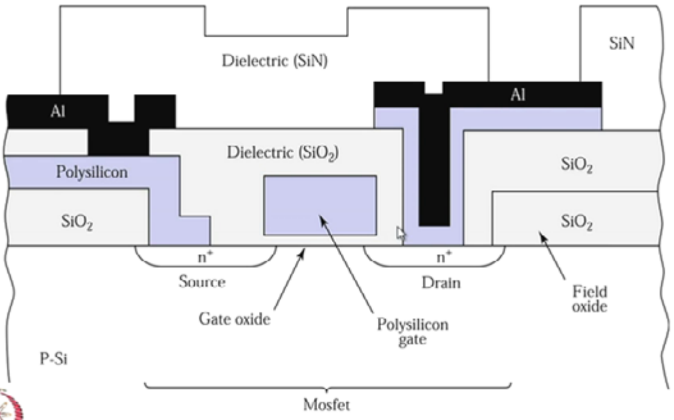
Processing of Semiconducting Materials

Prof. Pallab Banerjee
Department of Material Science
Indian Institute of Technology, Kharagpur

Lecture - 35
Oxidation – I

(Refer Slide Time: 00:24)

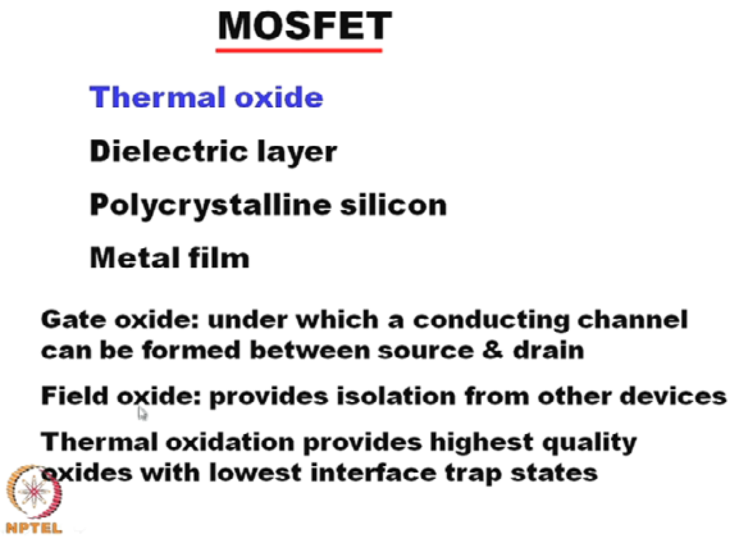
MOSFET



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

Today's topic of discussion is the oxidation, and you can see from this view graph that there are different types of layers that we use for making a discrete device or an i c, they are say gate oxide then there can be field oxide, the poly silicon gate or some dielectrics and finally the metal layers.

(Refer Slide Time: 00:40)



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

And we see that so far as the thermal oxide is concerned, it can be field oxide or the gate oxide as is evident from this view graph. The main function of the gate oxide is that under which a conducting channel is formed between the source and the drain. And also there is a field oxide, which provides isolation among the devices, and also you see that apart from this gate oxide and field oxide, there can be dielectric layer.

(Refer Slide Time: 01:12)

MOSFET

Thermal oxide

Dielectric layer

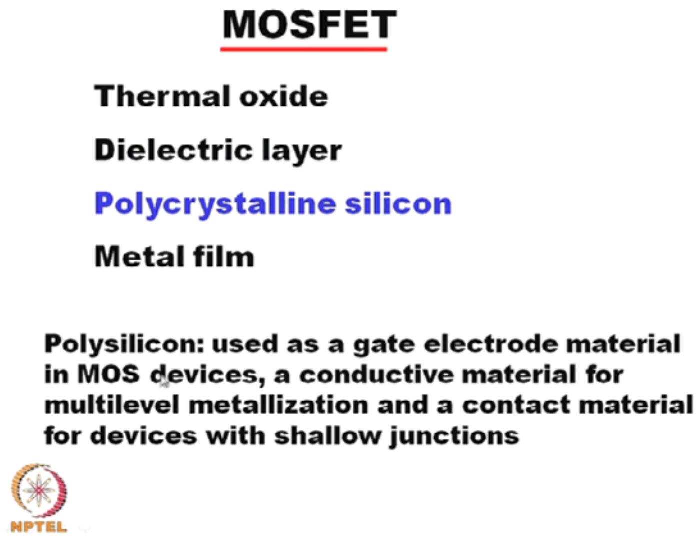
Polycrystalline silicon

Metal film

Used for insulation between conducting layers, for diffusion & ion implantation masks, for capping doped films to prevent the loss of dopants and for passivation to protect devices from impurities, moisture and scratches.

And this dielectric layer is used for insulation between conducting layers for diffusion and ion implantation masks, for capping doped films to prevent the loss of dopants and for passivation to protect devices from impurities, moistures and scratches. Here in this diagram, you can see that this is the dielectric layer silicon nitride is deposited at the top throughout the devices to prevent this kind of scratches or to protect the devices from impurities, moisture, etcetera.

(Refer Slide Time: 01:55)



MOSFET

Thermal oxide

Dielectric layer

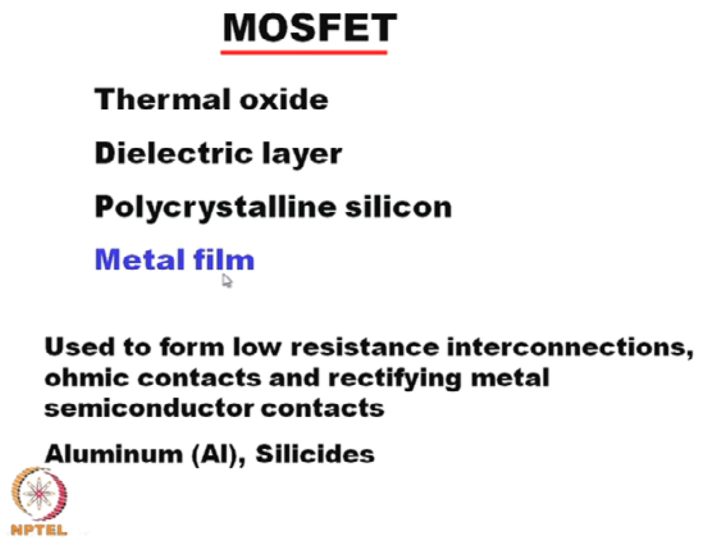
Polycrystalline silicon

Metal film

Polysilicon: used as a gate electrode material in MOS devices, a conductive material for multilevel metallization and a contact material for devices with shallow junctions

Another important layer you see is the polysilicon layer; this blue region is the polysilicon layer and this polysilicon layer are nothing but the polycrystalline silicon which is used as a gate electrode material in MOS devices, a conductive material for multilevel metallization and a contact material for devices with shallow junctions.

(Refer Slide Time: 02:14)



MOSFET

Thermal oxide

Dielectric layer

Polycrystalline silicon

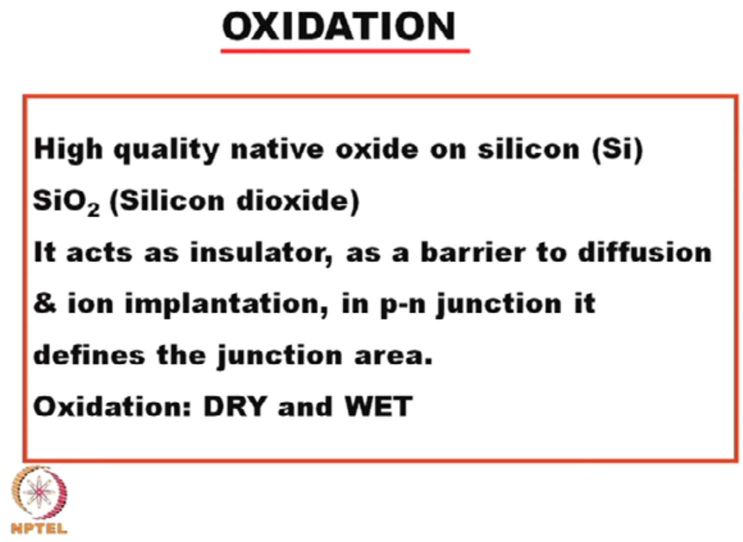
Metal film

Used to form low resistance interconnections, ohmic contacts and rectifying metal semiconductor contacts

Aluminum (Al), Silicides

And the last one is the metal film which is used to form low resistance interconnections, ohmic contacts between the metal and semiconductor and rectifying metal semiconductor barriers. And in this case in later on we will find that aluminum and silicides are widely used for making the metal films.

(Refer Slide Time: 02:31)



OXIDATION

High quality native oxide on silicon (Si)

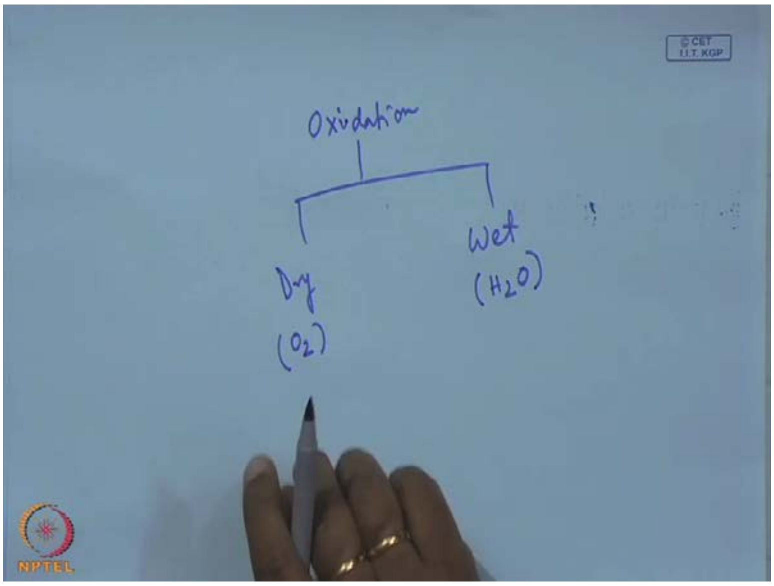
SiO_2 (Silicon dioxide)

It acts as insulator, as a barrier to diffusion & ion implantation, in p-n junction it defines the junction area.

Oxidation: DRY and WET

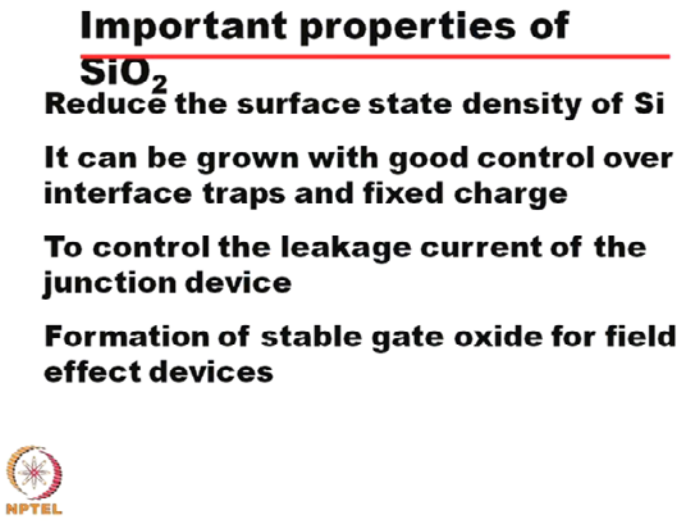
Now, so for as the oxidation is concerned, a high quality native oxide on silicon or is used basically in semiconductor technology, and it acts as insulator, and as a barrier to diffusion and ion implantation, and in p-n junction. It defines the junction area also. Now, the oxidation can be made two types.

(Refer Slide Time: 02:59)



There can be two type of oxidation; one is the dry oxidation and the second one is the wet oxidation, so depending on the source of oxygen available in the oxidation process. For dry oxygen generally oxygen high purity oxygen gas is used whereas, for wet oxidation high purity water vapour or steam is used. So, depending on the source that you use for an oxidation process, it can be termed as a dry or wet oxidation.

