VLSI Technology
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Lecture - 12
Oxidation II - Oxidation Rate Constants

So, we have been discussing the kinetics of thermal oxidation in silicon and I have told you that Deal and Grove suggested the model which we have been discussing and eventually we came to the differential equation. That was the step where we stopped in the last class and this differential equation says N 1 into dx dt is equal to K S C star divided by 1 plus K S by h plus K S x by D.

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$$N_1 \frac{dx}{dt} = \frac{K_S C^*}{1 + \frac{K_S}{h} + \frac{K_S x}{D}}$$

Let me quickly remind you what all these terms stand for. N 1 is the number of oxidant molecules per unit volume of the oxide, dx dt is the oxide growth rate, x being the oxide thickness and small t being the time, K S is the reaction rate constant, C star is the equilibrium constant of the oxidant species in the oxide, h is a multiple constant, you know, it contains the gas phase mass transfer coefficient and Henry’s constant and KT, and D is of course the diffusion coefficient. So, this is the differential equation and now we must solve this differential equation in order to obtain the oxide growth rate characteristics. That is how does the oxide thickness increase with time ....

It stands to reason that if you carry out oxidation for a longer time the oxide thickness will increase, but how exactly does it increase. That is the point where this equation is going to help us. So, very simply we can start by transposing.

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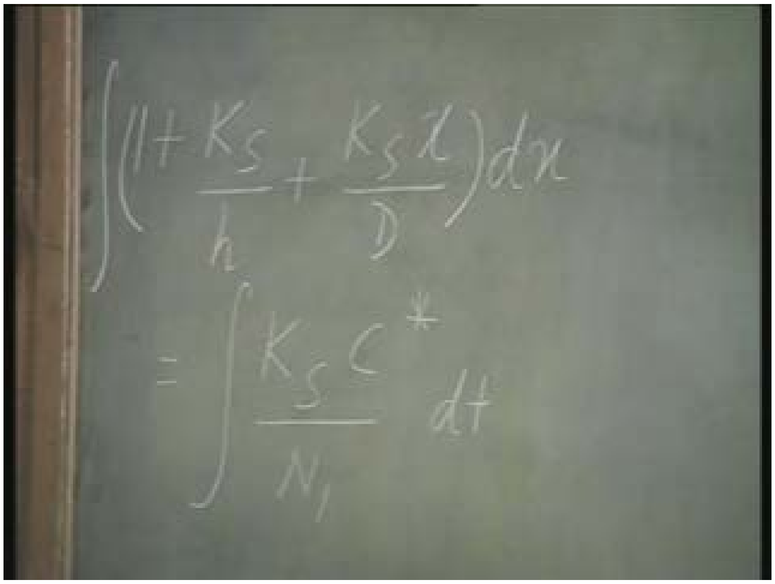

$$\int\left(1+\frac{K_S}{h}+\frac{K_S x}{D}\right)dx = \int \frac{K_S C^*}{N_1}\,dt$$

By transposing and integrating this is what we get.

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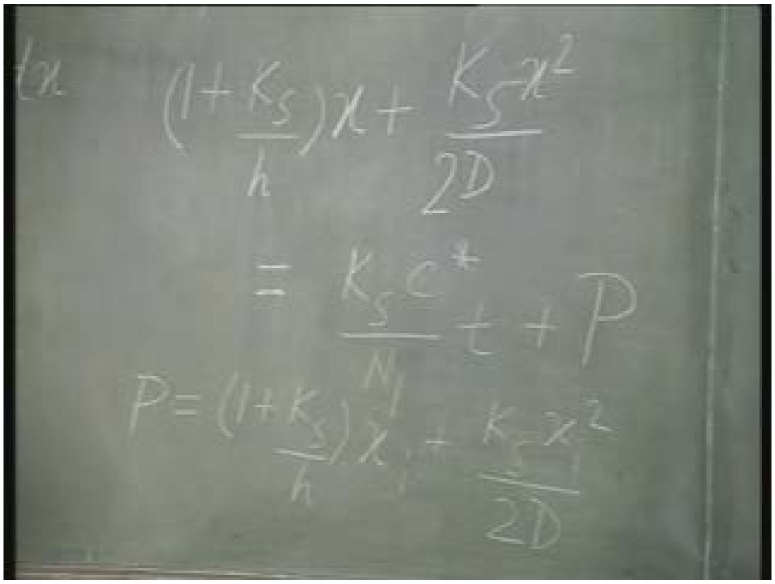

$$\left(1+\frac{K_S}{h}\right)x+\frac{K_S x^2}{2D}$$

$$=\frac{K_S C^*}{N_1}t+P$$

$$P=\left(1+\frac{K_S}{h}\right)x_i+\frac{K_S x_i^2}{2D}$$

Let us carry out the integration and see what happens or I could say, I can say, 1 plus K S by h multiplied by x plus K S x square by 2 D plus is equal to K S C star by N 1 times t plus the integration constant, P and in order to evaluate this integration constant, I must focus our attention to the initial condition that is at the beginning of time. In a general case I can say that when the oxidation started, let us assume that the silicon already had an initial oxide thickness present on it. That is the most general case, right, that initial thickness could be zero, could also be not zero.

So, in order to maintain generality, let us say that when we started the oxidation, the initial oxide present on silicon, let us call it x suffix i that is initial oxide thickness. If that is so, then I can say that ...... P then can be evaluated by putting t equal to zero and assuming that this x is equal to x i and this is what we get. So, I can rewrite this equation, I can modify this equation and write it like this.

