VLSI Technology

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Lecture - 11
Oxidation I – Kinetics of Oxidation

So, the unit process step that we are going to discuss today is oxidation of silicon. We have already discussed, many times we have already talked about the importance of this unit process step. Oxide is used as masking element, it is used for surface passivation and it is also used for gate oxide in MOS devices. In addition to that, you will also find that oxide can be used as isolation between devices. Now, silicon has a great affinity for oxygen. It is very simple to oxidize silicon. This oxidation can be done in various methods. That is if you boil silicon in nitric acid for example, you will form an oxide layer. This is called chemical oxidation.

If you use silicon in an electrolytic bath, use silicon as anode and noble metal as cathode in an electrolytic solution, pass, apply a voltage between the two electrodes, then also a layer of oxide will form on silicon. That is called anodic oxidation. But, the most important oxidation technique, most important from the point of view of VLSI technology is thermal oxidation of silicon. The quality of thermal oxidation is by far the best; of all the oxides that is grown on silicon, the quality of thermal oxide is the best and therefore thermal oxidation is widely used in VLSI technology.

The principle of thermal oxidation is very simple. You take silicon sample, put it inside a furnace, raise the temperature of the furnace and allow either oxygen or water vapour to flow and silicon will react either with oxygen or with water to form silicon dioxide.

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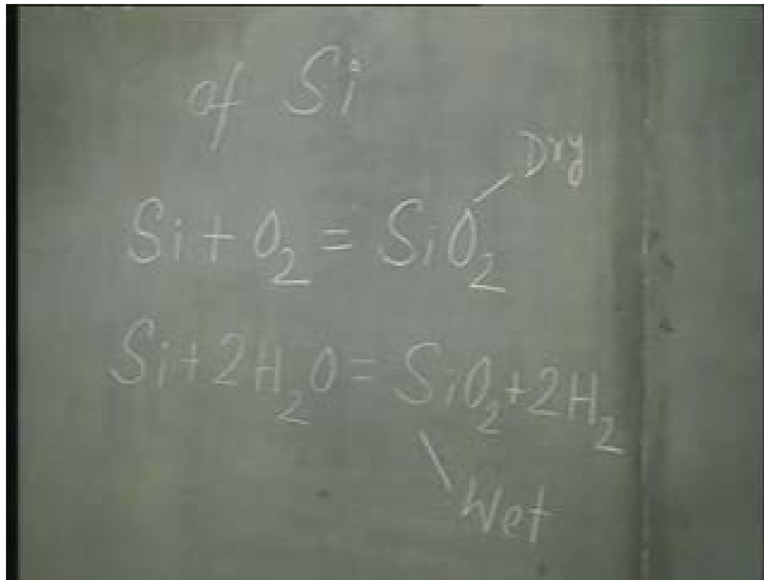

This is usually referred to as dry oxidation and this is as wet oxidation. Names are self explanatory, right. We will discuss more about the dry and wet oxidation later on. First of all let us concentrate, let us focus our attention on what is happening when the thermal oxidation of silicon is taking place. First of all, let me tell you that it has been established by using radioactive tracers that the oxidizing species, by oxidizing species I mean either oxygen or water vapour as the case may be, that is referred to as the oxidizing species or sometimes as the oxidant, the one which is oxidizing silicon, right. So, by radioactive tracers it has been established that it is the movement of the oxidizing species into the silicon that is causing the oxidation. It will become more clear if I draw this.

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On this side, is my silicon. So you see, when the oxide is growing there are two possibilities. One possibility is silicon can move out and react on the outer surface that is to the left of this interface and the oxide can grow like this. Then, a thin layer of oxide is grown. Silicon continues to move out and a further layer of oxide grow like this. That is always the oxide growth is happening towards the left of the interface. This is one possibility.

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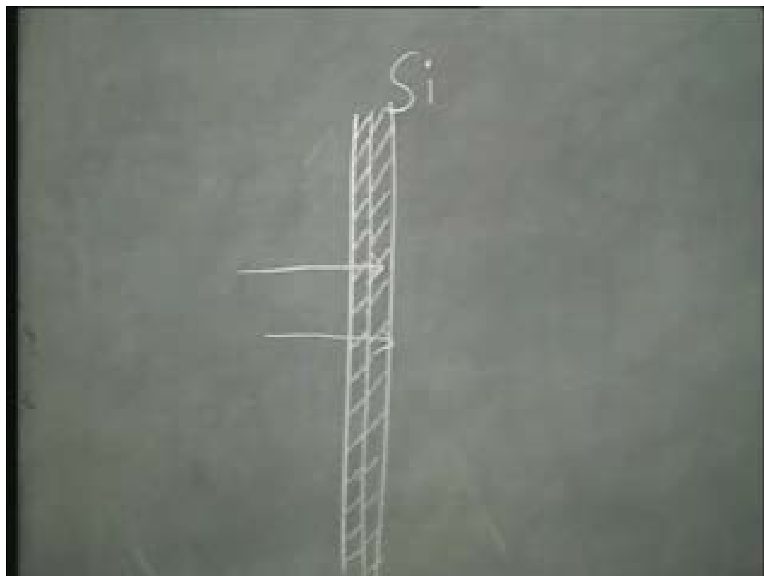

The other possibility, the oxidizing species move in and react at the right of this interface, so that oxide is formed like this. Then, this whole layer is converted into oxide. Oxidizing species continue to move in, so further reaction takes place again on the right of this interface. In other words, the oxide grows in this direction. Which of the two models is true? By radioactive tracers that is by using radioactive oxidizing species, it has been found that it is the movement of the oxidizing species into the silicon and not the movement of silicon out, right. So, during thermal oxidation process, the oxidizing species move inside, move through the oxide layer and reacts with the silicon at this interface. This is a property of thermal oxide. Let me tell you at this point itself that I just now mentioned that it is also possible to grow oxide by anodic oxidation, right. In case of anodic oxidation, the movement is in the reverse direction. That is there silicon moves out and reacts at the outer surface. Do you understand the fallout of this?

In case of thermal oxide, therefore you see, oxide is growing in this direction. That means the interface is not the original surface. Do you see? The original surface was here. Now, the interface is here, it is not the original surface. What is the advantage? You know, the original surface is actually the source of all kind of contamination, because that is the layer which is exposed to the surroundings. So, in thermal oxidation, you have a major advantage in that all this contamination, it is on the outer surface of the oxide and it does not affect the interface. In fact that is one of the secrets why thermal oxide is the best. This is one of the reasons for that. In contrast, if we are talking about anodic oxide, then you can easily visualize that the original surface is the interface. Therefore whatever the original contaminations were present on the surface that same thing will be present at the interface and the quality of the interface will be poorer. That is why thermal oxide and only thermal oxide is used as gate oxide on MOS devices. Because, that is where the interface qualities are of primary importance and this is the reason why thermal oxide gives you the best quality of oxide.

