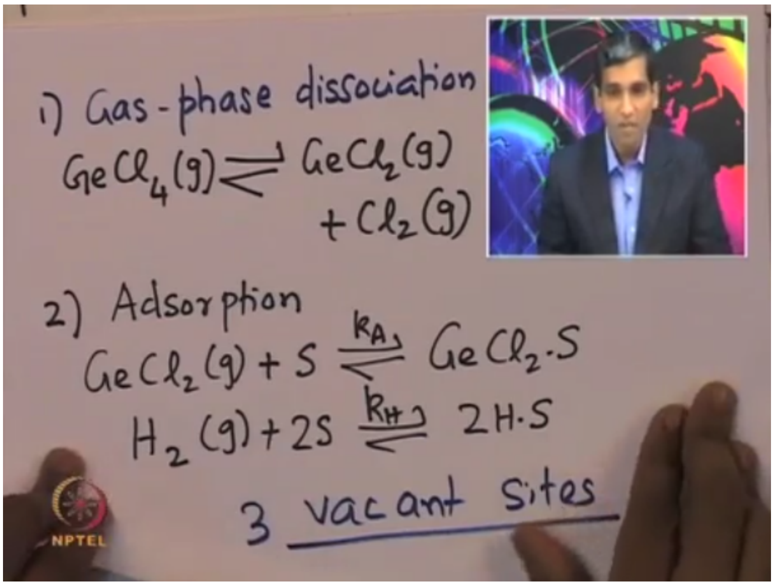

i) Gas-phase dissociation

$$GeCl_4(g) \rightleftharpoons GeCl_2(g) + Cl_2(g)$$

2) Adsorption

$$GeCl_2(g) + S \underset{}{\overset{k_A}{\rightleftharpoons}} GeCl_2 \cdot S$$

$$H_2(g) + 2S \overset{k_H}{\rightleftharpoons} 2H \cdot S$$

3 vacant sites

First step is the gas-phase dissociation step. Now, in the gas-phase dissociation, what happens is that the germanium chloride G e C l 4 in the gas phase; now that reversibly gets converted into the germanium C l 2 in the gas phase + C l 2 + chlorine. And the second step is the adsorption process where the germanium chloride G e C l 2 in the gas phase, it adsorbs onto the catalyst site, and it is an equilibrium process.

If k A is the specific constant corresponding to that and G e C l 2 dot S which is the, which basically represents the adsorption of germanium chloride onto the catalytic site. Now, here the germanium chloride actually reacts with the hydrogen. And so, in this particular case, the hydrogen gas in the gas phase also get adsorbed to the catalyst site. So, it actually interacts with 2 catalyst, 2 vacant catalyst site.

And so, if I, if there is specific constant for that particular forward step or adsorption step is k H, then it leads to, so, 1 molecule of hydrogen actually binds to 2 sites, 2 vacant sites which is available. And so, there are now 3 sites which are actually, so there are 3, 3 catalytic sites are actually involved. 3 vacant sites are required for this process, this catalytic process. And so, then the next step is basically the surface reaction. So, the next step is the surface reaction process where;

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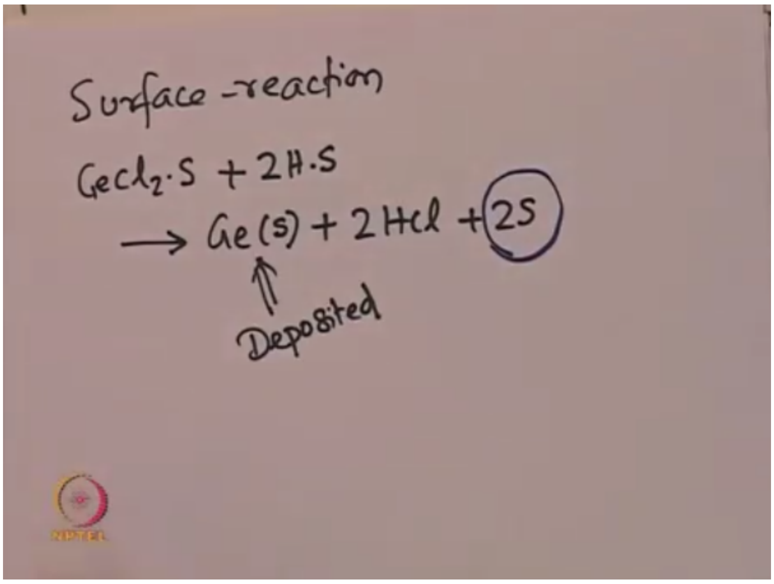

Surface -reaction

$GeCl_2 \cdot S + 2H \cdot S$

$\longrightarrow Ge(s) + 2HCl + \textcircled{2S}$

$\Uparrow$

Deposited

It is the surface reaction process. where the germanium chloride which is now adsorbed to the catalyst site, interacts with the hydrogen atoms which are actually adsorbted to vacant sites, 2 sites leading to formation of germanium in the solid form which is actually deposited on the surface of the substrate, + 2 H C L + 2 vacant sites. Now, so basically the, this is the one which is deposited.

