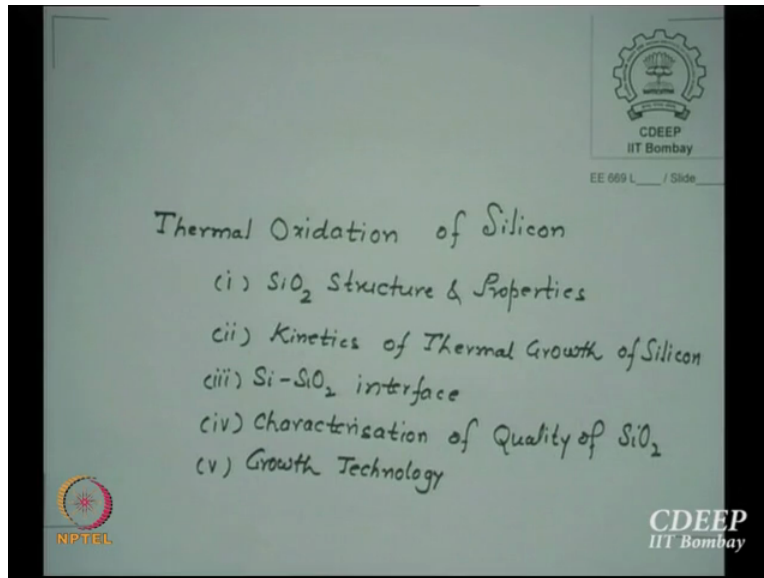


Fabrication of Silicon VLSI Circuits using the MOS technology
Professor. A N Chandorkar
Department of Electrical Engineering
Indian Institute of Technology Bombay
Lecture 11
Thermal Oxidation of Silicons

(Refer Slide Time: 0:19)



Okay, we start with the new topic today, thermal oxidation of silicon. SiO_2 is most important material in VLSI technology. And since it is very very important, we will like to study it little more carefully if not in that detail. So look into the structure of SiO_2 and their properties and its properties. We look into kinetics of thermal growth of silicon. This is necessary for modeling of the oxidation process. We will also look into Si- SiO_2 interface. This is very important for the electrical properties of a MOS transistor or a MOS capacitor or a FinFET or whatever it is.

And therefore we look into it, not so much detail from the face point of view but at least characterization and see what parameters we are looking into to interface circuiting models. Then we look into how some of those properties are characterized and we will finally look into how oxides are actually grown. So this is the some kind of content of these lectures or this area. I repeat this is nothing to remember, this just to say.

(Refer Slide Time: 1:35)

MOS Technology is used in creation of Silicon ICs, owe most of it's credit to Si-SiO₂ system. In fact more than calling ICs as Silicon ICs, we should really call ICs as SiO₂ ICs. SiO₂ is used in VLSI Technology as

- (i) Field Oxide (4000 Å to 1.4 μm)
- (ii) Masking Oxide (600 Å to 4000 Å)
- (iii) Gate Oxide (Gate Dielectric) [1nm to 1000 Å]
- (iv) Pad Oxide (100 to 400 Å)
- (v) chemical oxide ; During RCA cleaning

Logos: NPTEL, CDEEP IIT Bombay, EE 669 L / Slide

If you look at the history of MOS circuits, the technology of MOS is used in creation of silicon ICs, owe most of its credit to Si-SiO₂ system. In fact when we started calling silicon IC, we should have really called silicon dioxide ICs. If there would not have been silicon dioxide, pure silicon ICs would not have existed except for bipolars but certainly not MOS. Or even bipolar making would have been impossible. So of course, that is why we say SiO₂ is the most important material in VLSI.

We need to grow different kinds of oxides and different thicknesses for variety of steps in the interior circuit fab. First is field oxide which is typically can be as low as, maybe even these days it may be 2,000 Armstrongs as well. But typically 4,000 to 1.4 micron is the field oxide. Then we need to create a mask many time even for implant or even for impurities not to go through we need oxides should be kind of 600 Armstrong or 4,000 Armstrongs. And then we need gate oxidation if you are making MOS transistors and with no high k right now, then you forget dialectic.

We will require a good gate oxide and typically it may be 10 Armstrong to 1,000 Armstrong depending on the node of technology. For example, 1,000 Armstrong was useful for 1 micron technology, maybe even more whereas 1 nanometer and equivalent of that or less than that is recently going for 45 nanometer down. Then we also need to have a pad oxide and we will see what is one of the spacer technology in the case of FinFET, has some kind of padding.

Then we also see a chemical oxide which is naturally grown or by during RCA cleaning. And that also is, this may be very thin, maybe of the order of 10 Angstroms to 15 Angstroms. But these are all kinds of oxides are grown and required in the case of making an IC. These oxide thicknesses of course varies and therefore many of the process steps may vary for different oxide. For example, if you are doing a field oxide of very thickness 1 micron or so, the gate oxidation is very small, very thin. So the same technique cannot be used for field oxide because the time taken then will be very huge.

So we will change the technology as and when it needed and we will see how SiO₂ is grown in variety of methods. And here are few of the methods if you have noted down. The word field essentially means all along, we will see what exactly that around.

(Refer Slide Time: 4:31)

The slide is titled "Technologies used for creation of SiO₂". It lists two main categories:

1. Thermal Oxidation
 - (a) Dry Oxidation
 - (b) Wet Oxidation
2. Deposition techniques
 - (a) Chemical Vapour Deposition
 - (b) Physical Vapour Deposition
 - (c) Rapid Thermal Oxidation
 - (d) Sol.-gel Process
 - (e) Plasma Oxidation

Below the list, it states: "Thermal Oxidation is most basic oxidation technique and is most important step in creation of Gate-Oxide in a MOS Transistor."

The slide includes logos for NPTEL (National Programme on Technology Enhanced Learning) in the bottom left and CDEEP (Center for Design and Engineering Education) at IIT Bombay in the bottom right. A small gear logo with "CDEEP IIT Bombay" is also in the top right. The slide number "EE 669 L / Slide" is visible in the top right.

Technologies which are used for creation of SiO₂ are generally two kinds. There is one more which I forgot, maybe I will add, which is what current we are doing. This process was actually we worked in 1994-96 and was given out. Now suddenly with thin oxide requirement, this process has come after 25 years back in a big way. So when we grew in 1986-85, people were saying that who is going to use this oxide but now it is found that, that is very important process.

