Fundamentals of Micro and Nanofabrication
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Lecture - 12
Native Films

Today we are going to talk about another additive processing step: Native Oxide. Native oxide is basically referring to the fact that these films are directly grown from the wafer itself. The chemistry involves the wafer which is one of the precursors of the reaction. Silicon dioxide is I guess, the most important insulator in semiconductor fabrication. It is used for several things; the most important is the gate oxide.

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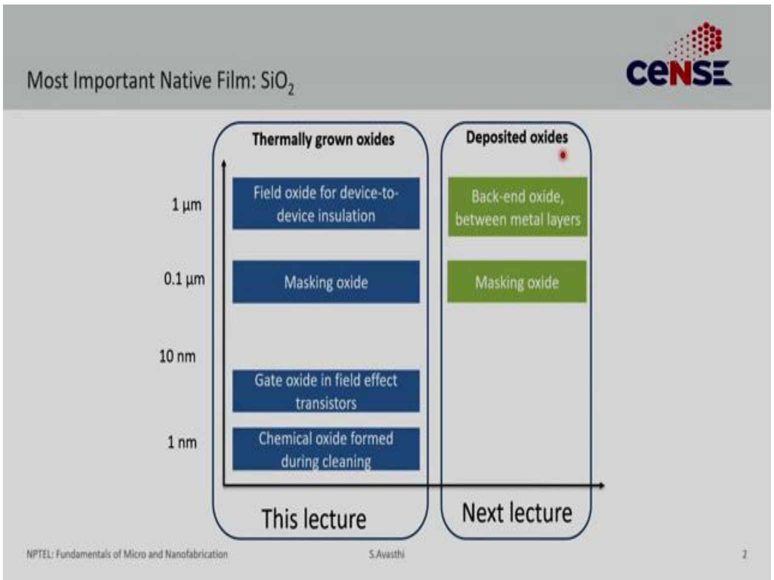

Most Important Native Film: SiO$_2$

Thermally grown oxides

1 µm — Field oxide for device-to-device insulation

0.1 µm — Masking oxide

10 nm — Gate oxide in field effect transistors

1 nm — Chemical oxide formed during cleaning

This lecture

Deposited oxides

Back-end oxide, between metal layers

Masking oxide

Next lecture

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Gate oxide in the field-effect transistors is where the silicon dioxide is used and used most successfully, but there are other aspects of silicon dioxide where silicon dioxide is used in common CMOS fabrication. We have already looked at how chemically formed silicon dioxide was used to do cleaning, by dissolving it into HF. It is also used as a masking oxide during diffusion to create patterns in the doping profile. A device-related issue that we have not discussed, but you can appreciate that in a typical process you would need to electrically insulate a device from another device even though the wafer is the same. We use field oxides to do that.

Oxides are actually also used to insulate metal layers. In a chip, you have not just one but multiple layers of metals and we will come to that when we discuss metallization, but each of those layers has to be isolated from one another (imagine over bridges and under bridges on the road; a similar thing with metals!). Those are back-end metal oxides.

You can grow silicon oxide in two ways. One is a thermally grown oxide from the wafer itself and another is a deposited oxide. This lecture is going to be about thermally grown oxides and we will talk about the deposited one later.