The germanium which is formed because of this reaction is the one which is deposited on the substrate. After the reaction it may appear that there are only 2 sites which are actually left out. It may appear that there are only 2 vacant sites. Now, that is not true because the germanium which is deposited also becomes active. And so, subsequently the deposited germanium in its solid form also acts as an active site for binding of germanium chloride or the hydrogen atom itself.

So, therefore, in addition to the 2 vacant sites which are created, the germanium deposit also acts as an active site. And so, totally there are 3 vacant sites, 3 active sites that actually created because of the reaction. So, really there is no loss of active sites on the catalyst because of the reaction.

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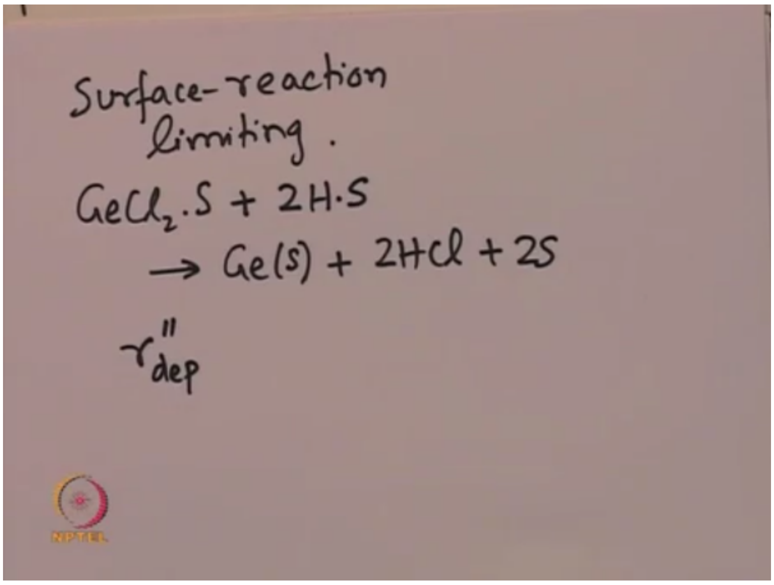

Surface-reaction limiting.

$GeCl_2 \cdot S + 2H \cdot S$

$\rightarrow Ge(s) + 2HCl + 2S$

r''_{dep}

So, now if I assume that the surface reaction is the limiting reaction. Then, I can write a, I can find out what is the rate of deposition of germanium. So, the surface reaction is G e C l 2 which is adsorbed to the surface + the 2 hydrogen atoms which are adsorbed to the surface leads to deposition of germanium in the solid form + 2 H C L + 2 vacant sites. So now, based on this reaction we can actually write a rate of deposition of germanium.

And so, the rate of deposition of germanium must be a function of the total number of active sites which are actually present, total number of active sites on which the germanium chloride is adsorbed. And also, the total number of active sites on which the hydrogen atoms are adsorbed.

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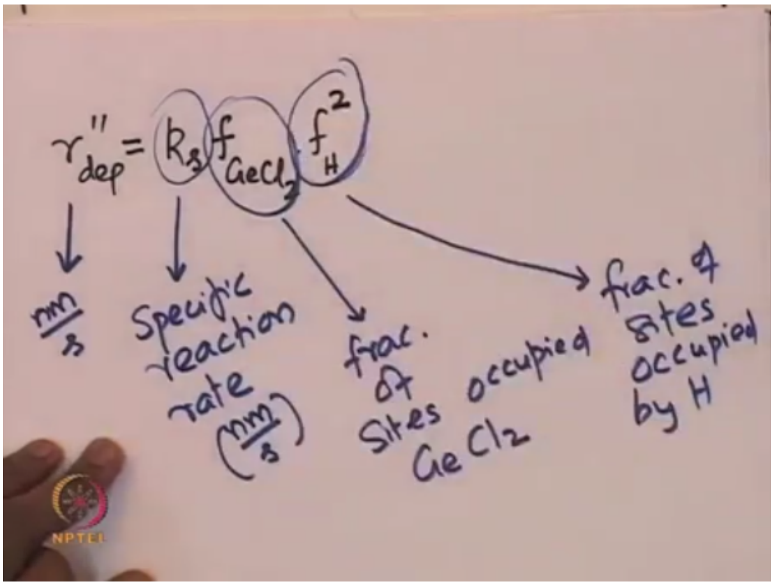