Now that we have established that it is the movement of oxidizing species inside the silicon, let us discuss about the kinetics of the oxide growth. Kinetics of the oxide growth that is exactly how the species are being transported, what are the fluxes?

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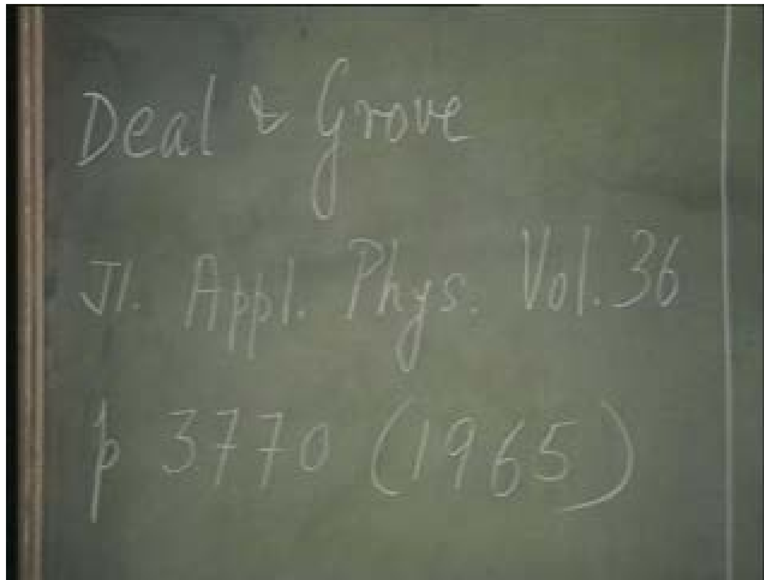

What is happening during the oxidation process that is the kinetics of oxidation and the kinetics of oxidation was predicted by Deal and Grove more than 30 years ago in their pioneering paper in Journal on Applied Physics in 1965 and the funniest thing is it is one of the longest standing models. You see, in 33 years, Deal and Grove's model have withstood the onslaught of all experiments. That is the experimental data, whatever experimental data has been generated so far on oxidation, Deal and Grove model can explain that quite adequately in most of the regions. There are a few problem areas, but overall Deal Grove's model is a very good model, very sturdy model. It explains the principle of silicon thermal oxidation quite adequately, except in a few pockets, right.

So, let us move on to Deal and Grove's model. First of all, let me draw your attention to this chart.

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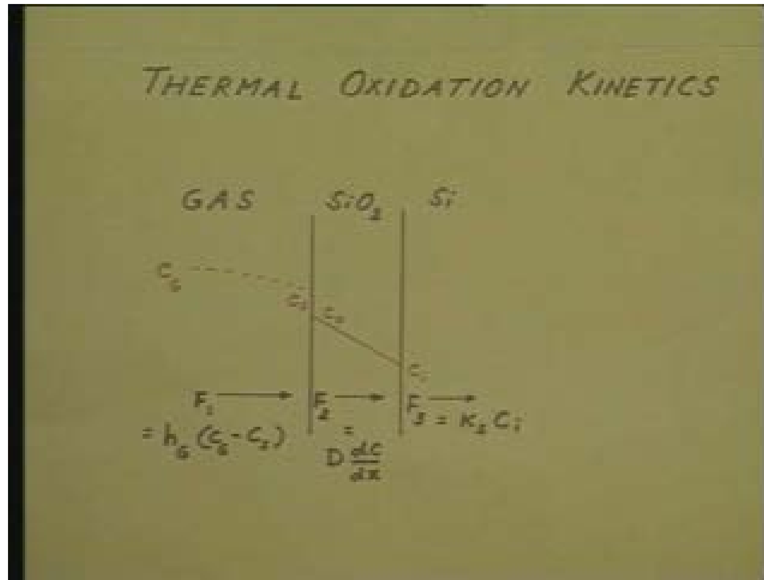

What do I have here? This is a perfectly generalized situation when silicon is getting oxidized. So, I have silicon and because I want to make it general, I have taken a non-zero silicon dioxide layer. That is you see, initially you may say that the oxide layer is not there, it is zero. But then as the oxidation process is proceeding, you have an oxide layer on silicon, right. Further oxidation is proceeding in the presence of this already grown oxide layer. That is why in order to maintain generality, I have taken silicon and then silicon dioxide and then I have the gas surrounding it. Now, what are the things that are happening? What are the processes that are happening in order to, in order that the oxidation process goes on what are the other things that must be taking place?

First of all, we have oxidizing species in the gas. From the gas stream it must be transferred to the oxide gas interface, right. So, that is number 1. Once these oxidizing species have reached the oxide gas interface, it must diffuse through the existing oxide layer in order to reach the silicon oxide interface, because you know the oxidation is taking place by the movement inside of oxidizing species. So, if they want to react with silicon, they must move through the already existing oxide layer into the silicon-silicon dioxide interface that is this interface, right. So, that is process number 2 and process number 3, once these oxidizing species reach the silicon-silicon dioxide interface, it must

react with silicon there. Isn't it. So, I have the movement of oxidizing species governed by these three phenomena.

One is movement of the oxidizing species from the gas stream to the oxides gas interface, then the movement of the oxidizing species through the existing silicon dioxide layer and then finally, the reaction of the oxidizing species at the silicon-silicon dioxide interface. Therefore I have, I can say three fluxes associated with this. The three fluxes are marked here as F 1, F 2 and F 3. Now, let us see what are these fluxes? But before I go on to define these fluxes, I have to take note of the concentration of the oxidizing species in the various regions.

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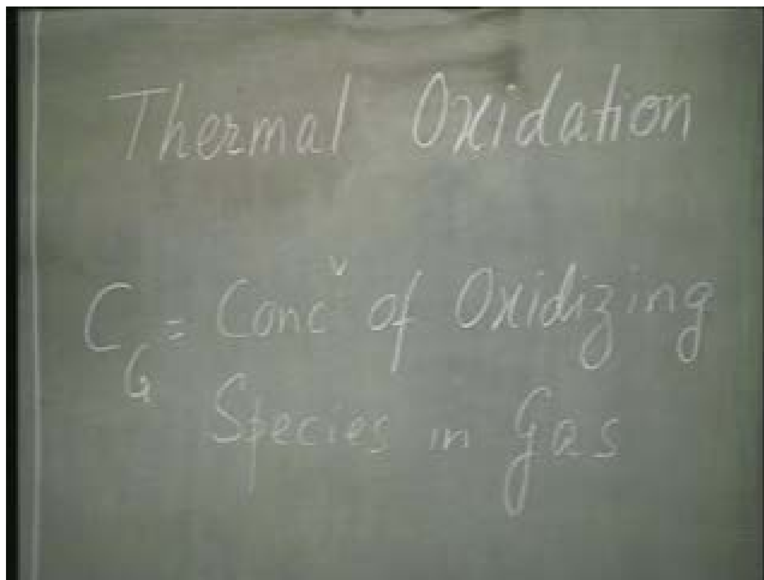

I have written C G here, C suffix G that is the concentration of oxidizing species in the bulk of the gas, C suffix G. C stands for concentration, G stands for gas, so concentration of the oxidizing species in the bulk of the gas. I have also written C S there.