(Refer Slide Time: 03:35)



Important properties of SiO_2

Reduce the surface state density of Si

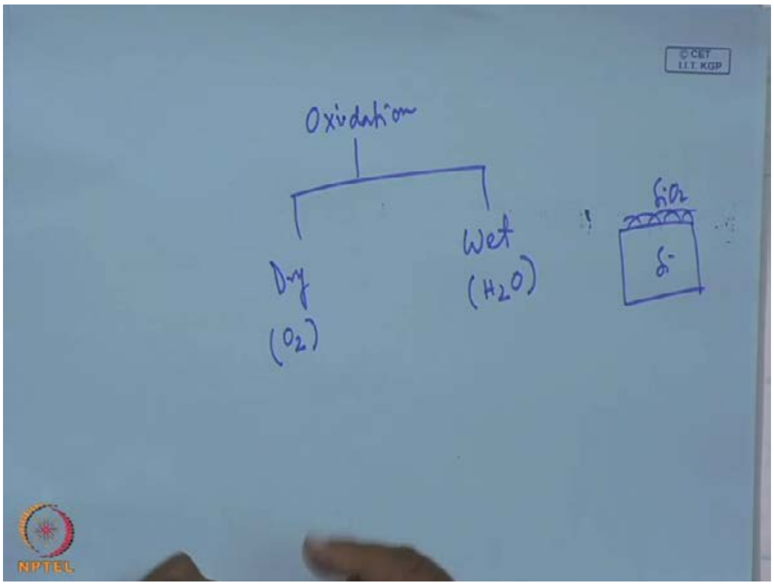
It can be grown with good control over interface traps and fixed charge

To control the leakage current of the junction device

Formation of stable gate oxide for field effect devices

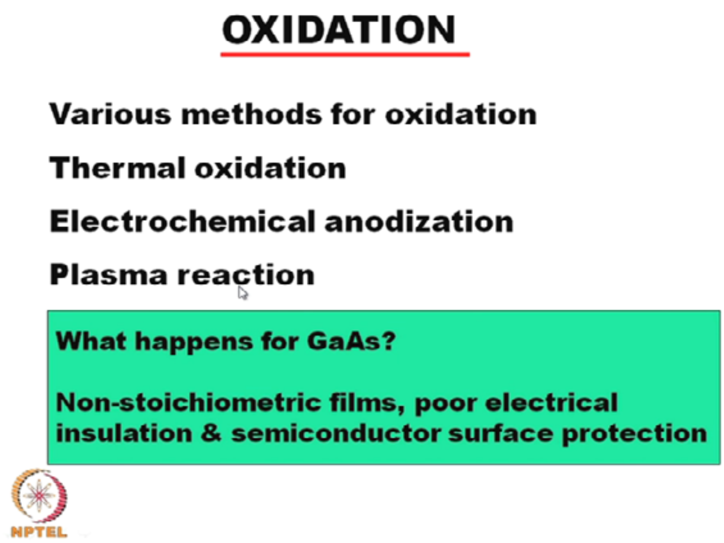
Then you see that there are some important properties of S i O 2, it reduce the surface state density of silicon.

(Refer Slide Time: 03:44)



And you know that if you keep a silicon substrate open in normal laboratory atmosphere, we will find that some dangling bonds are formed on the top are taking the arial oxygen and it is very prone to oxides. So, a large number of interface traps will be formed in the the surface state density will be quite high, because of such dangling bonds.

(Refer Slide Time: 04:33)



OXIDATION

Various methods for oxidation

Thermal oxidation

Electrochemical anodization

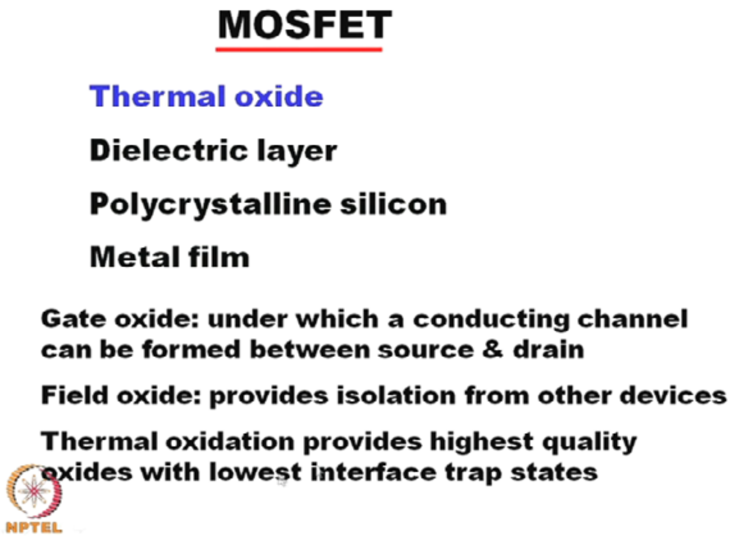
Plasma reaction

What happens for GaAs?

Non-stoichiometric films, poor electrical insulation & semiconductor surface protection

So with the application of S i O 2 on silicon, you will find that it can reduce the surface state density and it can be grown with good control over interface traps and fixed charge, to control the leakage current of the junction device, and formation of stable gate oxide for field effect devices below which the conducting channel is formed in a MOS device. So, these are the important properties of S i O 2, and you see that so far as the oxidation is concerned, various methods are used for oxidation, one can be thermal oxidation, another can be electrochemical anodization, third one can be plasma reaction and in your text books. You will find that a large number of oxidations processes are there using which you can make oxidation but among these three thermal oxidation, electrochemical and plasma reaction, we shall find that thermal oxidation is the best one.

(Refer Slide Time: 05:09)



MOSFET

Thermal oxide

Dielectric layer

Polycrystalline silicon

Metal film

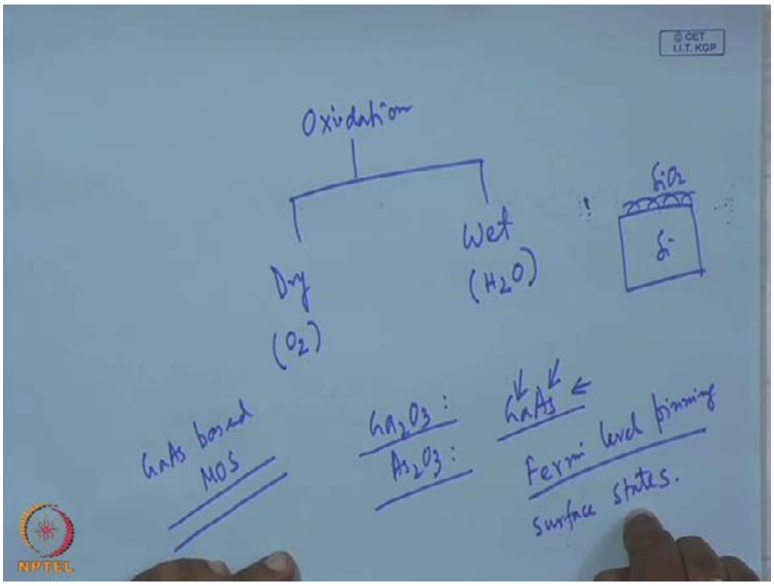
Gate oxide: under which a conducting channel can be formed between source & drain

Field oxide: provides isolation from other devices

Thermal oxidation provides highest quality oxides with lowest interface trap states

Because this thermal oxidation provides, the highest quality oxides with lowest interface trap states. So, in that sense the thermal oxidation is the best one and option that can be available. And this is true for S i, S i O 2 system for silicon S i O 2 is a stable oxide, it makes the interface traps very low and it is very stable and then what is what about gallium arsenide? What about gallium arsenide?

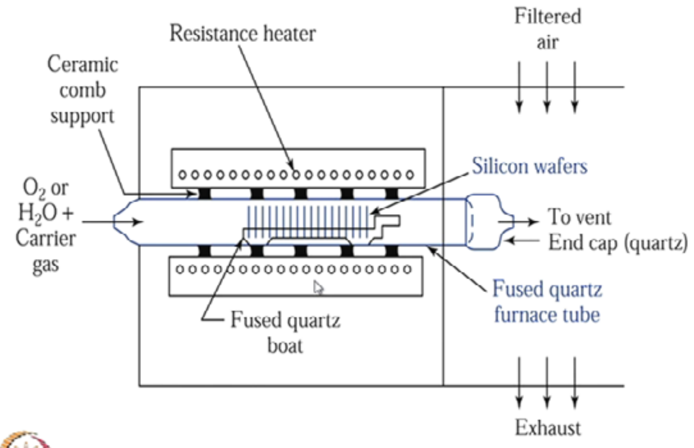
(Refer Slide Time: 05:40)



What happens? If gallium arsenide is tried to oxidation, now you see that since in the gallium arsenide that is; there are two types of atomic arrangements; one is gallium another is arsenic say, because it is the binary semiconductor. So, you will find that always, it will lead to non-stoichiometric films, these non-stoichiometric and and you see that G a 2 O 3 or A s 2 O 3. That means, the gallium oxide or the arsenic oxides are formed, it gives to very poor electrical insulation and semiconductor surface protection, so these are not used, because though it is the native oxides for gallium arsenide.

However, these oxides lead to fermi level pinning which is very important in the device application, and because of the fermi level pinning, you will find that a large number of surface states are formed on the gallium arsenide and which prevents processing of the gallium arsenide based MOS devices. So, that is important characteristics and basically this is the negative feature of the gallium arsenide oxidation, so apart from non-stoichiometric, poor electrical insulation, etcetera. The fermi level pinning is very important which gives rise to surface states and which prohibits gallium arsenide based MOS devices application.

(Refer Slide Time: 07:14)



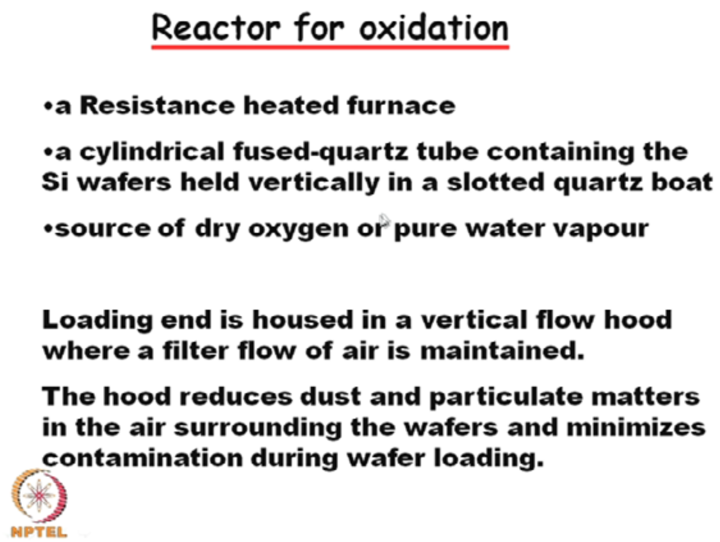
Source: Semiconductor Devices, 2/E by S.M. Sze. Copyright © John Wiley & Sons, Inc.

Now, this is a typical oxidation reactor, you see that in oxidation reactor, there are many components available in the oxidation reactor; one is the resistance heater which is used to heat the substrates, there is a quartz boat on which the silicon wafers are placed vertically, you can find that a large number of silicon wafers are kept here in the vertically in a vertical position on the quartz boat, and oxygen or H 2 O is passed through the quartz reactor.

And depending on the source, you can say that whether it is a dry oxidation or it is wet oxidation, and this oxygen or water vapour is transported to the reactor side by using a carrier gas which may be nitrogen which may be argon, it must have, it must be a gas having inert quality and the loading end through which you will load the silicon wafers onto the vertical quartz boat inside the reactor. You see that the loading end is fitted in a vertical hood, and the arrow gives the direction of the filtered air which is coming through the above and passing through the lower end.

So, making this portion free, relatively free from the dust or the particulate matters so; that means, thereby reducing the contamination of the wafers during the loading or unloading process. So essentially, it is basically a fused quartz tube furnace, and you will find that for diffusion, for or oxidation, for doping, these kind of a furnace is widely used, also for the processing of during the rapid thermal annealing and this quartz tube, furnace tube is heated through some resistance heater, here it is resistance heater this is used or in some cases the induction type or lamp fitting furnace one can make.

(Refer Slide Time: 09:31)



Reactor for oxidation

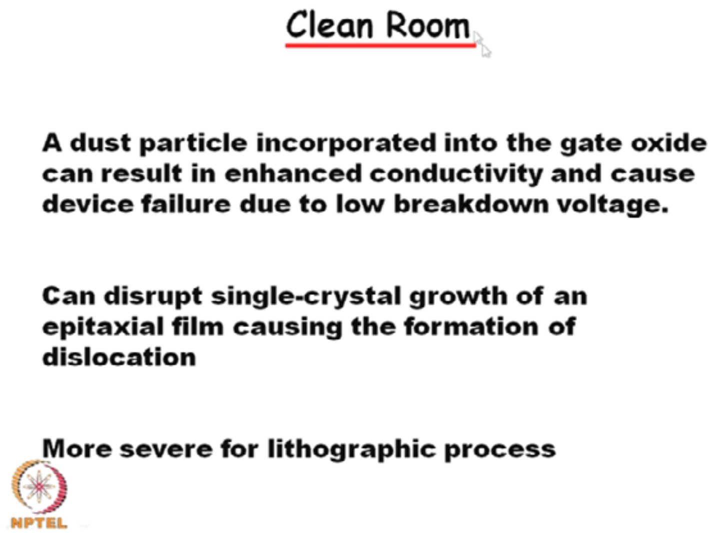
- **a Resistance heated furnace**
- **a cylindrical fused-quartz tube containing the Si wafers held vertically in a slotted quartz boat**
- **source of dry oxygen or pure water vapour**

Loading end is housed in a vertical flow hood where a filter flow of air is maintained.

The hood reduces dust and particulate matters in the air surrounding the wafers and minimizes contamination during wafer loading.

