Processing of Semiconducting Materials
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Lecture - 33
Oxidation – II

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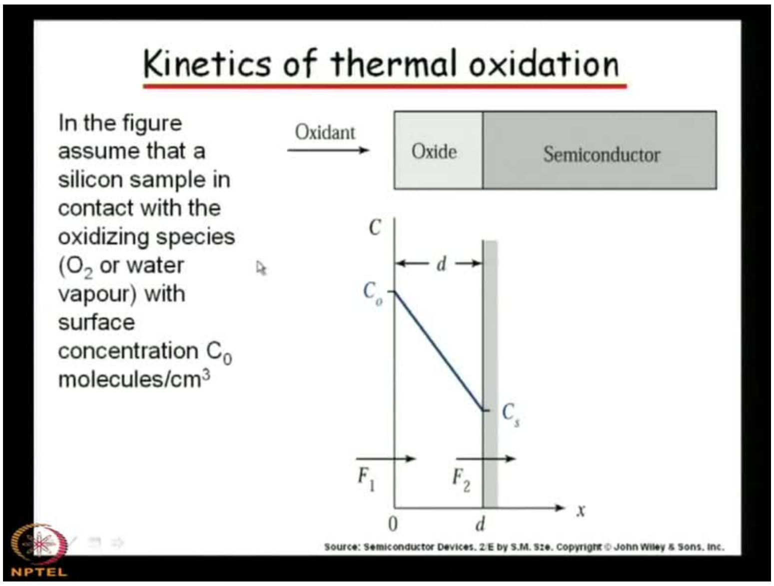

Kinetics of thermal oxidation

In the figure assume that a silicon sample in contact with the oxidizing species (O_2 or water vapour) with surface concentration C_0 molecules/cm^3

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Sir, start. In the earlier class we have discussed about the thermal oxidation, which is one of the most important process steps in the process engineering of silicon or in any other device technology. So, today we shall discuss about the kinetics of thermal oxidation. And you can find that in this view graph that this is the semiconductor piece of sample, let it be silicon and the oxide has been formed at one of it send through the oxidants; that means we have assumed that a silicon sample in contact with the oxidizing species.

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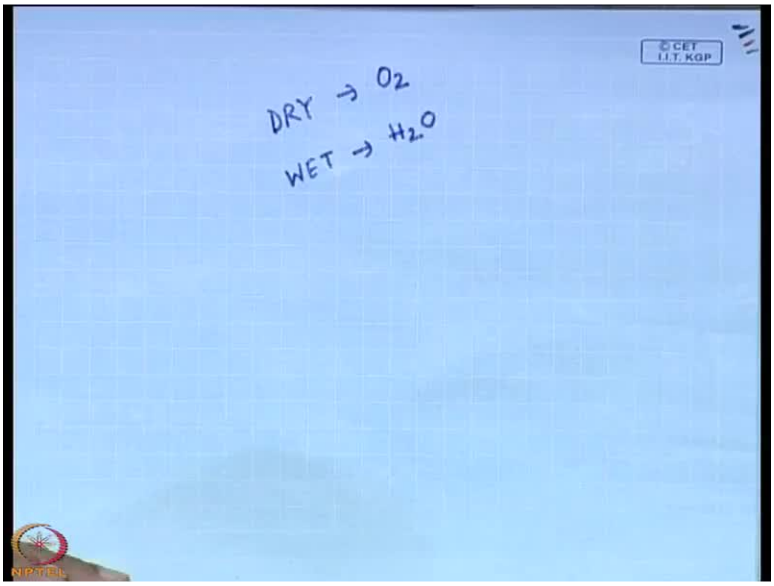

The oxidizing species can be oxygen or the water vapor, because we have discussed earlier that the oxidation can be done by two process; one is the dry oxidation, another is the wet oxidation. And in dry oxidation generally oxygen is used and in wet oxidation water vapor or steam is used. So, in the view graph you can see that when we talk about the oxidizing species. Basically this could be oxygen or water vapor depending on the oxidation is dry or wet with surface concentration C 0 molecules per centimeter cube. Now, next step is that, what what is the value of this C 0?

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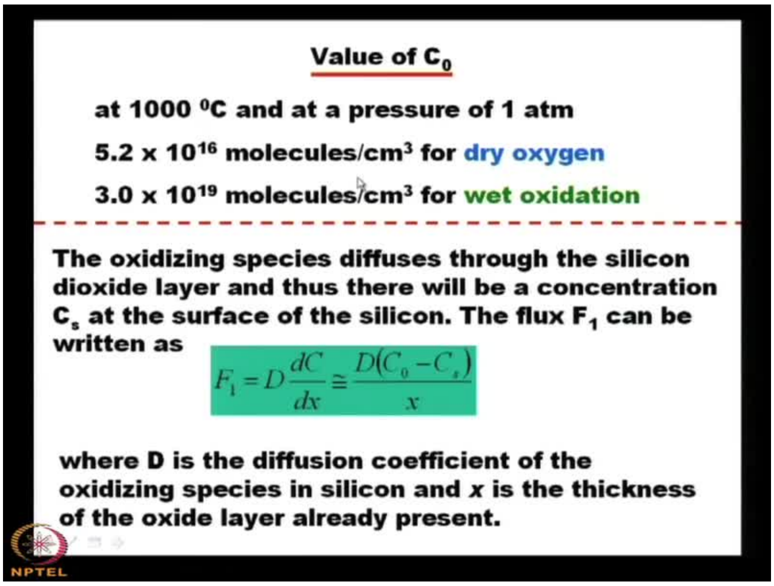

Value of C_0

at 1000 ^{0}C and at a pressure of 1 atm

5.2×10^{16} molecules/cm^3 for dry oxygen

3.0×10^{19} molecules/cm^3 for wet oxidation

The oxidizing species diffuses through the silicon dioxide layer and thus there will be a concentration C_s at the surface of the silicon. The flux F_1 can be written as

$$F_1 = D\frac{dC}{dx} \cong \frac{D(C_0 - C_s)}{x}$$

where D is the diffusion coefficient of the oxidizing species in silicon and x is the thickness of the oxide layer already present.

The value of this C 0 for dry oxygen is 5.2 into 10 to the power 16 molecules per centimeter cube, and for wet oxidation its value is somehow higher it is 3 into 10 to the power 19 molecules per centimeter cube, it is at the 1000 degree centigrade and at a pressure of 1 atmosphere. Now, if you change the process condition, suppose if you increase or decrease the temperature or if you increase or decrease the pressure the values will be changed. So, this is the value of C 0, which we have assumed that it is the concentration at the surface, then what happens?

Then the oxidizing species diffuses through the silicon dioxide layer because remember here, since there is a oxide layer already formed on the semiconductor surface. Now, the oxidant oxidants or the oxidizing species must diffuse through the oxide layer to reach to the semiconductor surface. Once they reach at the semiconductor surface, they will be react with the semiconductor for the formation of SiO2. So, the the oxidizing species diffuses through the silicon dioxide layer and thus there will be a concentration C s at the surface of the silicon.

This is the C s of the surface of the silicon, so this d is the thickness of the oxide already formed and the oxidizing species must diffuse through the oxide species. Now, we have to calculate the flux at this f one that means between the oxide and the oxidizing species and also at this surface where it is between the oxide already formed and semiconductor so let us calculate the flux at F 1 and F 2. Now, if you calculate the flux at F 1 that can be written as d d C by d x, which is equals to d C 0 minus C s by x. So, remember that this is the C 0 and this is the C S. So, C 0 minus C s by x is the concentration gradient because d C d x is the concentration gradient, where d is the diffusion coefficient of the oxidizing species in silicon and x is the thickness of the oxide layer already present.

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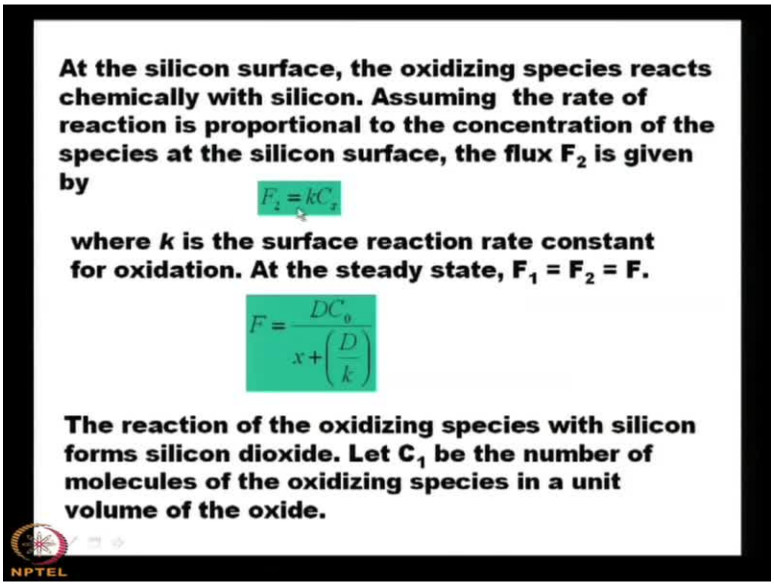

At the silicon surface, the oxidizing species reacts chemically with silicon. Assuming the rate of reaction is proportional to the concentration of the species at the silicon surface, the flux F_2 is given by

$$F_2 = kC_s$$

where *k* is the surface reaction rate constant for oxidation. At the steady state, $F_1 = F_2 = F$.

$$F = \frac{DC_0}{x + \left(\frac{D}{k}\right)}$$

The reaction of the oxidizing species with silicon forms silicon dioxide. Let C_1 be the number of molecules of the oxidizing species in a unit volume of the oxide.

At the silicon surface the oxidizing species reacts chemically with silicon, assuming the rate of reaction is proportional to the concentration of the species at the silicon surface the flux F 2 in given by F 2 equals to k into C s.

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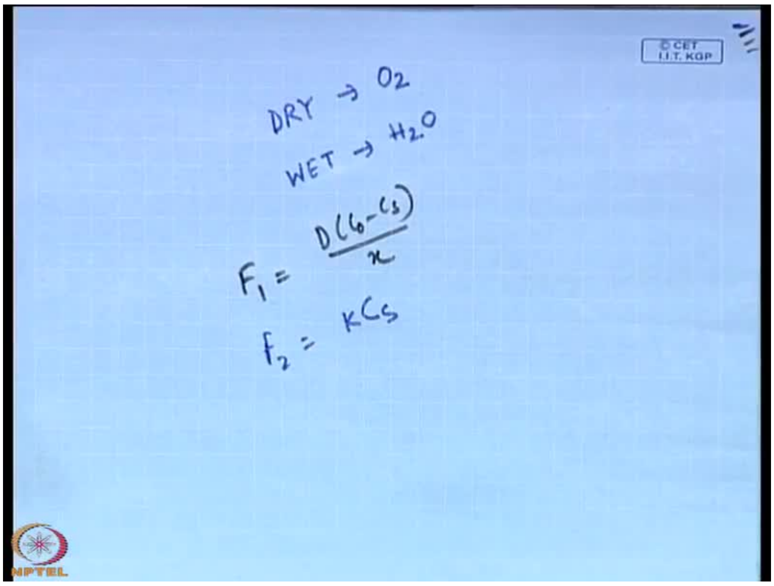

DRY → O_2

WET → H_2O

$$F_1 = \frac{D(C_0 - C_s)}{x}$$

$$F_2 = kC_s$$

So, what we find that first this F 1 which we can write as d of C 0 minus C s by x and F 2 which we can write as k into C s. This C s is the concentration at the surface of the silicon. This is the concentration of the surface of the silicon then what is k? k is a surface reaction rate constant for oxidation. At the steady state this F 1 and F 2 will be equal and at the steady state this F 1 equals to F 2 equals to F.