So, therefore we can write this reaction rate as r deposition is = the specific reaction rate multiplied by the fraction of sites which are occupied by the germanium chloride multiplied by the fraction of sites which is occupied by the hydrogen atom and a square of that. So, the reason why there is a square here, because for every reaction, every surface reaction which is assumed irreversible there are 2 catalytic sites are actually involved in the surface reaction, 2 catalytic sites containing adsorbed hydrogen atoms are actually involved in the reaction.

And therefore, the rate of deposition has to be some constant reaction, specific reaction rate multiplied by the fraction of sites on which the germanium chloride is adsorbed and multiplied by the square of the fraction of sites on which the hydrogen atom is adsorbed. And the units of the rate is actually nanometres per second. So, that is the rate. This can actually be converted into the molar units by multiplying the molar density.

And this is the specific reaction rate. And the units are nanometres per second. And this is the fraction of sites occupied by germanium chloride. And this is the fraction of sites occupied by hydrogen atom. So, this sort of captures the rate of deposition of germanium on the substrate. So, now the exercise is to find out what is the fraction of germanium chloride which is adsorbed onto the surface. And what is the fraction of the hydrogen atom which is adsorbed onto the surface.

So, this can be obtained by looking at the expression, looking at the adsorption process. And so, the adsorption step, so let us look a little more deeply into the adsorption steps. There are

2 adsorption steps. One is the germanium chloride which adsorbed onto the vacant sites and the hydrogen adsorbs onto 2 vacant sites.

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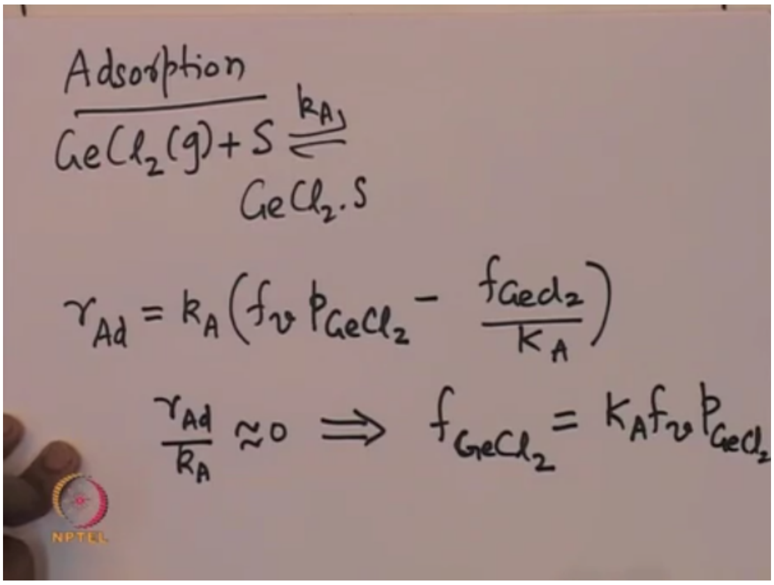

Adsorption

$$GeCl_2(g) + S \overset{k_{A1}}{\rightleftharpoons} GeCl_2 \cdot S$$

$$r_{Ad} = k_A \left(f_v p_{GeCl_2} - \frac{f_{GeCl_2}}{K_A} \right)$$

$$\frac{r_{Ad}}{k_A} \approx 0 \Rightarrow f_{GeCl_2} = K_A f_v p_{GeCl_2}$$

So, the first adsorption step is G e C l 2 in the gas phase + a particular vacant site. Reversibly it is an equilibrium process. And if the, k A is the corresponding specific constant, it gets adsorbed and leads to the adsorbed, germanium chloride adsorbed to the active site. So, the rate of adsorption is given by k A multiplied by the fraction of vacant sites f v multiplied by the partial pressure of the germanium chloride in the gas phase – the fraction of sites onto which the germanium chloride is adsorbed, divided by the corresponding equilibrium constant.