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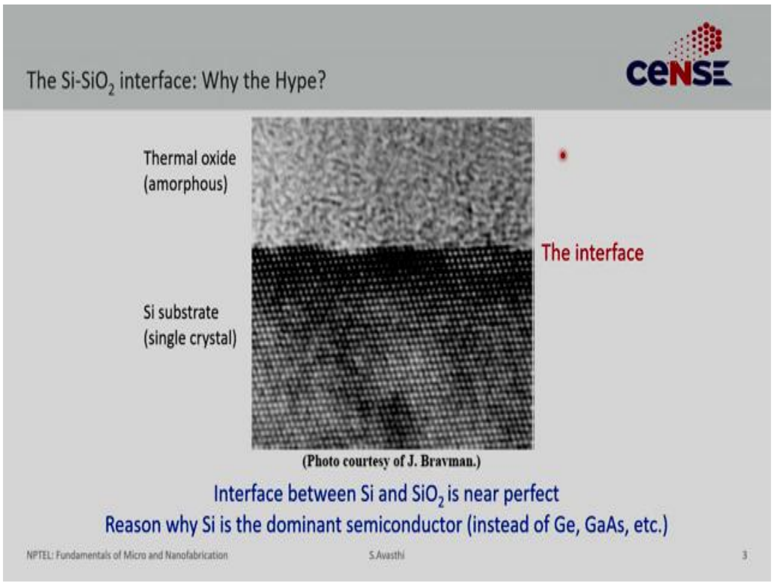

The Si-SiO$_2$ interface: Why the Hype?

Thermal oxide (amorphous)

Si substrate (single crystal)

The interface

(Photo courtesy of J. Bravman.)

Interface between Si and SiO$_2$ is near perfect

Reason why Si is the dominant semiconductor (instead of Ge, GaAs, etc.)

Why is the silicon-silicon dioxide interface hyped so much? In the introductory lecture, we briefly discussed this. Silicon dioxide is an amorphous film, while silicon is a single crystalline film and you would expect that the interface between them would be fairly defective because there is a transition from a crystalline phase to an amorphous phase. This is a TEM image. These dots represent actual atoms.

You would expect a lot of defects and this transition to be not very sharp but it turns out that it is not the case; the transition is extremely sharp a few atoms thick, and the number of defects is very low. So in fact, from a materials perspective, silicon-silicon dioxide interfaces are one of the best interfaces we know how to grow. This is a reason why silicon is the dominant semiconductor. Gallium oxide, arsenide, germanium all of these semiconductors have been the materials of the future and will remain so because they cannot beat the quality of the silicon-silicon dioxide interface. Only very recently have we started getting that good of quality of interface from gallium arsenide and some other semiconductors.

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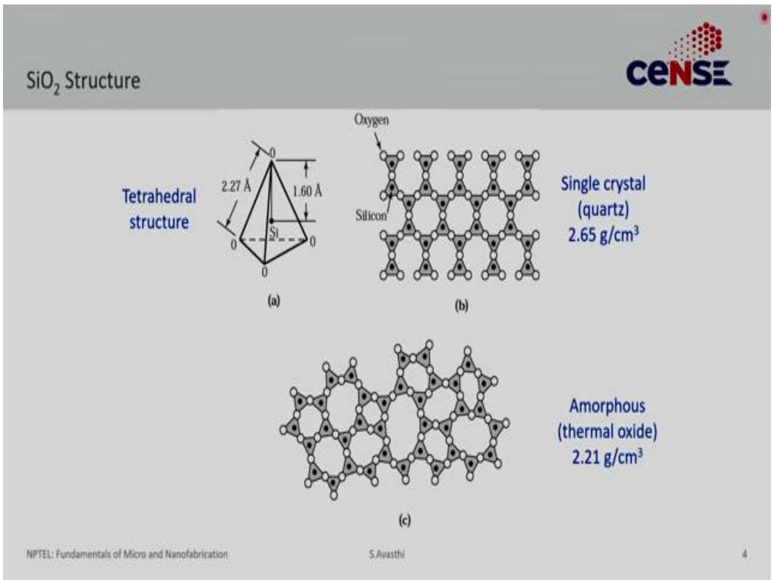

SiO$_2$ Structure

Tetrahedral structure

Single crystal (quartz) 2.65 g/cm^3

Amorphous (thermal oxide) 2.21 g/cm^3

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The crystalline version of silicon dioxide - quartz is also tetrahedral like silicon. The silicon-oxide bond length is 1.6 Å and the oxygen-oxygen bond length is 2.7 Å, but if you compare this with a silicon lattice, silicon dioxide lattice is not matched with silicon lattice and that is why you cannot grow crystalline silicon dioxide on top of the silicon. The density of crystalline silicon dioxide or quartz is ~ 2.65 g/cm^3 but what you end up growing is an amorphous thermal oxide with a significantly lower density ~2.1 g/cm^3.