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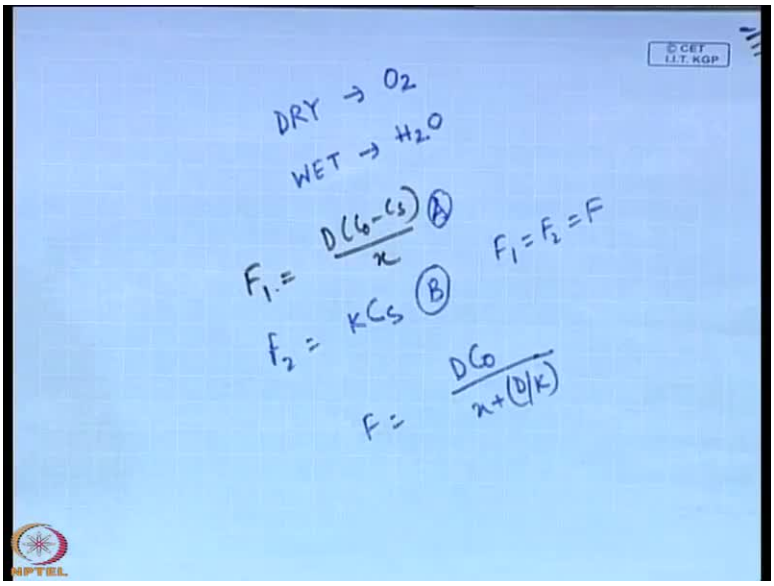

DRY → O_2

WET → H_2O

$$F_1 = \frac{D(C_0 - C_s)}{x} \quad Ⓐ$$

$$F_2 = kC_s \quad Ⓑ$$

$F_1 = F_2 = F$

$$F = \frac{DC_0}{x + (D/k)}$$

Now, if you equate this equation suppose it is A and it is B, put the value of C s in terms of F, then what we find then F becomes d C zero by x plus d upon k. So, C 0 is the initial surface concentration of the oxidizing species and d is the, this d is the diffusion coefficient or diffusivity. So, the reaction of the oxidizing species with silicon from silicon dioxide, let us even be the number of molecules of the oxidizing species in a unit volume of the oxide. Remember that this C 1 we have assume that it is the number molecules of the oxidizing species in a unit volume of oxide.

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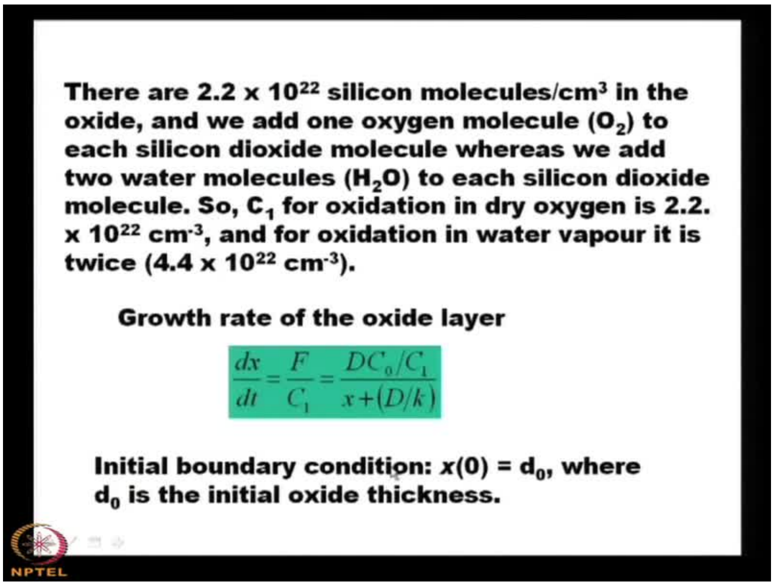

There are 2.2×10^{22} silicon molecules/cm^3 in the oxide, and we add one oxygen molecule (O_2) to each silicon dioxide molecule whereas we add two water molecules (H_2O) to each silicon dioxide molecule. So, C_1 for oxidation in dry oxygen is 2.2. $\times 10^{22}$ cm^{-3}, and for oxidation in water vapour it is twice (4.4×10^{22} cm^{-3}).

Growth rate of the oxide layer

$$\frac{dx}{dt} = \frac{F}{C_1} = \frac{DC_0/C_1}{x+(D/k)}$$

Initial boundary condition: $x(0) = d_0$, where d_0 is the initial oxide thickness.

Then what will happen then we must be interested about the value of C 1, so there are 2.2 into 10 to the power 22 silicon molecules per centimeter cube in the oxide and we add 1 oxygen molecule to each silicon dioxide molecule, whereas we add 2 water molecules to each silicon dioxide molecules. Because 1 oxygen molecule is oxygen is diatomic, so it is O2. Here in water molecule only one atom of oxygen is there, so to make it oxygen molecule there must be 2 water molecules, so this 2.2 into 10 to the power 22, this will be 4.4 into 10 to the power of 22 centimeter cube, if the oxidation takes place due to the water vapor. So, C 1 value for dry oxygen and water vapor and and for wet oxygen it is different, it is twice because of the oxygen diatomicity.

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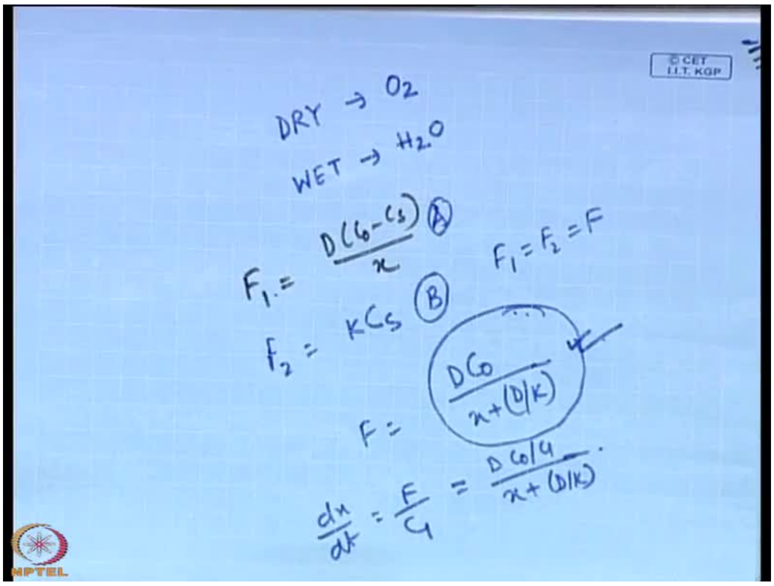

DRY → O_2

WET → H_2O

$$F_1 = \frac{D(C_0 - C_s)}{x} \quad Ⓐ$$

$$F_1 = F_2 = F$$

$$F_2 = KC_s \quad Ⓑ$$

$$F = \boxed{\frac{DC_0}{x + (D/K)}} \checkmark$$

$$\frac{dx}{dt} = \frac{F}{C_1} = \frac{DC_0/C_1}{x + (D/K)}.$$

Then growth rate of the oxide layer which is given by d x by d t it is equals to F by C 1 and that is equals to if we put the values of F. Then because F is equals to d into C 0 by x plus d by k, this is the value of F. So, if we put this F equals to F by C 1 that is the growth rate, it is the growth rate d x d t of the oxide layer. So, if we put this F by C 1 here, so what we get? That d C 0 by C 1 by x plus d upon k, so this is the growth rate of the oxide layer and the initial boundary condition is that at t equals to 0, already there is an initial oxide thickness that we have shown here also. Already there is an initial oxide thickness and this oxide thickness can be a result of earlier oxidation or p oxidation and in dry oxide condition, we know that already there is an oxide layer forms at the surface of the silicon wafer.

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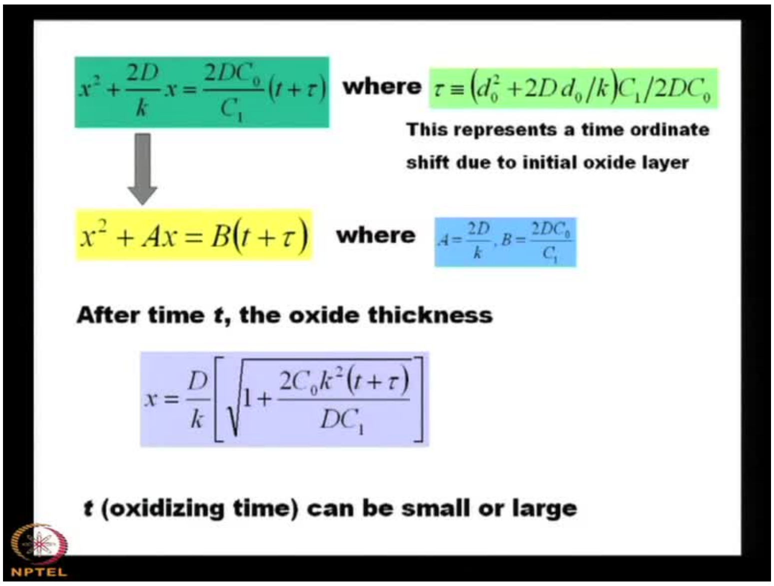

$$x^2 + \frac{2D}{k}x = \frac{2DC_0}{C_1}(t+\tau)$$ **where** $\tau \equiv \left(d_0^2 + 2D\,d_0/k\right)C_1/2DC_0$

This represents a time ordinate shift due to initial oxide layer

$$x^2 + Ax = B(t+\tau)$$ **where** $A = \frac{2D}{k},\ B = \frac{2DC_0}{C_1}$

After time *t*, the oxide thickness

$$x = \frac{D}{k}\left[\sqrt{1+\frac{2C_0k^2(t+\tau)}{DC_1}}\right]$$

***t* (oxidizing time) can be small or large**

So, with this initial condition that d 0 is the initial oxide thickness, we can write that x square plus 2 d by k into x equals to 2 d C 0 by C 1 into t plus tau. So, these equation and where tau is is a time ordinate shift due to initial oxide layer that can be represented by the value d 0 square plus twice d small d 0 by k multiplied by C 1 by twice d C 0 and this equation can be written as x square plus A x plus B into t plus tau, where A is equals to twice d by k and B equals to twice d C 0 by C 1.

Now, after time t the oxide thickness can be written as x equals to d by k root over of 1 plus twice C 0 k square t plus tau by d C 1. So, it is the solution of this equation where t is the oxidizing time that can be small or large, because here it is very much important that when t is small, one thing will happen and when t is large the other thing will happen. So, throughout the time axis you can consider that the oxidation layer will not be uniform. For small t we shall see that it will varies linearly with time and for large T we shall find that it will be parabolic. So, the rate constant will be different and we shall analyze that thing and for small t, this because this is the equation that x equals to this is the reaction.

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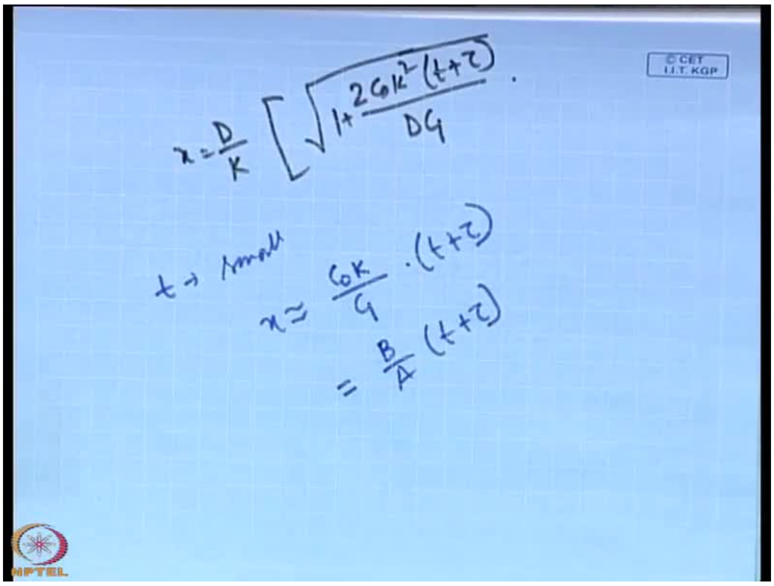

$$x = \frac{D}{K}\left[\sqrt{1+\frac{2C_0K^2(t+\tau)}{DC_1}}\right.$$

$t \to$ small

$$x \simeq \frac{C_0K}{C_1}\cdot(t+\tau)$$

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

That x equals to d by k root over of 1 plus twice C 0 k square t plus tau by d C 1. Now, when t is small, for t is small that can be approximated to x is equivalent to C 0 k by C 1 into t plus tau. How this can be approximated? That in that case we can consider that the numerator of the of this fraction numerator of this fraction is very, very greater than 1 and we can write in this manner and which is equals to B by A into t plus tau. This B by A is equals to C 0 k into by C 1 that can be written from here that B by A, k we have assumed that what is the value of A and what is the value of B and if you take the ratio of B by A you will find that will arrive at this expression.