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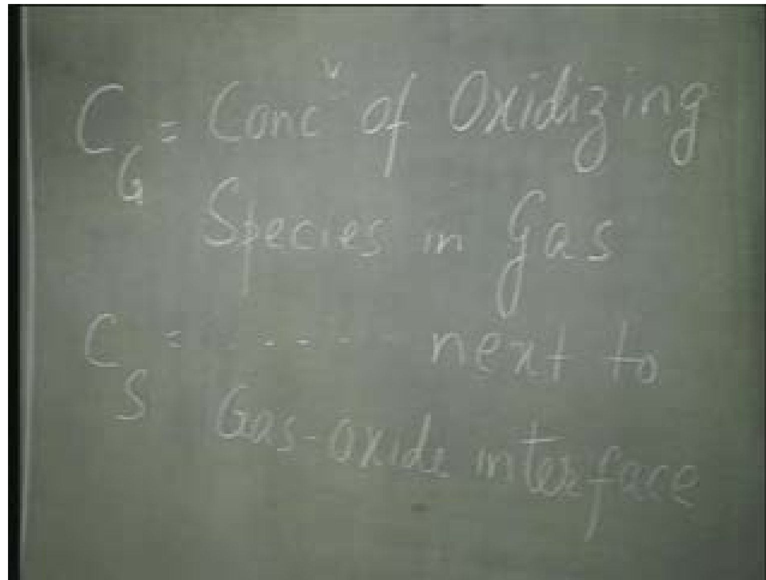

Again you know, C stands for concentration of the oxidizing species and S says that this is right next to the gas oxide surface. So, this is concentration of the oxidizing species right next to the gas oxide interface. Similarly, I have also defined two other concentrations C 0 and C i. C 0 is the concentration of the oxidizing species at the outer oxide surface, zero or o, o stands for outer surface, outer oxide surface. You see, this is the oxide. It has two surfaces - this is the outer surface, this is the inner surface. So, concentration of the oxidizing species at the outer surface is called C naught and concentration of oxidizing species at the inner surface is called C i.

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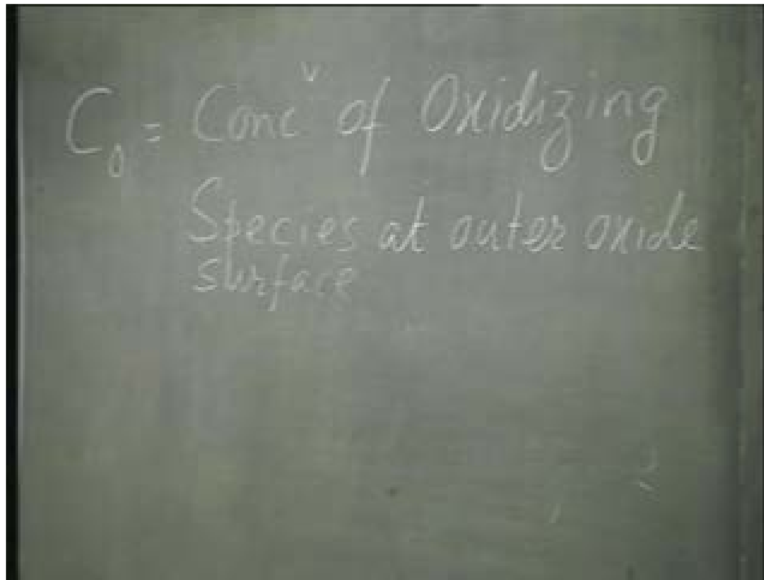

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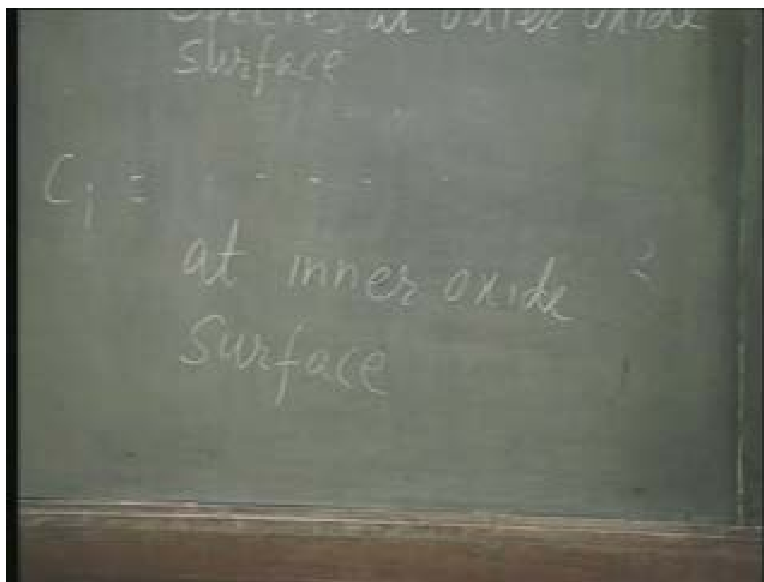

So, I have defined four concentrations.