And you see that these reactor for oxidation, if we describe in detail that apart from, a resistance heated furnace, a cylindrical fused quartz tube containing the silicon wafers held vertically in a slotted quartz boat; that is shown by this blue vertical lines, these are basically the silicon wafers, it can be 2 inch 4 inch 6 inch diameter and source of dry oxygen or pure water vapour; that is shown on the left side of this diagram. Loading end is housed in a vertical flow hood, where a filter flow of air is maintained. The hood reduces dust and the particulate matters in the air surrounding the wafers and minimizes contamination during wafer loading that we have discussed earlier.

(Refer Slide Time: 10:16)



Clean Room

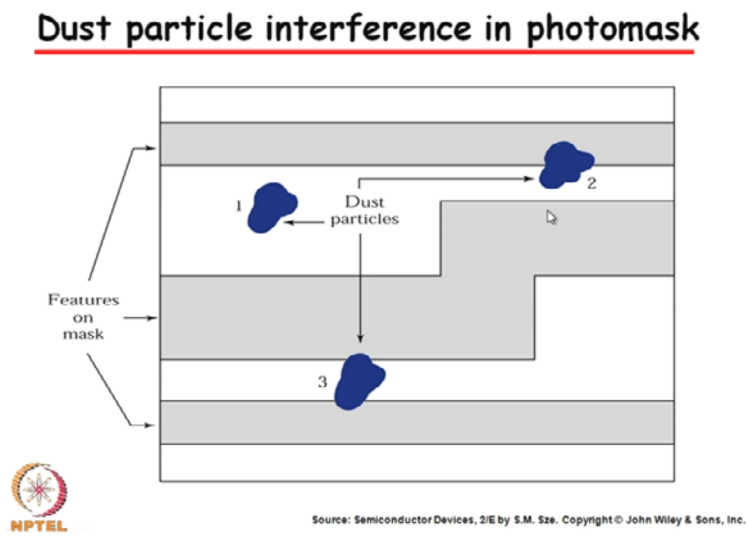
A dust particle incorporated into the gate oxide can result in enhanced conductivity and cause device failure due to low breakdown voltage.

Can disrupt single-crystal growth of an epitaxial film causing the formation of dislocation

More severe for lithographic process

Now, one cannot think of the possessing in a a normal room, because clean room is essential in making any device processing, all kind of processing is made on a clean room. A clean room is a a room; it is free from any dust particle or particulate matters. So, a problem with the dust particle which is incorporated into the gate oxide, it can result in enhanced conductivity and cause device failure due to low breakdown voltage, because it acts as an impurity or it can disrupt single-crystal growth of an epitaxial film causing the formation of dislocation. And this is the the presence of this particulate matter or dust is severe for lithographic process as we shall see later on; that essential clean room is the is a must in case of a lithographic process.

(Refer Slide Time: 11:16)

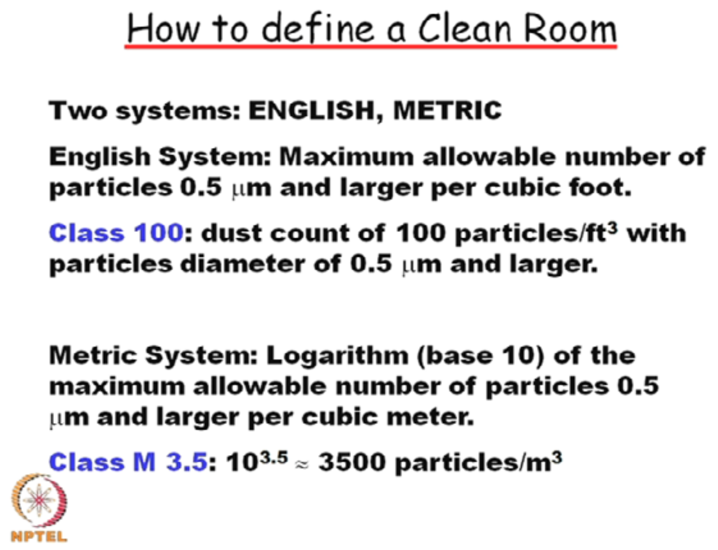


Dust particle interference in photomask

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

Because, you see that, if there is a particle or a dust here, so what will happen that this will constrict the flow of the current and also here it will see that it will interconnect between these blue region and this blue region; it will act as a conducting, and also it will give rise to some defect. So, you see that depending on the position of the dust particles, since the dimension is very narrow of the less than 1 micron. So, these dust particle can cause above during the semiconductor processing.

(Refer Slide Time: 11:57)



How to define a Clean Room

Two systems: ENGLISH, METRIC

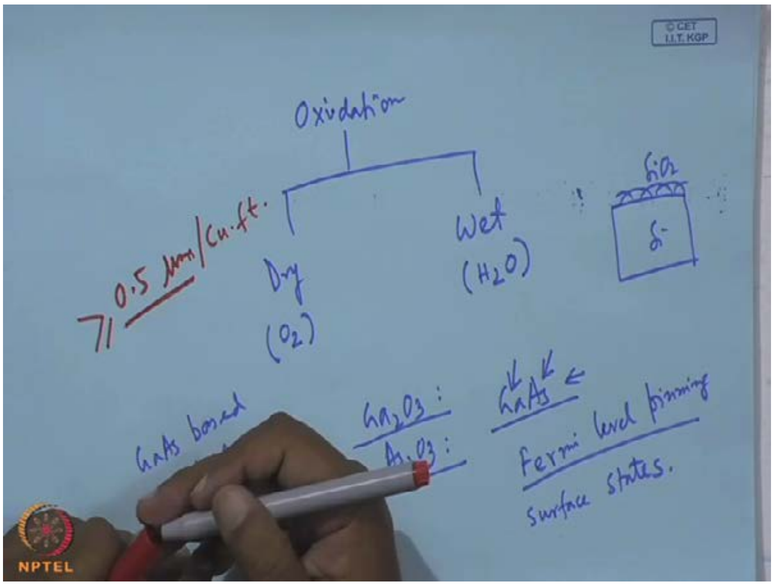
English System: Maximum allowable number of particles 0.5 μm and larger per cubic foot.

Class 100: dust count of 100 particles/ft^3 with particles diameter of 0.5 μm and larger.

Metric System: Logarithm (base 10) of the maximum allowable number of particles 0.5 μm and larger per cubic meter.

Class M 3.5: $10^{3.5} \approx$ 3500 particles/m^3

(Refer Slide Time: 12:19)

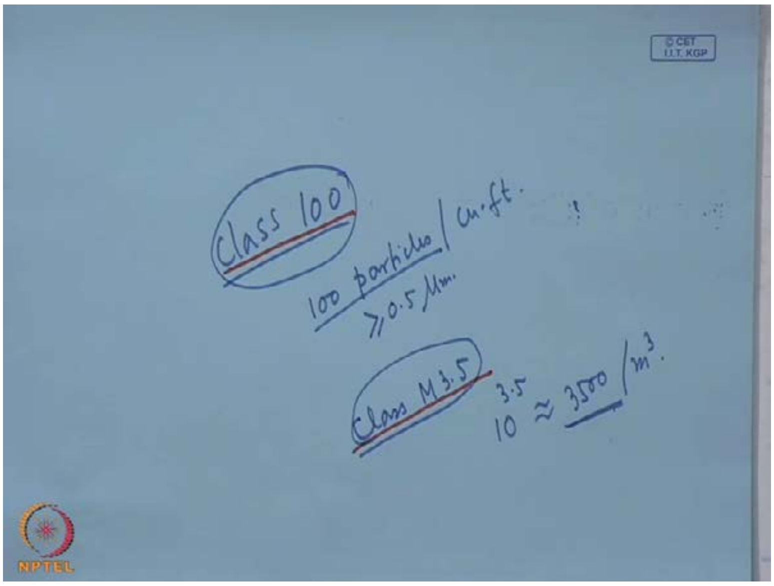


So you must have a clean room, now how to define a clean room? There are two systems using which we can define a clean room; one is the English system, another is the metric system. In English system, this maximum allowable number of particles is 0.5 micron, you see that it is 0.5 micron or above and a per cubic feet.

So, if have a particle above or equals to greater than equals to 0.5 micron per cubic feet then you can see that that is the maximum allowable limit and if it is greater than that, then you cannot term that it is a clean room; that means, the size; size is very important here 0.5 micron or greater. Now, what is the definition of a class 100 clean room? In a class 100 clean room, you see that the dust count of 100 particles per cubic feet with particles diameter of 0.5 micron and larger.

So you see that if you have a clean room then you can say that it is a class 100 clean room, if the particles, dust particles or count of the particles is 100 particles per cubic feet, so in 1 cubic feet of air, you can have at the maximum 100 particles then what is the dimension of the particles? Dimension of the particles is greater than equals to 0.5 micron or large that means; either it can be 0.5 micron or larger and maximum allowable particles are 100 per cubic feet.

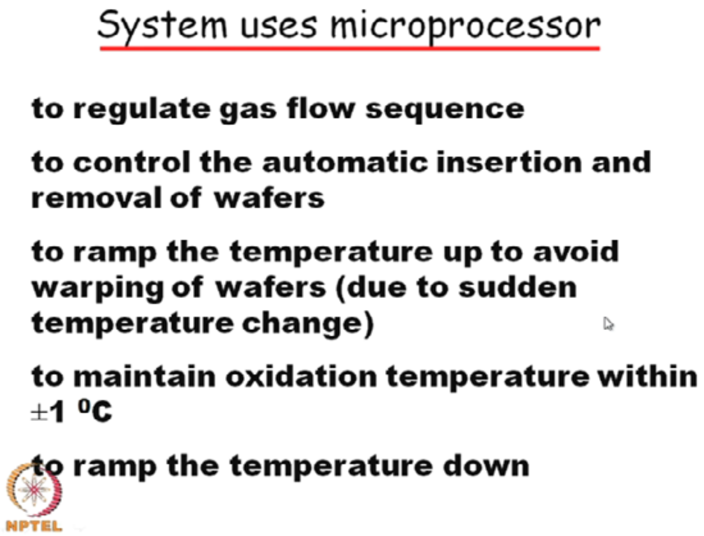
(Refer Slide Time: 14:12)



So, this is known as the class 100 clean room or in metric system, you see that it is a a logarithm of the maximum allowable number of particles and the particle size is same in this case also, it is 0.5 micron and larger per cubic meter. So, in metric system, it is per cubic meter and in English system it is per cubic feet. Now, what is a class M 3.5? M stands for metric, 3.5 it it means 10 to the power 3.5 or at the most 3500 particles per cubic meter per cubic meter it is allowed.

So, a class 100 clean room is equivalent to class M 3.5 clean room. So, these two clean rooms are essentially equivalent that means class 100 and class M 3.5, why because the number of particles 100 particles per cubic feet is equal to 3500 particles per cubic meter and the dimension of the particle in both the cases are same; it is 0.5 micron or larger; that means, in diameter.

(Refer Slide Time: 15:19)



System uses microprocessor

to regulate gas flow sequence

to control the automatic insertion and removal of wafers

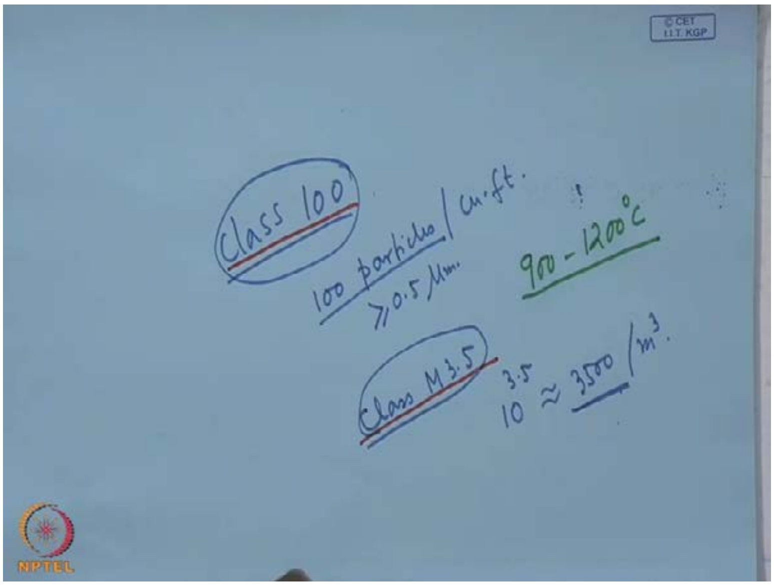
to ramp the temperature up to avoid warping of wafers (due to sudden temperature change)

to maintain oxidation temperature within ±1 ^{0}C

to ramp the temperature down

So, there are there can be 1000 class, there can be 10000 class, so different kind of classes are available to obtain a clean room and the efficiency of a clean room will be proved during the process of lithography. In this case, you see that the system uses microprocessor to regulate gas, gas flow sequence. So that means here, if you come down to the reactor, for the oxidation; this is basically a microprocessor controlled system and here you see that to control the automatic insertion and removal of wafers. That means, here the automatic insertion and removal of wafers that is done by the microprocessor control, and to regulate gas flow sequence, gas flow sequence means; this is the gas flow sequence either it can be oxygen or it can be water wafer, but it must be carried over the carrier gas and what is the forehead of the carrier gas how long it will flow.