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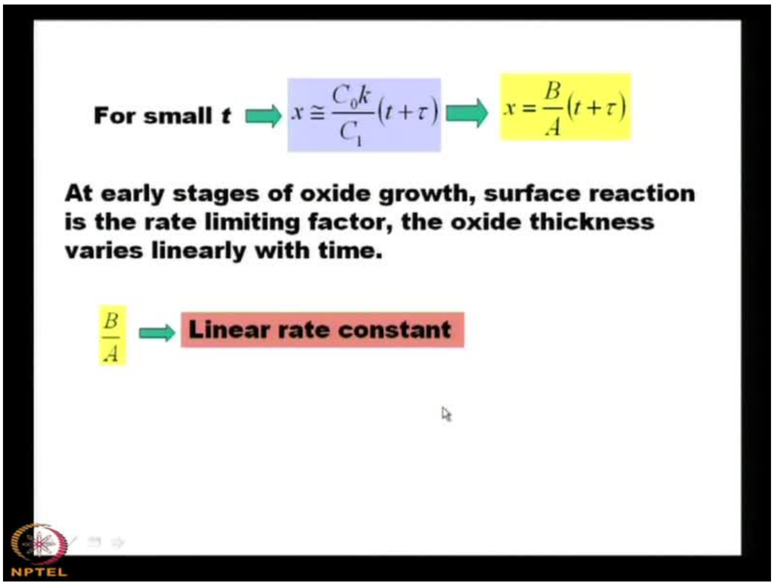

For small *t* → $x \cong \frac{C_0 k}{C_1}(t+\tau)$ → $x = \frac{B}{A}(t+\tau)$

At early stages of oxide growth, surface reaction is the rate limiting factor, the oxide thickness varies linearly with time.

$\frac{B}{A}$ → **Linear rate constant**

So, at early stages of oxide growth, surface reaction is the rate limiting factor. At early stages of oxide growth surface reaction is the rate limiting factor the oxide thickness varies linearly with time and this B by A is known as the linear rate constant. So, we shall arrive at two types of rate constant; one is the linear rate constant and another is that we shall discuss now it is for large T, when we shall find that this will vary as the parabolic nature.

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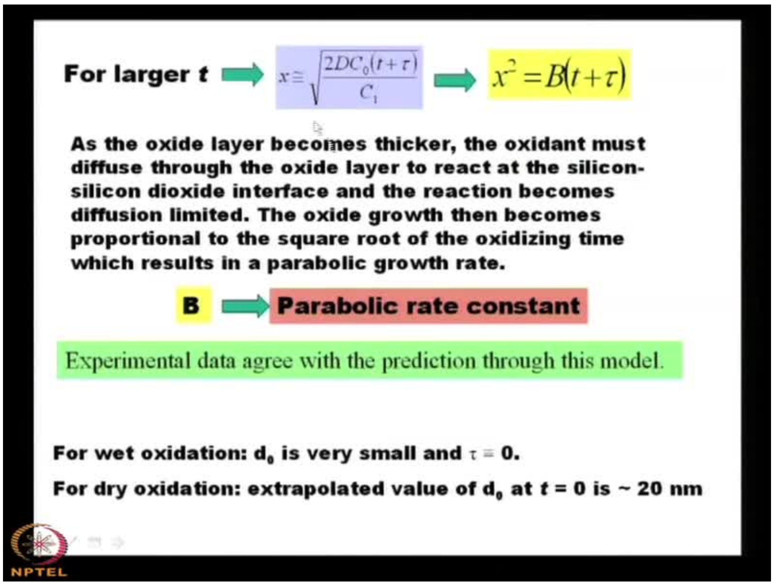

For larger *t* ⇨ $x \cong \sqrt{\frac{2DC_0(t+\tau)}{C_1}}$ ⇨ $x^2 = B(t+\tau)$

As the oxide layer becomes thicker, the oxidant must diffuse through the oxide layer to react at the silicon-silicon dioxide interface and the reaction becomes diffusion limited. The oxide growth then becomes proportional to the square root of the oxidizing time which results in a parabolic growth rate.

B ⇨ **Parabolic rate constant**

Experimental data agree with the prediction through this model.

For wet oxidation: d_0 is very small and $\tau = 0$.

For dry oxidation: extrapolated value of d_0 at $t = 0$ is ~ 20 nm

For larger t, x will be equals to twice d C 0 t plus tau by C 1. In this case it will be x square equals to B t plus tau, so as the oxide layer becomes thicker the oxidant must diffuse through the oxide layer to react at the silicon silicon dioxide, silicon and silicon dioxide interface and the reaction becomes diffusion limited. The oxide growth then becomes proportional to the square root of the oxidizing time which results in a parabolic growth rate. So, it is the equation of a parabola x square equals to B t plus tau and this B is known as the parabolic rate constant.

And this is basically a rate constant this is a kinetic kinetic thermal oxidation, so that is a model and we have seen that experimental data agree with the prediction through this model. Now, let us again consider the case of small t and large T to explain what is the linear rate constant and what is the parabolic rate constant? You see that at the onset of oxidation when it is just starting, the oxidizing species reacts with the semiconducting material. So, if the semiconducting material is silicon and oxidizing species is oxygen then oxygen reacts with silicon and so that is a rate limited case.

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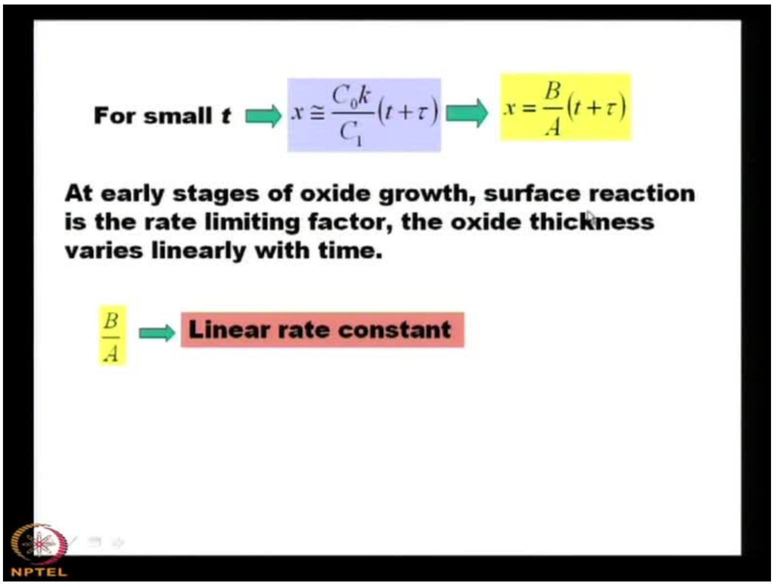

For small t $\Rightarrow$ $x \cong \frac{C_0 k}{C_1}(t+\tau)$ $\Rightarrow$ $x = \frac{B}{A}(t+\tau)$

At early stages of oxide growth, surface reaction is the rate limiting factor, the oxide thickness varies linearly with time.

$\frac{B}{A}$ $\Rightarrow$ **Linear rate constant**

So, surface reaction is a rate limiting factor say it is a surface reaction and and the oxide thickness varies linearly with time. Now, when there will be an oxide layer already present, so what will happen? The oxidizing species must diffuse through the oxide layer to reach at the semiconductor surface. In that case as the oxidant must diffuse through the oxide layer to react at the silicon silicon dioxide interface and the reaction becomes diffusion limited. Then it becomes the it becomes proportional to the square root of the oxidizing time.

So, there are two rate constant one is the linear rate constant another is the parabolic rate constant. For wet oxidation this d 0 is very small and tau is almost equals to 0. For dry oxidation extrapolated value of d 0 at t equals to 0 is almost 20 nanometer. So, at the onset already we can assume that a 20 nanometer oxidation layer is formed on the surface of the semiconducting wafer for dry oxidation. Now, if we now consider the SiO2 structure, what what is about the SiO2 structure?

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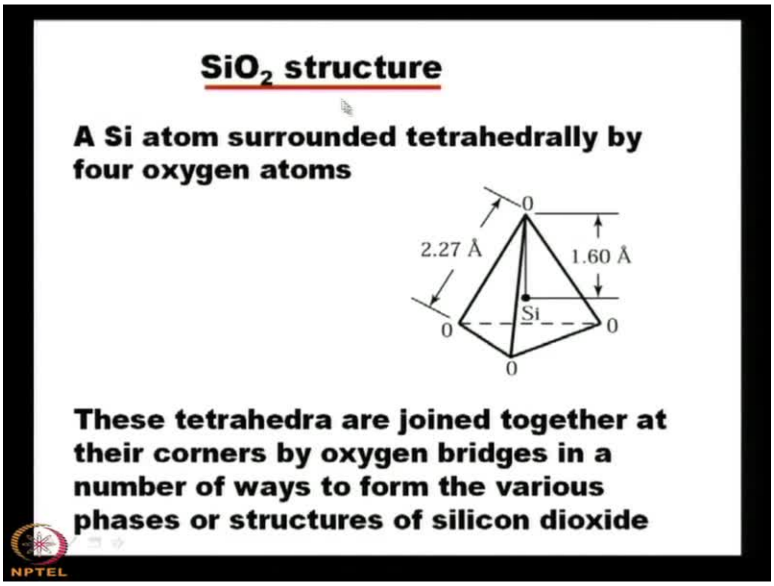

SiO$_2$ structure

A Si atom surrounded tetrahedrally by four oxygen atoms

These tetrahedra are joined together at their corners by oxygen bridges in a number of ways to form the various phases or structures of silicon dioxide

Here you see that a silicon atom is surrounded tetrahedrally by 4 oxygen atom. So, this is the silicon atom and it is surrounded tetrahedrally by 4 oxygen atom, 1, 2, 3 and 4 oxygen atoms, and the distance between the internuclear distance between the oxygen and silicon is 1.6 angstrom and the internuclear distance between oxygen and oxygen is 2.27 angstrom. So, this is the the the structure and these tetrahydra are joined together at their corners by oxygen bridges in a number of ways to form the various phases or structure of silicon dioxide.

So, depending on how the oxygen bridges are formed, the the silicon dioxide structures will be different and one type of structure could be say the amorphous structure that we shall discuss, another type of structure could be the crystalline structure or the quartz. In SiO2 sometimes you know that it is known as the silica and silica can have two type of crystal structure; one is the crystalline nature, which is the quartz and another is the amorphous structure that we shall discuss now.

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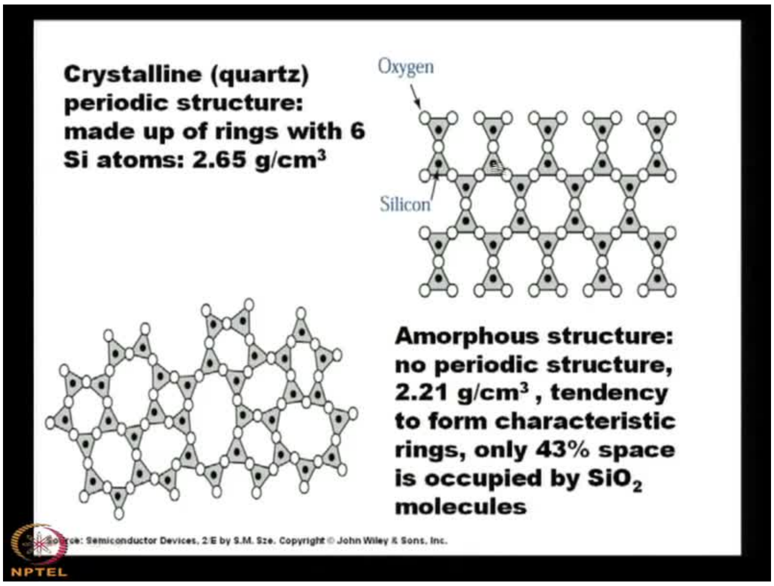

Crystalline (quartz) periodic structure: made up of rings with 6 Si atoms: 2.65 g/cm^3

Amorphous structure: no periodic structure, 2.21 g/cm^3, tendency to form characteristic rings, only 43% space is occupied by SiO_2 molecules

Source: Semiconductor Devices, 2/E by S.M. Sze. Copyright © John Wiley & Sons, Inc.