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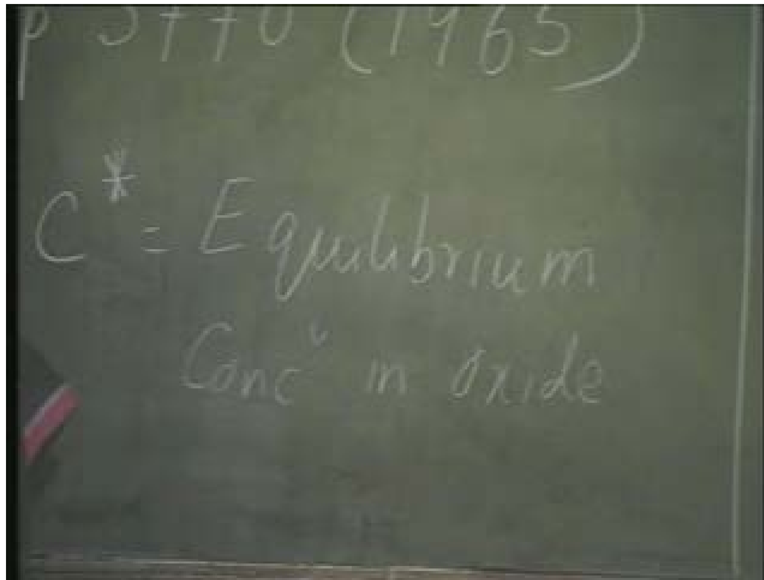

In addition, I want to define a concentration term C star and C star is defined as the equilibrium concentration of the oxidizing species in the oxide, equilibrium concentration. This is called the equilibrium concentration of the oxidizing species in the oxide. Remember, whenever I am saying concentration, actually I mean concentration of the oxidizing species.

Now that we have defined all these concentrations, let us see what are the three different fluxes. That is what are F 1, F 2 and F 3. F 1 is the flux of the oxidizing species in the bulk of the gas, from the bulk of the gas right next to the oxide gas interface.

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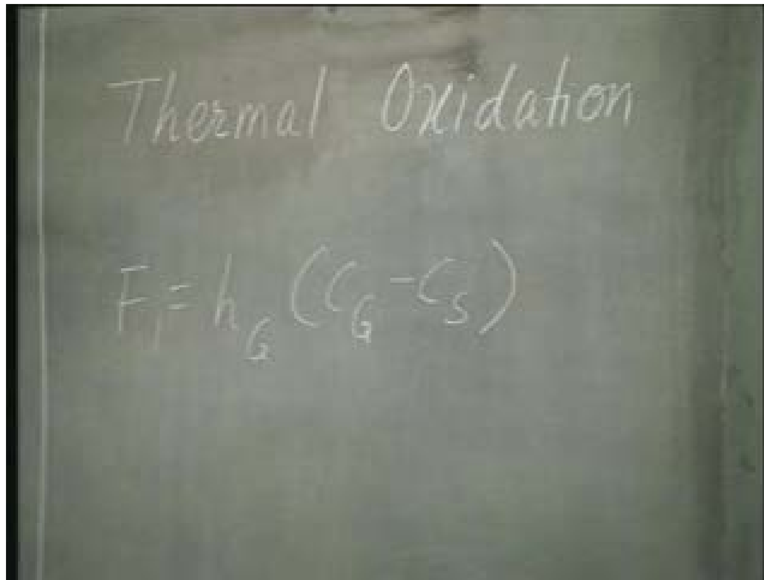

So, this flux is governed definitely by the concentration difference at these two points, isn't it and this is therefore given by C G minus C S. This is proportional to C G minus C S, C G being the concentration of the oxidizing species in the gas, C S being the concentration of oxidizing species right next to the oxide gas surface and h G is called the proportionality constant that is the gas phase mass transfer coefficient. Now, you see by gas laws I could replace C G and C S by the pressure of these oxidizing species, the partial pressure of these oxidizing species p v equal to KT.

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So, I could write this as, can I not? At this point, we invoke a law called Henry's law and Henry's law states this - that in equilibrium the concentration of a species within a solid is proportional to the partial pressure of that species in the surrounding gas. Think about it more carefully. The concentration of a species within a solid is proportional to the partial pressure of that species in the surrounding gas. I have already defined C star as the equilibrium concentration of the oxidizing species in oxide, in the solid, the solid being the oxide. So, by Henry's law you know C star is going to be proportional to the partial pressure of this oxidizing species in the surrounding gas that is P G. In other words, by Henry's law I could say C star is equal to Henry's constant times P G.

Now, what is C naught? C naught is the concentration of the oxidizing species at the outer surface of the oxide. So, C naught is going to be proportional to P S, where P S is the partial pressure of the oxidant right next to the gas oxide surface. Now you see, it is possible for me to write the flux equation in terms of C star and C naught, because I know C star is proportional to P G and C naught is proportional to P S, isn't it.

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So, what I can do is I can replace P G by, right and in order to simplify matters further, let me use a constant H.

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In other words, I have related the flux F 1 to the equilibrium concentration of the oxidizing species and the concentration of the oxidizing species at the outer surface of the oxide and I have seen that it is proportional to the difference of these two concentrations.

So, this is all about flux one. What about flux two that is F 2? F 2 is related to the movement of the oxidizing species through the existing oxide layer.

Why should the oxidizing species move through the oxidizing layer? Because of the concentration gradient, it is diffusing across the existing oxide layer. It is diffusion of oxidizing species through the already existing oxide layer and you know, diffusion is always proportional to the concentration gradient. If I make a linear approximation as I have done here, you know concentration of the oxidizing species at the outer surface is given by C naught, concentration of the oxidizing species at the inner surface is given by C i, then the concentration gradient will be given by C naught minus C i divided by the oxide thickness. So, F 2 should be proportional to that and the proportionality constant is called the diffusion constant, x is the existing oxide thickness and finally we come to flux number three, F 3 and what is F 3?

F 3 is related to the reaction of silicon with the oxidizing species and since I have an abundance of silicon at the interface, lots of silicon is present, the reaction will be governed by the availability of the oxidizing species, isn't it. The more oxidizing species I have, the faster will be the reaction, the more will be the reaction. So, this flux will again be proportional to the concentration of the oxidizing species at the oxide silicon interface that is the availability of the oxidizing species. In other words, F 3 will also be proportional to C i and I will call this proportionality constant K S, which is also referred to as the reaction rate constant.

I now have three equations governing the three fluxes. Under steady state condition, these three fluxes must be equal, agreed. So, if I now equate these fluxes what do I get? Let me first try to equate two and three.