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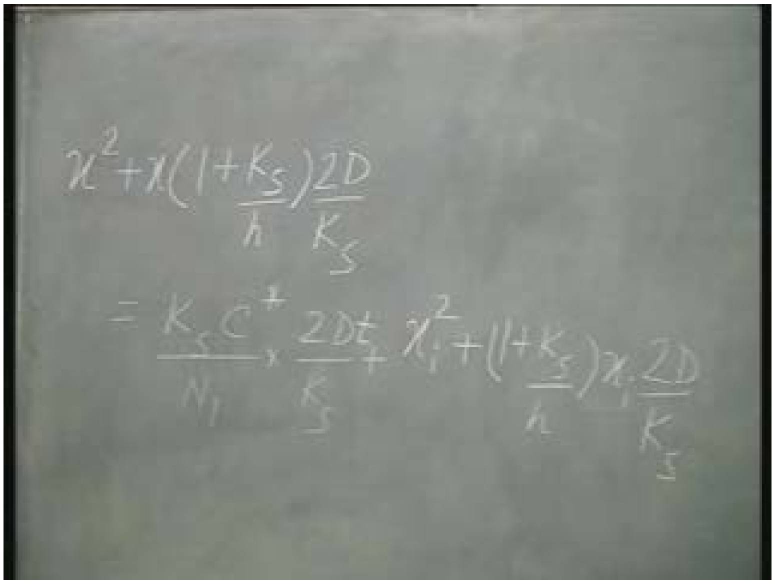

$$x^2 + x\left(1+\frac{K_s}{h}\right)\frac{2D}{K_s} = \frac{K_s C^*}{N_1} \times \frac{2Dt}{K_s} + x_i^2 + \left(1+\frac{K_s}{h}\right)x_i\frac{2D}{K_s}$$

I have simply divided both sides, both left hand and right hand side by, 2 D by K S. Therefore I get, x square plus x multiplied by 1 plus K S by h multiplied by 2 D by K S is equal to K S C star by N 1 into 2 D by K S into t and instead of writing P, I have written it in terms of x i. So, I get plus x i square plus 1 plus K S by h into x i into 2 D by K S, agreed.

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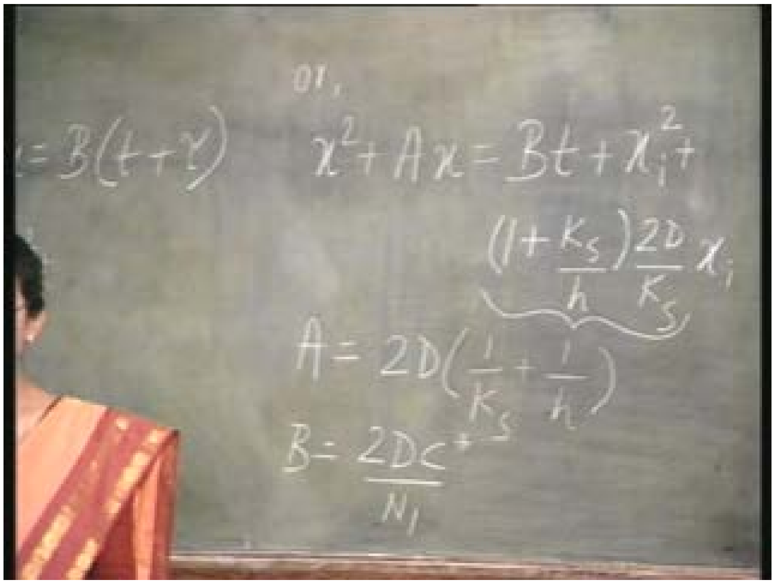

$= B(t+\tau)$

or,

$$x^2 + Ax = Bt + x_i^2 + \underbrace{\left(1+\frac{K_s}{h}\right)\frac{2D}{K_s}}\,x_i$$

$$A = 2D\left(\frac{1}{K_s} + \frac{1}{h}\right)$$

$$B = \frac{2DC^*}{N_1}$$

Since this looks too confusing, let me give it simple nomenclature and let us write, never mind, Bt, that is x i square plus 1 plus K S by h, where A can be written, if you just compare this equation with the equation I have written on the right side, you can see that A is actually nothing but 2 D into 1 upon K S plus 1 upon h. B is nothing but 2 D C star by N 1, K S K S cancels each other, right. I would like to further simplify this equation.

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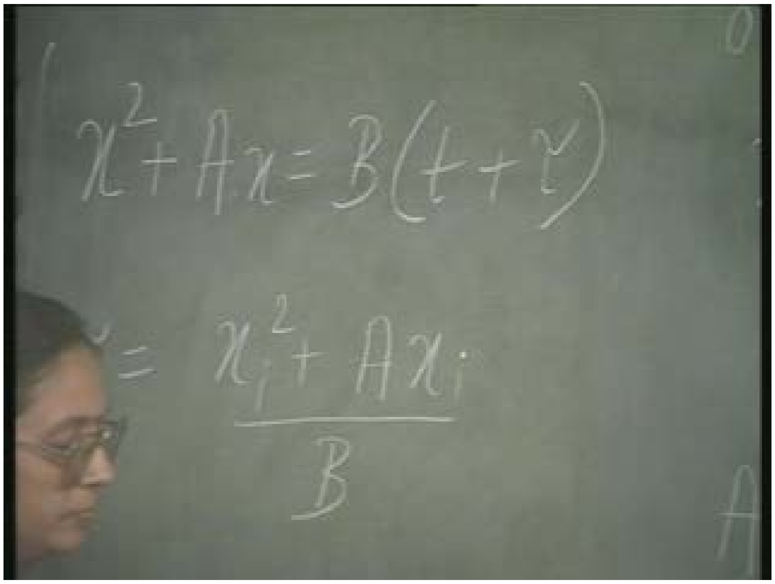

So, what I would like to have is ....., where, what is this? In terms of A and B, what is this term? This is nothing but A.