So thermal oxidation of two kinds we will use, dry oxidation and wet oxidation. Wet stand for H₂O, deposition techniques we will have CVDs, PVDs. PVD includes sputtering and also plasma oxidation is also partly physical vapor depositions. Rapid thermal oxidation and sol gel

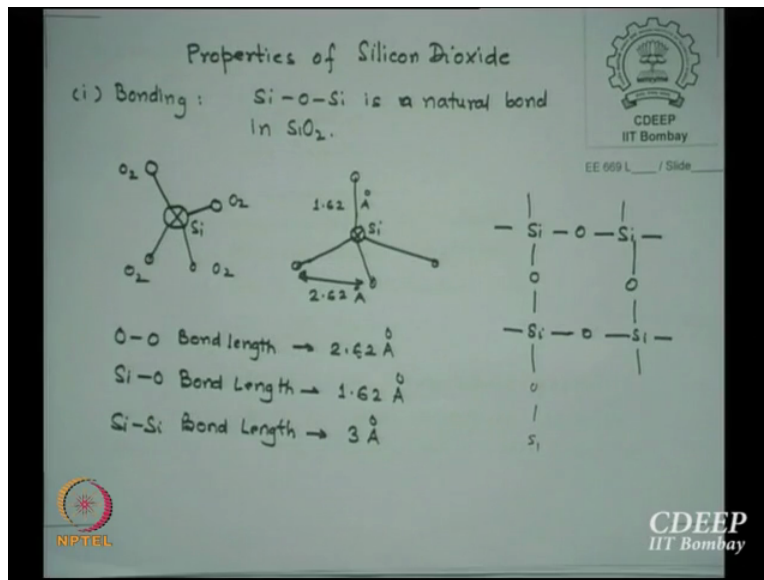
process, solution gel process which is mostly used by solar cell people. Thermal oxidation is most basic oxidation and is most important step in creation of gate oxide in a MOS transistor and therefore we will look into what is the growth techniques, what is the property, what are the properties of this gate oxide which is needed to have a good electric parameters for MOS transistors.

So I repeat there are mostly two techniques in which oxide can be grown, one is thermal oxidation which actually silicon converts into silicon dioxide by thermal process. Whereas in the other case substrate is immaterial, we can deposit on any substrate including silicon. So the deposition technique has advantage that it can be deposited on any surface. Whereas thermally grown oxide has to be out of silicon because that is what it is oxidizing. So the property obviously one can see that thermal oxides will have better properties compared to any deposited oxide.

So as I say we will look into variety of oxidation procedures. However we will model these two and I will not model here this CVD and PVD because there is a separate chapter or separate part of the course we will discuss about CVDs, PVDs or different materials. And during that time we will actually model CVD process and PVD process. PVD is essentially sputtering, evaporation and that kind. We will see in molecular beam epitaxy, all these are PVDs. So we will look into model for them in general and not necessary for oxide.

It can be nitride, it can be metals, it can be anything. So deposition can be any material on any material, other material. So we will see there. But we will certainly look into the models which are related to thermally grown oxides, typically by two processes, dry oxidation and wet oxidations. I said okay, this is what we are really looking for.

(Refer Slide Time: 7:47)



Before we start, let us look into basic properties of SiO_2 , why it became so popular actually. So let us look at this first thing we want to see a bond, bonding situation. The natural bond for SiO_2 is Si-O-Si. And typically the figure which is shown here if this is your silicon atom, it is surrounded by four oxygen atoms, slightly shown better way same figure. The distance, bond length as it is called, oxygen to oxygen bond has a length of 2.62 Armstrongs, silicon to oxygen has a bond length of 1.62 Armstrongs and silicon to any other next silicon is bond length around 3 Armstrongs.

If you see Si-O bond, the silicon lattice, oxide lattice may look Si-O-Si, Si-O-Si, Si-O-Si, and if you keep doing this, O-Si, and so on and so forth. So this is how silicon dioxide lattice is created, so one can see from here which is most important thing we will see, oxygen is not free, it is bonded on both sides by silicon atoms. And this is a very strong bond, this is very, of course it is not stronger than silicon to silicon which is the strongest but at least it is still quite a strong bond. So if I want to take oxygen, I will have to break this and I must apply energy to break this bond actually.

We will see this, this is most important in actually growth models. If you have seen these lengths are just for the sake of it, I mean just to give an idea what kind of lattice structures one has. If you have noted down, then we will start ahead. Why we are using SiO_2 in a MOS technology, please forget material in specific or otherwise.

(Refer Slide Time: 9:51)

SiO_2 is a Dielectric Material and is available in (i) Amorphous Phase (ii) Crystalline Phase \rightarrow Quartz

Thermally grown oxides are Amorphous in nature. Typical atomic structure of SiO_2 with some impurities or ions is as below:

Labels in diagram: Bridging OH, Network Modifier, Non Bridging, Network Former

Logos: CDEEP IIT Bombay, NPTEL, CDEEP IIT Bombay

EE 669 L / Slide

Because it is excellent dielectric material. And since it is a very good dielectric material, it is used in the field effect transistors because it does not allow DC current to flow through it. It is excellent dielectric material. It is available in two phases, amorphous phase and crystalline phase. Already I have told you, crystalline phase of SiO_2 is quartz whereas the oxide which we use in all VLSI technology is always in amorphous phase. As I just now said thermally grown oxides are amorphous in nature and typical atomic structure of SiO_2 with some impurities or ions are shown below. The lattice is random. This is say for example Si-O-O this but this oxygen or ion is also connected to another say silicon atom. Then it is called bridging bond.

Whereas this silicon atom and if I create another oxygen on this, this is free to it and it is called non-bridging. It does not have another silicon on the other side and it is called non-bridging. So to break a non-bridging bond is easier compared to a bridge bond because bridge bond means two silicon will hold it. And if one oxygen is free other side, that oxygen probably can be taken away. There can be possibility of some kind of impurities inside the lattice which is at interstitial sites. These are called network modifier and network formers and we will look into it.

There is also a possibility between silicon atoms or oxygen atom, there may be a formation of OH ions or OH bonding and this is very important in many cases, at least for wet oxides. The silicon is going to oxygen and there is no silicon ahead. So the oxygen is dangling right now, the

other bond. So it is free to get out very fast. It is not bonded other side, so non-bridged. Like this OH has nothing here, OH is also non-bridged. Anything connected other side it bridged.

So based on this lattice there are some observations we can make and of course as I say these are not the way book tried but I think I will give simplest observations out of all the structure. If you have drawn this, this is given in a book, Plummer's book and any other book. There is a book by (())(12:23), microelectronics technology or something, old book but has, new edition has come, I am told (())(12:29), I am not sure whether we have one. But many of the old technology models and everything are well given in (())(12:38) book.

(Refer Slide Time: 12:44)

Some observations:

(i) From the lattice structure of SiO_2 , we observe that- if Si has to leave SiO_2 lattice, it must break 4 Si-O bonds. While if Oxygen atom has to leave SiO_2 lattice, it needs to break only one bond.

(ii) SiO_2 with no impurities like diffusing impurities, or Sodium, Lead, Borium etc, is called Intrinsic Silica. While SiO_2 with impurities is called Extrinsic Silica.