The structure is maintained a tetrahedral unit cell. You still a stoichiometric mixture but it is not crystalline. Amorphous oxide has an undefined crystal structure, but despite that, its electrical properties are excellent which is a happy surprise. What is the mechanism of oxide growth? Since this is a native film, one of the precursors is the silicon wafer itself.

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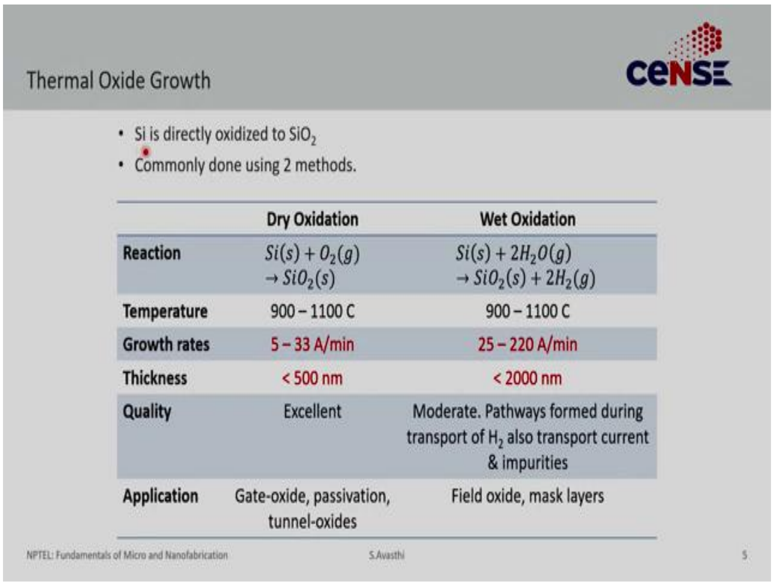

Thermal Oxide Growth

- Si is directly oxidized to SiO_2
- Commonly done using 2 methods.

	Dry Oxidation	Wet Oxidation
Reaction	$Si(s) + O_2(g) \rightarrow SiO_2(s)$	$Si(s) + 2H_2O(g) \rightarrow SiO_2(s) + 2H_2(g)$
Temperature	900 – 1100 C	900 – 1100 C
Growth rates	5 – 33 A/min	25 – 220 A/min
Thickness	< 500 nm	< 2000 nm
Quality	Excellent	Moderate. Pathways formed during transport of H_2 also transport current & impurities
Application	Gate-oxide, passivation, tunnel-oxides	Field oxide, mask layers

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Silicon gets directly oxidized to form SiO_2. There are two ways you can do that. One is dry oxidation, another is wet oxidation. The dry oxidation uses oxygen gas, which is the simplest thing you can do; just expose silicon wafer to oxygen and form silicon dioxide. You need temperatures 900-1100^{o}C to get a meaningful rate. Around 800^{o}C, oxidation starts at a very low growth rate and becomes reasonable at 900^{o}C. For most of the cases, you need an oxide ~ 10-100 nm thick or growth rates ~ 0.33-0.5 nm/min. You have a growth window of a few minutes to a few hours. Usually, you do not grow > 500 nm thick films with this method because it is very slow. The quality, however, is excellent and it is the best silicon dioxide we can grow. For the best quality oxides, we use dry thermal oxidation, for example, for gate oxide, for passivation or tunneling oxides, we use this.