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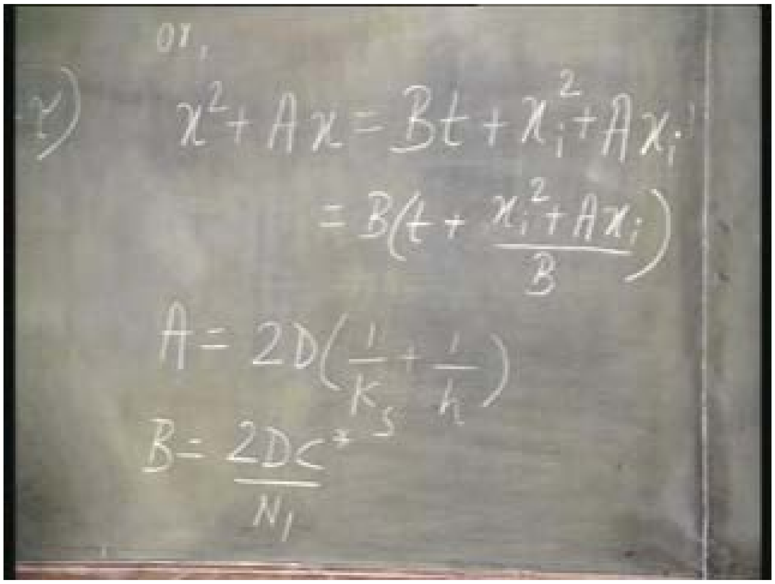

or,

$$x^2 + Ax = Bt + x_i^2 + Ax_i$$

$$= B\left(t + \frac{x_i^2 + Ax_i}{B}\right)$$

$$A = 2D\left(\frac{1}{K_s} + \frac{1}{h}\right)$$

$$B = \frac{2DC^*}{N_1}$$

So, I can simply write it as..... and therefore I can further modify it and this is what I am going to call tau.

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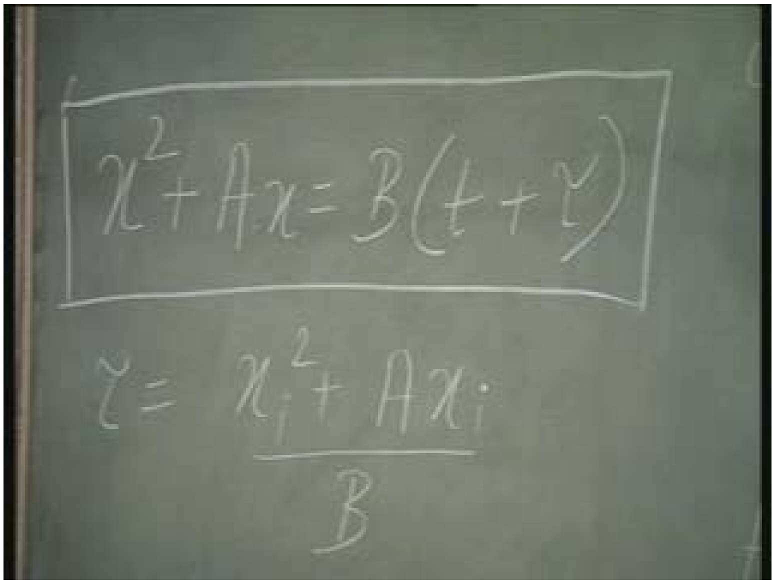

$$\boxed{x^2 + Ax = B(t + \tau)}$$

$$\tau = \frac{x_i^2 + Ax_i}{B}$$

So, this is my final form, x square plus A x is equal to B into t plus tau, where A is 2 D into 1 upon K S plus 1 upon h. B is 2 D C star by N 1 and tau is x i square plus A x i divided by B. This is the famous Deal and Grove oxidation kinetics equation, which predicts the growth of thermal oxide on silicon quite accurately.

Let us now examine this equation more carefully and see what does it really predict. First of all you will notice that this is a quadratic equation, right, it is a quadratic equation. So, you all know how to find out the roots of this quadratic equation. So, from this quadratic equation our first job will be to find the actual oxide thickness x, in terms of B and A and t and everything. We will just put them all on this side, tau is this.

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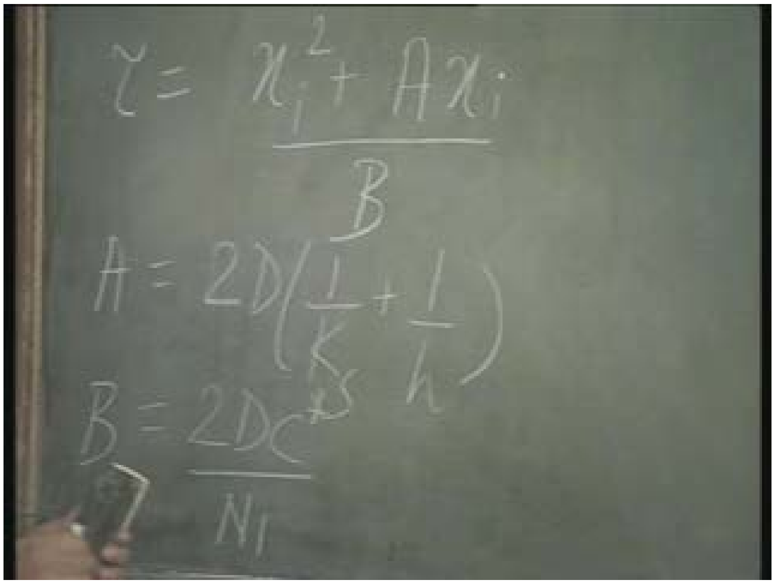

$$\tau = \frac{x_i^2 + A x_i}{B}$$

$$A = 2D\left(\frac{1}{k_s} + \frac{1}{h}\right)$$

$$B = \frac{2DC^*}{N_1}$$

Let us not disturb this part.