Now, because we assume that the surface reaction is the limiting reaction, the rate of adsorption has to be approximately 0. So, therefore the rate of adsorption divided by k A is approximately 0, from which one can estimate that the fraction of sites on which the germanium chloride is adsorbed, is given by K A into fraction of the vacant sites multiplied by the partial pressure of germanium chloride in the gas phase. Similarly, we can look at the other adsorption process which is the adsorption of hydrogen.

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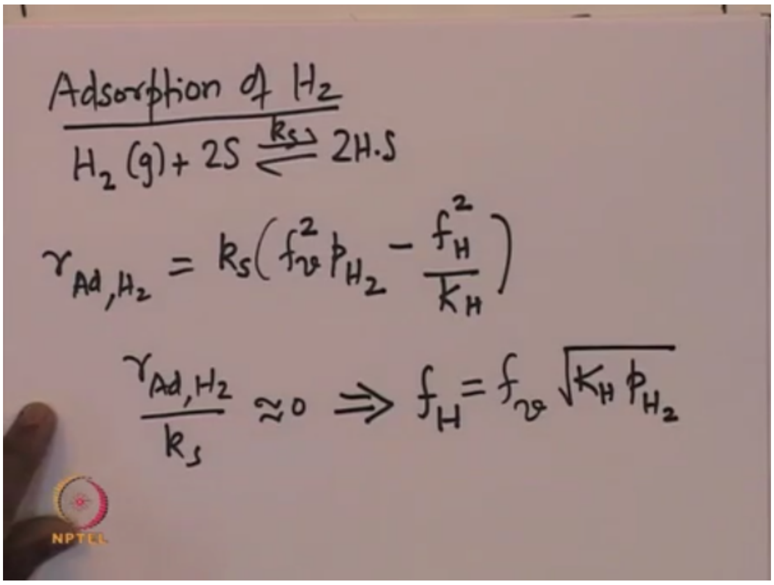

Adsorption of H_2

$$H_2(g) + 2S \overset{k_S}{\rightleftharpoons} 2H.S$$

$$r_{Ad,H_2} = k_S\left(f_v^2 p_{H_2} - \frac{f_H^2}{K_H}\right)$$

$$\frac{r_{Ad,H_2}}{k_S} \approx 0 \Rightarrow f_H = f_v\sqrt{K_H p_{H_2}}$$

And, so this, the reaction that corresponds to the adsorption desorption step is hydrogen + 2 catalytic vacant sites. If k s is the corresponding specific constant, leads to 2 sides in which the hydrogen atoms are bound. So, now the rate of adsorption of hydrogen is given by a specific constant k S multiplied by the, so it needs 2 vacant sites. So, the rate will be given by f v square multiplied by the partial pressure of hydrogen – the fraction of sites that are actually occupied by the hydrogen atom f H square divided by the corresponding equilibrium constant.

Because we assume that the surface reaction is a limiting reaction, we can actually say that the rate of adsorption of H 2 divided by k S is approximately 0. And from here, one can estimate that the fraction of sites to which the hydrogen atom is bound is given by the vacant sites f v multiplied by square root of the equilibrium constant for hydrogen adsorption multiplied by the partial pressure in the gas phase of hydrogen in the gas phase. So now, the total number of sites which is present in the catalyst is actually a constant, because it is a conservation property.

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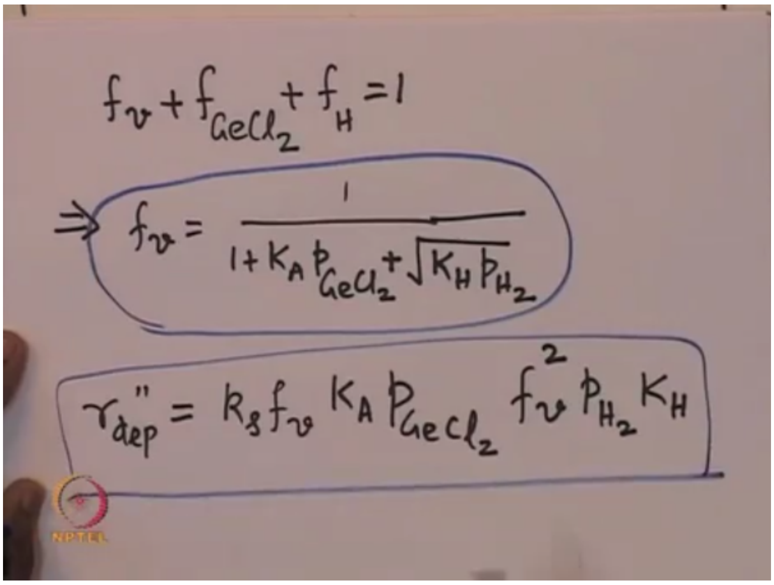