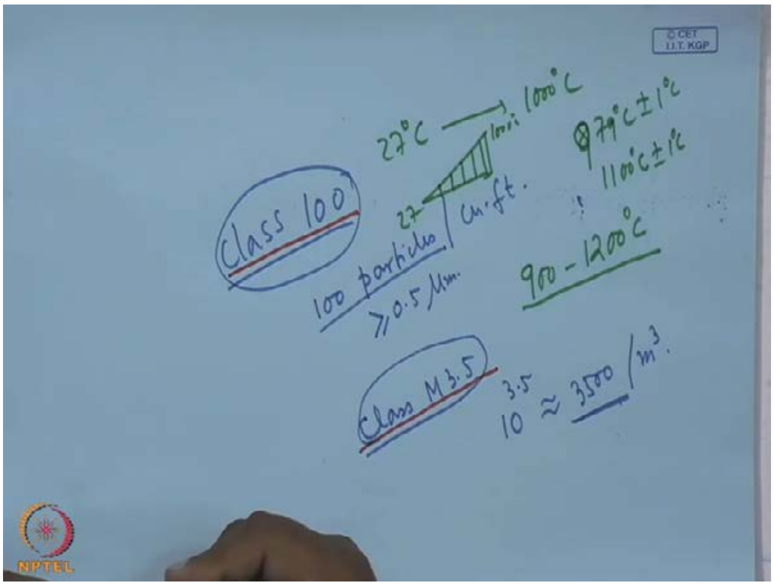
(Refer Slide Time: 16:33)



So, everything will be settled by the microprocessor control and in this case you see that apart from these gas flow sequence and automatic insertion and unloading of wafers temperature you have to increase, because the temperature required in this case is normally 900 to 1200 degree centigrade, this is the temperature required for the oxidation.

Now, to ramp the temperature up to highest temperature, to ramp the temperature up to say the oxidation temperature, you have to ramp the temperature why? Because, otherwise if there is a sudden change of temperature the, there will be thermal shock to the wafers and you will not be able to avoid warping of wafers. So; that means, there can be some cracks etcetera, air like cracks also and that is the warping and to avoid warping, you have to ramp the temperature very slowly.

(Refer Slide Time: 17:18)

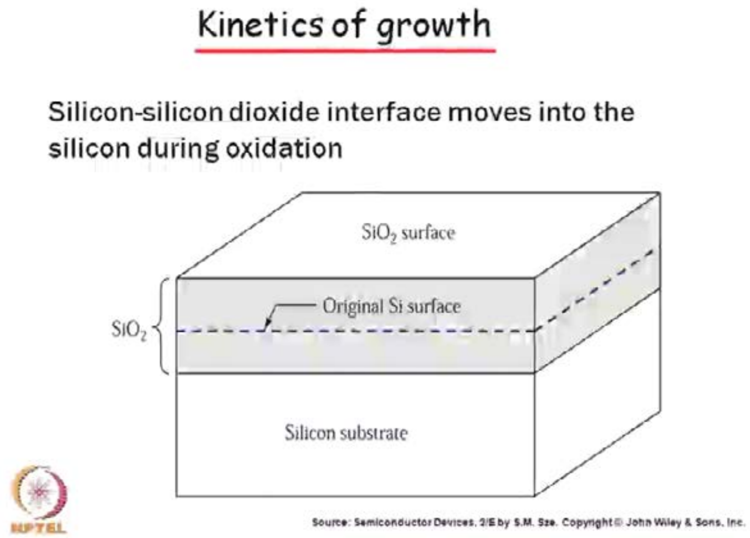


So, from room temperature say your room temperature is 27 degree centigrade, from 27 degree centigrade to say 1000 degree centigrade, we have to ramp the temperature very slowly. So that you can have here from 27 to 1000 degree centigrade, you can have, you can avoid the warping of the wafers, and to maintain the oxidation temperature within plus minus 1 degree centigrade.

So, it is very important; if you need say 879 degree sorry, 979 degrees centigrade or 1100 degree centigrade temperature. So, it must be plus minus 1 degree centigrade, plus minus 1 degree centigrade. So, such kind of precision is required in case of a oxidation system, and again when the oxidation is completed then to ramp the temperature down to room temperature from say 1100 degree centigrade or 979 degree centigrade or 1200 degree centigrade to ramp down the temperature, you have to use the microprocessor.

So; essentially, we find that the oxidation furnace which is used in case of the oxidation process, it must have some computer control or microprocessor control using which you can load, unload the wafers. You can ramp the temperature up to the oxidation temperature which is quite high to keep the temperature at that point very precisely up to plus minus 1 degree centigrade then loading unloading of the wafers, to control the gas flow, the timing and the flow rate etcetera, all such thing and when it is over; the oxidation is over. You have to ramp down the temperature from the oxidation temperature down to your room temperature all such jobs are processed by the microprocessor or in a computer controlled system.

(Refer Slide Time: 19:19)

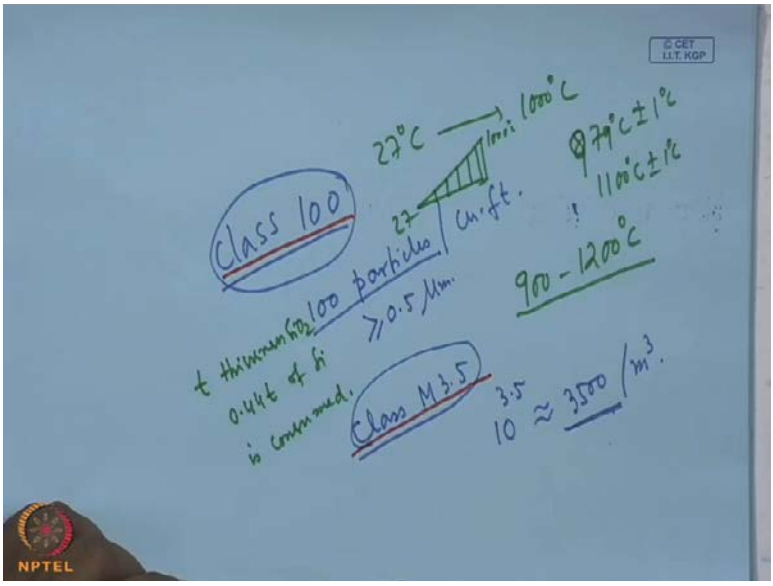


Kinetics of growth

Silicon-silicon dioxide interface moves into the silicon during oxidation

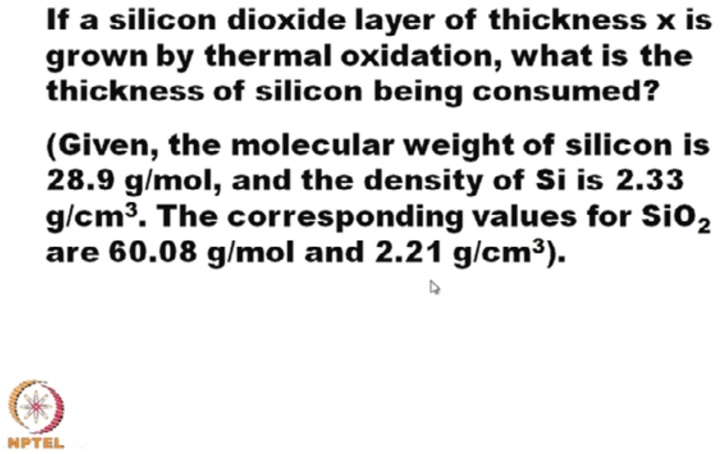
Source: Semiconductor Devices, 2/E by S.M. Sze. Copyright © John Wiley & Sons, Inc.

(Refer Slide Time: 19:36)



Now, it is very interesting to have the kinetics of growth, because you see that, when S I 2 is grown on a silicon, silicon is consumed and we shall see that if you want t thickness of the oxide film, t thickness of S i O 2, if you need, so 0.44 t of silicon is consumed. So, that is very important thing and if we discuss the kinetics of growth of silicon oxide, you will find that this silicon-silicon dioxide interface moves into the silicon during oxidation. So, if this is the interface this is, this is the dotted line is the original silicon surface, this dotted line is the original silicon surface and this original silicon surface is basically moves downward so; that means, as the S i O 2 is grown these interface comes down slowly.

(Refer Slide Time: 20:30)

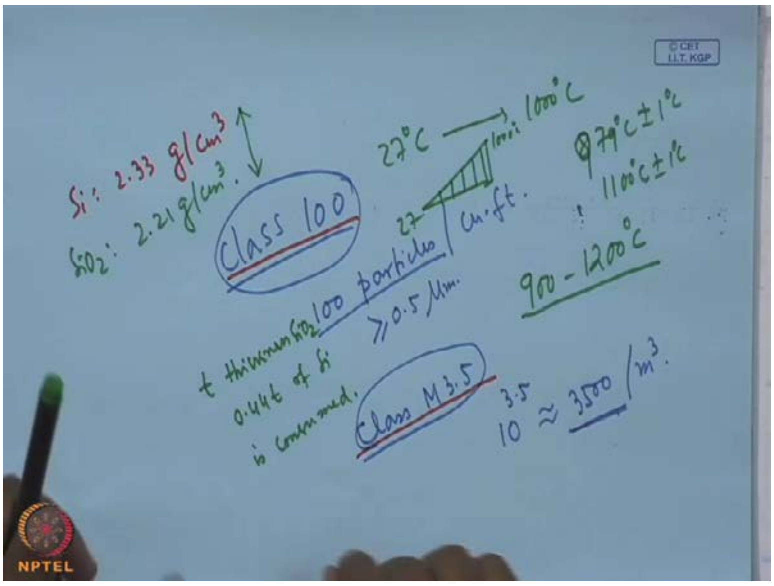


If a silicon dioxide layer of thickness x is grown by thermal oxidation, what is the thickness of silicon being consumed?

(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).

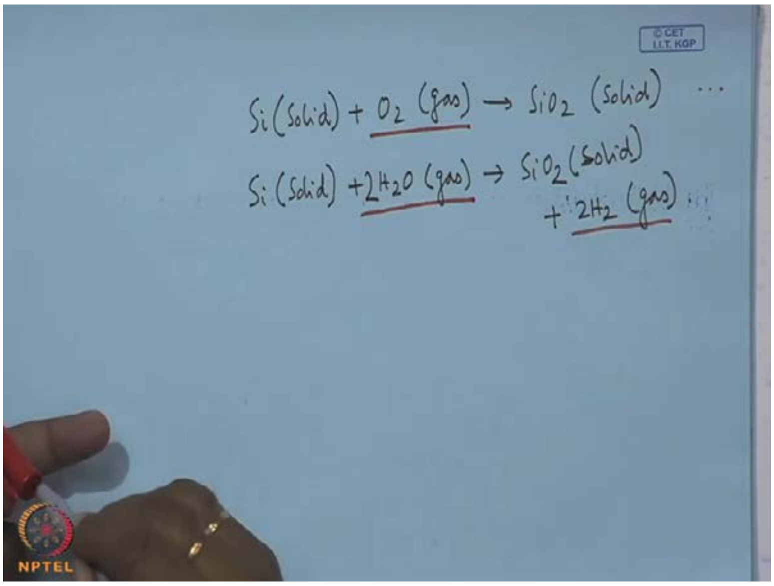
If a silicon dioxide layer, you see of thickness x is grown by thermal oxidation, what is the thickness of silicon being consumed? So, that is very interesting thing and the values are given, the molecular weight of silicon is 28.9 gram per mole and the density of silicon is 2.33 gram per centimeter cube.

(Refer Slide Time: 21:18)



The corresponding values; that means, the molecular weight of silicon dioxide is given as 60.08 gram per mole and 2.21 gram per centimeter cube is the density of S i O 2. So obviously, you see that the density of S i O 2 is less than the density of Si, Si density is 2.33 gram per centimeter cube, whereas for S i O 2 it is 2.21 gram per centimeter cube so; obviously, if you compare with the silicon the porosity is larger in case of S i O 2.