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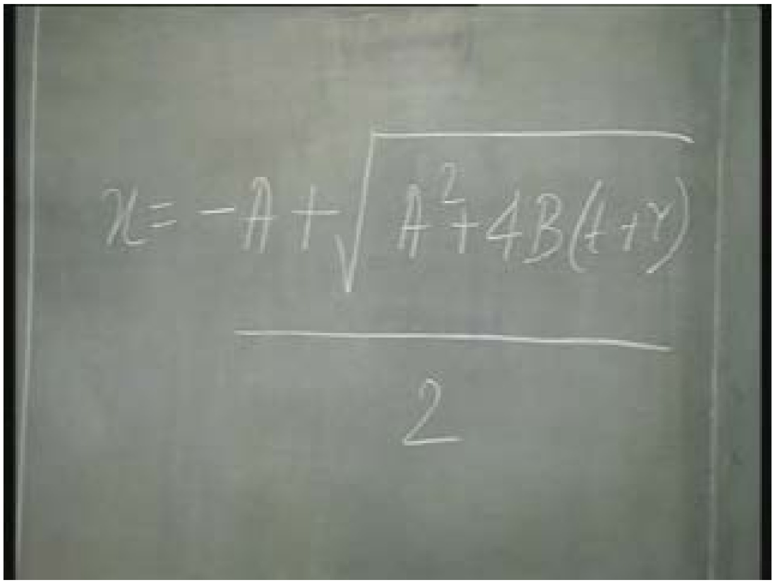

$$x = \frac{-A + \sqrt{A^2 + 4B(t+\tau)}}{2}$$

In order to find the roots of this quadratic equation, I can write x is ...... I am taking only one root, because the other root would give me a negative oxide thickness, which is practically impossible. So, I have to take only one root. Now, let us consider two limiting cases. The first case is when t is very small.

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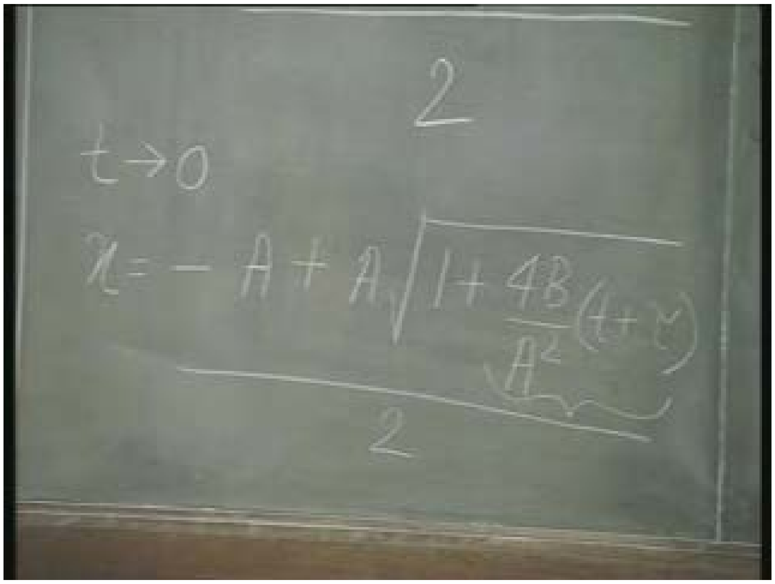

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$t \to 0$

$$x = \frac{-A + A\sqrt{1 + \underbrace{\frac{4B}{A^2}(t+\tau)}}}{2}$$

I am oxidizing for a very short duration of time, t tends to zero; t is not actually zero, t is very, very small. What is the significance of this, that t is very, very small. All I am trying to say is if I write x as minus A plus .... and if I say that t is tending to zero, then the significance is that under this square root, the second term is much smaller than the first term, that is 1. In other words, I am considering, when t is very small I am considering that this whole term is much, much less than 1, right. So, in that case I can approximate this term under the square root as this becomes like 1 plus epsilon to the power half which can be approximated as 1 plus half epsilon, right.

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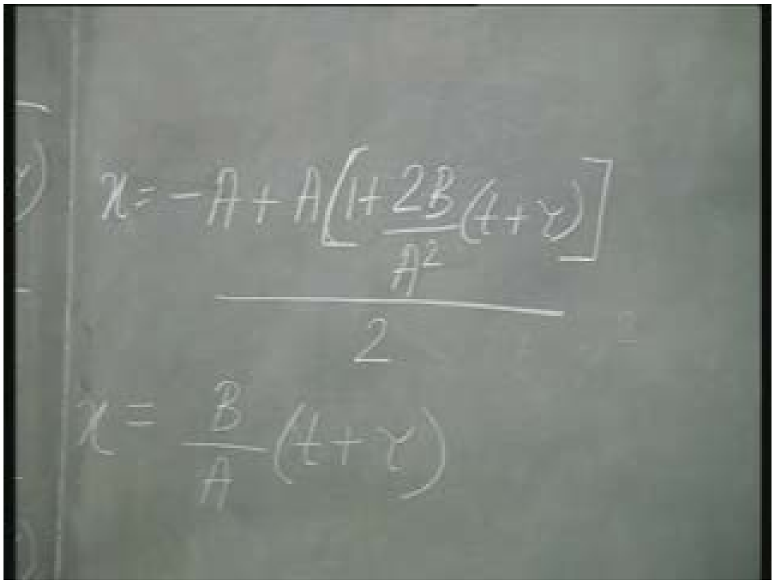

$$x = \frac{-A + A\left[1 + \frac{2B}{A^2}(t+\tau)\right]}{2}$$

$$x = \frac{B}{A}(t+\tau)$$

So, then I can write ...., agreed. This gets cancelled out, so what I have is simply B by A into t plus tau. In other words, when the oxidation time is really short, so that this term 4 B by A square into t plus tau is much, much smaller than 1, in that case the oxidation follows a linear growth rate curve; x is linearly proportional to time, right. That is one end of the spectrum, one limiting case that is when t is very, very small.