$$f_v + f_{GeCl_2} + f_H = 1$$

$$\Rightarrow \boxed{f_v = \frac{1}{1 + K_A p_{GeCl_2} + \sqrt{K_H p_{H_2}}}}$$

$$\boxed{r''_{dep} = k_s f_v K_A p_{GeCl_2} f_v^2 p_{H_2} K_H}$$

So, therefore that can be written, the conservation property can be written as f v which is the total fraction of vacant sites + the sites on which the germanium chloride is bound + the total fraction of sites on which the hydrogen atom is bound, that should be = 1, because the total number of sites which is present in the catalyst is a constant. And from here we can express that f v =, we can find, we can substitute the fractional sites on which the germanium chloride is bound and the fractional sites on which the hydrogen is bound.

And from this conservation property we can estimate that the fraction of vacant sites which is present is given by 1 divided by 1 + K A into partial pressure of germanium chloride in the gas phase + square root of the equilibrium constant for hydrogen adsorption multiplied by the partial pressure of hydrogen in the gas phase. So now, we can plug all these expressions into the rate of deposition. So, the rate of deposition is now given by k s into f v into K A. f v is the vacant site, number of vacant sites which is present.

Multiplied by the equilibrium constant for adsorption of germanium chloride, multiplied by the square of the number of vacant sites which is present multiplied by the partial pressure of hydrogen in the gas phase into the equilibrium constant for hydrogen. So, now we know the, we know what is the relationship between the vacant sites which is available and the partial pressure of the germanium chloride in the gas phase and the partial pressure of hydrogen in the gas phase. So, we can relate, we can plug in this expression in the reaction rate, deposition rate expression.

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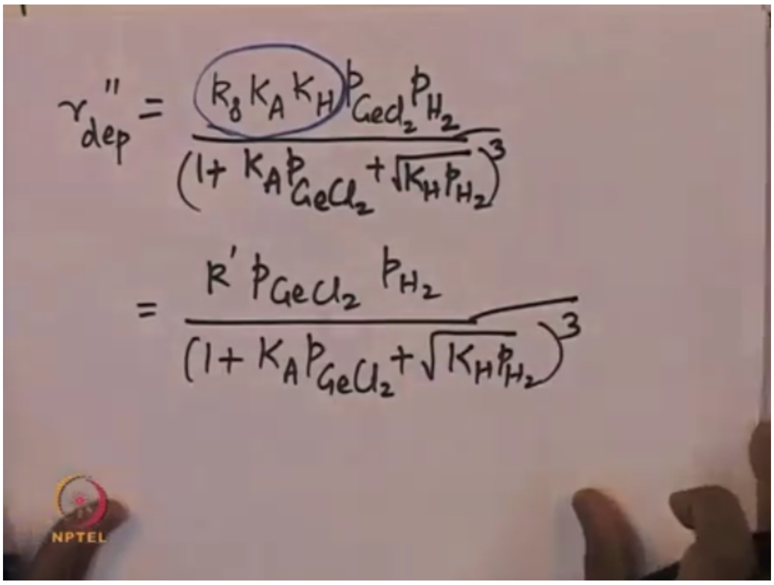

$$r''_{dep} = \frac{\boxed{k_s K_A K_H} p_{GeCl_2} p_{H_2}}{\left(1 + K_A p_{GeCl_2} + \sqrt{K_H p_{H_2}}\right)^3}$$

$$= \frac{k' p_{GeCl_2} p_{H_2}}{\left(1 + K_A p_{GeCl_2} + \sqrt{K_H p_{H_2}}\right)^3}$$

And so, we can rewrite the deposition rate expression as r deposition is = k s K A K H multiplied by the partial pressure of germanium in the gas phase multiplied by the partial pressure of hydrogen in the gas phase divided by 1 + K A partial pressure of germanium chloride in the gas phase + the square root of K H into P H 2 whole cube. So, now we can plugin we can actually collate these 3 constants, we can collate these 3 constants together and we can write it as 1 constant k prime.