(Refer Slide Time: 21:56)

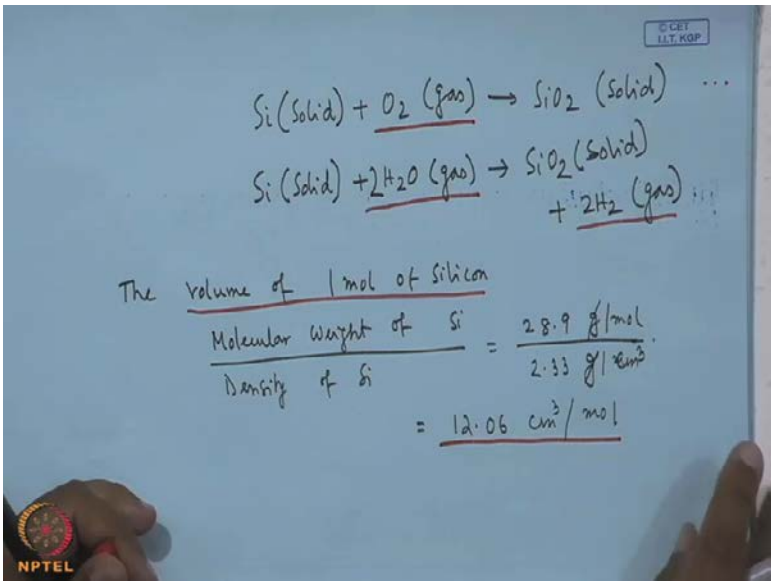


Now, with this value, let us consider that how this S i O 2 layer is grown? In this case, the S i O 2 layer is grown, suppose you have S i which is nothing but the solid it reacts with oxygen which is gas and S i O 2 is formed which is obviously solid or you can have silicon substrate which is a solid material and it reacts with, it reacts with water vapour which is basically the gas; that means, the steam is used. So, here you see, S i O 2 solid is formed and along with the S i O 2, there will be hydrogen gas.

So, depending on the source, in this case you see that the source is oxygen, no hydrogen is there; in this case the source is the water vapour or the steam hydrogen gas emits and; obviously, because of the presence of hydrogen gas, you see from this reactor that to vent. Vent means this hydrogen must pass out from the quartz tube reactor to the scrubber before sending it to the atmosphere, and in the scrubber, there can be some charcoal at maintain at a particular temperature heated charcoal is there and the hydrogen is passed through that heated charcoal, and finally to air.

So, not directly it is sent back to the atmosphere, so the in this case you see that depending on the source of the oxygen, there can be the presence or the emission of hydrogen gas or not now. In this case, if we consider this problem that if a silicon dioxide layer of thickness x is grown by thermal oxidation, then what is the thickness of silicon being consumed with this value.

(Refer Slide Time: 24:05)



$$\mathrm{Si\,(Solid)} + \underline{\mathrm{O_2\,(gas)}} \rightarrow \mathrm{SiO_2\,(Solid)} \;\ldots$$

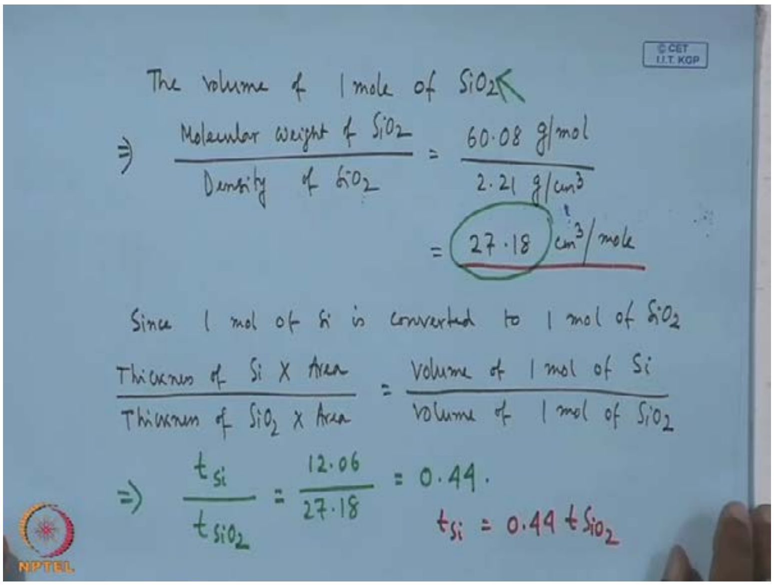
$$\mathrm{Si\,(Solid)} + \underline{\mathrm{2H_2O\,(gas)}} \rightarrow \mathrm{SiO_2\,(Solid)} + \underline{\mathrm{2H_2\,(gas)}}$$

The $\underline{\text{volume of 1 mol of Silicon}}$

$$\frac{\text{Molecular Weight of Si}}{\text{Density of Si}} = \frac{28.9\ \mathrm{g/mol}}{2.33\ \mathrm{g/cm^3}} = \underline{12.06\ \mathrm{cm^3/mol}}$$

So, let us calculate say say the volume of 1 mole of silicon, volume of 1 mole of silicon if we write then you have to write that molecular weight of silicon by the density of silicon. Now, what is the molecular weight of silicon it is given, 28.9 gram per mole, you see that it is given here it is 28.9 gram per mole and what is the density of silicon it is also given 2.33 gram per centimeter cube.

(Refer Slide Time: 25:21)



The volume of 1 mole of SiO_2

$$\Rightarrow \frac{\text{Molecular weight of } SiO_2}{\text{Density of } SiO_2} = \frac{60.08 \text{ g/mol}}{2.21 \text{ g/cm}^3}$$

$$= \boxed{27.18} \text{ cm}^3/\text{mole}$$

Since 1 mol of Si is converted to 1 mol of SiO_2

$$\frac{\text{Thickness of Si} \times \text{Area}}{\text{Thickness of } SiO_2 \times \text{Area}} = \frac{\text{Volume of 1 mol of Si}}{\text{Volume of 1 mol of } SiO_2}$$

$$\Rightarrow \frac{t_{Si}}{t_{SiO_2}} = \frac{12.06}{27.18} = 0.44.$$

$$t_{Si} = 0.44\, t_{SiO_2}$$

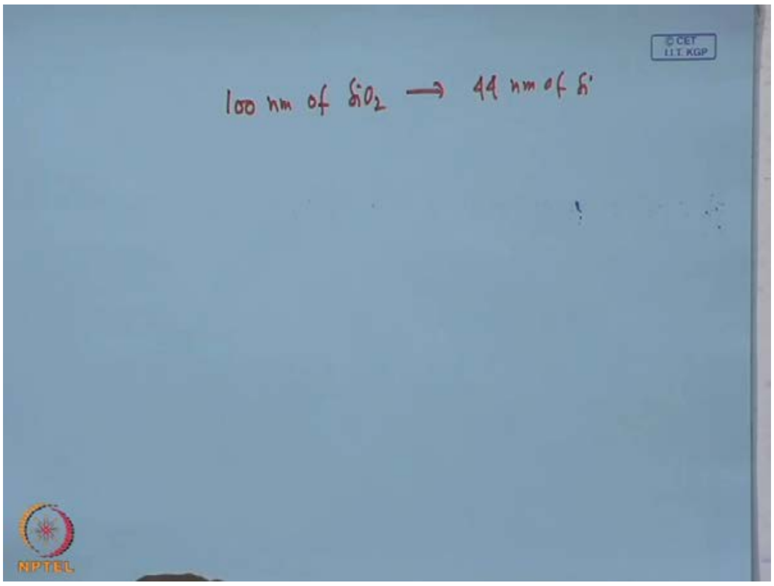
Now, with this value if we take the final result; that means, 28.9 by 2.33, you will get it is 12.06 centimeter cube by mole. So, with this with, this value we can calculate this volume of 1 mole of silicon. Later we shall see that what is the volume of 1mole of silicon dioxide, the volume of 1 mole of silicon dioxide here also, we can calculate by the same ratio, you see that here we have taken the molecular weight of silicon to the density of silicon here we shall take, the molecular weight of S i O 2 by the density of S i O 2, and in this problem you see that it is given that it is 60.08 gram per mole.

So, it is 60.08 gram per mole to the density of S i O 2 is 2.21gram per mole, so it is 2.21 gram per centimeter cube and with this value, we can calculate the volume of 1 mole of S i O 2 as 27.18 centimeter cube by mole. So, what are the values, we get here we have obtained 12.06 here, we obtain 27.18 centimeter cube by mole that is for S i O 2 and this one for silicon.

Next is that since 1 mole of silicon is converted to 1 mole of S i O 2, so we can write that the thickness of silicon multiplied by area, because if you multiply thickness with area you will get the volume, by the thickness of S i O 2 multiplied by the area. So, you will get volume of 1 mole of silicon to the volume of 1 mole of S i O 2.

Now, we have already calculated what is he volume of 1 mole of s i? Or what is the volume of 1 mole of S i O 2? Now, you can write from this equation that if you cancels out the area, thickness of silicon let us denote it by T s i to the thickness of S i O 2 thickness of the silicon dioxide and that is equals to volume of 1 mole of S i volume of 1 mole of s i is 12.06. So, let us write down as 12.06 divided by the volume of 1 mole of S i O 2 it is 27.18, this is S i O 2 so it is 27.18 and if you take the final output it is 0.44, so we can write that the thickness of silicon will be 0.44 times of S i O 2 thickness. So, that we have started earlier that 44 percent of the silicon is consumed.

(Refer Slide Time: 29:23)



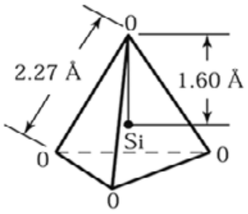
©CET I.I.T. KGP

100 nm of SiO_2 → 44 nm of Si

(Refer Slide Time: 29:41)

SiO_2 structure

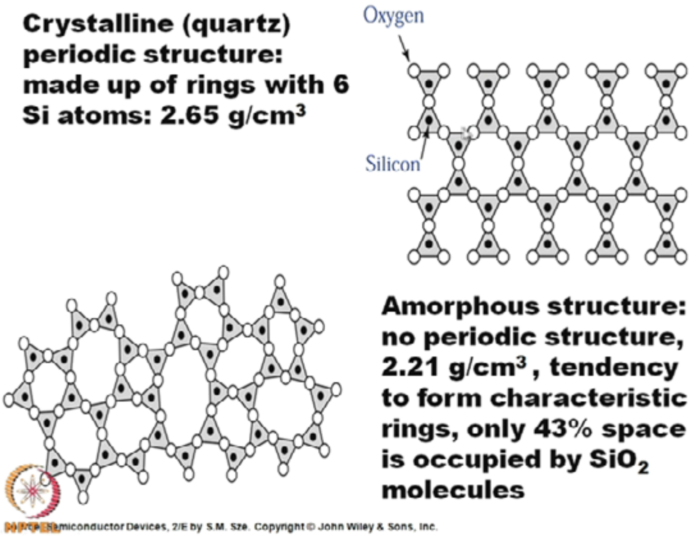
A Si atom surrounded tetrahedrally by four oxygen atoms



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

So; that means, the the concept is that if you want to grow 100 nanometer of S i O 2, how much silicon is consumed 44 nanometer of silicon is consumed, so that is the kinetics of growth for S i O 2. And you see that what is the S i O 2 structure? S i O 2 structure is basically in a S i O 2, a silicon atom is surrounded tetrahedrally by 4 oxygen atoms, and you see that a silicon atom is tetrahedrally surrounded by 4 oxygen atoms and what are the values of those oxygen atoms? 1 oxygen atom you see that between oxygen atom to atom, the inter-nuclear distance is 2.27 angstrom, the inter-nuclear distance is 2.27 angstrom while between oxygen and silicon; these distance is 1.6 angstrom only.

(Refer Slide Time: 30:56)



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

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

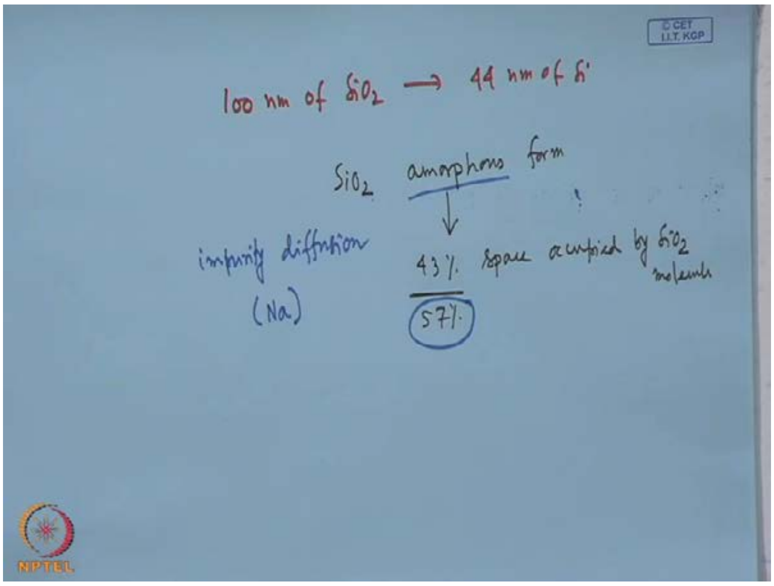
So, now when such kind of arrangements of silicon atoms surrounded tetrahedrally by 4 oxygen atoms, they are joined; this tetrahedra are joined together at their corners by oxygen bridges in a number of ways to form the various phases of structures of silicon dioxide. So, it depends on how they are joined by the oxygen bridges and we shall see that this is one type of bridge, where the oxygen makes the bridges or here different types of bridge. So, depending on how they are joined; that means, the tetrahedra are joined together at their corners by the oxygen bridges, they, they form different kind of structures.