The slide includes logos for CDEEP IIT Bombay (top right), NPTEL (bottom left), and CDEEP IIT Bombay (bottom right). The text 'EE 609 L / Slide' is visible in the top right corner of the slide content.

From the some observations about the lattice, from the lattice structure of SiO_2 we observed that if silicon has to leave SiO_2 lattice, it must break, force oxygen bonds, Si-O bonds. It is bonded on the four sides, so it must leave all four of them. While if oxygen atom has to leave, it needs only one bond if it is non-bridging, two bonds if it is bridging. SiO_2 with no impurities like diffusing impurities or sodium, lead or borium is called intrinsic silica. If there are no impurities in oxide, then it is called intrinsic silica or intrinsic SiO_2 .

While if there are impurities, then we call it is extrinsic silica. So these are few these, there are few more if you note down, I repeat the Si-O, when silicon leaves the SiO_2 bond, it needs, it is very difficult because it needs four bonds to be broken whereas oxygen is only two. Or non-

bridging, it is only one, so it just goes away. This property has been used during oxidation, that this oxygen is available, I can break it. Is it okay?

Our ultimate aim today is to actually go through the model but let us see how fast we go so that I can ask tomorrow some question on models. I keep telling you our interest in the course is manifold. One is to understand the material property so that at least one out of 100 are people here. Let us say giant technology and also thinks 20 years ahead what he can do to become entrepreneur of his own technology fab house in India somewhere.

(Refer Slide Time: 14:45)

iii) Boron, Phosphorus & Arsenic (etc.) replace Silicon and hence create bond between Oxygen & them. Such Impurities are called Network former.

However if Impurities sit in Interstitial Sites, then they modify the Network of SiO_2 , and hence called Network Modifier. Na_2O , Pb_2O_3 , Ba_2O_3 are such Modifier

(iv) If SiO_2 is put into water, we can have reaction as

$$\text{Si-O-Si} + \begin{array}{c} \text{H} \\ | \\ \text{OH} \end{array} \rightarrow \begin{array}{c} \text{SiOH} \\ | \\ \text{SiOH} \end{array}$$

It is also to be noted that SiO_2 is strong Hydrophilic in nature.

EE 669 L / Slide

CDEEP IIT Bombay

NPTEL

CDEEP IIT Bombay

The boron, phosphorus or arsenic or such impurities in silicon and hence create bond between oxygen and them. Such impurities are called network formers because oxygen will also get bonded to them. However if impurities sit in the interstitial side and then they modify the, see example, these impurities can sit on a silicon. So instead of silicon your impurity in four oxygen bonds, similar, I mean similar as Si-O bond it will be impurity O-Si bond.

Whereas if the impurities sitting in interstitial side, it still will form a bond with oxygen and they will modify the structure of network. Such materials which do that is called, is because of Na_2O , barium oxide, then there is a lead oxide, Pb_2O_3 . Then comes another phase of Pb which is PbO . There is thin oxide which I forgot, these are called network formers or modifiers. Whereas the impurities when they replace silicon, these are called network formers. Please remember these impurities are only present in some traces, one part per billion or lower but it is not they are 0.

Because due to the processing we pass gases, we heated materials around, so some impurities will be always there. How small we make them is most important.

If we have SiO_2 is put into water, it is very interesting thing that this Si-O-Si bond reacts with H-OH which is water to form SiOH-SiOH bond. This is very important, silicon hydroxyl bonds. This is silicon hydroxyl, two such molecules actually get bonded and this is the most important thing why wet oxides can be grown. One more interesting feature of SiO_2 is that it is a strong hydrophilic, water attracts to the surface of SiO_2 and bonds and actually create these hydroxyl bonds. So one test that we have a silicon surface or oxide surface is just dip it into water. If water sticks, that means there is SiO_2 layer. If water does not stick, it is a silicon layer.

So these some properties of these and we also know when Na_2O kind of structure gets into silicon dioxide lattice, we call soda glass. These are very bad kind of glasses, very impure, large amount of potassium, sodium, first group elements actually forms oxides there. And they are not very good as far as the properties of MOS structures are concerned. So we must avoid sodium, potassium, barium in the lab as much as possible, preferably 0 but nothing is 0, so something lower than 0.

That is why I say the other one we of course said that if there is an impurity oxides along with the silicon dioxide, these are called silicate glasses. If you have boron, then it is boro-silicate glass. If it is phosphorus, it is called phosphosilicate glass. If it is arsenic, then it is arsenosilicate glass. So these glasses are good, sometimes they are used as impurity sources because they have the impurity in them. But the mixture is called glasses, silicate glasses. Pyrex is essentially borosilicate glass, Borosil is the company in India which manufacture Pyrex.

(Refer Slide Time: 18:28)

(v) Physical Properties of SiO_2

1. $\rho \approx 10^{-16}$ mhos/cm
2. Bandgap $E_g \approx 9$ eV
3. Refractive Index $n = 1.45$
4. Density = 2.22
5. No. of atoms/cc = 2.3×10^{22} /cc
6. Dielectric Constant $K_{\text{SiO}_2} = 3.9$
7. Dielectric Strength = 10^7 V/cm.

(vi) SiO_2 has strong utility in IC processing as

- (a) Easy to Etch $\text{SiO}_2 + 4\text{HF} \rightarrow 4\text{SiF}_4 + 2\text{H}_2\text{O}$
- (b) Excellent Insulator with High Dielectric Strength

Logos: NPTEL, CDEEP IIT Bombay, EE 669 L / Slide

Okay, there are certain properties of SiO_2 which are very relevant for our, at least some electrical properties are relevant for us, even these days optical properties. Because silicon has been used in optic devices, not necessarily for electrical behavior, for optical greetings. Many of the communication people are now looking for optical communication and greetings are one of the most important element in optical communication. So you need to know greetings index, so how do you change the index?

So okay, typical resistivity of SiO_2 is very high, 10 to power 16 ohm centimeter or conductivity should be less than 10 to power minus 16 mhos per centimeter. The band gap of SiO_2 , actually this is slightly misnomer. Why I say misnomer? The band gaps are only available for crystalline materials because there is a periodicity. There is no periodicity in amorphous materials. So there is, this is only a matter of conjecture that there is a band gap in a small crystallite and that band gap is typically of the order of 9 electron volts.

What (essentia), what is the silicon band gap? 1.1 electron volt, so it is much easier even at room temperature to create hole electron pairs because the band gap energy is very small. Germanium, it is 0.6 , so even more easy. So the intrinsic carrier concentration of germanium is higher than silicon because its band gap is lower. If the band gap of 9 electron volt, so at room temperature it will be almost impossible for hole electron pair to form and therefore no conduction and therefore large resistivity.