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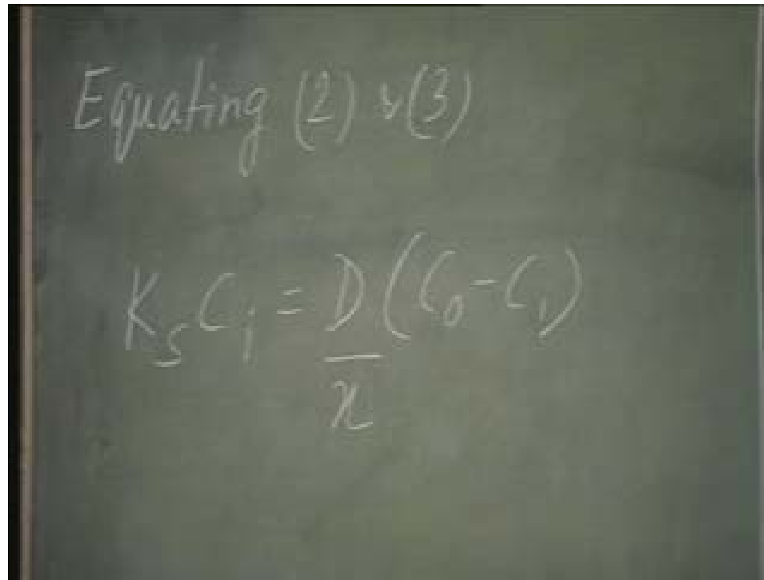

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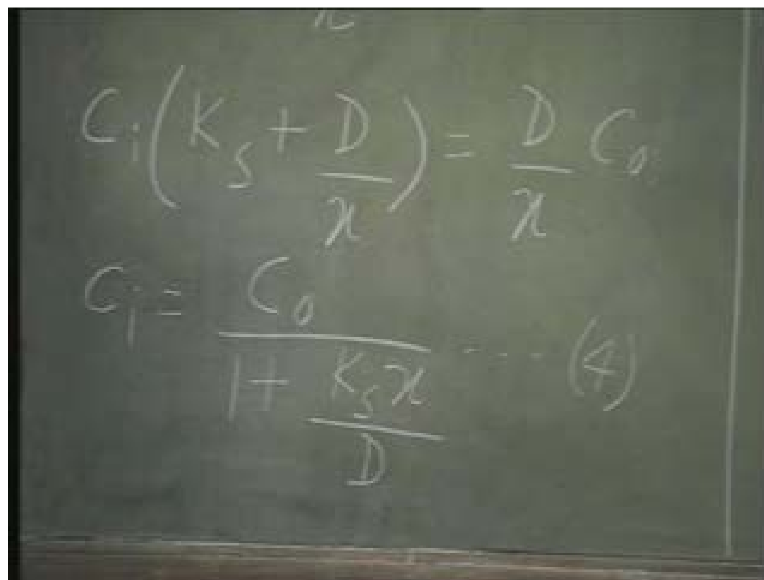

I can write or I could say ...., I have related the concentration of the oxidizing species in the inner surface with the concentration of the oxidizing species in the outer surface and you can see that if x is very small, I have a very thin oxide layer, then C i is going to be nearly equal to C naught. The thicker the oxide layer is, the smaller, C i becomes correspondingly smaller than c naught, obviously. Now, I have obtained this expression for C i. Let me use this expression in this equation 3.

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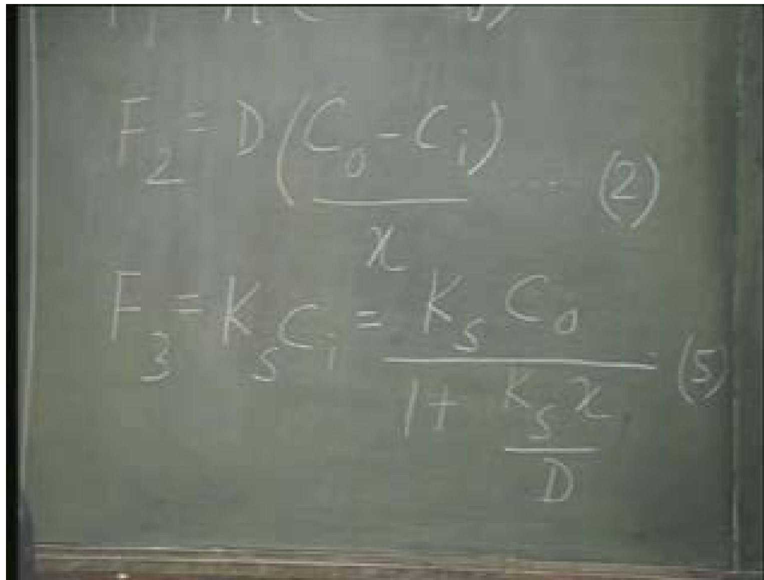

So, I could write that F 3 is equal to K S C naught by 1 plus K S x by D. Replacing C i with this expression, you can write that? Now so, let me call this my equation 5. Now, see if I equate F 1 and F 3, because under steady state condition as I have told you, all the three fluxes are equal, so now, if I equate F 1 with F 3, what do I get?

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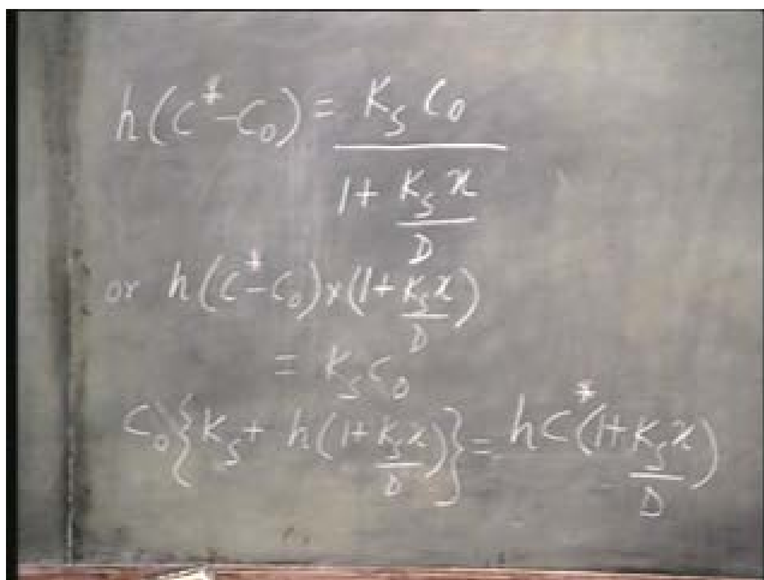

I get or I could say..... Now, if I collect all the terms containing C naught then I will get ....

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Finally, therefore I can write that C naught is equal to ......, right or I could further simplify it and write it like C star divided by, dividing it by h, I could write it as 1 plus K S by h plus K S x by D into 1 plus K S x by D, right. I have divided it by h, both numerator and denominator. So, this is going to be my equation number 6. Now you see, I have an expression for C naught in terms of the equilibrium concentration C star. All the others are constant. K S is the reaction rate constant, h is the gas phase mass transfer coefficient and Henry's coefficient put together and D is the diffusion coefficient and x is the existing oxide layer thickness.

Now, if you look at equation number 4, here you find that C i is given as C naught by 1 plus K S x by D.