So, different crystalline structure are possible as mentioned earlier, one such structure is known as the quartz or S i O 2 is also called silica, those silica can be one form of silica can be quartz which is crystalline in nature. So, different crystalline forms are available in nature and one amorphous form is also there, and here you see that depending on the oxygen bridges. Here, two types of bridges we have, we have shown; one is the here, the oxygen bridges made 6 made of 6 rings with silicon atoms.

So, this is silicon atoms, so you see that 1,2,3,4,5,6, here you see 1,2,3,4,5,6, so, these 6 silicon atoms, they made of rings and this is basically a crystalline structure, this is known as the quartz and… And here this is the amorphous structure, because there is no periodic structure, here a periodic structure is formed, here no periodic structure is formed, here in all the cases; it is made up of 6 silicon atoms, here you see that there is a tendency to form the characteristics ring, but but exactly the structure, no periodic structure is formed only 43 percent space is occupied by S i O 2 molecules and the rest of the space is void.

Also if you compare the density, it is 2.21gram per centimeter cube, here it is 2.65 gram per centimeter cube is the density of, of the quartz form, that means; the crystalline form, here it is the amorphous form and because of this 43 percent void space, you can see that with this void space, what happens that there can be contamination impurity.

(Refer Slide Time: 33:19)



100 nm of SiO_2 $\longrightarrow$ 44 nm of Si

SiO_2 amorphous form

$\downarrow$

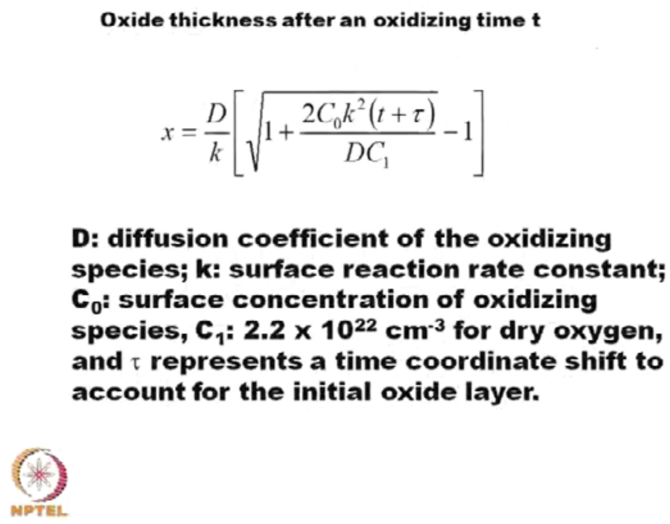
impurity diffusion (Na)

43% space occupied by SiO_2 molecules

$\boxed{57\%}$

So ,in S i O 2 amorphous form, you see that there is 43 percent space occupied by S i O 2 molecules, so almost 57 percent is void and this 57 percent void space. This 57 percent void space has some bad effect, in the sense that there can be impurity diffusion as it is amorphous in nature. So, impurity diffusion will be there particularly sodium and because of this impurity diffusion or inter-diffusion of some impurities, the stability of the device or the structure or will be a very small and so care must be taken, to avoid this kind of a structure, if we use this S i O 2 for some application in the i c technology.

(Refer Slide Time: 34:37)



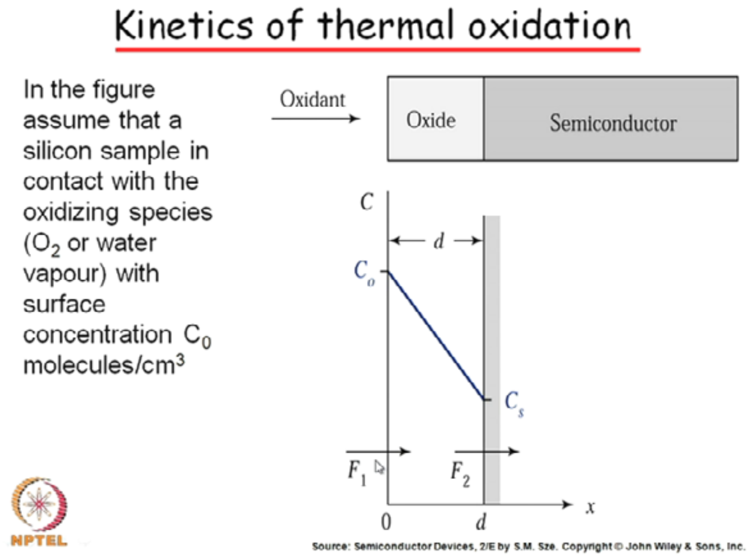
Oxide thickness after an oxidizing time t

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

D: diffusion coefficient of the oxidizing species; k: surface reaction rate constant; C_0: surface concentration of oxidizing species, C_1: 2.2 x 10^{22} cm^{-3} for dry oxygen, and τ represents a time coordinate shift to account for the initial oxide layer.

NPTEL

(Refer Slide Time: 34:42)



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

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

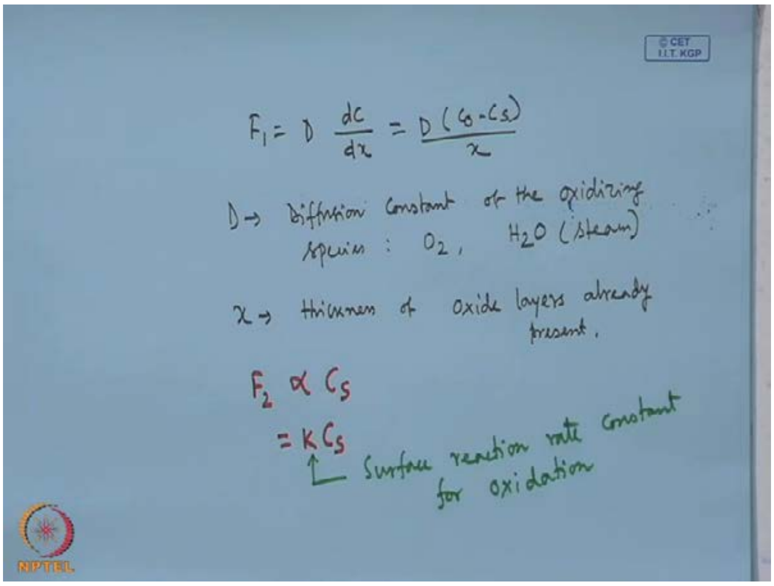
NPTEL

Now, if we model the growth, what is the kinetic of thermal oxidation? We see that let us have, let us take a semiconductor sample and the oxidant species can be oxygen or water vapour, but there can be oxide layer, so if C 0 is the surface concentration and of the species oxidizing, species oxidizing species are basically the water vapour or the oxygen molecules, these are the oxidizing species.

So, they have to diffuse through this oxide layer and C s is the surface concentration at the semiconductor; that means, at the interface between the oxide and the semiconductor, this C s is the surface concentration. So, we can calculate the flux F 1 and F 2, which will give us some insight about the kinetics of thermal oxidation and as mentioned earlier that let us consider that d thickness of oxide is formed, already it can be formed by some other process or already there is a presence of oxide with thickness d.

So, we have to consider two surfaces flux between the oxidizing species and oxide that means; at this interface, where the oxidizing species enters the system and between the oxide and the semiconductor F 2 flux, we have to consider because that is the surface where C s concentration of molecules per centimeter cube is available. So obviously, if you plot with the distance x verses c the concentration, the concentration is lower in case of the semiconductor surface compared to the oxide surface, where there is the availability of the oxidizing species is very high.

(Refer Slide Time: 36:51)



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

$D \rightarrow$ Diffusion Constant of the oxidizing species : O_2, H_2O (steam)

$x \rightarrow$ thickness of oxide layers already present.

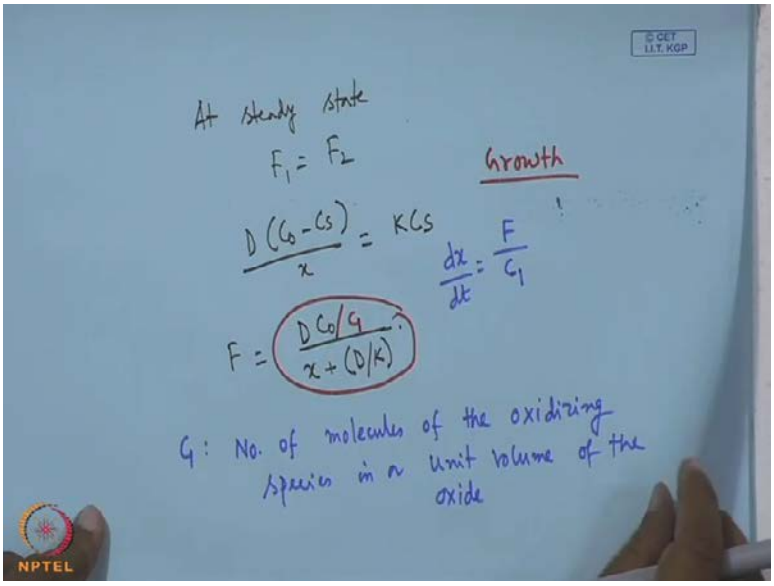
$$F_2 \propto C_s$$
$$= K C_s$$

↑ Surface reaction rate constant for oxidation

Now, with this idea, so let us consider that F 1 is the flux, which we can say that it is equals to D and d c by d x, where D is the diffusion constant of the oxidizing species that means; oxidizing species may be, it can be oxygen molecules or water vapour. That means, steam, now this is equals to, we can write D C 0 minus C s by x as you can find, that it is C 0 minus C s by x, so what is x? x is the thickness of oxide layers already present or already formed, it can be formed by some other process as well.

Now, this is F 1; now, what about F 2? F 2 we can write, it is proportional to the surface concentration and this C s, you see that it is this is coming through the diffusion through the oxide layer at the surface of the semiconductor. So, this is we can write equals to k some constant into C s. Now, what is k? k is basically surface reaction rate constant for oxidation, so we so we get two types of thing, one is this F 1 another is F 2, the two fluxes at the two surfaces, one at the oxide surface, another at the semiconductor surface.

(Refer Slide Time: 39:25)



At steady state

$F_1 = F_2$

Growth

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

$$\frac{dx}{dt} = \frac{F}{C_1}$$

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

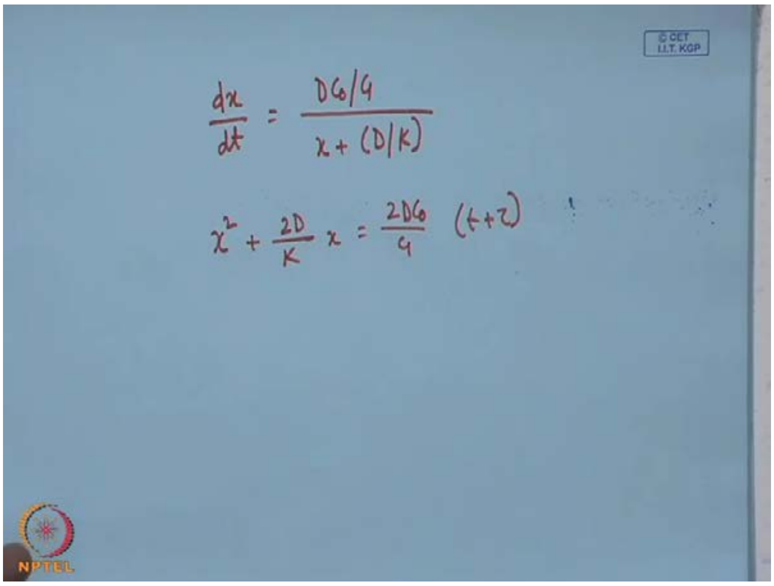
C_1 : No. of molecules of the oxidizing species in a unit volume of the oxide

Now, at steady state, what will happen at steady state? These two will be equal at steady state, you see that what happens at steady state? At steady state, F 1 will be equals to F 2 and say that is we can write F 1 is basically these thing, so D C 0 minus C s by x and that is equals to k C s and we can write that F equals to in, in this case F equals to dc 0 by x plus D by k as mentioned earlier that, D is the diffusion constant or the diffusivity of the oxidizing species in silicon and x is the thickness of the oxide layer already formed and C 0 is the surface concentration and and k is the surface reaction rate constant for oxidation.

Now, what is the growth rate? This is the flux, it is the overall flux at the steady state then what is the growth rate? The growth rate is very important, because finally, it is the growth rate which will give us the data for any kind of oxidation, and this growth rate you can see that we can write the growth rate can be F by C 1, so d x d t is the growth rate. Let us consider that d x d t is the growth rate, rate of growth of oxide with time, it is F by C 1, now what is C 1? C 1 is the number of molecules of the oxidizing species in a unit volume of the oxide.

So, this is the number of molecules of the oxidizing species in a unit volume of the oxide and if we divide this flux by these number of molecules of the oxidizing species then we can achieve the growth rate of the oxide layer. Now, if we divide F by C 1, so you see that this is the expression for f, so just divide it by C 1, so it will be D C 0 by C 1.