Typically flat index for SiO₂ is 1.45, density is 2.22. The number of, you should write grams per cc. Normally this definition was slightly, I did not write specific because there is something in the case of molecular densities. There is (20:28) number appears. So think of it why I did not write the full density units. The number of atoms per cc is 2.3×10^{22} per cc. Dielectric constant of silicon dioxide is 3.9. This is one of the major parameter in decision of the MOS transistor performance, epsilon. And we know we are trying to go for higher epsilon oxides, high k materials because of some reasons, we will see them later.

Another problem which most of the oxide particularly gate oxide, you are applying a VGS across the gate and thickness is very thin because you are scaling down, so the voltage is not scaling down. So voltage divided by the thickness of oxide is the field across the oxide which is increasing as the technology node is reducing. Now this field which you are getting should be less than 10^7 because at 10^7 all bonds can be broken and we say dielectric ionization will start. So anything voltage you can apply is as much as that the field at least order or half of 10^6 , 5×10^6 , or 4×10^6 , should be the best of hole per centimeter should be the applied fields.

So safety, you do not, actually most of the oxide even do not reach 10^7 . Most oxide in our lab you may strengths of 4×10^6 , 5×10^6 . So safe oxide fields are only 10^6 volt per centimeter. So your thickness if you decide, then your voltage is essentially decide that it should reduce the field below 10^6 . This is compulsory requirement. That is otherwise in a circuit I may go verily 5 volt for 10 Armstrong circuit also, what is the bad thing in that. I will push it but by then oxide will puncture.

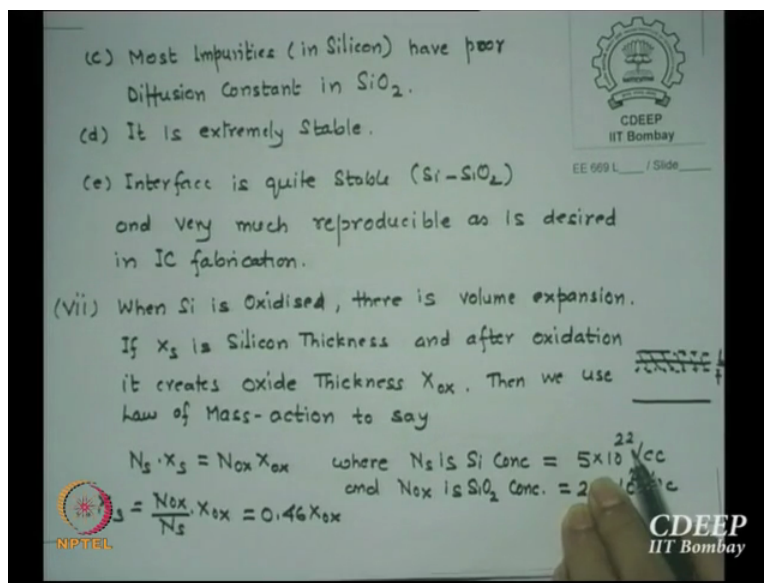
So this is important property which SiO₂ has. Not most materials have this high strengths, even hafnium oxide is lower than this. So the major problem with many other high k is dielectric strength is as, is not as good as SiO₂ and therefore SiO₂ is sticking for last 50 years, they do. Of course now we have to change for some reasons, we will see later. SiO₂ has strong utility of IC processing. Why we want to use SiO₂? Firstly of course its electrical properties are great and everything is fine. But it is much easier to create as well as to etch.

Silicon dioxide etches into, for example, SiO₂ plus let us say HF, so I want 4, it can give me 4 SiF₄ which is plus H₂O. SiF₄, Silicon fluoride is soluble in water, so if I put my silicon dioxide

wafer into HF, then it will get removed all of the HF, in the HFs forming silicon fluorides and water, inside the water. So it is very easy to etch and therefore, of course fluorine has its own advantages and disadvantages, some other day.

So please remember that SiO₂ has, is much easier to grow, much easier to etch, much easier to control in every sense, best dielectric strengths, very good easy, very good insulator and refractive index is also very good for many optical circuits. So all and all glass is very good and glass of something is even better.

(Refer Slide Time: 24:28)



The other properties which you see in the case of, most impurities in silicon have poor diffusion coefficient in SiO₂. Like silicon arsenic, antimony, phosphorus, all these impurities are, boron, everything has a very poor diffusivity in SiO₂ compared to silicon. So they act like a mask, no impurity can easily pass through oxide compared to what it will go into silicon. Another important feature of SiO₂ is extremely stable. What do you mean by stable? Its structure does not change easily and it remains for all full processing, SiO₂ properties do not change.

So essentially it is stable with temperature, with everything it is very-very stable material and therefore extremely useful in all IC because ICs have to last tens of years or at least these 3 to 4 years. So why the light is not now ten years which earlier we used to say? Companies will collapse if things work out for 10 years, what will they do then now? So they finish 3 years, it must go. Another advantage of silicon is, silicon dioxide is the interface between Si and SiO₂ is

ideal if not, it is very good if not ideal and it is extremely reproducible many number of times in any IC processing. Any number of times you go, you can have control on this interface.

That is why it is very good. When silicon is oxidized, there is a volume expansion and this is very important. When silicon is oxidized, there is a volume expansion total. Here is shown here. The dark one is silicon which you have and I started putting oxygen ambient and oxidizes. So what it does is it consumes certain amount of silicon to convert into SiO₂ but the volume of that is larger than the silicon volume which you consume. This is essentially because of the law of mass action. Ns axis must be equal to Nox Xox and since the Nx, Nox have the ratio on silicon SiO₂ concentration is given this, typical ratio of this number of atoms per cc is 5 and 2.3 ratio, is actually appearing in the ratio of silicon to oxide ratio.

And so one can see 0.46 of silicon, 0.46 of micron of silicon will grow how much oxide? 1 micron of oxide, is that clear to you? 0.46 Armstrongs, microns of silicon will consume to create 1. So oxide will grow above, 0.46 will go inside and 0.54 will go above and this is the figure which shows this. 0.46 inside and so volume expansion and essentially because of the density ratio or because of the concentration ratio essentially. So that is important.

If someone says I have only this much surface of silicon, so please remember when you oxidize it, its volume will increase, at least 50 percent above and 50 percent below. And accordingly oxide will be available. So you can see from here there is an oxide layer. Say let us say I do selective maybe and that is very important. If you have noted down, I will just show you a figure which is called local oxidation. So silicon thickness is roughly 0.46 or for simplicity you may say 50-50, 50 percent Si will convert it to 1, 100 percent SiO₂.