So, depending on the oxygen bridges, the crystalline or the amorphous structure is formed. Here you see that when this oxygen bridge is there and forms a ring, it is a ring like structure made up of 6 silicon atoms. This is 1 silicon atom, 1, 2, 3, 4, 5 and 6. So, 6 silicon atoms are there, if you consider here there is also 6 silicon atoms, so they formed a periodic structure. This periodic structure it has a it has density of 2.65 gram per centimeter cube.

Since, it is periodic structure we can say that it is crystalline in nature and if this tetrahydra are joined together at the corners by oxygen bridges in this manner, then we can say that it is a quartz structure. This silica structure is a quartz structure. But if we consider that the structure is like this that the that the tetrahydra are joined together at their corners by oxygen bridges in this manner, and here though there is a tendency to form the characteristics ring here, there is a characteristics ring with 6 silicon atoms. Here there is a tendency, but it is not periodic in the sense that sometimes it is more than 6, sometime it is less than 6, there is a tendency to form the characteristic rings, but they could not make it.

So, only 43 percent space is occupied by SiO2 molecules and 57percent space is not occupied by the SiO2 molecules. So, what happens that there are many spaces or wide spaces available in this kind of a structure and so predictably the density is 2.21 gram per centimeters cube. If you if you compare this value of 2.21 gram per centimeter cube, you will find that in for crystalline structure is 2.65, so here the structure is more closely packed than this type of a structure. And this is a amorphous structure because there is no periodicity, though there is a tendency. So, depending on the structure there could be other type of structures also…

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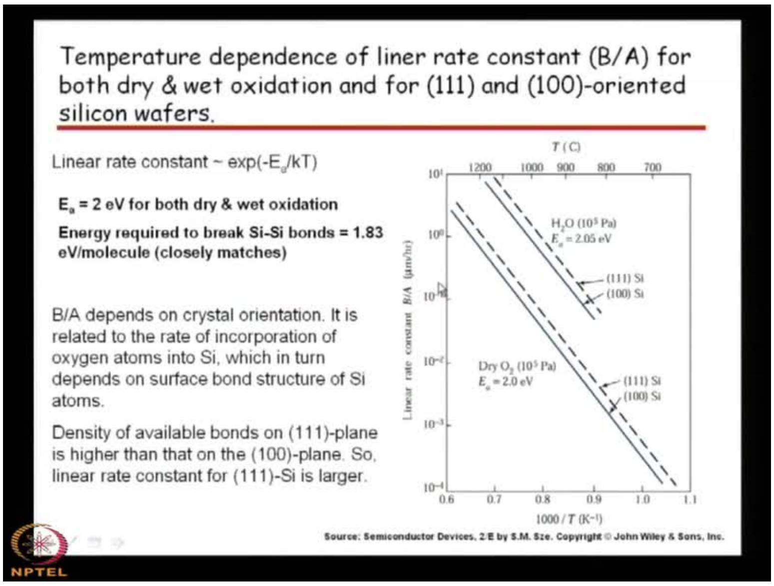

Temperature dependence of liner rate constant (B/A) for both dry & wet oxidation and for (111) and (100)-oriented silicon wafers.

Linear rate constant ~ exp(-E_a/kT)

E_a = 2 eV for both dry & wet oxidation

Energy required to break Si-Si bonds = 1.83 eV/molecule (closely matches)

B/A depends on crystal orientation. It is related to the rate of incorporation of oxygen atoms into Si, which in turn depends on surface bond structure of Si atoms.

Density of available bonds on (111)-plane is higher than that on the (100)-plane. So, linear rate constant for (111)-Si is larger.

Source: Semiconductor Devices, 2/E by S.M. Sze. Copyright © John Wiley & Sons, Inc.

And here the parabolic rate constant or the linear rate constant we shall now, now see the variation of the temperature dependence or the temperature dependence of linear rate constant for two cases; one is when the wafer is 111 oriented or 100 oriented.

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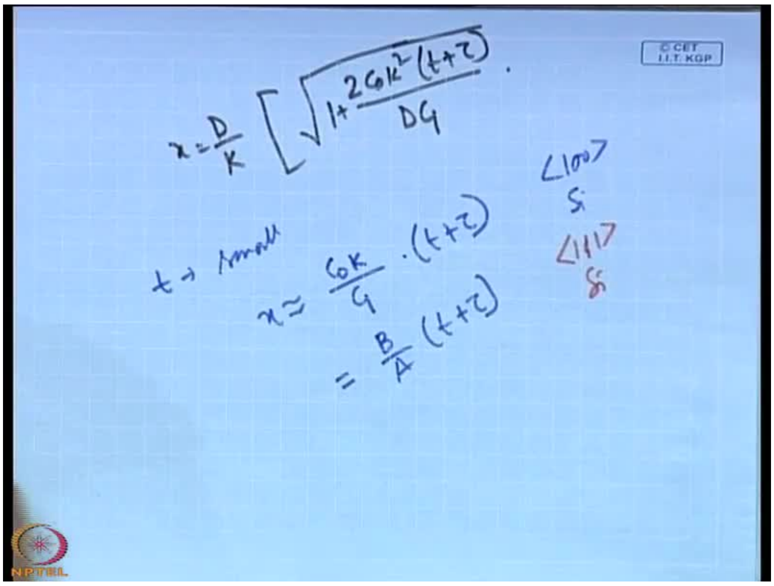

$$x = \frac{D}{K}\left[\sqrt{1+\frac{2C_0K^2(t+\tau)}{DC_1}}\right.\,.$$

$t \rightarrow$ small

$$x \simeq \frac{C_0K}{C_1}\cdot(t+\tau)$$

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

<100> Si

<111> Si

So, we have considered that silicon crystal can be two types of orientation; one is say silicon 100 another is silicon 111. So, both type of crystals orientation have been used for the growth of the oxides and some interesting features we shall now discuss. So, this is the temperature dependence of the linear rate constant B by A for both dry and wet oxidation for 111 and 100 oriented silicon wafers. So, what we see we see that in both the cases that is for dry oxidation or for wet oxidation the linear rate constant B by A which has its units micrometer per hour.

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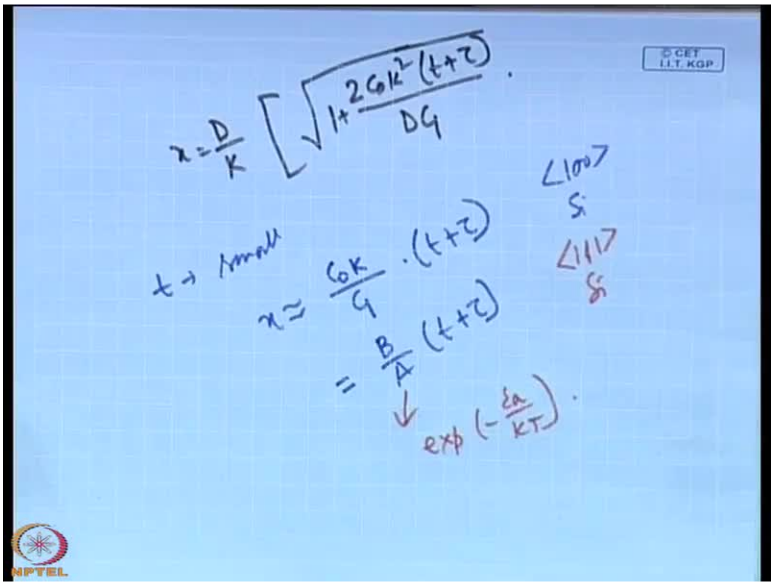

$$x = \frac{D}{K}\left[\sqrt{1+\frac{2C_0k^2(t+\tau)}{DC_1}}\right.$$

$t \rightarrow$ small

$$x \simeq \frac{C_0K}{C_1}\cdot(t+\tau)$$

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

$$\downarrow$$

$$\exp\left(-\frac{E_a}{KT}\right)$$

<100> Si

<111> Si

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It varies as exponential it varies as the rate constant is varies as exponential minus E a by k t it is it is E a by k t. So, obviously it is the activation energy this E a is the activation energy and that can be calculated from the arrhenius plot, which is nothing but 1000 by t in the x axis and linear rate constant at the y axis. We have calculated and what what is seen that the activation energy is 2 electron volt for dry oxidation here? Also for wet oxidation activation energy is 2 electron volt it is explicitly 2.05 electron volt and the condition is at 10 to the power 5 pascal pressure.

So, we can see that the activation energy is equal in both the cases. So, that means this two lines are parallel you can see. Now, this oxidation this activation energy 2 electron volt you can consider that to break a silicon silicon bond, how much energy is required? To break a silicon silicon bond we can see that the energy required is 1.83 electron volt per molecules.

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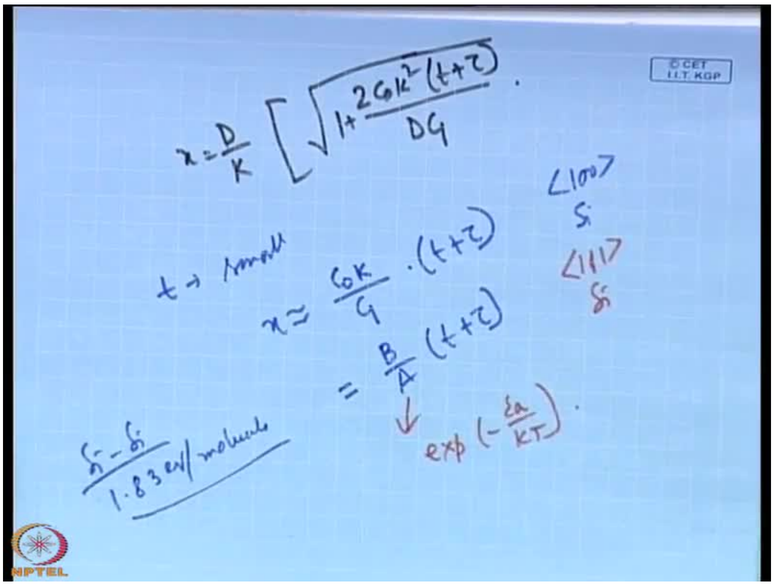

$$x = \frac{D}{K}\left[\sqrt{1+\frac{2C_0K^2(t+\tau)}{DC}}\right.$$

$t \to$ small

$$x \simeq \frac{C_0K}{C}\cdot(t+\tau)$$

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

$$\frac{B}{A} \downarrow \exp\left(-\frac{E_a}{KT}\right)$$

<100> Si

<111> Si

Si – Si

1.83 eV/ molecule

So, if the silicon silicon bond to break it the energy required is 1.83 electron volt per molecules so we can say that this closely matches with the value of the activation energy in case of both the dry and wet oxidation which is 2 electron volt. Also we see that this B by A that means the linear rate constant depends on crystal orientation, it depends on crystal orientation in the sense that 100 silicon has value smaller than 111 silicon. So, why why the value differs? Why it depends on the crystal orientation?

So, that is very important observation, which has been and observe by the investigators for SiO2 thermal oxidation and to make. It is related to the rate of incorporation of oxygen atoms in silicon it is related to the rate of incorporation of oxygen atoms into silicon, which in turn depends on surface bond structure of silicon atoms. So, how much oxygen atoms are incorporated into silicon and that obviously depend on the surface bond structure of silicon atoms. Now, density of available bonds on one one one plane is higher than that of the 100 plane. So, linear rate constant for 111 silicon is larger because available bonds density of available bonds is higher and obliviously it the rate constant will be higher in case of 111.