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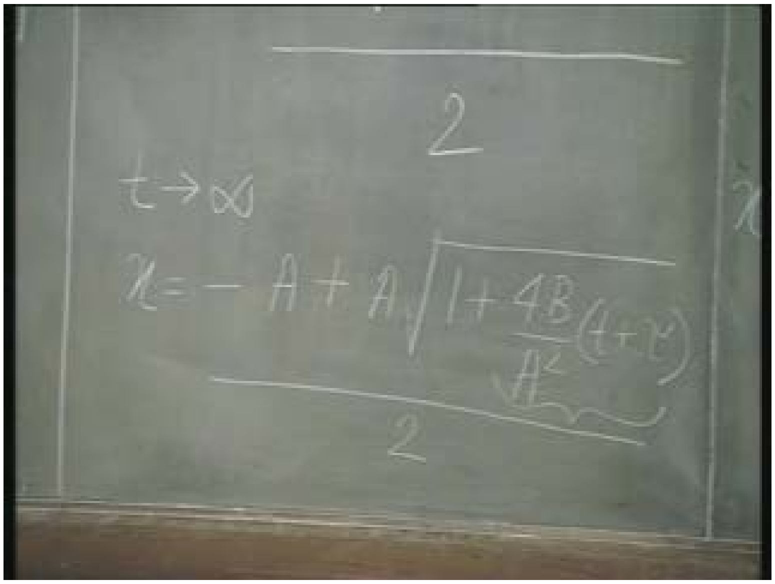

Let us look at the other end of the spectrum, t is very, very large. Again, this term is very significant.

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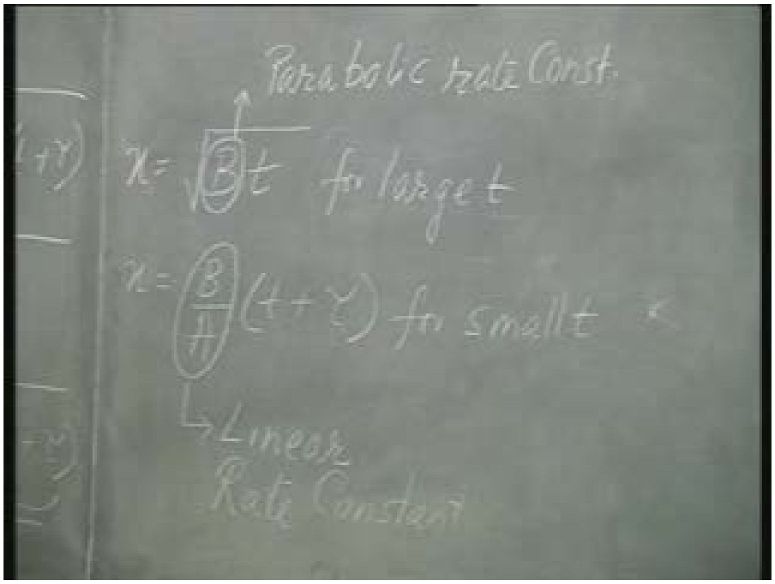

But now, the significance is that this is much, much greater than 1, so that the term under the square root can simply be approximated as, I can simply take this one out and say that x is equal to square root of B t. Essentially what I am trying to say is that this term and

this term does not have any significance. It is only this term that is dominating the procedure. So, the 4 goes out of the square root, it cancels with this 2. I have B into t plus tau. There again, since t is much, much greater, I can neglect tau and can simply say x is equal to square root of B t. That is when the time of oxidation is really very large, it no longer follows the linear rate of growth, but it now follows a parabolic rate of growth.
You would all know the equation of a parabola, y square equal to 4 A x, right, this is what you are seeing here, x square is equal to B t.

So, this is the famous Deal Grove linear parabolic equation of oxide growth rate, linear parabolic. That is when the oxidation time is short, the growth rate follows a linear rate of increase and when the time is much larger, then it follows a parabolic rate of growth. So, this is called the linear parabolic rate of oxide growth and this is the all important equation governing that growth rate that is x square plus A x is equal to B into t plus tau, with A, B and tau having their significance as given here. They are dependent on various constants. So, this is in general the oxidation growth rate.

Now, I have already told you that thermal oxidation of silicon is done either in presence of oxygen alone or in presence of water vapour. When it is done only in presence of oxygen, we call it dry oxidation. When it is done in presence of water vapour, we call it wet oxidation. So, dry and wet there are two types of oxidation. Let us see how the oxide growth depends on the type of oxidation. Before that, I would like to introduce two terms. So, you see x is square root of B t, this is for large t and x is equal to ....., for small t. This is called the linear rate constant and this B, this is called the parabolic rate constant. So, for any oxidation process, we have two rate constants associated with this. One is called the linear rate constant B by A, the other is B that is the parabolic rate constant. Any oxidation process can be defined by defining these two rate constants.

So, now let us have a look as to how this linear and parabolic rate constants depend on the type of oxidation that is whether the oxidation is dry or wet, also how they depend on temperature and why. Let us have a look at the table here.

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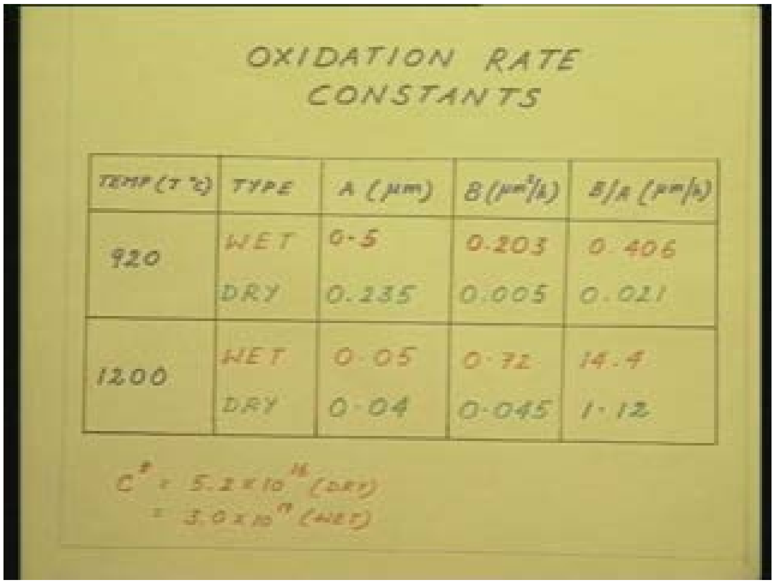