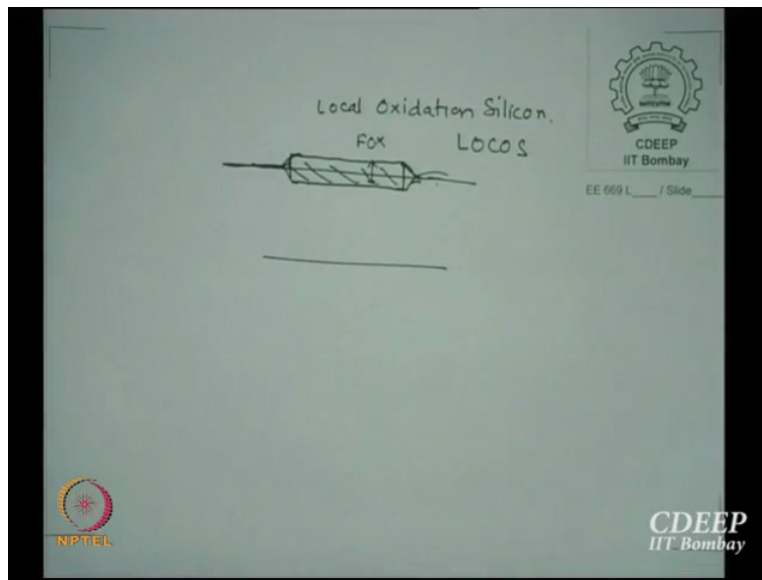
“Professor-student conversation starts.”

Student: What value of band thickness?

Professor: What value of, no, the ratio is 0.46. If it is 1 micron of this, then it is 0.46 micron. The ratio is 0.46. So if I want an oxide thickness of 1 micron, you must bear this that 0.46 micron of silicon must be made available to grow that much silicon dioxide. That is what I say, I will just show you a figure.

“Professor-student conversation ends.”

(Refer Slide Time: 28:42)



If this is my silicon surface and I restrictively do oxidation only here, so what will happen? I will get oxide something like this. The rest places, the surface is here but the selective oxidation process, part of the oxide is above and in fact there will be some, something called taper down. So now you can see this is how the oxides are actually protecting the rest of area. This much is near field oxide as we shall see this process, this selective this is called local, we will do process later, oxidation of silicon and is called locos.

So in actual IC making, wherever you do not want impurities to go, the field oxide is generally grown by process of low cost. Only those areas oxidize but the silicon surface is retained wherever your actual device is going to come. Is that correct? So that is very important that oxide thickness is roughly double that of silicon thickness consumed. So this roughly tells about the properties and some comments on SiO_2 , some observations.

Now we start today our basic modeling issue. We have discussed earlier the properties we will look into, so we looked into properties. We now start looking into the models or how oxide is actually grown. Is it okay everyone? The process of growth is essentially thermally related in thermal oxidation and the process is essentially whenever it is related to thermodynamics we say it is kinetics. There is some specie moving and reacting, reaction. Any reaction is, has a kinetic model. So we will look into kinetics or thermal oxidation of silicon.

(Refer Slide Time: 31:04)

"Kinetics of Thermal Oxidation of Silicon"

Silicon dioxide (SiO_2) is generally grown by Oxidation of Silicon at high temperatures (800°C to 1200°C) in Oxygen rich ambient. It could be pure O_2 or H_2O . Oxygen reacts with Silicon to form SiO_2 .

$$\text{Si} + \text{O}_2 \xrightarrow{\text{High T}} \text{SiO}_2 \Rightarrow \text{Dry Oxidation}$$

SiO_2 formation by oxidation of Silicon in Water Vapour may have a bit complicated reaction. Overall however it may be like:

$$\text{Si} + 2 \text{H}_2\text{O} \xrightarrow{\text{High T}} \text{SiO}_2 + 2 \text{H}_2 \Rightarrow \text{Wet Oxidation}$$

Logos: NPTEL, CDEEP IIT Bombay, EE 669 L / Slide

As I say silicon dioxide is generally grown by oxidation of silicon at high temperatures. Typical temperatures could be 800 degree to 1200 degree. Obviously one can think very simply that lower the temperature, thickness will be smaller. Larger the temperature, oxidation will continue at higher temperatures, will have higher oxidations rates. And generally done in oxygen ambient, typically ambient choose are either oxygen, pure oxygen or pure water. Of course there is a mixture of water and oxygen which is called partial pressures of oxygen, NH_2O or steam partial pressure in this ambient. These are called pyrogenic system, we will discuss this later.

So the wet oxide when I say next time, the wet oxidation is essentially not a steam oxidation, is that part clear? When the steam will come out, when the water is heated at what temperature steam comes? 100 degree. Wet oxides are not steam oxides, so we do 95 degree heating, so only water vapors come which are bubbling, I mean you see the bubbler system and they are used in this. But there is no full steam, so there is some oxygen content in the steam part and that is why it is called wet oxidation. It is not called steam oxidation.

The typical reactions which are very simple, Si plus O_2 at high temperatures of 800 to 1200 converts into SiO_2 and if the only oxygen is the ambient, then it is called dry oxidation. This is the most common oxide thickness, oxide growing procedure when you want thin oxides, dry oxidations. SiO_2 is also formed by oxidation of silicon in water vapors, actually it is process is called complicated. Maybe I will show quickly something. However overall when we say Si plus

2H₂O, is SiO₂ plus 2H₂, this is overall reaction, this is called wet oxidation. Those who have little more interest in models of chemistry or chemical engineering, or material science, here is what can happen.

“Professor-student conversation starts.”

Student: (0)(33:32)

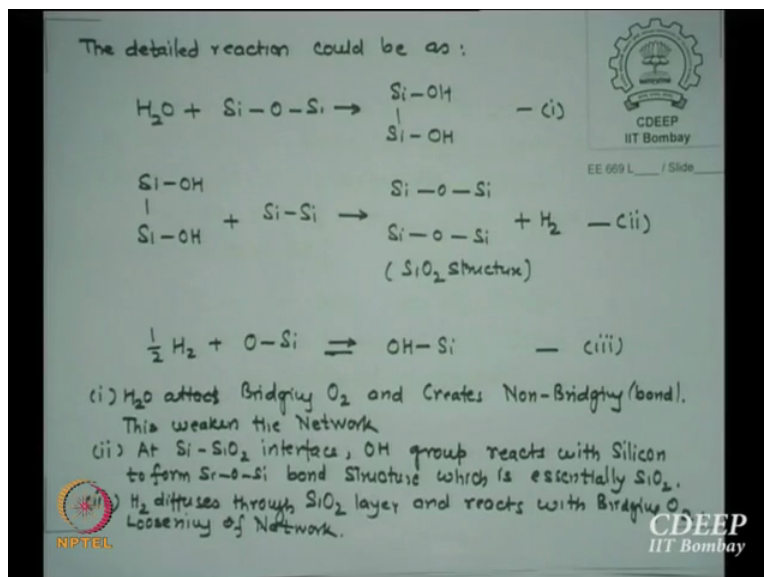
Professor: High temperatures. 800 to 1200 is high temperature, room temperature is 27 degree. Oxides cannot be grown below 800 is not correct statement. Any temperature it will grow but the required thicknesses cannot be attained at lower than 800.