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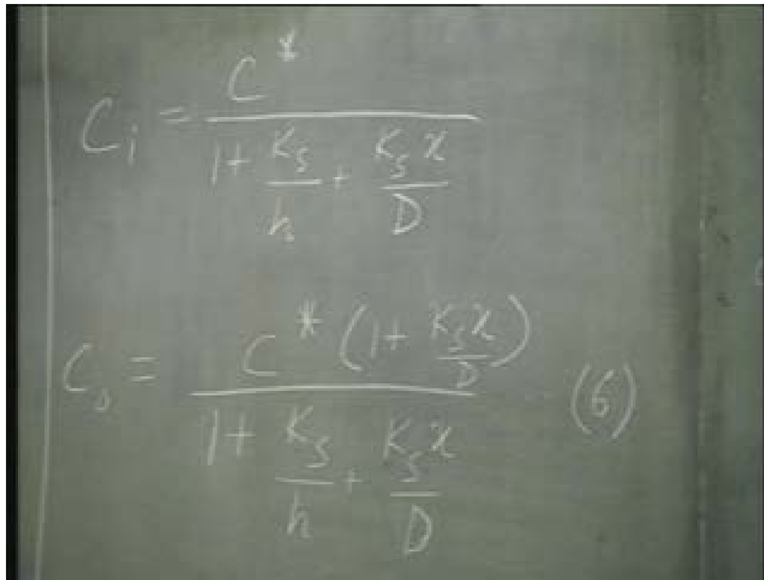

So, if I put this equation in equation number 6, then I find C i is given by, C i is given by C star divided by 1 plus K S by h plus K S x by D and C naught is given by C star into 1 plus K S x by D divided by 1 plus K S by h plus K S x by d. Now, after all these mathematical rigmarole, let us look at it a bit more physically.

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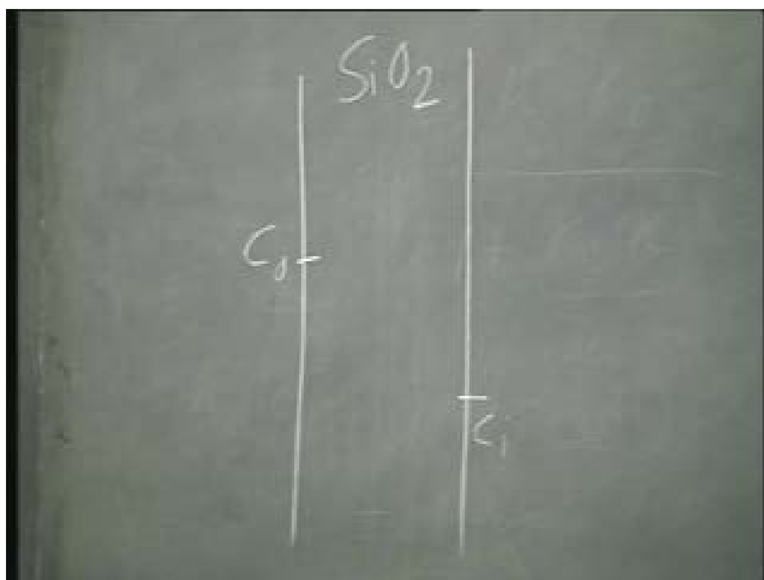

As I have told you, C naught and C i actually denotes the concentration here and the concentration here, isn't it, concentration of oxidizing species at the outer surface of the oxide and at the inner surface of the oxide. Now, from these relative expressions what do we see? We see two interesting cases.

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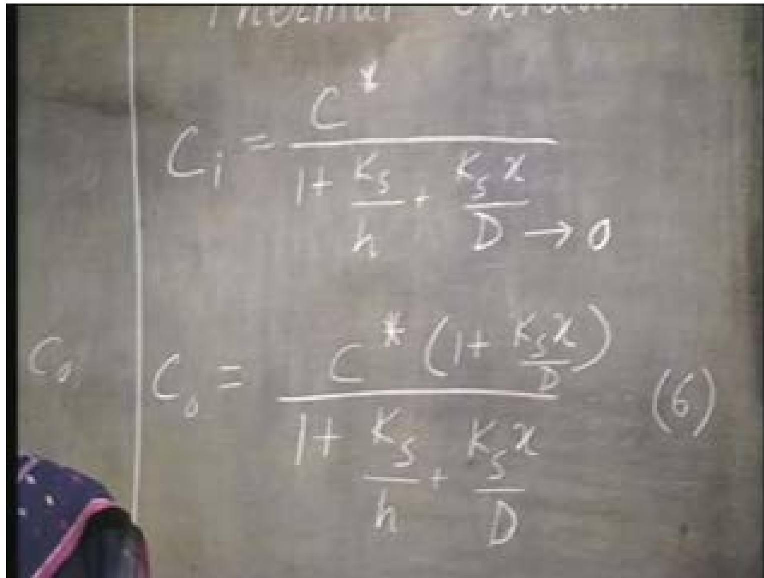

One case is suppose D is tending to zero that is my case number 1. If D tends to zero, then what happens? If D tends to zero, then this denominator becomes a very large quantity, agreed and therefore C i will become very small, C i will tend to zero.

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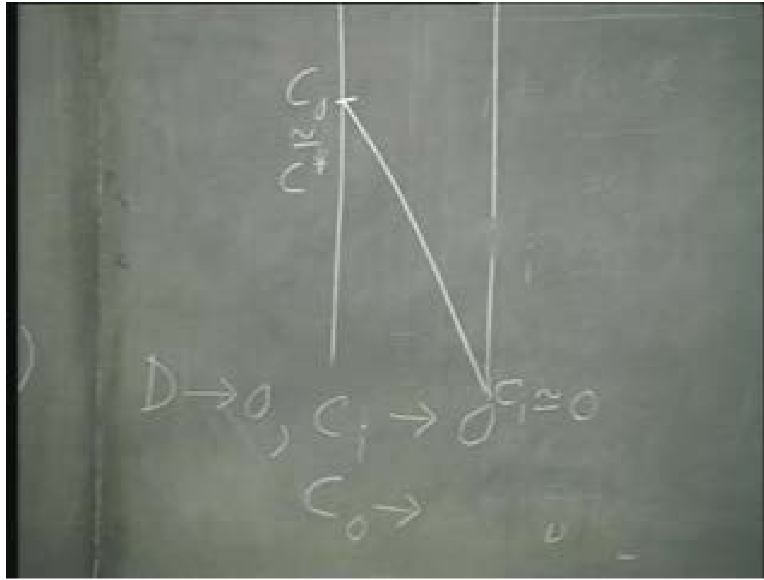

So, case one that is when D tends to zero, C i tends to zero. In other words, I have a case like this. Let us first see what C naught is going to be, then we will see the case as D tends to zero what is going to happen to C naught? You see, as D tends to zero, this K S x by D, it dominates the denominator as well as this numerator. So, we can cancel these two and C naught in the limiting case becomes approximately equal to the equilibrium concentration that is C star, agreed, yes. Yes or no?