(Refer Slide Time: 42:08)

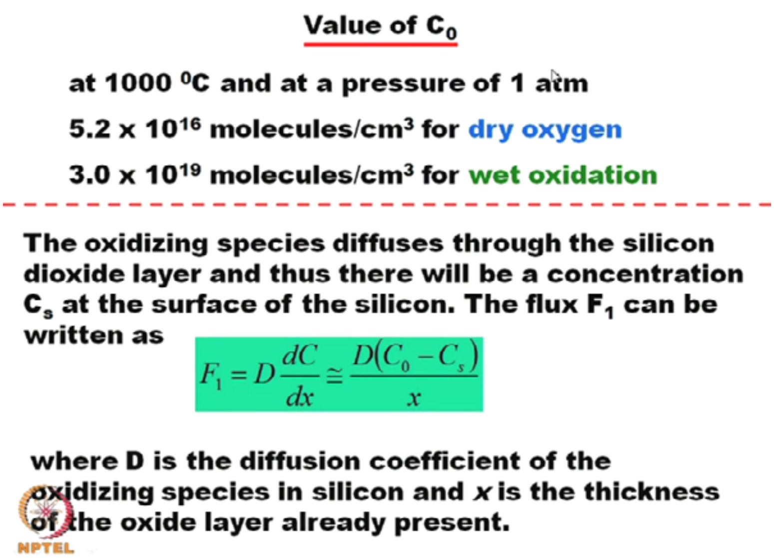


$$\frac{dx}{dt} = \frac{DC_0/C_1}{x + (D/K)}$$

$$x^2 + \frac{2D}{K}x = \frac{2DC_0}{C_1}(t+\tau)$$

So, finally, we can write that the growth rate, d x d t is equals to D C 0 by C 1 by x plus D upon k, you see that the same thing, we have written earlier that divided by C 1 in the previous expression.

(Refer Slide Time: 42:58)



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

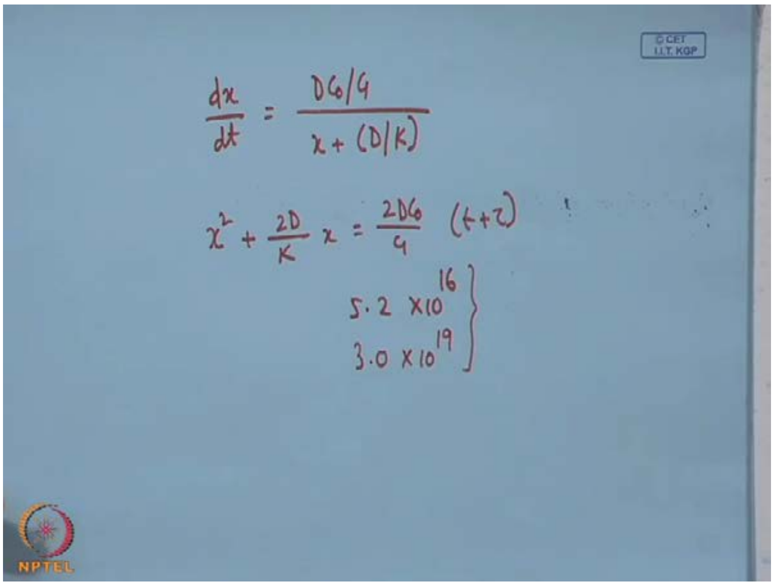
The oxidizing species diffuses through the silicon dioxide layer and thus there will be a concentration C_s at the surface of the silicon. The flux F_1 can be written as

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

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

Now, if we rearrange this equation, this will the equation than what we will get, we will get x square plus twice D k into x equals to twice D C 0 by C 1 t plus tau, why because there will be some boundary condition as we shall discuss here, you see that what is the value of this C 0, because we have used C 0 here. And what is the value of C 0, if we take that the oxidation of growth the temperature is 1000 degree centigrade and the pressure is 1 atmosphere then we can say that for dry oxygen, the value is 5.2 for dry oxygen, it is 5.2 into 10 to the power 16, where is for wet molecules or wet oxidation, it is 3 into 10 to the power 19.

(Refer Slide Time: 43:22)



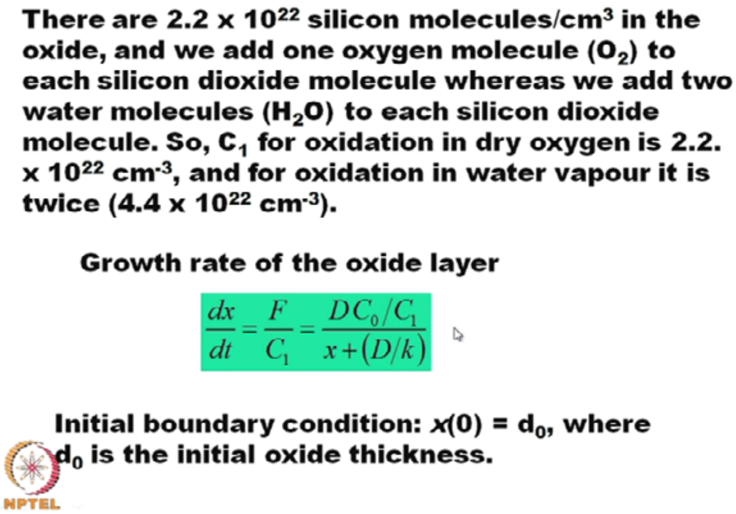
$$\frac{dx}{dt} = \frac{DC_0/C_1}{x + (D/K)}$$

$$x^2 + \frac{2D}{K}x = \frac{2DC_0}{C_1}(t+\tau)$$

$$\left.\begin{matrix} 5.2 \times 10^{16} \\ 3.0 \times 10^{19} \end{matrix}\right\}$$

So, this is the value and it is written over here, that at 1000 degree centigrade and at a pressure of 1 atmosphere 5.2 into 10 to the power 16 molecules per centimeter cube is the value of C 0 for dry oxygen, and 3 into 10 to the power 19 molecules per centimeter cube for wet oxygen or wet sorry, wet oxidation. Now, what is C 0? Here you see, C 0 is the surface concentration of the oxidizing species and another thing is that this C 1.

(Refer Slide Time: 44:07)



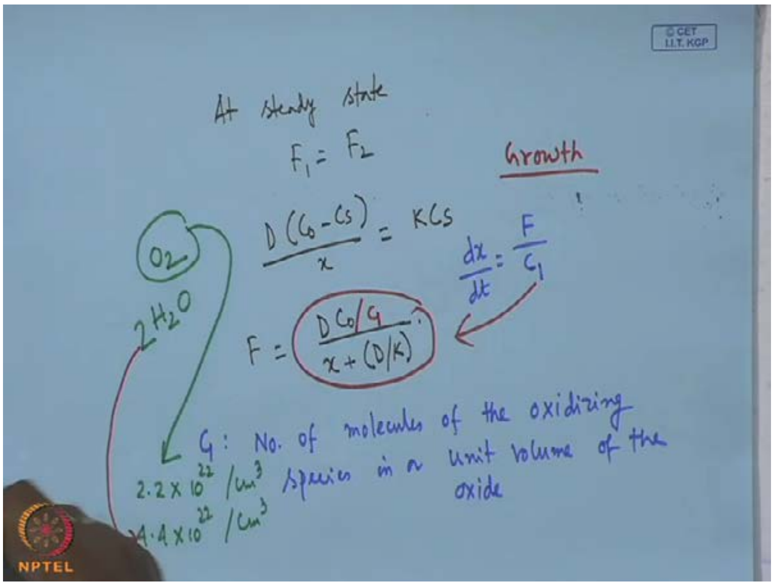
There are 2.2 x 10^{22} silicon molecules/cm^3 in the oxide, and we add one oxygen molecule (O_2) to each silicon dioxide molecule whereas we add two water molecules (H_2O) to each silicon dioxide molecule. So, C_1 for oxidation in dry oxygen is 2.2. x 10^{22} cm^{-3}, and for oxidation in water vapour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

(Refer Slide Time: 44:32)



At steady state

$F_1 = F_2$

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

Growth

$$\frac{dx}{dt} = \frac{F}{C_1}$$

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

O_2

$2H_2O$

C_1 : No. of molecules of the oxidizing species in a unit volume of the oxide

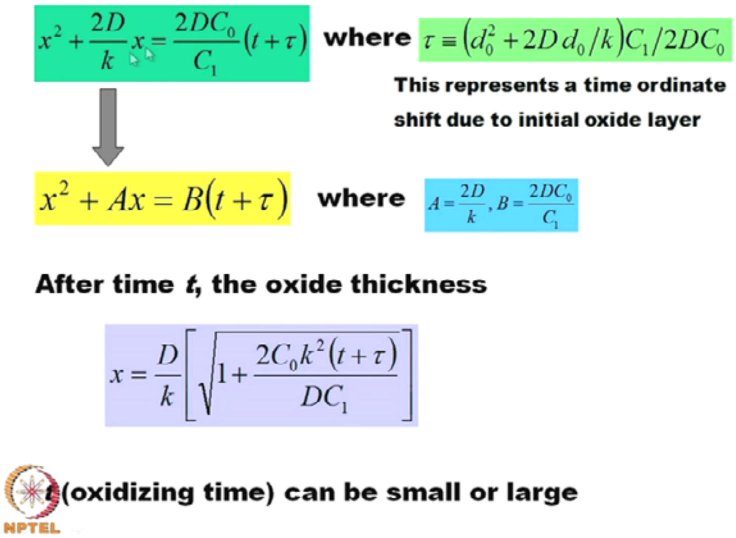
$2.2 \times 10^{22} /cm^3$

$4.4 \times 10^{22} /cm^3$

Value of C 1, C 1 we have taken as discussed earlier, that C 1 is the number of molecules of the oxidizing species in a unit volume of the oxide and what is its value? Now, its value is 2.2 in dry oxygen, 2.2 into 10 to the power 22. So, this value of C 1 is value of 2 C 1 is 2.2 into 10 to the power of 22 per centimeter cube in dry and 4.4 into 10 to the power 22 per centimeter cube in presence of water vapour, why it is multiplied by two? Because, you see the during oxidation, if you use 1 oxygen molecule and if you use 1 water molecule, in water molecule 1 atom is there, so if you need 2 molecules, 1 molecule of oxygen; that means, you have to use 2 H 2 O.

So, whatever be the value of oxygen, in case of water vapour, it must be multiplied by two, because in a water molecule only 1 atom of oxygen is there. However, you need 1 molecule of oxygen. Now, these expression; that means, d x d t equals to F by C 1 and it is equals to D C 0 by C 1, what we have deduce till, now it has a initial boundary condition that at x equals x 0, it is d 0 the value of d 0; that means, it is the initial oxide thickness at t equals to 0.

(Refer Slide Time: 46:02)



$$x^2 + \frac{2D}{k}x = \frac{2DC_0}{C_1}(t+\tau)$$ **where** $\tau \equiv \left(d_0^2 + 2Dd_0/k\right)C_1/2DC_0$

This represents a time ordinate shift due to initial oxide layer

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

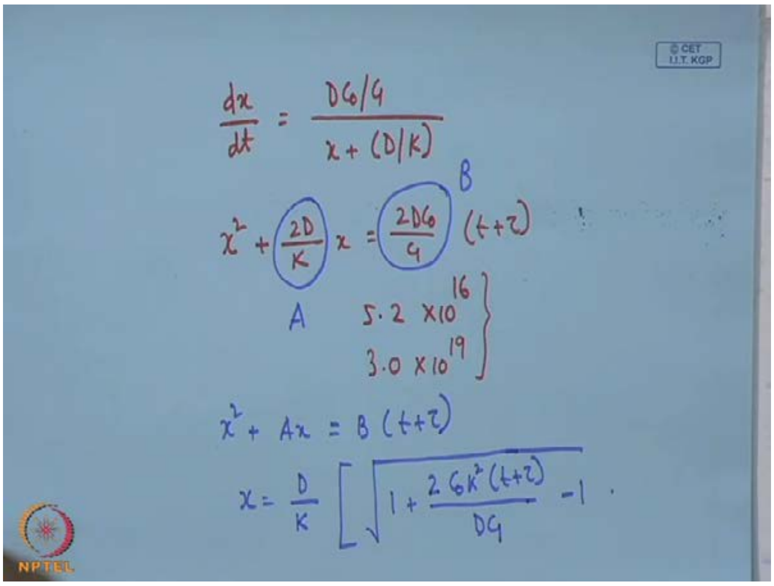
After time *t*, the oxide thickness

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

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

So; that means, we are considering that always, there is an oxidation layer, oxide layer formed at the surface of the silicon and so with this boundary condition, we can write this expression; that means, x square plus 2 D by k into x plus 2 D C 0 by C 1 into t plus tau. So this expression, we are achieving, and where tau is given by this expression, these represents a time ordinate shift due to initial oxide layer, because here, we are getting an initial oxide layer of d 0, so tau is not zero. Tau is some finite value having this because of the presence of d 0, you see d 0 square etcetera and so it is a time shift, it is a time ordinate shift due to initial oxide layer.