Student: I think you are saying that at 95.

Professor: Water vapor, oxidation is performed on the silicon which is heated to 800 to 1200, we will see the technology. Water vapors are coming and reacting with the silicon vapors which are held at 800 to 1200 degree centigrade. That is why it is high temperature. Water vapor is at 95.

“Professor-student conversation ends.”

(Refer Slide Time: 34:33)



Here is something what chemistry can do. An H₂O can react with Si-O-Si bond and form SiOH-SiOH hydroxyl bonds. These hydroxyl bonds can react with silicon-silicon bond and may form Si-O-Si, Si-O-Si plus what is hydrogen. This hydrogen may react with unfinished, unbridged

bonds or non-bridged bonds, O-Si and may convert into OH-Si. And this OH-Si is essentially going back, Si-OH and again it will react with silicon to form SiO₂. So this is a ring system and it keeps doing itself to get Si-O-Si bonds.

So if you really see a chemistry at a given temperatures, some may dominate, some may not, so some thickness may not be correct. So those who are really looking for very thin oxide models, these equations may be of relevance. Water attacks O₂ bond and creates non-bridging bond. This weakens the network, first part. Si-SiO₂ interface, OH group react with silicon to form Si-O bond which is the structure for SiO₂. And hydrogen also actually diffuses through SiO₂ layer and react with bridging oxygen and loses the network as it shows.

The basic idea how much oxidant can go inside is there must be some structure in which oxygen can flow ahead. This is how network can loosen and can allow oxidant to move in. That is what the chemistry is about. Anyway if you forget, it is fine but if you, those who are very keen should know that there is lot of chemistry goals, lot of thermodynamics associated. For example, say rest of the time I did not show but in this case this is both side reaction and I must maintain certain temperatures to actually have a forward reaction on, when was backward reactions.

Particularly in CVD we will come back and look into forward and reverse reactions very seriously because what is reverse? Etching. Forward, depositions. So if you are depositing, it may etch. If you are etching, it may deposit. So we will have to see when I deposit, I deposit. When I etch, it does not deposit. So that time we will come back and do lot of thermodynamics to see when the reaction is favored on one side or the other.

Way back in 1965 two scientists from Intel actually first time suggested the kinetic model for oxidation, thermal oxidation and these names are very famous in MOS technology, this is called Bruce Deal and Andy Grove. Deal is still around, so is Andy. Deal is still working on SiO₂ after 60 years, great man, 50 plus years and of course who was the chief of Intel few years ago. And he is not well these days but still on the board of Intel. He is the founder member of Intel. Is that okay?

(Refer Slide Time: 38:06)

Bruce Deal and Andy Grove were first to model the process of Thermal Oxidation. (Ref: J. Appl. Phys., vol. 36, p 2770, 1965) Hence the Model is called 'Deal-Grove' Model.

This model provides kinetics of growth of SiO_2 (X_{ox}) as a function of temperature and time.

Model Assumptions

- Initially there is a finite (Thin) oxide layer, before oxidation ($t=0^-$) starts
- The Oxidant Gas specie impinges on this SiO_2 layer and diffuses through the Oxide-layer and reaches Si-SiO_2 interface.

NPTEL CDEEP IIT Bombay EE 669 L / Slide

In 1965 they suggested the model and till very late as maybe around 1995 to 2000, this Grove-Deal model or Deal-Grove model remained as the only model available. When the oxide thickness started reducing further and further, modifications to Grove-Deal models started coming in but these are the words modification. That means the basic tenets of Deal-Grove model remained even now sufficiently valid though there are ways of saying that they are not correct in every case.

What actually Deal-Grove model is suggesting or what are the assumptions it starts with? It actually why we are looking into? I want to grow SiO_2 of thickness X_o or X_{ox} and I want to see how it is related to temperature and time. I have silicon wafers pushed into a furnace of high temperature. I pass oxygen ambient and I expect thickness of my choice by deciding the temperature and time. Now this model should do that, it should be able to be, X_o must be proportional to temperature and time.

If it shows that, that means I can decide how much oxide thickness I will get at a given temperature after how much time of oxidation. Or given a time oxidation fits, if I change the temperature I can change the thickness. This is what my aim, and therefore I will like to see what the model is so that I will be able to derive that part or other day when I was showing you some graphs, I have oxide thickness versus time at different temperatures, 111, 100 wafers. Those graphs have been derived out of this model. So for our quick calculations we can use those

graphs directly, time versus thickness at different temperature at different concentrations of wafers. One can immediately read out how much oxide thickness.

So the model assumes there is a finite layer of thin oxide layer present at on the silicon at t is equal to 0 minus. Before, that means before the oxidation start, already there is very thin layer of oxide exist. Now this is an issue which is challengeable at times. So if someone actually etches the silicon pure and push it, we mean to say oxide will not start, oxidation it does. But the model expects that there is a finite thickness of oxide at t is equal to 0 minus. And 0 plus means oxidation starts just before there is a thin oxide, very very thin oxide. Next it says that the oxidant gas specie impinges on this SiO_2 layer and not silicon oxide. So here is before I write this, do not write, I will just show you figure and then we will, you may write.

(Refer Slide Time: 40:57)

© The Oxidant specie then reacts with Silicon atoms at the Interface and creates newer oxide layer.

This process continues and Sidioxide layer keeps growing to a thickness by end of time of Oxidation. This process is depicted in the Fig. below

Gas SiO_2 Silicon

There are Three Fluxes in Gas, SiO_2 and Silicon regions.
 Let F_1 be oxidant flux in Gasphase
 F_2 be oxidant flux in SiO_2
 F_3 be oxidant flux for reaction at Silicon.

The diagram shows a vertical cross-section of the oxidation process. It is divided into three regions: Gas, SiO_2 , and Silicon. Concentration profiles are shown as lines: C_a in the gas, C_s at the gas-oxide interface, C_i at the oxide-silicon interface, and C_o in the silicon. Fluxes F_1 , F_2 , and F_3 are indicated by arrows pointing right. A distance x_{ox} is marked at the bottom.

This is the physics, physical model or picture of that. This is the gas ambient, this is that thin oxide and this is silicon. So gas oxidant come here and actually impinges on this SiO_2 layer surface. Now we are saying how much it will reach here, then how much it will reach to the silicon interface to, please remember oxide can be grown only when there is a reaction with silicon. So how much oxidant from the gas will actually reach to the interface to oxidize further silicon, that is the model we are looking for.

You start with huge amount of gases. There is a silicon wafer, thin oxide, partly it does not allow all of it to go or how much it goes and reacts with silicon to form new SiO_2 . Is that clear? If

SiO₂ is grown further, the flux which is going through may be further reduced because now oxide thickness will be increasing. So we will see what is the model of growth of X_o. This is the figure. Please note down this figure, then I will come to those ABCs again so that you know what I am talking about.