Students: yes.

Yes, so, then in that limiting case, C naught is approximately equal to C star and from there, there is a deep fall like this, C i is tending to zero. This is a situation when the diffusion coefficient is tending to zero. But again, I am doing only mathematics. What is the physical significance of this? The physical significance is diffusion is controlling the oxidation. The oxidation is called diffusion limited. It is like you know the bottleneck, the bottleneck is because not enough oxidizing species can reach the interface, diffusion coefficient is tending to zero, C i is tending to zero. So, the bottleneck in the oxidation process, the movement of the oxidizing species is hampered by this, the process of diffusion. So, this is called the diffusion limited regime of oxidation and of course you

can understand, it is very easy for you to intuitively understand, that the thicker the oxide layer becomes, the more difficult it becomes for diffusion to take place, right. You see in this case, I have taken D tending to zero. I could have achieved the same thing by assuming x tends to infinity, right. Basically the point is this factor x by D is becoming very large, agreed. So, physically speaking this is the diffusion limited regime of oxidation.

Now, look at the other possibility. What is the other extreme?

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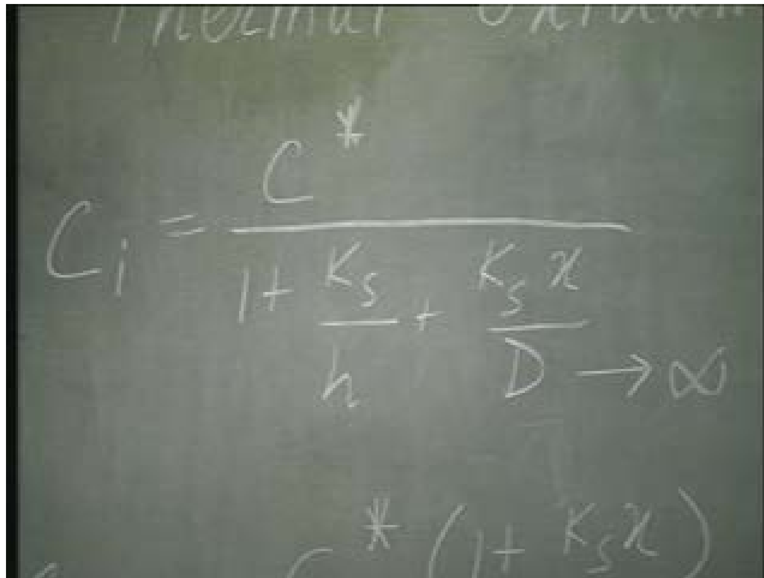

D tends to infinity or let us say x by D is very, very small.

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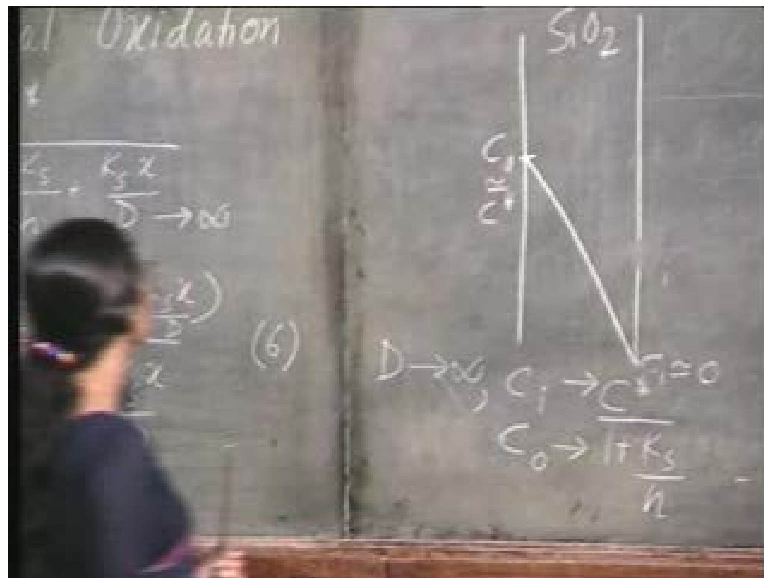

When x by D is becoming very, very small or in other words, D is tending to infinity, then C i is going to be C star divided by 1 plus K S by h. This is tending to infinity, this term is zero. So, this is C star divided by 1 plus K S h and what about C naught? C naught is also the same thing, C star divided by 1 plus K S by h.

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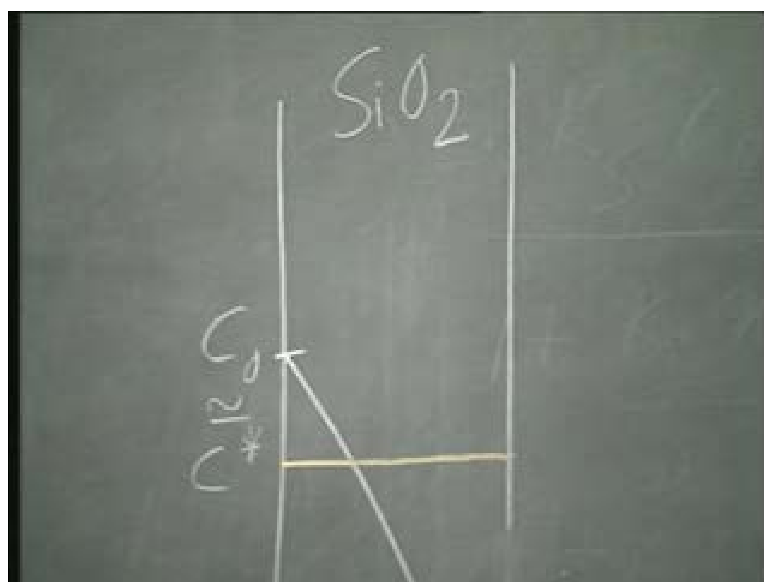

In other words, there is no difference between the concentration of oxidizing species from the outer surface to the inner surface. That is physically speaking, what I am trying to say is that the availability or the diffusion of oxidizing species through the oxide is not posing a problem. The problem is after the oxidizing species have reached the interface, how fast can they react with silicon. That is what is going to govern the oxidation rate. So, the oxidation is called reaction limited for this case. When D tends to infinity, this is called reaction limited. So, we have identified two cases.