(Refer Slide Time: 47:07)



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

$$x^2 + \underset{A}{\boxed{\frac{2D}{K}}}\,x = \overset{B}{\boxed{\frac{2DC_0}{C_1}}}\,(t+\tau)$$

$$\left.\begin{array}{l} 5.2 \times 10^{16} \\ 3.0 \times 10^{19} \end{array}\right\}$$

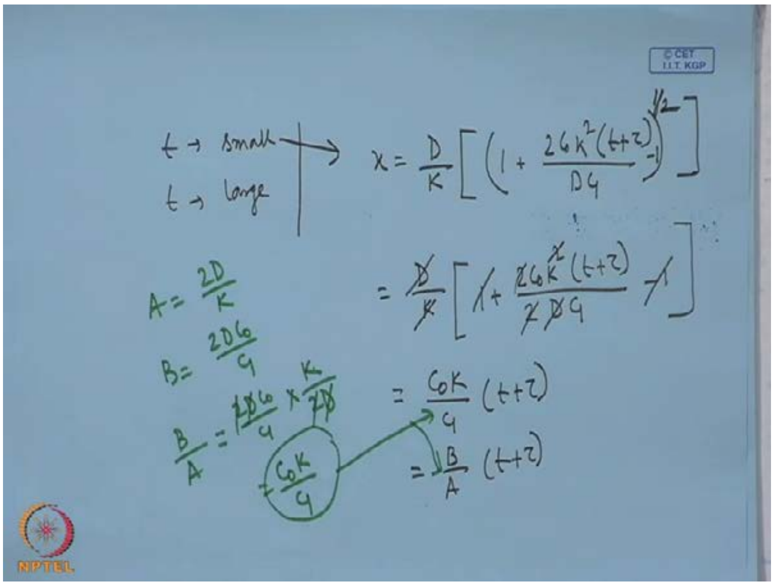
$$x^2 + Ax = B(t+\tau)$$

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

Now, this can be written as x square plus A x plus B into t plus tau so; that means, A is written A, this is replaced by A and B replaces this 2 D C 0 by C 1, so that means; this is replaced by A. So, we can write x square plus A x that is equals to it is replaced by B. So, it is B into t plus tau, so A and B can have value like this, A equals to twice D by k and B equals to twice D C 0 by C 1 than after time t, what should be the oxide thickness? then you have to take the value of x equals to D by k root over of 1 plus twice C 0 k square t plus tau by d C 1 minus 1, so this is the value of the oxide thickness after time t. So, this t, that means how long we are oxidizing the material? In this case the silicon it, it depending on how much it is there? We can have t larger or t smaller. So, we shall discuss both the cases, when t is large or when t is small.

So, what we are doing, first we have taken a semiconductor and we have considered that a d 0 oxide layer is there, at t equals to 0 some oxide layer is there, oxidizing species are coming on the surface of the oxide layer having surface concentration C 0. These oxidizing species can be water vapour steam or oxygen dry then it will diffuse through the oxide layer to reach the semiconductor surface with the surface concentration of C s and we have calculated two fluxes here F 1 and F 2 at steady state. This F 1 and F 2 becomes equal and we have achieved that F equals to this at steady state, and finally we have solved this equation to obtain the value of x equals to D by k root over of 1 plus 2 C 0 k square t plus tau by D C 1 minus 1, and now we shall solve for two cases when t can be small when t can be large.

(Refer Slide Time: 49:52)

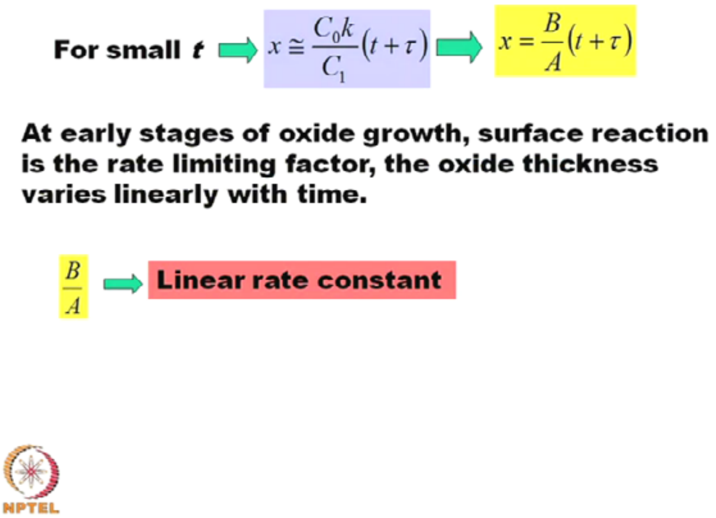


So; that means, for small oxidizing time, what happens when t is small and when t is large; two distinct cases we shall consider with this relation; that means with this relation when t is small or when t is large, now when t is small, what happens for small t? You can write that for small t, that for small t x equals to D by k in to 1 plus 2 C 0 k square t plus tau by D C 1 to the power half, because square root is there minus 1.

So, this is equals to D by k 1 plus 2 C 0 k square t plus tau by here it is half power is half. So, 2 will be there multiplied by D C 1 minus 1, so this will cancel out this D will go. And we will, we will find that we can write this C 0 k, because this k will cancel out, C 0 k, one k will be there, this 2 will also cancel out by C 1 into t plus tau. Now, what is this C 0 k by C 1, we can write it as B by A into t plus tau, why because you see that here we have considered what is the value of B? And what is the value of A?

Here, the value of A is twice D by k, the value of A we obtained as twice D by k and B is twice D C 0 by C 1, twice D C 0 by C 1, so if you take the ratio of B by A, you will get as twice D C 0 by C 1 multiplied by k by twice D. So, k C 0 by C 1 is obtained and this is nothing but these and we can write B by A into t plus tau.

(Refer Slide Time: 52:44)



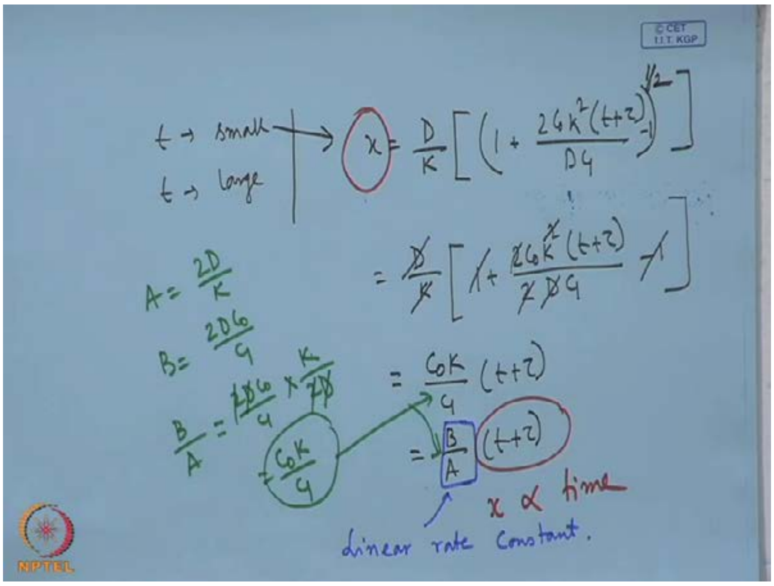
For small *t* ⟹ $x \cong \frac{C_0 k}{C_1}(t+\tau)$ ⟹ $x = \frac{B}{A}(t+\tau)$

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, that is for the small t, now for the small t, we see that this is nothing but an a rate limiting factor at early stages of the oxide growth surface reaction is the rate limiting factor. And the oxide thickness varies linearly with time, because this oxide thickness x propositional to time.

(Refer Slide Time: 53:00)



t → small

t → large

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

$$= \frac{\cancel{D}}{\cancel{K}}\left[\cancel{1} + \frac{\cancel{2}C_0K^{\cancel{2}}(t+\tau)}{\cancel{2}\cancel{D}C_1} - \cancel{1}\right]$$

$$= \frac{C_0K}{C_1}(t+\tau)$$

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

$x \propto$ time

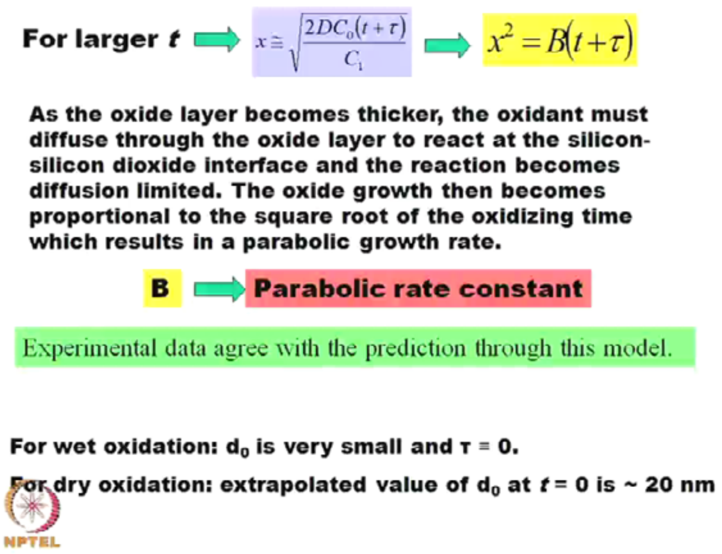
linear rate constant.

$A = \frac{2D}{K}$

$B = \frac{2DC_0}{C_1}$

$\frac{B}{A} = \frac{\cancel{2D}C_0}{C_1} \times \frac{K}{\cancel{2D}} = \frac{C_0K}{C_1}$

(Refer Slide Time: 53:52)



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

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**

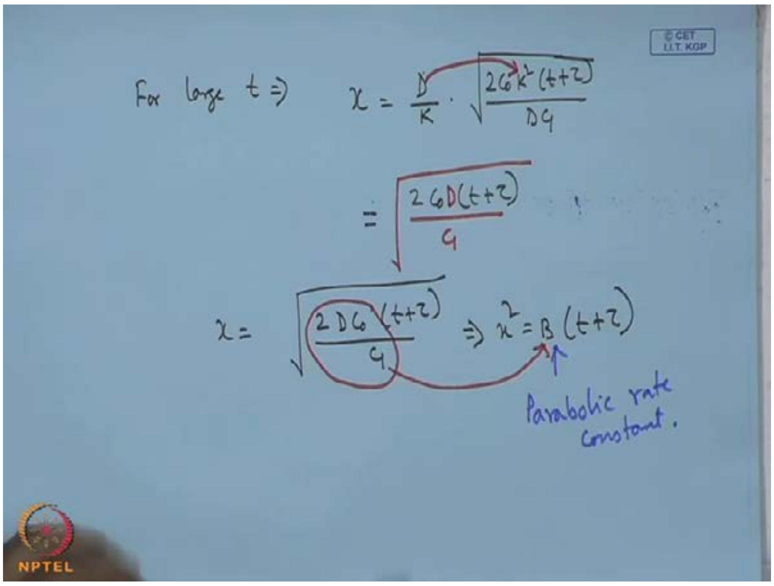
Experimental data agree with the prediction through this model.

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

It is a constant; this B by A is known as the linear rate constant, because this is A linear process, here you see that x propositional to time as the time grows thickness increases, and so since it is a line a expression. So, this B by A can be termed as the linear rate constant, next is that what happens when t is large? When t is large? We shall see that when t is large? it is very straight forward, for larger t we shall get the expression here is, this is the expression that we obtained this is the expression for x and when, when t is large basically it is the square root of this thing.

(Refer Slide Time: 54:18)



For large $t \Rightarrow \quad x = \dfrac{D}{K} \cdot \sqrt{\dfrac{2C_0K^2(t+\tau)}{DC_1}}$

$$= \sqrt{\frac{2C_0D(t+\tau)}{C_1}}$$

$$x = \sqrt{\frac{2DC_0(t+\tau)}{C_1}} \Rightarrow x^2 = B(t+\tau)$$

Parabolic rate constant.

So, we can write that for large t, we can write x equals to D by k root over of twice C 0 k square into t plus tau by D C 1, and which boils down to 2 C 0 t plus tau D is here. So, if we put D inside this root, so one D will be there, because of the denominator, there is one D by C 1 is there, so it will be root over of this. So, the final expression is x is equals to twice D C 0 t plus tau by C 1 root over of and that is equals to we can write x square is equals to B t plus tau. And you see that here, we have used this D twice D C 0 by C 1 as B, because earlier we have use this B as twice D C 0 by C 1.

So, this twice D C 0 by C 1 is nothing but B and so we can write that it is equals to B t plus tau. And we see that this is not a linear equation, it is basically a parabolic equation. And we shall discuss in the next class that what is the implication of this parabolic expression? When large t is there. And because this is a parabolic equation B is known as the parabolic rate constant, B is known as the parabolic rate constant.

So in the next class, we shall consider individually, what happens? If t is large or what happens when t is small or what is the bearing of this oxidation on the different crystal plane, why what is the effect of dry oxidation wet oxidation, how they are differ; those things, we shall discuss in the next class.

Thank you.