OXIDATION RATE CONSTANTS

TEMP (T °C)	TYPE	A (µm)	B (µm²/h)	B/A (µm/h)
920	WET	0.5	0.203	0.406
	DRY	0.235	0.005	0.021
1200	WET	0.05	0.72	14.4
	DRY	0.04	0.045	1.12

$C^* = 5.2 \times 10^{16}$ (DRY)

$= 3.0 \times 10^{19}$ (WET)

Concentrate only on one temperature first, let us say 920 degrees centigrade. I have two types of oxidation - red is for wet, green is for dry. So you can see for the wet oxidation, A, that is given in micrometer, please notice the units carefully, A is given in micrometer that is 0.5. B that is micrometer square per hour, that is given as 0.203 and B by A that is the linear rate constant is given as 0.406. So, this is the linear rate constant, this is the parabolic rate constant. B is the parabolic rate constant, B by A is the linear rate constant. Compare these values with that of the dry oxidation case. For the dry oxidation, B by A is 0.021, 20 times less. Am I correct? It is 20 times less, right. Similarly, B is 0.005, 40 times less. So, you can see that both the linear as well as the parabolic rate constants for the wet oxidation is much, much larger than in case of dry oxidation. Same thing, same trend you will see even at a different temperature.

Even when I go to 1200 degree centigrade, you find that B by A for wet oxidation is 14.4, whereas that in case of dry oxidation is only 1.1 and B is 0.72 for wet oxidation, 0.045 in case of dry oxidation. So, of course, first of all we have to understand why is it that in case of wet oxidation we have a much faster growth rate; that is what it signifies. Both B and B by A are so much larger, why is it that in case of wet oxidation we have so much larger growth rate? Let us look at this, the fact that both B and B by A in case of wet oxidation is so much larger, the key factor in it is because of B. Now, what is B? B is 2 D C star by N 1. Now, you know actually N 1 is larger for wet oxidation, because in order to grow one molecule of silicon dioxide we needed two molecules of water. So, number of oxidant molecules per unit volume of oxide, this is actually double in case of wet oxidation than in case of dry oxidation, remember. So, N 1 for wet oxidation is actually larger. So, you would expect that B for wet oxidation should actually be smaller, but this difference is more than offset if I look at C star that is the equilibrium concentration of the oxidant species in the oxide.

In case of dry oxidation, the equilibrium concentration of the oxidizing species is given as 5.2 into 10 power 16, whereas for wet oxidation this value is 3 into 10 power 19. Remember, I am giving these values only at a particular temperature. At a given temperature, the equilibrium concentration for dry oxide is more than three orders of magnitude less compared to the wet oxidation, about three orders of magnitude less, right, 10 power 16 in one case and 10 power 19 in the other case. So, obviously it stands to reason that B in case of wet oxidation will be much higher and therefore B by A will also be much higher.

So, now it brings me to the practical utility point of view that is when I want to grow thicker oxide, therefore it makes more sense to grow it using steam ambient, because the oxide growth rate will be much faster and that is what is done, actually. When you need thicker oxide for masking or field oxide then you use wet oxidation. On the other hand, dry oxidation quality will be much better, we will discuss that later on; quality will be much better and I will have controlled thinner growth of oxide. So, dry oxidation is used mostly for gate oxidation that is where you are bothered more about the quality of oxide, not the quantity. You do not want a very thick oxide, you want moderate thicknesses of oxide, but you are particular about the quality, then you will use dry oxidation.

There are certain other interesting points associated with this rate constants that is B and B by A. From this table, you have seen the values of B at two particular temperatures and see that B actually increases with an increasing temperature, right. At 920 centigrade, you have seen that B was 0.203 for wet oxidation and at 1200 degree centigrade, it has increased to 0.72. This is an increase which can be explained by this diffusion coefficient D. D is the diffusion coefficient which increases exponentially with temperature.

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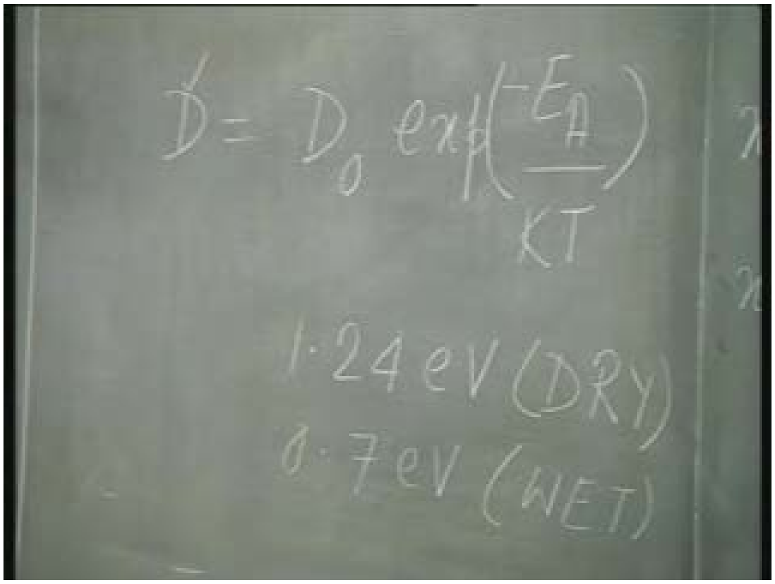

$$D = D_0 \exp\left(\frac{-E_A}{KT}\right)$$

1.24 eV (DRY)

0.7 eV (WET)

That is to say, D can be written as D 0 exponential minus E A by KT, where this E suffix A is called the activation energy, T is the temperature and the value of this E A is actually 1.24 electron volt and 0.7 electron volt. This is for dry oxidation, this is for wet oxidation and the interesting thing is it sort of matches with the diffusivity of oxygen and of water vapour through silicon dioxide signifying that this process is actually governed by diffusion. The activation energy matches with the diffusivity. This is a further proof to Deal and Grove's model.