That will be k prime into partial pressure of germanium chloride into partial pressure of hydrogen in the gas phase, divided by 1 + K A into partial pressure of germanium chloride whole cube. So now, when we, the germanium chloride is actually in the form of G e C l 4 C l 4 and not G e C l 2 which is the one which gets adsorbed onto the surface.

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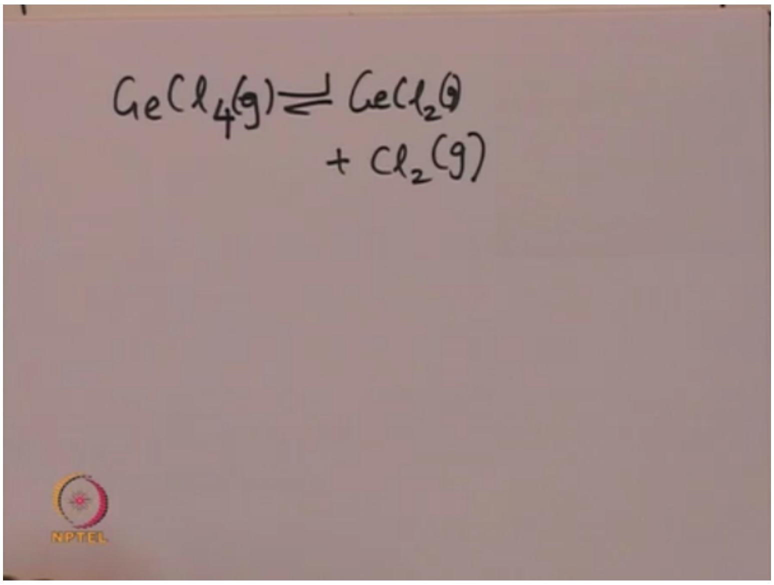

$$GeCl_4(g) \rightleftharpoons GeCl_2(g) + Cl_2(g)$$

So now, there is a gas phase reaction which actually is responsible for the conversion of or transformation of G e C l 4 into the C l 2 form. And so, the gas phase reaction is given by G e C l 4 in the gas phase C l 2 + chlorine. So, that is the gas phase reaction. Now one can write a an expression relating the gas phase partial pressure of the germanium chloride G e C l 4 and the germanium chloride G e C l 2. So, that can simply be written as, because it is a equilibrium conditions.

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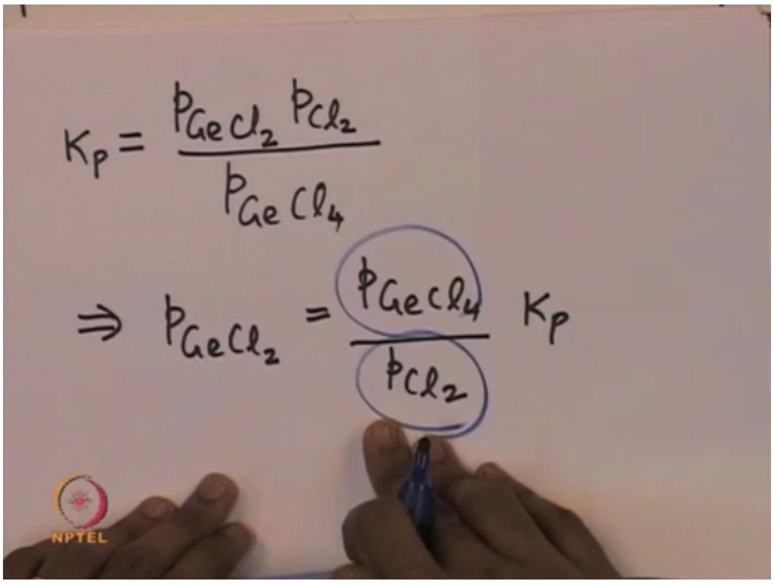

$$K_p = \frac{p_{GeCl_2}\, p_{Cl_2}}{p_{GeCl_4}}$$

$$\Rightarrow p_{GeCl_2} = \frac{p_{GeCl_4}}{p_{Cl_2}} K_p$$

We can write it as K P which is the corresponding equilibrium constant. And that should be = partial pressure of G e C l 2 multiplied by partial pressure of chlorine, divided by partial pressure of germanium C l 4. So, from here, we can find out what is the partial pressure of germanium G e C l 2 which is given by C l 4 divided by partial pressure of C l 2 multiplied by K P.