So, we see that both for dry oxidation and wet oxidation 111 silicon has higher value of linear rate constant compared to 100 silicon, because of the availability of the bonds, which is higher in number in case of 111 than the that of 100. So, that is a characteristics of silicon 111 and 100. So, what we find that if you have a sample say 111 silicon and 100 silicon you have two sample suppose and that two samples must have the linear rate constant different. For 111 the linear rate constant will be higher than the 100 because for 111 the number of available bonds is higher in case of the silicon. Then what about the parabolic rate constant? This was the the temperature dependence of the linear rate constant.

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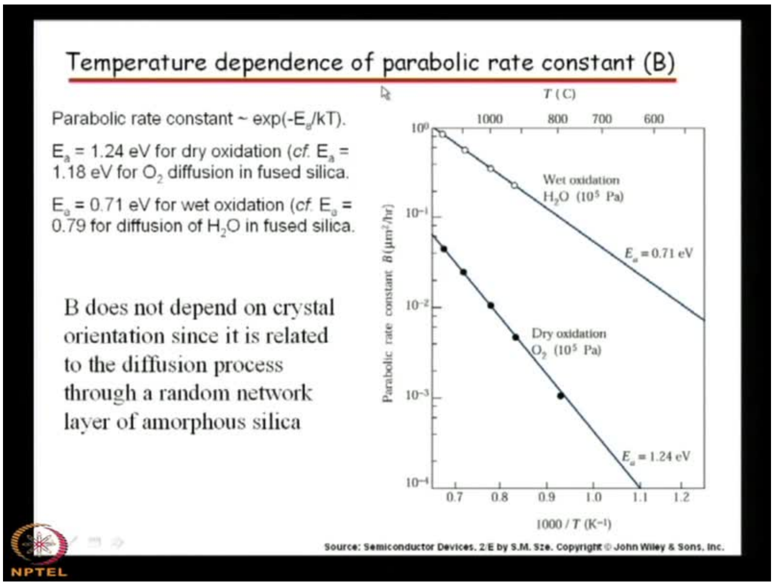

Temperature dependence of parabolic rate constant (B)

Parabolic rate constant ~ exp($-E_a/kT$).

E_a = 1.24 eV for dry oxidation (*cf.* E_a = 1.18 eV for O_2 diffusion in fused silica.

E_a = 0.71 eV for wet oxidation (*cf.* E_a = 0.79 for diffusion of H_2O in fused silica.

B does not depend on crystal orientation since it is related to the diffusion process through a random network layer of amorphous silica

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And this is the temperature dependence of parabolic rate constant parabolic rate constant B and quickly we can see that what is B? B is twice d C 0 by C 1, this d is the diffusivity or the diffusion constant, C 1 what are what are C 0 and C 1. C 1 is the value for for dry oxidation this is the number of molecules of the oxidizing species in a unit volume and C 0 is the oxidizing species at the surface. So, C 0 and C 1 we understand and from that we can know what is B the parabolic rate constant?

The parabolic rate constant also its unit is micrometer square per hour. Here you see that it is micrometer per hour. So, obliviously the parabolic rate constant value will be different and it is also varies as exponential minus E a by k t where E a is the activation energy and as usual if you have to calculate the activation energy in this in such process, so what we should do? That we must take help of the arrhenius plot on the x axis, you plot 1000 upon t and the x axis in the y axis you plot the rate constant be it parabolic or linear to calculate the activation energy.

So, that is a standard technique and here also we see that we have plotted thousand by t in the x axis and parabolic rate constant in the y axis this activation energy, which was calculated from the arrhenius plot is o1.24 for dry oxidation for dry oxidation oxygen is used and for wet oxidation water vapor or steam is used in both the cases pressure maintained is 10 to the power 5 pascal. So, activation energy in case of dry oxidation, we find that it is 1.24 electron volt and we can compare this 1.24 electron volt for the activation energy of oxygen diffusion in fused silica in fused silica. the value is 1.18 electron volt. so the value quite matches well.

Similarly, for wet oxidation the activation energy is found to be 0.71 electron volt and this 0.71 electron volt. If we compare the value with a diffusion of water vapor in fused silica, we find that the value is 0.79. So, in both the cases diffusion through fused silica whether it is by oxygen molecules or by the water vapor where depending on whether it is the dry oxidation or wet oxidation, we find that the activation energy values are quite matches well.

However, one important difference between this parabolic rate constant and this linear rate constant is, this in linear rate constant we have seen that the crystal orientation has a has an effect profound effect. However, for parabolic rate constant we find that it does not depend on crystal orientation. Why it does not depend on crystal orientation, because it is related to the diffusion process through a random network layer of amorphous silica. So, since there is a random network layer of amorphous silica and it is a diffusion process. So, it is a random process and in random process the orientation dependence does not exist.

So, what was the difference between the parabolic rate constant and linear rate constant. That the difference is the parabolic rate constant does not depend on crystal orientation. However, the linear rate constant depend on crystal orientation second important difference is that the activation energy for parabolic rate constant is different for wet oxidization and for dry oxidization. However, linear rate constant for wet oxidization and dry oxidization is same it is almost 2 electron volt and the activation energy for linear rate constant is higher than that of the wet oxidation. Activation energy for wet oxidation you see that it is 2 electron volt and here it is 1.24 electron volt and 0.71 electron volt. So, we can summarize this findings that the activation energy dependence; one is the linear rate constant and number two is the parabolic rate constant.

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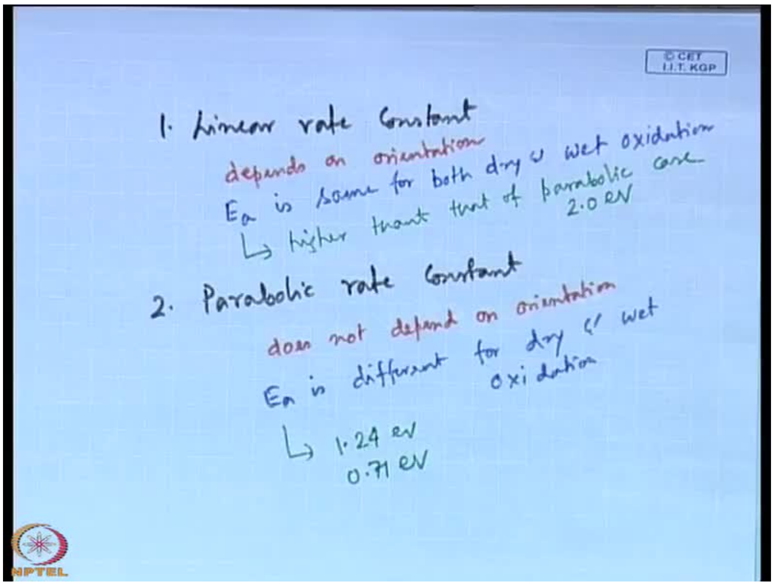

1. Linear rate Constant
   depends on orientation
   E_a is same for both dry & wet oxidation
   ↳ higher thant that of parabolic case
   2.0 eV
2. Parabolic rate Constant
   does not depend on orientation
   E_a is different for dry & wet oxidation
   ↳ 1.24 eV
   0.71 eV

This parabolic rate constant orient does not depends on orientation linear rate constant, it depends on orientation. Then in linear rate constant the value of activation energy E a is same for both dry and wet oxidation here E a is different from dry and wet oxidation. The third difference which is the value of E a that E a this value it is higher than that of parabolic rate constant and this is lower than the linear rate constant. It is 2 electron volt here it is 1.24 electron volt and 0.71 electron volt.

So, ultimately the activation energy it is basically the process of diffusion and for for the parabolic rate constant. Obliviously it is the process of diffusion and through fused silica either oxygen or water vapor and in case of linear rate constant, it is the reaction at the silicon surface with the oxygen and the energy required to break the silicon silicon bonds. So, the mechanism is different it is well understood.

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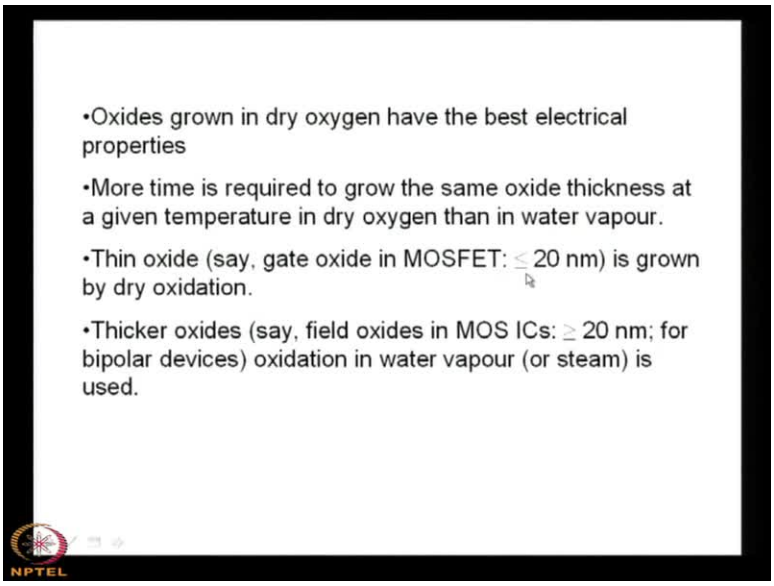

- Oxides grown in dry oxygen have the best electrical properties
- More time is required to grow the same oxide thickness at a given temperature in dry oxygen than in water vapour.
- Thin oxide (say, gate oxide in MOSFET: $\leq$ 20 nm) is grown by dry oxidation.
- Thicker oxides (say, field oxides in MOS ICs: $\geq$ 20 nm; for bipolar devices) oxidation in water vapour (or steam) is used.

Now, now, some comments about the thermal oxidization that this is the oxides grown in dry oxygen have the best electrical properties more time is required to grow the same oxide thickness at a given temperature in dry oxygen than in water vapor. So, that means dry oxidation is very slow process and if you want to grow say 50 nanometer or 20 nanometer oxide layer by dry oxygen, if the time required using dry oxidation is t 1 and that using water vapor is t 2, the same thickness say thickness is 50 nanometer or say x nanometer.

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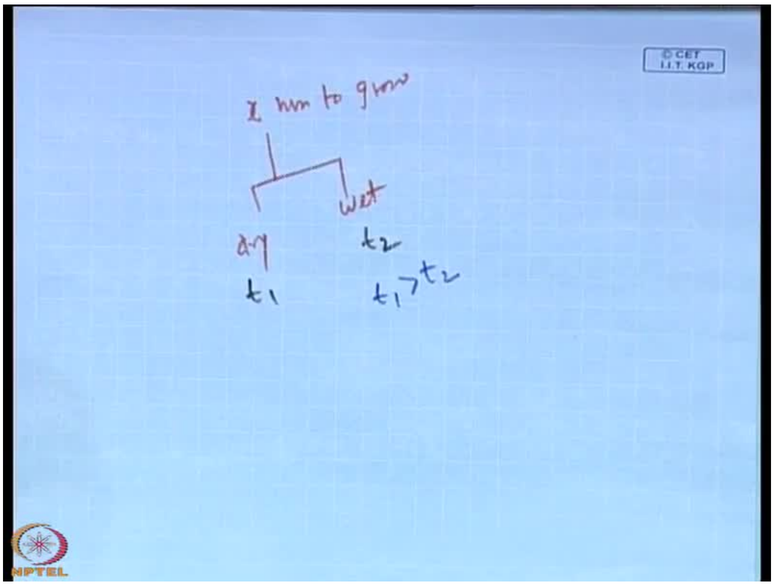

Then we can say that for x nanometer to grow for x nanometer to grow either by x nanometer to grow either by i say dry oxidation or by wet oxidation the time required is say t 1 and t 2. Obviously t 1 must be greater than t 2, so more time is required to grow the same oxide thickness at a given temperature in dry oxygen than in water vapor and thin oxide is grown by dry oxidation. Thin oxide means gate oxide in MOSFET whose value is less than equals to 20 nanometer or thicker oxides say field oxides in MOS integrated circuits, it is greater than 20 nanometer for or for bipolar devices, where the thicker oxides are required oxidation in water vapor or steam is used.