If you have drawn the figure, few names I have suggested here. This is CG, G. This at the surface is C S or s. There is, just below that there is a C star, just below that there is a C₀. At the silicon-silicon dioxide concentration is C_i which has a gradient and there are three fluxes associated. One in the gas phase, other in the oxide and third entering the silicon, three fluxes. Flux means amount of oxidant per unit area per unit time, flux.

So there are three fluxes. F₁ is the oxidant flux in a gas phase, F₂ in the SiO₂ phase, F₃ is what is reaching at the silicon. Now this figure is the model figure for Bruce Deal and Andy Grove's model which is most important model in thermal oxidations. This the text part, I will now explain once you have drawn the figure and maybe if you wish these fluxes I have written. The ABC I will repeat again. This figure I will redraw again but since, if you have drawn now, it will be, you do not have to redraw it again. So is that model clear what we are saying?

There is a thin oxide present. From the gas stream some oxidant arrive at the surface of SiO₂, then it goes through oxide with some flux, reaches silicon and oxidizes. This is the model. Have you drawn the figure?

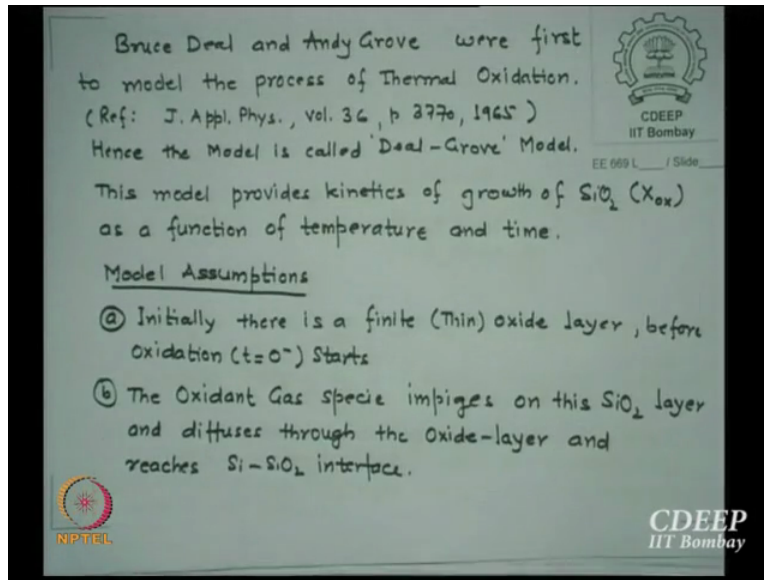
(Refer Slide Time: 43:57)

Bruce Deal and Andy Grove were first to model the process of Thermal Oxidation. (Ref: J. Appl. Phys., vol. 36, p 2770, 1965) Hence the Model is called 'Deal-Grove' Model.

This model provides kinetics of growth of SiO_2 (X_{ox}) as a function of temperature and time.

Model Assumptions

- Initially there is a finite (Thin) oxide layer, before oxidation ($t=0^-$) starts
- The Oxidant Gas specie impinges on this SiO_2 layer and diffuses through the Oxide-layer and reaches Si- SiO_2 interface.

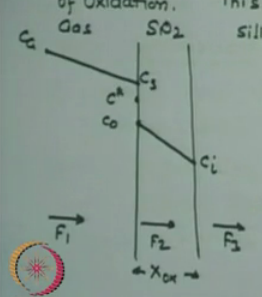


So I come back to this. So as I just now said, initially there is a finite thickness, yes, initially there is a finite thickness. Oxidant gas specie impinges on SiO_2 layer.

(Refer Slide Time: 44:11)

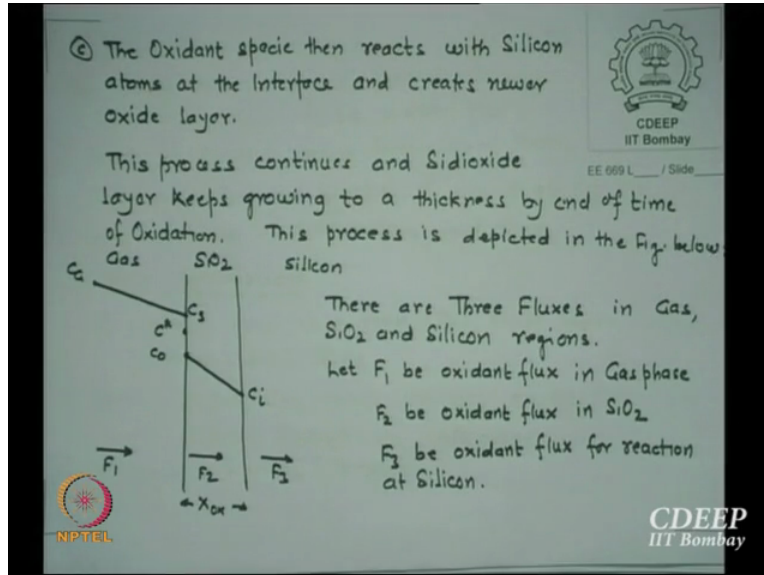
③ The Oxidant specie then reacts with Silicon atoms at the Interface and creates newer oxide layer.

This process continues and SiO_2 layer keeps growing to a thickness by end of time of Oxidation. This process is depicted in the Fig. below



There are Three Fluxes in Gas, SiO_2 and Silicon regions.

Let F_1 be oxidant flux in Gasphase
 F_2 be oxidant flux in SiO_2
 F_3 be oxidant flux for reaction at Silicon.



And now the oxidant specie then reacts with silicon as much as it goes through the oxide and creates new oxide layer. This is the model we have suggested, not we, Deal and Grove. This process continues as long as your oxidant is available and oxides keep growing. Assumption is temperature is held constant. At a given temperature the gas ways are also constant but gas is

flowing all the time. And as long as that flows, silicon dioxide will keep increasing its thickness. This is the model.

Now we must see that therefore one thing we are clear that as the time increases, oxide thickness will grow. So one requirement I said, I want to know what is the oxide thickness at end of my oxidation cycle. Further I have temperature this, right now I kept one temperature. If I change the temperature, I will see how much additionally oxide may grow. Is that okay?

(Refer Slide Time: 45:20)

The slide contains the following text:

- Ⓐ Transport of Oxidant from the Furnace ambient to the Oxide surface takes place with Flux F_1 .
- Ⓑ Oxidant specie Diffuses through SiO_2 layer with a Flux F_2 .
- Ⓒ Oxidant reacts with Silicon with Flux F_3 .