So, this is required to complete the problem because what is practically measurable quantity is actually the partial pressure of G e C l 4 and the partial pressure of chlorine. So, therefore it is required to express the partial pressure of G e C l 2 in the gas phase in terms of the measurable quantities. So, plugging in these measure, these expressions we can find that the net rate of deposition r dep.

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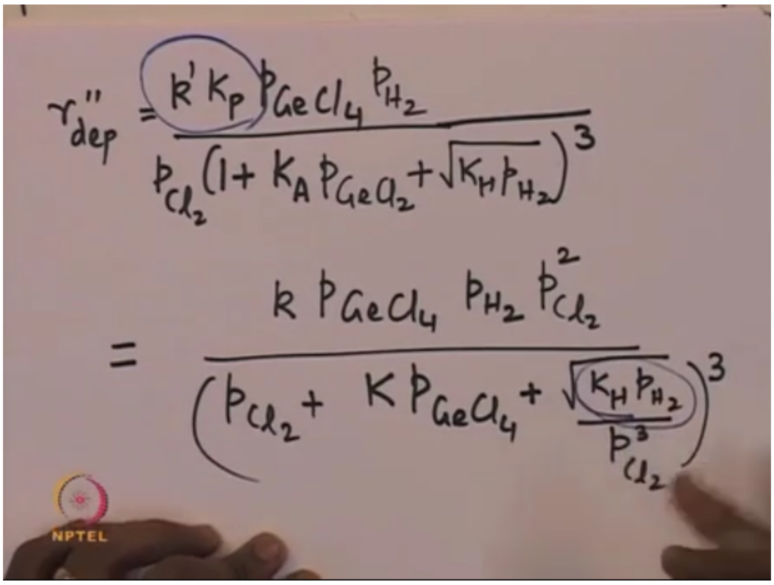

$$r''_{dep} = \frac{\boxed{k' K_P}\, p_{GeCl_4}\, p_{H_2}}{p_{Cl_2}\left(1 + K_A p_{GeCl_2} + \sqrt{K_H p_{H_2}}\right)^3}$$

$$= \frac{k\, p_{GeCl_4}\, p_{H_2}\, p_{Cl_2}^2}{\left(p_{Cl_2} + K p_{GeCl_4} + \sqrt{\frac{\boxed{K_H p_{H_2}}}{p_{Cl_2}^3}}\right)^3}$$

Net deposition rate is actually given by k prime K P into partial pressure of germanium chloride G e C l 4 into partial pressure of hydrogen divided by partial pressure of C l 2 into 1 + equilibrium constant K A multiplied by partial pressure of G e C l 2 + square root of K H into partial pressure of hydrogen, the whole cube. So, we can easily rewrite this expression as, with a little bit of algebra, we can rewrite this expression as k which is basically k prime into K P.

So, we can club these 2 constants here into 1 constant k multiplied by the partial pressure of G e C l 4 multiplied by the partial pressure of H 2 into partial pressure of C l 2 square, divided by the partial pressure of C l 2 + constant K into partial pressure of G e C l 4 + the square root of K H into partial pressure of H 2 divided by partial pressure of C l 2 cube, the whole cube. So now, suppose if the partial pressure of hydrogen in the K H into partial pressure of hydrogen is very small. Suppose if this quantity is very small, then we can rewrite this expression as r deposition.

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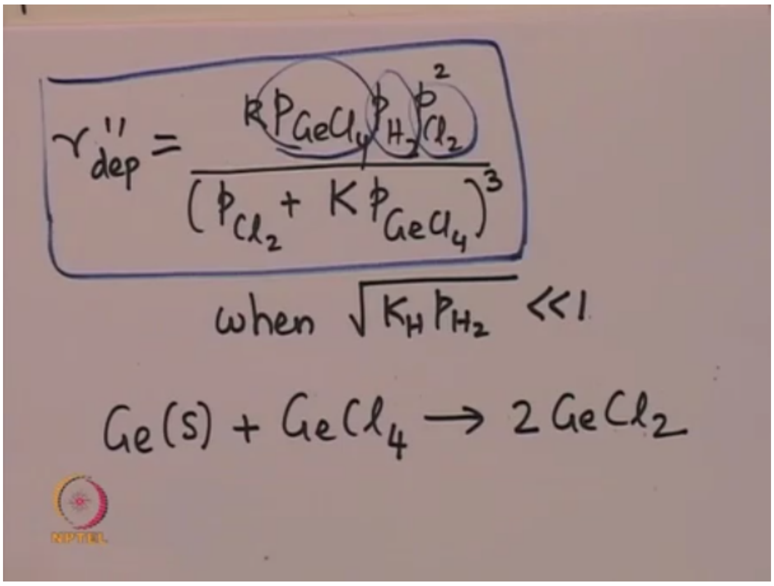