So, the limiting factor or the factor that must be chosen for growing the thin oxide or the thicker oxide is the thickness of the oxide layer if it is less than 20 nanometer. One should go go for the thin oxide or if it is 20 nanometer greater than equals to nanometer, it one should go for the thicker oxides, and thicker oxides are grown using water vapor. Now, here we have mentioned that gate oxide field oxide, what are those? Let me very quickly refresh your memory that what is the gate oxide and what is the field oxide.

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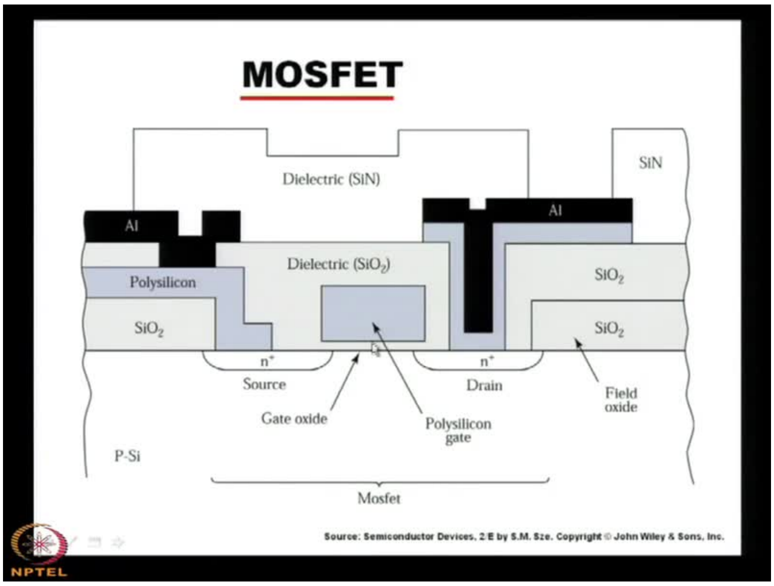

MOSFET

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If you see this diagram you can find, you can find that this is the block diagram for a MOSFET metal oxide semiconductor field effect transistor, it has grown using p silicon substrate. So, this is the field oxide, this is field oxide SiO2 and this is gate oxide, this is less then equals to 20 nanometer, this gate oxide. All are SiO2, but the field oxide thickness is greater than 20 nanometer it is used for the isolation or the passivation, and this less than 20 nanometer it is for the gate oxide to make for the MOSFET. Now, with this idea we can say that for 20 nanometer we can use the dry oxidation process and for greater than 20 nanometer we can use the thicker oxide, which is the result of the water vapor used.

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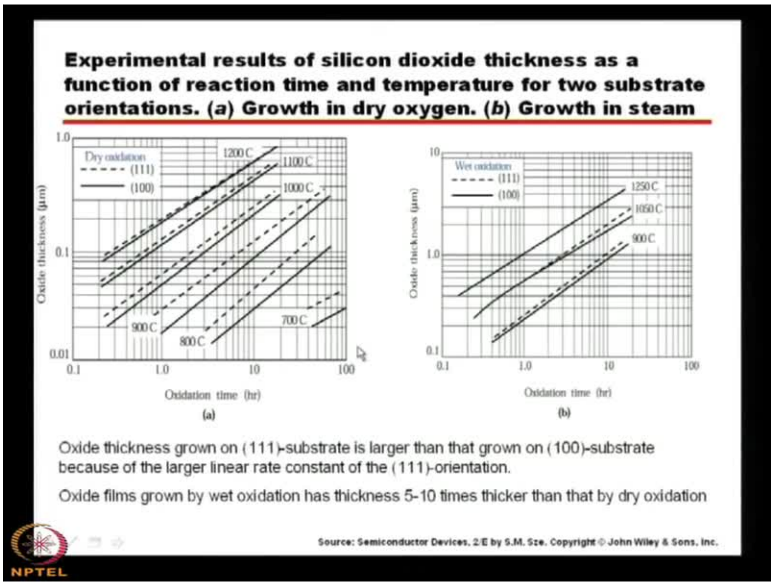

Experimental results of silicon dioxide thickness as a function of reaction time and temperature for two substrate orientations. (*a*) Growth in dry oxygen. (*b*) Growth in steam

Oxide thickness grown on (111)-substrate is larger than that grown on (100)-substrate because of the larger linear rate constant of the (111)-orientation.

Oxide films grown by wet oxidation has thickness 5-10 times thicker than that by dry oxidation

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Now it is the experimental results of silicon dioxide thickness as a function of reaction time and temperature for two substrate orientations. Two substrate orientations means; one is 111, another is 100 because we have seen that crystal orientation has a profound effect on the oxidation. So, in this two view graphs, we have shown you the oxide thickness which is in micrometer as a function of oxidation time as a reaction time and temperature also you see that in this graph it is for dry oxidation and it is for wet oxidation.

Here the temperature used is 700 degree centigrade to 1200 degree centigrade. So, both for the low and high temperature oxidation here used low temperature means, say 700 to 900 and high temperature is almost 1000 to 1200 degree centigrade. This dotted curves or is for the 111 orientation crystal or substrate and 100 is the solid curve. Here, the same thing here at three different temperatures it has been shown one is 900 another is 1050 degree centigrade and third one is 1250 degree centigrade.

Remember that here also the dotted curves are for the 111 substrate and solid curve is for 100 crystal orientation of the substrate. This is when the growth of the SiO2 has taken place in steam or water vapor, and this is the growth of the oxidation oxide layers in dry oxygen. Then now what we find we find that oxide thickness grown on 111 substrate is larger than the dotted curves. These are the 111 it is larger than that grown on 100 substrate because of the larger linear rate constant of the 111 orientation that we have discussed earlier also, that because the density of the bonds is higher in case of 111 orientation.

Then here the growth rate is higher linear rate constant is higher and so the oxide thickness grown is also higher and oxide films grown by wet oxidation method has thickness 5 to 10 times thicker than that by dry oxidation at any temperature, say 9, 900 degree centigrade. Suppose this is the curve for 900 degree centigrade, the solid one is for 100 and oxidation time is on the x axis. So, let us take the value at 1 hour, what is the thickness for 900 degree centigrade growth? We will see that it is 0.01 so it is less than 0.02 somehow here.

So, it is less than 0.02 micron 1 hour here. For 1 hour it is greater than 0.2 micron. This is 0.1 so it is 0.2 and even it is greater than 0.2 micron. So it is less than 0.02 micron, less than 0.02 micron. In case of the dry oxidation and where as in it is greater than 0.2 micron for wet oxidation. So, we can say that it is 5 to 10 times thicker than that by dry oxidation. However, this thick layer is electrically not the best one dry oxygen oxides oxides grown in dry oxygen have the best electrical properties.

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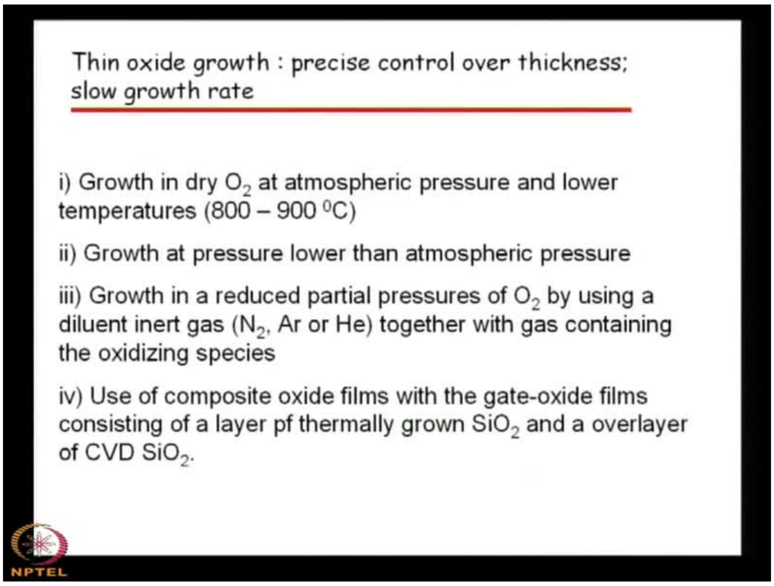

Thin oxide growth : precise control over thickness; slow growth rate

i) Growth in dry O_2 at atmospheric pressure and lower temperatures (800 – 900 ^{0}C)

ii) Growth at pressure lower than atmospheric pressure

iii) Growth in a reduced partial pressures of O_2 by using a diluent inert gas (N_2, Ar or He) together with gas containing the oxidizing species

iv) Use of composite oxide films with the gate-oxide films consisting of a layer pf thermally grown SiO_2 and a overlayer of CVD SiO_2.

Another important thing from from this from this studies is that thin oxide growth thin oxide to grow précised control and to make the precise control over thickness slow growth rate is important slow growth rate is important where one can precisely control the thickness, because one can see that in process technology when we talk about the oxidation that this is the oxidation it is one of the process steps by planar technology.

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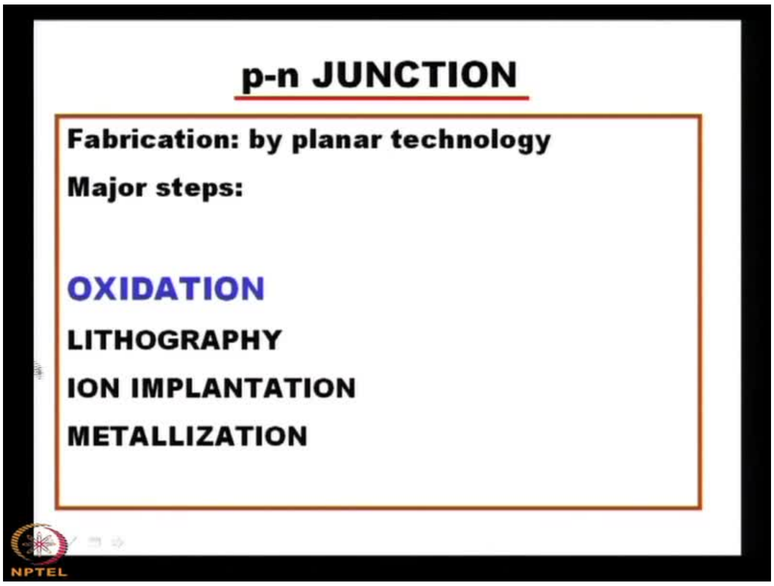

p-n JUNCTION

Fabrication: by planar technology

Major steps:

OXIDATION

LITHOGRAPHY

ION IMPLANTATION

METALLIZATION

We can see that oxidation is the first one with lithography ion implantation metallization etcetera and this oxidation step very good quality gate oxide is required. Otherwise what will happen the leakage current will increase like anything, and because the leakage current increased and the interface states will be more in case of the leakage. So, gate oxide must have good electrical property and this electrical property can be achieved if we use the oxide grown by the dry oxygen method.

So, that is a important consideration in case of the oxidation this is the thermal oxidation because we shall come across other oxidations also like the c v d of silicon or say for other types of oxidation we shall find that there are other applications also, not that it is only used for making the gate oxide, in some cases for the isolation, for some cases to making the mask for the diffusion or lithographic pattern and thick oxide layers are grown and in that case obliviously we will not use the dry oxidation, rather we shall go for the wet oxidation or the oxidation by the c v d technique or other techniques that that we shall discuss in later stages.

So, control is very important, precise control is important and then the growth rate must be slow enough then what are the processes. What are the major steps that people have taken or the industry have taken? So, the formalities are one is the growth in dry oxygen at atmospheric pressure and lower temperatures. Lower temperatures means 800, 900 degree centigrade, so here you see that it is 800 900 degree centigrade atmospheric pressure and low temperature, this is dry. Another protocol can be growth at pressure lower than atmospheric pressure, so then it becomes more slow. Atmospheric pressure and lower the atmospheric pressure it can be more slow, the rate will be less.