However in Steady State we can say that-

$$F_1 = F_2 = F_3 = F$$

The diagram shows a furnace with a rack of wafers inside. An arrow labeled O_2 points into the furnace from the left. The temperature is indicated as $800^{\circ} \text{ to } 1200^{\circ} \text{C}$. Logos for NPTEL, CDEEP, and IIT Bombay are present.

So there are three fluxes which we talked about. Three processes, so what are three requirement for oxidation is transport of oxidant from the furnace. Please remember the way, we will discuss the technology later but maybe I will show you the furnace. And this is the rack, everything is in quartz. These are my wafers sitting on a rack. This temperature could be adjusted to 800 to 1200 degree. Sometimes 1250 we could have done, nothing very serious.

An oxygen is entering. So this is the gas ambient. At least between this, so this is called the mid zone. So mid zone temperature, the gas is heated to this mid zone temperature but the gas is everywhere. This is the concentration flux which is entering. From here is everywhere. Then it actually reaches to the surface of silicon, it impinges on silicon. This flux which actually impinges on silicon surface or silicon dioxide surface because we assume there is oxide, is essentially flux F_1 .

(Refer Slide Time: 46:47)

(A) Transport of oxidant from the furnace ambient to the oxide surface takes place with flux F_1 .
 (B) Oxidant species diffuses through SiO_2 layer with a flux F_2 .
 (C) Oxidant reacts with silicon with flux F_3 .

However in steady state
 $F_1 = F_2 = F_3 =$

Here:
 C_a - Oxidant conc. in Bulk-Gas
 C_s - Oxidant conc. at Oxide Interface in Gas-Phase.
 C_i - Equilibrium oxidant conc. in Solid - related to C_a
 C_o - Equilibrium Oxidant conc. - related to C_s
 C_i - Oxidant conc. at SiO_2/Si interface

F_1 in Gas ambient is essentially governed by Mass-Transfer, which can be expressed as
 $F_1 \propto (C_a - C_s)$ or $F_1 = h_a(C_a - C_s)$
 where h_a is called Mass Transfer Coefficient.

NPTEL CDEEP IIT Bombay

The oxidant species then before we, this word, it has already impinged here. Then it gets inside SiO_2 by the process of diffusion because there is no oxidant here. There is oxidant here, there is a gradient creation. So oxidant species diffuses in the SiO_2 to reach silicon-silicon dioxide interface.

(Refer Slide Time: 47:09)

(A) Transport of Oxidant from the Furnace ambient to the Oxide surface takes place with Flux F_1 .
 (B) Oxidant species Diffuses through SiO_2 layer with a flux F_2 .
 (C) Oxidant reacts with Silicon with flux F_3 .

However in Steady State
 $F_1 = F_2 = F_3 =$

NPTEL CDEEP IIT Bombay

So the second flux is diffuses through SiO_2 with a flux F_2 .

(Refer Slide Time: 47:17)

(A) Transport of oxidant from the ambient place

(B) Oxidant diffuses through SiO_2 layer

(C) Oxidant reacts with silicon

Here:

- C_a - Oxidant conc. in Bulk-Gas.
- C_s - Oxidant Conc. at Oxide Interface in Gas-Phase.
- C^* - Equilibrium oxidant conc. in Solid - related to C_a
- C_o - Equilibrium Oxidant conc - related to C_s
- C_i - Oxidant Conc. at SiO_2 -Si interface

ambient is essentially governed by Mass-Transfer, which can be expressed as $F_1 = h_c(C_a - C_s)$ or $F_1 = h_c(C_a - C_i)$

called Mass Transfer Coefficient

And the third before I come back again, it reaches silicon surface or silicon-silicon interface and reacts with silicon to form new oxide.

(Refer Slide Time: 47:22)

(A) Transport of Oxidant from the Furnace ambient to the Oxide surface takes place with Flux F_1 .

(B) Oxidant specie Diffuses through SiO_2 layer with a Flux F_2 .

(C) Oxidant reacts with Silicon with Flux F_3 .

However in Steady State we can say that-

$$F_1 = F_2 = F_3 = F$$

200 to 1200°C

So oxidant reacts with silicon with flux F_3 . However in, there are two things we say in devices as well as in any process for that matter, thermodynamic process. There are two terms which we use, thermal equilibrium and steady state. What does that say? In the case of thermal equilibrium as there is no external force applied. The system is only by thermodynamically adjusting its energy to the minimum. This is the entropy, this relationship.

So first law of thermodynamics says that it should remain valid for any temperature you fix. It is equilibrium with the ambient. However what we are saying now is we are passing gases, so there is a force going on. So it is not equilibrium, thermal equilibrium situation. However the gas is constant. If the gas is constant, some oxidant is getting in, some is impinging, some is reacting, so system is time invariant. That is called steady state. So we are looking of a case when it is steady state.

“Professor-student conversation starts.”

Professor: Yes.

Student: There is no oxygen atoms that form SiO₂, from the SiO₂ interface that....

Professor: No, it does not because there is no Si-O-Si bond. Oxygen, it will actually break it. So it does not help us actually.

Student: As we provide the temperature around 800 degree centigrade.....

Professor: But Si-O-Si bond does not break at 800 degree. As I say it is one of the strongest bond. Si-Si bond is even stronger, Si-Si breaks it at 1412. That is even higher temperature but 800, that is why 1200 I said. I did not say 1400. Is that okay? So it does not happen. So that is why we say it impinges, diffuses and reacts. And even if, I mean of course it is not true but even if I take a word, this is not Deal-Grove model. This is what Deal is suggesting. Firstly it is not true but even if it is true, you may say modify whatever is good name, you could say modify Deal-Grove model by so and so, publish it.

“Professor-student conversation ends.”

(Refer Slide Time: 49:52)

(A) Transport of Oxidant from the Furnace ambient to the Oxide surface takes place with Flux F_1 .

(B) Oxidant specie Diffuses through SiO_2 layer with a Flux F_2 .

(C) Oxidant reacts with Silicon with Flux F_3 .

However in Steady State we can say that

$$F_1 = F_2 = F_3 = F$$

Diagram: A furnace tube containing a silicon wafer. An arrow labeled O_2 points into the tube. The temperature is indicated as $900 \text{ to } 1200^\circ\text{C}$.

Logos: CDEEP IIT Bombay (top right), NPTEL (bottom left), CDEEP IIT Bombay (bottom right).

Aajkal sab yahi kar rahe na? x plus dx , ek paper. $2dx$, dusara paper. So F_1 , see Grove-Deal, Deal-Grove model was suggested in 1965, pachas saal ho gaye hai, hila nahi abhitak. Is not it? Ek paper hi sufficient hai na? So that is what I think, world has I think now thinking 2 lakh papers have the best scientist, contribution 0. So F_1 is equal, so what is in steady state we say? All three fluxes must be, so let us stop now because there is nothing we can do.