Experimentally it is verified that this activation energy if you plot B versus 1 by KT, you get that this activation energy is 1.24 for dry oxidation, which sort of matches with the diffusivity of oxygen through silica and for wet oxidation this value is seen to be about 0.7 electron volt, which again matches with the diffusivity of water vapour through silica. So, this is an experimental verification, an indurate experimental verification of Deal and Grove's model. So, B increases with temperature primarily because of this.

Let us look at the linear rate constant B by A. B by A for wet oxidation at 920 degree centigrade it was 0.406 micrometer per hour and at 1200 degree centigrade, it has increased to 14.4. Now, what is B by A? If I look at B by A, see this D term will get cancelled. So, this increase in B by A with temperature is actually not because of the diffusion coefficient, it is because of this term K S. K S is the reaction rate constant and K S increases with temperature, therefore B by A will also increase with temperature. So, the properties of both the parabolic rate constant and the linear rate constant can be easily explained, you see. But there is one very funny problem.

What happens to A? If you notice, A actually decreases with temperature. In this particular example that I have taken, A actually decreases with temperature. At 920 degree centigrade, A was 0.5 and at 1200 degree centigrade, it has decreased to 0.05. Why should it be so? That is because A has D in the numerator and K S in the denominator, both of them are increasing with temperature. So, what actually happens to A depends on which one is dominating, D or K S. That is why we find that A is actually decreasing with temperature, although both the linear and the parabolic rate constants increase with temperature.

So, now therefore we have seen that the oxidation growth rates are higher for wet oxidation than for dry oxidation and also the growth rates will be higher at higher temperature, right. That is if you carry out the oxidation at higher temperature, for a given amount of time you would expect to grow thicker oxide.

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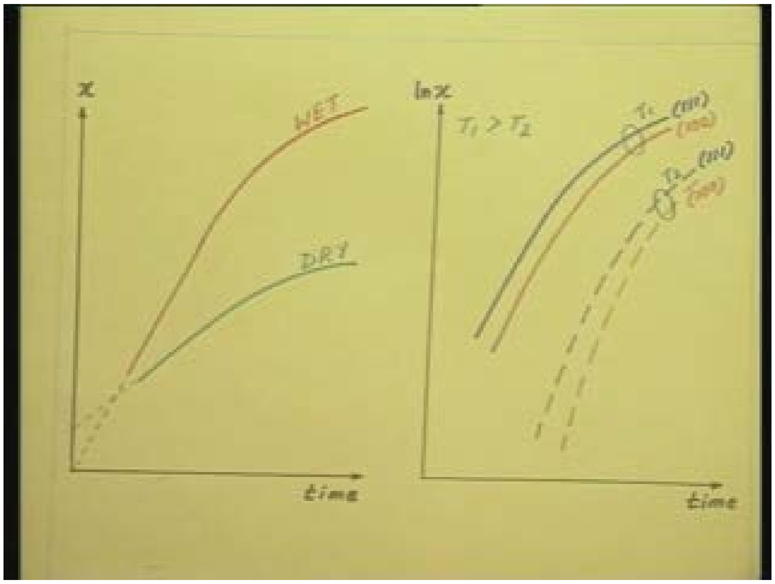

This is something I have tried to depict pictorially. Look at this graph on the left. I have plotted x versus time. x is actually the oxide thickness and assume that both these oxidations are carried out at same temperature. Both of them will exhibit the famous linear parabolic relationship. That is it starts off with linear and then becomes parabolic and the wet oxidation is going to give rise to a much thicker oxide in the same time. So far, so good. This is what Deal Grove's model also predicts. However there is a, there is a quite an interesting point, if you look more carefully at this graph. I have tried to extrapolate these two curves. Now you see, if I started with a fresh silicon surface, I know I have made sure that there is no oxide on it at the time of starting the oxidation process, then I would expect that both these curves will pass through the origin. That is at t equal to zero, the oxide thickness should be zero, because I know, I have made sure.

However experimentally, both these curves are experimental curves, right, experimentally when you generate this curve and then try to extrapolate it, you find that even though the wet oxidation curve passes through the origin, the dry oxidation curve does not pass through the origin. Instead it gives a non zero intercept on the x-axis that is on the thickness axis. That means it is as if even at the beginning of oxidation there is a finite thickness of oxide present. In other words, I have a non zero x i, non zero initial oxide thickness. This is almost the only place where there is a departure, deviation between Deal Grove's model and the experimental curves. Otherwise Deal Grove's model hold up very well, it holds up very well. It can explain all the experimental data.

The only problem starts when you are going to grow very thin oxide by dry oxidation on silicon, very thin oxide. That is according to Deal Grove's model, it should have passed through the origin, but in the experimental, I always find there is a non zero intercept on the x-axis. So, what happens actually in the initial region during oxidation? One way to explain this is of course, you assume that initially the oxide growth rate is much faster than that predicted by Deal and Grove.

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That is to say I have ..... This actually means that the initial rate of growth was much faster and then it has caught up with the model predicted by Deal and Grove. So, this portion is not explained by the Deal Grove model. That initial region of faster oxide growth is not adequately explained by Deal and Grove's model. That is why very thin oxidation on silicon is still quite a challenge and you know the importance of this thin oxidation is increasing, because now we are talking about gate oxides with less than 100 Angstrom thickness, 40 Angstroms. Intel is now making gate oxides with 40 Angstrom thickness. This is because this intercept is about 270 Angstrom. So, anything less than 270 Angstrom is difficult to explain by Deal Grove's model. Whenever you are going to an oxide thickness less than this value, it cannot be adequately explained by Deal Grove's model, it is more difficult to predict. So, now when we are going to get oxide thicknesses of less than 100 Angstrom, this thin oxide growth is coming under more and more scrutiny. A lot of research is being carried out in this region to explain how this thin oxide growth rate is taking place. So, this is one interesting point.