Growth in a reduced partial pressure of oxygen by using a diluent inert gas, the inert gas can be nitrogen, argon or helium together with gas containing the oxidizing species. So, that means we can reduce the partial pressure. How to reduce the partial pressure or we can use some inert gas to dilute it, that inert gas can be inert gas can be this argon, nitrogen or helium. Then if the reduced if it is grown by reduced partial pressure, then obviously the growth rate will be very, very slow and another process that can be used is the use of composite oxide films with the gate oxide films consisting of a layer of thermally grown SiO2 and a over layer of c v d SiO2.

So, that means you can use composite oxide films with the gate oxide films, consisting of a layer of thermally grown SiO2 and over layer of c v v d. SiO2 means silicon dioxide made made by chemical vapour deposition. So, these are the processes that can use there are many other processes also people have reported, but mostly the industry adopted this one that is the growth in dry oxygen at atmospheric pressure and lower temperature.

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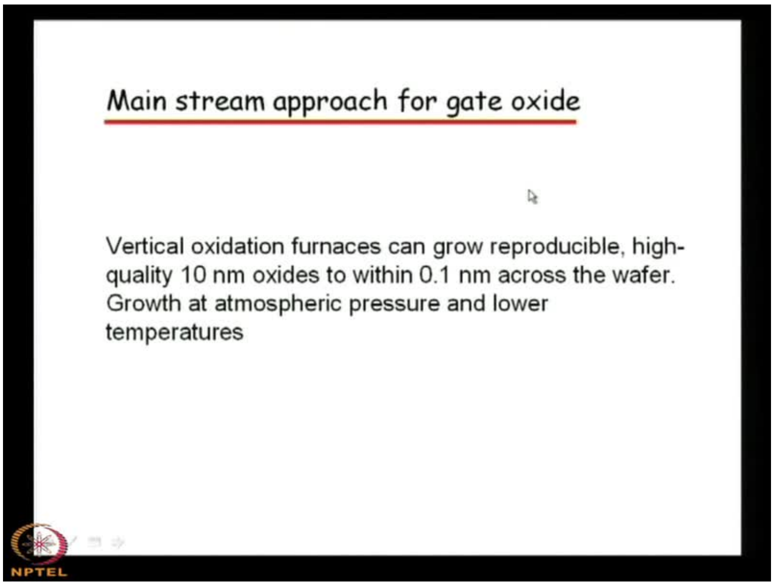

Main stream approach for gate oxide

Vertical oxidation furnaces can grow reproducible, high-quality 10 nm oxides to within 0.1 nm across the wafer. Growth at atmospheric pressure and lower temperatures

So, main stream approach for gate oxide is that one can use the vertical oxidation furnaces I have shown you the oxidation furnaces this is the oxidation furnace that we have discussed earlier. It is a horizontal type of thing and you see that here on the silicon wafers are placed on the fused quartz boat a large number of silicon wafers.

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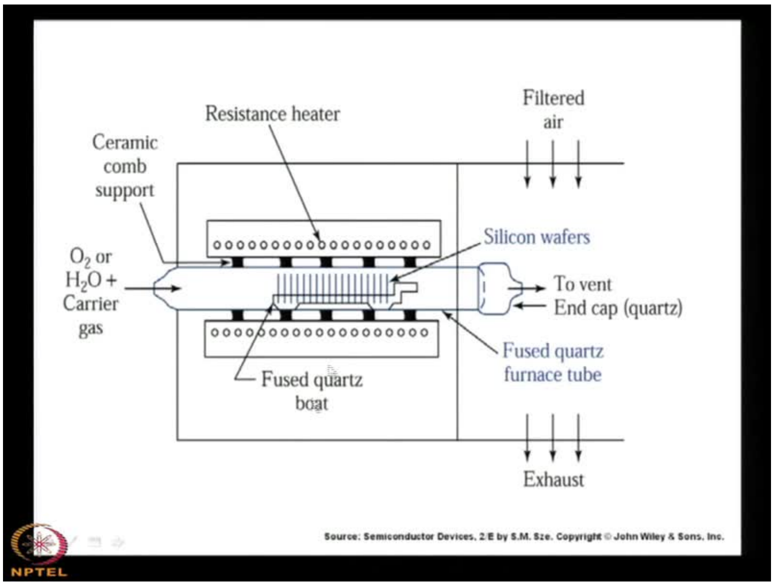

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You can use then there is a resistance heater or the heater can be other types of say it is a lamp glow or it can be microwave, so any kind of heating can be accomplished mainly the resistance heater is used and there is the oxygen or H2O plus carrier gas the carrier gas can be high purity nitrogen or argon, which will transport the oxygen or the water vapor to the silicon wafers or the furnace region, where the actual reaction and the diffusion will take place.

Obviously there will be vent the un reacted gases or that will build up that will be vented out from this quartz tube reactor and then there will be exhaust. So, this is the standard protocol that we have used and obviously we have discussed that that this must be accompanied by the clean room this must be accompanied by the clean room because without clean room one cannot make this oxidization very good.

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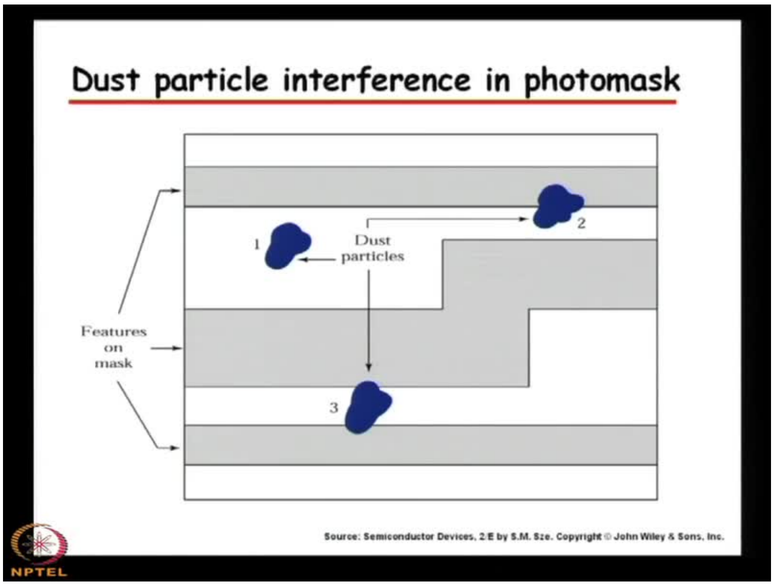

Dust particle interference in photomask

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Otherwise there will be a large number of dust particles that will have its own imprint or signature on the other surfaces or on the wafer surfaces in the later stage. So, what we see that this oxides, which are grown at the furnace that furnace can be a vertical 1. Vertical oxidation furnace can grow reproducible high quality 10 nanometer oxides to within 0.1 nanometer across the wafer.

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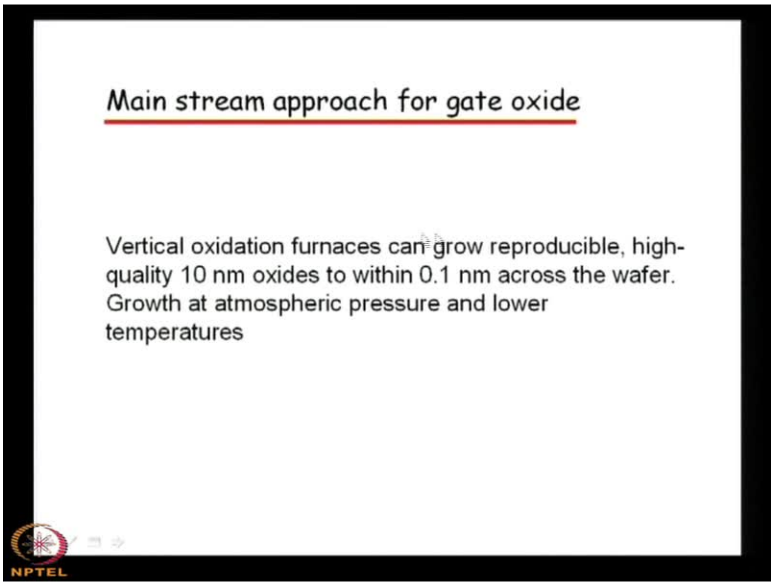

Main stream approach for gate oxide

Vertical oxidation furnaces can grow reproducible, high-quality 10 nm oxides to within 0.1 nm across the wafer. Growth at atmospheric pressure and lower temperatures

So, if you have a wafer say of 6 inch and the growth can be oxide layers can be of say 10 nanometer plus minus 0.1 nanometer plus minus 0.1 nanometer. So, that is very, very precise and this 10 nanometer is nothing but where we have we have seen that it can be it is it is used in case of the gate oxide in moss technology, and also the growth at atmospheric pressure and at lower temperatures.

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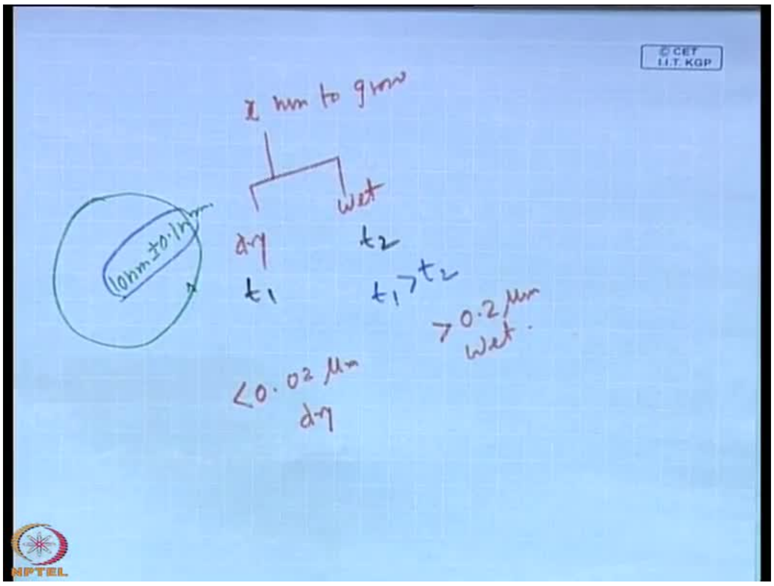

So, that is the main stream approach for gate oxide which has been done in case of the industry. Now, we see that vertical furnace is the most efficient furnace and it is horizontal one and where at atmospheric pressure normal atmospheric pressure that means 76 centimeter of 76 millimeter of mercury and also that low temperature. Low temperature means 800, 900 degree centigrade. So, that it becomes a slow process the thermal shock is not there and at one go a large number of silicon wafers can be made to oxidized.

So, these are the advantages and so the vertical furnace has its own own own efficiency now till now what we have discussed that in oxidation the oxidation can be a dry one. This this is a dry one, and you see that first there is a silicon silicon dioxide interface and that moves into silicon during oxidation; first silicon silicon dioxide interface and its moves.

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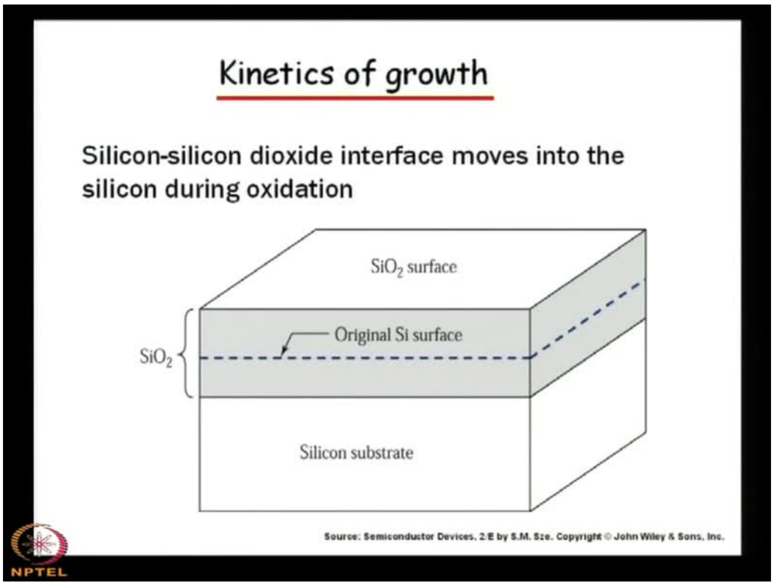

Kinetics of growth

Silicon-silicon dioxide interface moves into the silicon during oxidation

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So, more and more silicon is consumed for the for the formation of SiO2 and one example that you can and try to solve if a silicon dioxide layer of thickness x is grown by thermal oxidation. What is the thickness of silicon being consumed? So, if it is x, then how much thermal oxidation and will be the silicon dioxide if a silicon dioxide layer of thickness x is grown by thermal oxidation?