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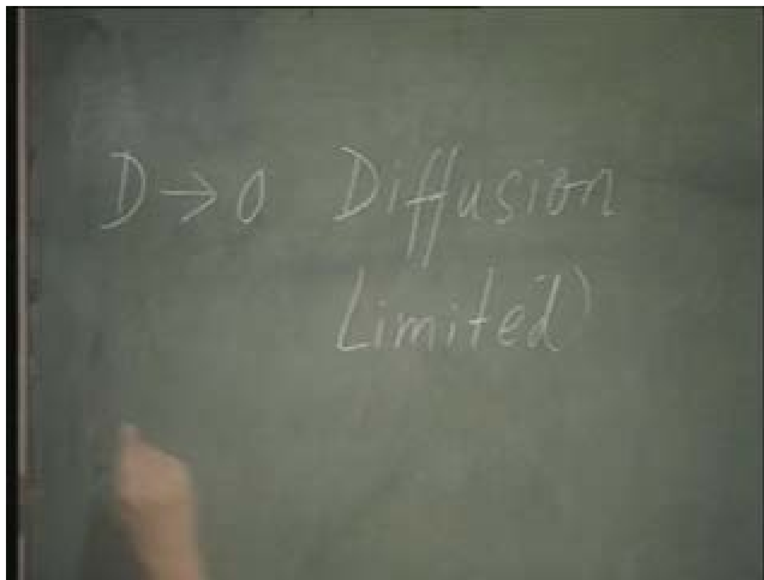

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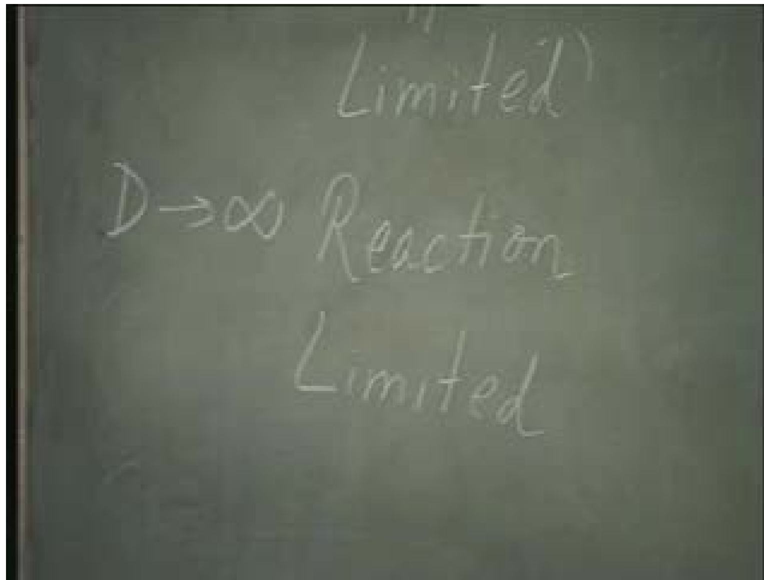

Two regimes of oxidation - diffusion limited case and reaction limited case. That is in both cases I am looking at the slowest process that is the process where the bottleneck is. When D is tending to zero, the bottleneck is in the diffusion of the oxidizing species. That is why it is called diffusion limited. When D is tending to infinity, then diffusion is not the bottleneck. The bottleneck is the reaction rate between silicon and oxidizing species. So, now that we have obtained all these expressions for the fluxes and from there we could relate the concentration of the oxidizing species with the equilibrium concentration and the known constants, we have to find out the oxide growth rate, right.

How do you find the oxide growth rate, that is the next problem. You know, one molecule of silicon reacts with one molecule of oxygen to give one molecule of silicon dioxide or one molecule of silicon is going to react with two molecules of water to give one molecule of silicon dioxide. I wrote those two equations at the beginning of these classes.

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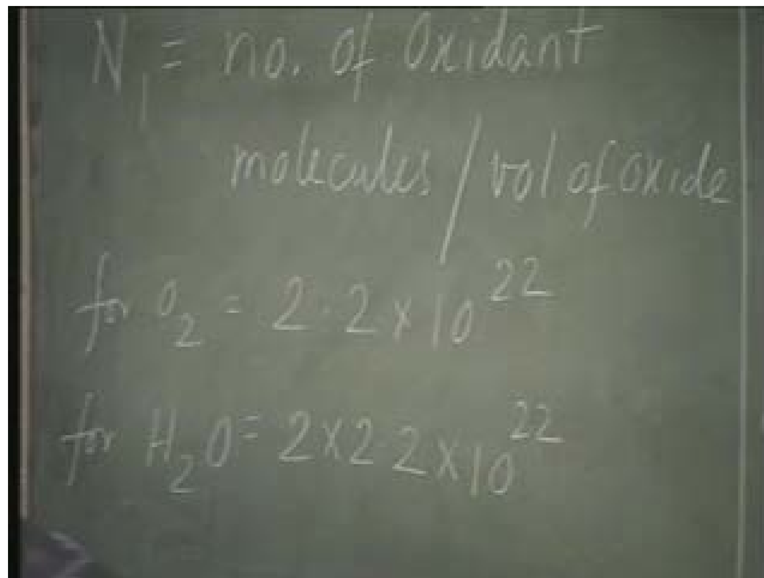

Now, let me define a term N 1 that is number of oxidant molecules; it can be either oxygen or water vapour per unit volume of oxide, number of oxidant molecule per unit volume of oxide. So, obviously for oxygen being the oxidant molecule, I need one molecule of oxygen in order to get one molecule of oxide. So, N 1 for oxygen it is 2.2 into 10 to the power 22 and for water it is going to be double the number, because per molecule of silicon dioxide needs two molecules of water vapour in contrast to one molecule of oxygen, right. So, this is going to be 2 times this. Important numbers these, right, N 1 that is the number of oxidant molecules per unit volume of oxide.

So you see, as the oxide is growing, the growth rate is given by dx dt, so and N 1 is the number of oxidant molecules incorporated per unit volume. So, N 1 times dx dt is nothing but the flux of the oxidizing species, isn't it.

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So, I could say that can be given as the flux. Since all the fluxes are identical under steady state condition, I could say N 1 dx dt is equal to F 3 that is equal to K S C star divided by 1 plus K S by h plus K S x by D, agreed. I have got a differential equation and in the next class I am going to solve this differential equation subject to the initial conditions and obtain an expression for relating the oxide thickness with the time of oxidation. That is called the oxide growth rate equation. So remember, this is my most important expression. I have obtained, this is actually K S times C i. I have related C i with C star. C star divided by 1 plus K S by h plus K S x by D and now I am going to equate that with the number of oxidant molecules per unit volume multiplied by the oxide growth rate, dx dt. I will equate that, solve the differential equation subject to the initial conditions and obtain the expression for oxide growth rate, in the next class.