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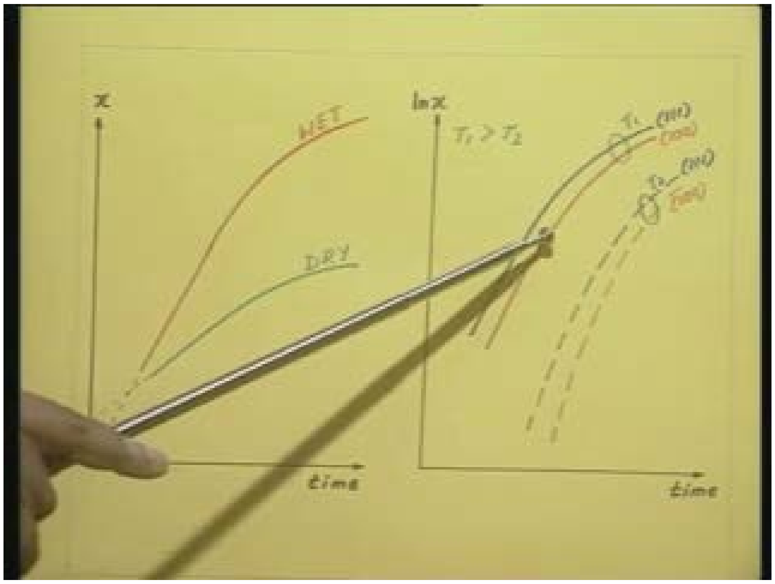

Notice that, for wet oxidation I do not have anything like this. For wet oxidation, it passes straight through the origin. Only for dry oxidation I have this problem, it shows a non zero intercept of about 270 Angstrom. The other interesting point to notice, look at any two black curves or any two red curves. The black curve here, this is for T 1, a temperature T 1 and this dotted curve is for a temperature T 2. T 1 is greater than T 2. So, obviously the growth rate is higher for the higher temperature. This is what we have seen from the table also just now, that both the linear growth rate as well as the parabolic growth rate is going to increase and therefore at higher temperature the oxidation will grow, the oxide will grow faster.

But now, I have added another twist to this. That is I have plotted the curves both for 1 1 1 and 1 0 0 oriented crystal and you see that the 1 1 1 oriented crystal shows a higher rate of oxide growth than the 1 0 0 oriented crystal. This is true for T 1 as well as for T 2. While you know that 1 1 1 oxidizes faster, because it has more number of atoms per unit area, more number of silicon atoms per unit area. Therefore, particularly in the linear region, for smaller oxidation time where the oxidation is dependent mostly on the reaction rate, there 1 1 1 will oxidize faster, because there are more number of silicon atoms waiting to be oxidized. This is what we see. For smaller time, you see, the two curves are widely separated, here as well as here; the two curves are widely separated.

However, as the oxide grows in thickness, the oxidation becomes, from the linear region it enters the parabolic region and then the advantage of this, having this larger number of silicon atoms is somewhat lost, because then the oxidation is dependent more on the diffusion of the oxidizing species, because already a thick enough oxide is grown. So, it depends on the availability of the oxidizing species. The oxidizing species now must diffuse through the existing oxide layer and then reach the silicon-silicon dioxide interface. So, the oxidation rate is governed primarily by the diffusion. That is why you see as the time progresses, the two curves tend to come closer together. So, particularly in the linear region, you find there is quite a considerable difference between 1 0 0 and 1 1 1 oriented crystals. However as time progresses, the oxide thickness sort of tends, they tend to catch up with each other.

I will just mention one more interesting point. We carry out the oxidation, right and the silicon wafer is doped. It can be doped either p-type or n-type, it can either be doped very heavily or moderately. Will the oxidation rate depend on the doping also? The answer is yes, if it is very heavily doped. It is found that if the silicon wafer is doped p-plus that is you know, for p-type doping we always use boron. So, if it is heavily doped with boron, then it oxidizes faster than a moderately doped sample. It oxidizes faster at all temperatures. No matter what the oxidation temperature is, compared to a moderately doped sample a heavily doped p-type sample will always oxidize faster.

If it is heavily doped n-type, even then it is n-type, the most common dopant is phosphorus. So, you have to consider phosphorus doped silicon. Even then we find that it oxidizes faster, but only at lower temperature. At higher temperature, the oxidation rates tend again to be equal. The heavily doped and the moderately doped samples tend to have equal oxide growth rate, but at lower temperature the heavily phosphorus doped sample oxidize faster. This is because when you are talking about heavily boron doped sample, the oxidation rate is faster because boron converts the oxide into borosilicate glass and diffusion of the oxidizing species is faster through this boron doped silicon dioxide, which I am calling borosilicate glass. So, both the rate constants are getting affected by that, whereas in case of phosphorus doped sample, it creates a defect region, sort of a defect region, at the silicon-silicon dioxide interface, which increases the reaction rate. That is why when you have a phosphorus doped sample, the higher oxidation rate is visible only for lower temperature that is where the linear rate is dominating, where it is reaction rate limited, only there heavily phosphorus doped samples tend to oxidize faster. Whereas, if we have a heavily boron doped sample, since it is the diffusion of the oxidizing species that is getting facilitated, we have a higher oxide growth rate at all temperature.

Now, why should this happen? Why should phosphorus create a sort of damaged region at the silicon-silicon dioxide interface and why should boron convert the silicon dioxide? Why should boron affect the properties of silicon dioxide? These are some things we will discuss in the next class. That is in other words, we are going to discuss in the next class when the silicon is doped p-type or n-type, what happens to the impurity when it is getting oxidized? Do I have impurities in equal proportion in silicon and silicon dioxide or does it come preferentially into the silicon dioxide or does it go back preferentially in silicon? What happens to the dopants when silicon is getting converted in the silicon dioxide? That is what we will start discussing in the next class.