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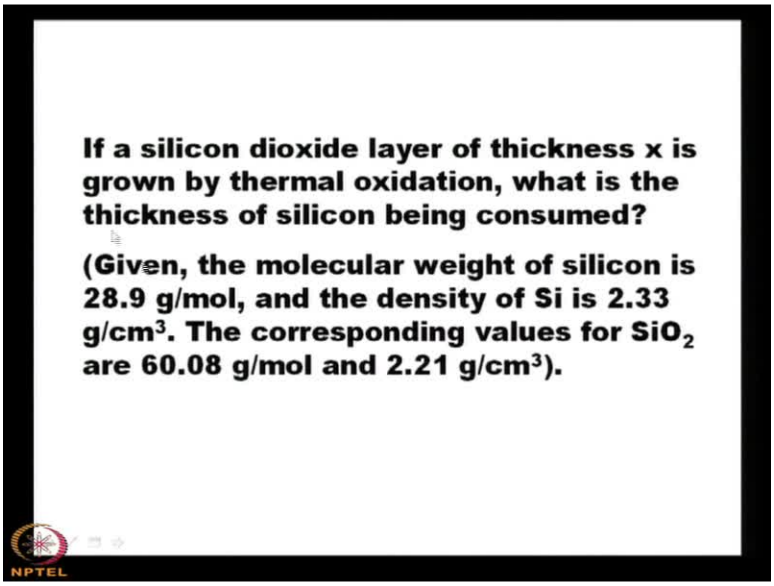

If a silicon dioxide layer of thickness x is grown by thermal oxidation, what is the thickness of silicon being consumed?

(Given, the molecular weight of silicon is 28.9 g/mol, and the density of Si is 2.33 g/cm^3. The corresponding values for SiO_2 are 60.08 g/mol and 2.21 g/cm^3).

What is the thickness of silicon being consumed and given the molecular weight of silicon is 28.9 gram per mole and the density of silicon is 2.33 gram per centimeter cube. The corresponding values for SiO2 are 60.08 gram per mole and 2.21 gram per centimeter cube. So, you can try this example to see what happens for and you will find that this silicon silicon dioxide interface moves into the silicon during oxidation and more and more silicon is consumed.

This is very, very interesting thing and once the SiO2 is is grown, then the oxidizing species must diffuse through the grown SiO2 to reach at the surface that means at the interface between the Si and SiO2 to make it at reacting with the silicon atoms for for the growth of SiO2. So, now we can summarize our lecture in the sense that in this way that the oxidation can be two types; one is the dry oxidation another is the wet oxidation, then dry oxidation we have seen that oxygen gas is used whether for wet oxidation H2O vapour.

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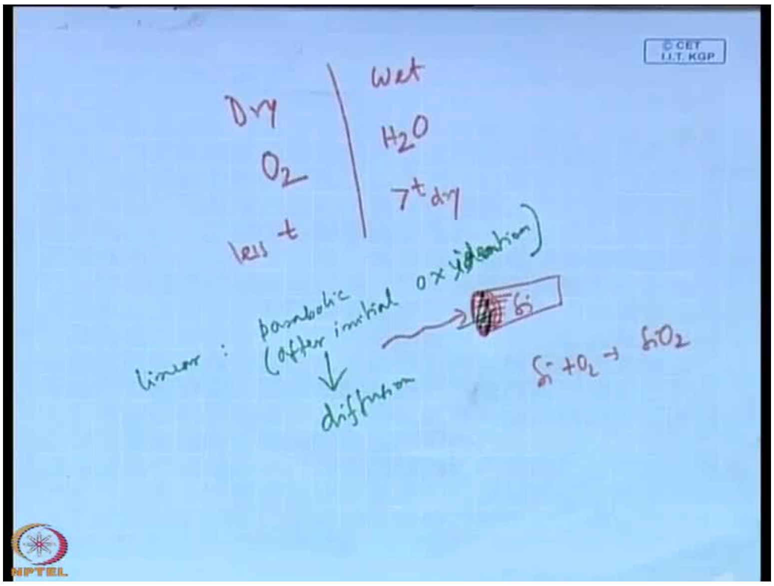

That means water vapour or steam is used. We have seen that this dry oxidation it is the thickness is less less value of t is less for wet oxidation it is greater than the t for the dry with the same condition. Also we have seen that the kinetics of growth is that first a layer of SiO2 is formed on the silicon and this silicon SiO2 layer moves. So, what happens the first it is the rate limiting factor that effects the reaction of the S i with oxygen to form the SiO2 that is the linear in nature, and the rate constant depends on rate constant depends linearly.

Then the oxidizing species diffuses through the SiO2 layer to reach the surface for the reaction. So, it can be the parabolic rate constant, so depending on that those model one is this that linear rate constant is there and it is different from the parabolic rate constant after the initial oxidation. This is after initial oxygen or oxidation initial oxidation because it is diffusion takes place through this initial layer of the oxidation.

So, linear rate constant, we have seen that it is very much depend on the orientation of the crystal that we have discussed. That the linear rate constant it depends on orientation parabolic rate constant does not depend on orientation than the linear rate constant the activation energy is same for both dry and wet oxidation.

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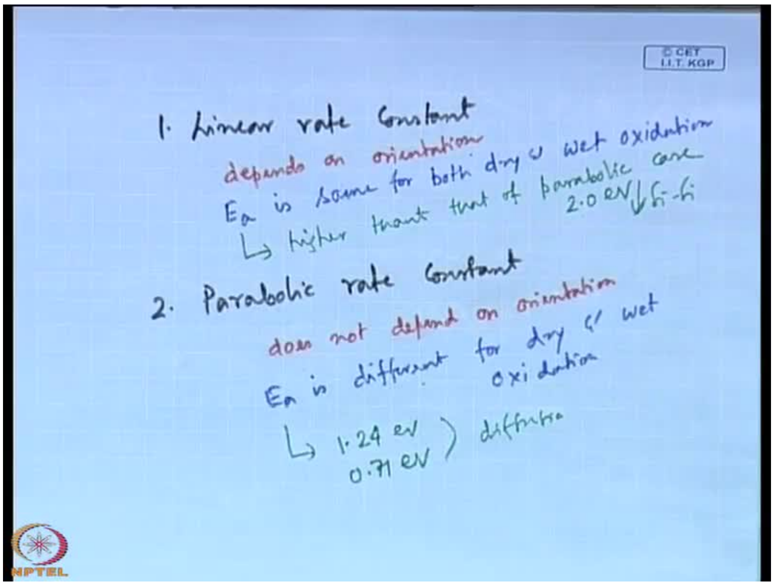

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1. Linear rate constant

depends on orientation

E_a is same for both dry & wet oxidation

↳ higher than that of parabolic case

2.0 eV ↓ Si-Si

2. Parabolic rate constant

does not depend on orientation

E_a is different for dry & wet oxidation

↳ 1.24 eV) diffusion

0.71 eV)

For parabolic rate constant that activation energy is different for dry and wet oxidation and also the value of the linear rate constant activation energy for the linear rate constant it is 2 electron volt it is higher. Why it is higher, because this is the amount of energy required to break the silicon silicon bond. Here it is for the diffusion only, then we have come across the different kinds of structures of the SiO2, one can be a quartz type of structure another can be of of say silicon, one is quartz type of structure another is amorphous type of structure.

We have seen that the density of the quartz structure is greater with with closely with with with its packing fraction is very high. Why it is so it is because it has a periodic nature and the silicon atoms form as ring of 6 atoms. It is perfectly crystal it is perfectly periodic in nature and for quartz for amorphous type of crystal structure of SiO2 we have seen that it is more or the density is very less. Why why because only less than 50 percent space is used by the SiO2 molecules and so the impurity particularly the sodium or that type of impurity can and diffuse through the SiO2 that thing must be taken care of. Then we have talked about a mathematical problem, which is given by this that silicon layer.

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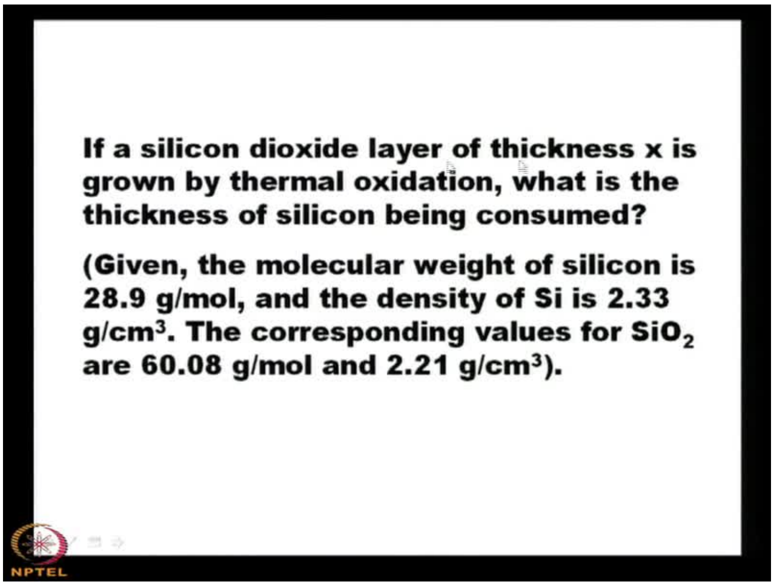

If a silicon dioxide layer of thickness x is grown by thermal oxidation, what is the thickness of silicon being consumed?

(Given, the molecular weight of silicon is 28.9 g/mol, and the density of Si is 2.33 g/cm^3. The corresponding values for SiO_2 are 60.08 g/mol and 2.21 g/cm^3).

Thickness to grow SiO2 layer thickness x is to grow how much silicon is being consumed so with this, we end the discussion on the oxidation that is we have discussed that it is one of the most important and gate oxide under which a constant conducting channel can be formed between source and drain.

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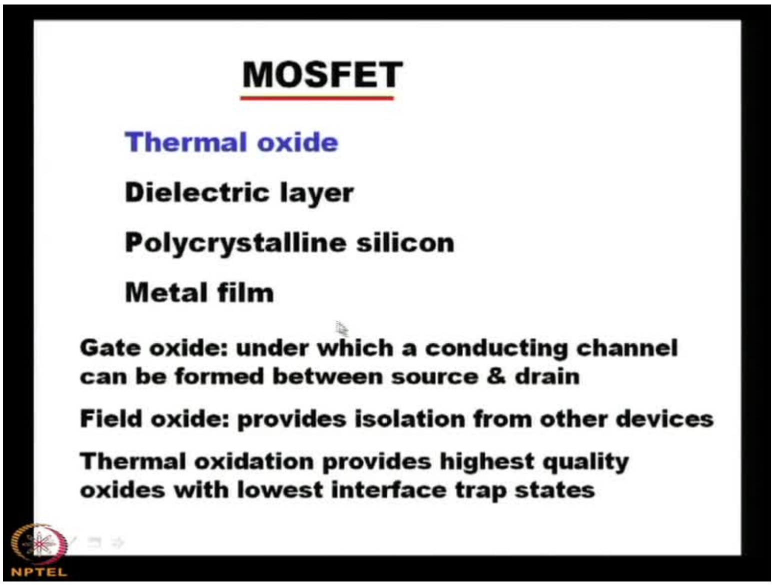

MOSFET

Thermal oxide

Dielectric layer

Polycrystalline silicon

Metal film

Gate oxide: under which a conducting channel can be formed between source & drain

Field oxide: provides isolation from other devices

Thermal oxidation provides highest quality oxides with lowest interface trap states

Then field oxide it is provides isolation from other devices and this two oxides are formed mainly by the thermal oxide, next day we shall discuss the dielectric layers or other polycrystalline silicon and metal film.

Thank you.