$$\boxed{r''_{dep} = \frac{K p_{GeCl_4} p_{H_2} p_{Cl_2}^{2}}{\left(p_{Cl_2} + K p_{GeCl_4}\right)^{3}}}$$

when $\sqrt{K_H p_{H_2}} \ll 1$

$$Ge(s) + GeCl_4 \rightarrow 2\,GeCl_2$$

The deposition rate is given by k into partial pressure of germanium chloride 4 multiplied by partial pressure of hydrogen multiplied by partial pressure of chlorine square divided by partial pressure of chlorine + modified constant K multiplied by the partial pressure of germanium chloride 4 in the gas phase whole cube. And this is valid only when square root of K H P H 2 is much smaller than 1. So, let us stare at this equation.

So, we will see that now we have expressed the rate of deposition as a function of the gas phase partial pressure of germanium chloride, which is a measurable quantity. And then, the partial pressure of hydrogen which is again a measurable quantity. And then, partial pressure of chlorine which is again a measurable quantity. So, from here we can find out what is the expression for the rate of deposition of germanium on the substrate.

Now, there is another process which can actually occur along with this. The germanium which is deposited onto the surface because of this reaction can actually react with the germanium chloride in order to form 2 germanium C l 2. So, this has actually being ignored in the current framework but in principle this can actually occur in reality. So, let us summarise what we have learnt today. So, what we have seen is we have, we completed the reactor design that we initiated in the last lecture.

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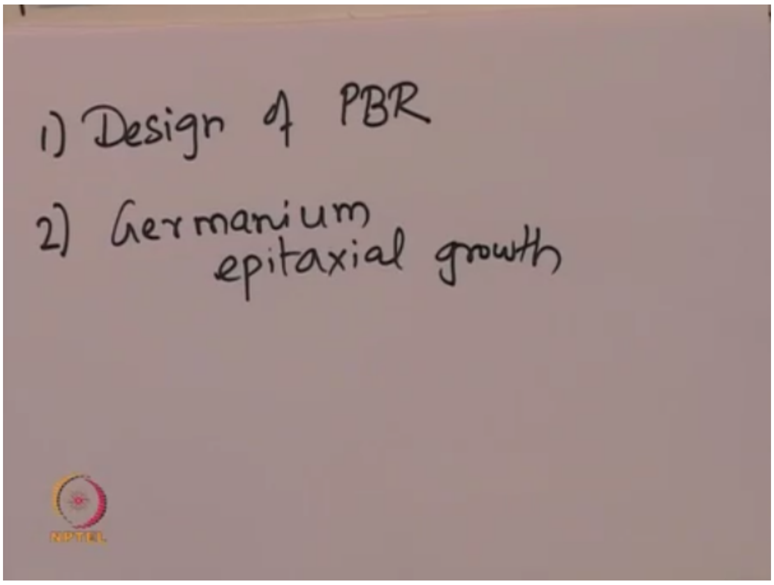

1) Design of PBR

2) Germanium epitaxial growth

So, we looked at the design of a packed bed reactor. And then we looked at how the conversion can be expressed in terms of the weight of the catalyst which is packed inside the reactor. And then we also looked at what should be the performance equation for a CSTR in case we want to find out what is the weight of the catalyst which is required to obtain the same conversion as that obtained in the packed bed reactor.

And then we went on to describe a case study of the germanium epitaxial film growth, so germanium epitaxial film growth. So, which also is, can be modelled as a heterogeneous catalytic process. And so, with these 2 examples of hydro demethylation of toluene and germanium epitaxial growth, what we have learnt is a systematic way to start from first principles by determining what is the mechanism of a particular catalytic reaction.

Find out what is the surface reaction, what is the limiting step. In both these cases we assume that it is the surface reaction which is the limiting step. And in principle the adsorption or desorption also can be a limiting step. So, it is important to note that, only the 75% of the heterogeneous catalytic reactions are actually surface reaction limiting. And so, in principle the same procedure can be followed if the adsorption and the desorption step were to be the limiting step.

So, using these rate law for hydro demethylation of toluene we estimated the rate parameters. And then, we went ahead to design a simple packed bed reactor model to find the relationship between the conversion and the weight of the catalyst that is actually packed inside the reactor. Thank you.