The wet oxide uses water as the oxidation source. The temperature remains the same, however, the growth rates are much higher compared to dry oxidation, which allows you to grow much thicker film; however, the quality is a little poorer. We use it for field oxide and masking layers where the electrical quality is not that important. Below 800^{o}C, the rate of oxidation is very small. This would be at odds with the statement that I have made in the past: silicon will form a native oxide if you leave it in air. So, how is it that we form a very thin silicon dioxide even at room temperature, but I am claiming that you will not have any growth rate all the way to 800^{o}C? The short answer is the surface and the bulk are different. All these things that we discussed were bulk properties. Surface often has very different energetics. The top surface of silicon gets oxidized even at room temperature and forms a very thin layer of oxide; however, once that oxide forms, it prevents the formation of more oxide. In order to continuously grow an oxide that is not self-limiting, you need a high temperature of around 800°C.

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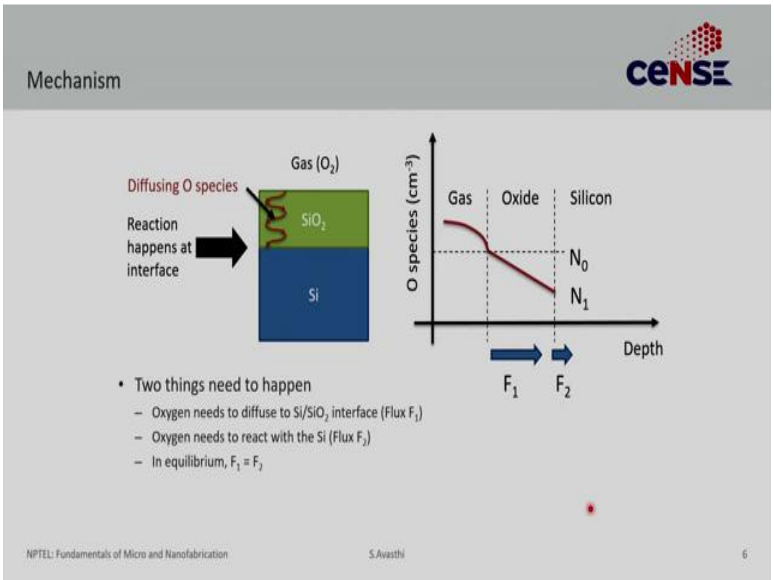

Mechanism

- Two things need to happen
  - Oxygen needs to diffuse to Si/SiO_2 interface (Flux F_1)
  - Oxygen needs to react with the Si (Flux F_2)
  - In equilibrium, $F_1 = F_2$

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Silicon oxide growth mechanism is one of the most studied and well-understood mechanism and the reason I would like to discuss this slowly and in detail is that it is a very good case study of how such mechanism studies are done. If you understand silicon oxide growth good, but more importantly try to appreciate the science behind it and how you can probably use some of these concepts in your own growth studies.

Let us start the oxidation process at t = 0, and start analyzing at t = 10 min, by this time some thickness of silicon dioxide as grown. Above this silicon dioxide, is your oxidation source - water or oxygen. Here, we are doing dry oxidation. This precursor (oxygen in this case) has to reach this interface in order to react with silicon. So, it must travel through the silicon dioxide through and reach the interface to react with silicon.

The only mechanism we know of pushing one type of material through another is diffusion. This is not an electrical species, so we cant put the electric field. You have some concentration of oxygen in the gas which diffuses from top to bottom, giving you this profile of oxygen concentration as a function of depth. There is some depletion of the oxygen precursor in the gas phase. The diffusion of oxygen through the oxide causes this concentration gradient. Finally, it reaches silicon and reacts to form silicon dioxide.

The concentration N_1 at the silicon interface will be lower than N_o at the gas interface. There are 3 fluxes, of which 2 are important. The first is within the gas itself; the oxygen species moves from the region of higher concentration to lower concentration. It turns out that depletion is very and can be ignored for the purposes of this discussion. When we talk about chemical vapor deposition, this may become the bottleneck. Second is the flux (F_1) of oxygen species within the oxide. The last is the flux (F_2) of the oxygen species reacting with silicon to form silicon dioxide at the interface. All of these fluxes are in series, so they must be similar otherwise there will be accumulation. In the steady-state, $F_1 = F_2$.

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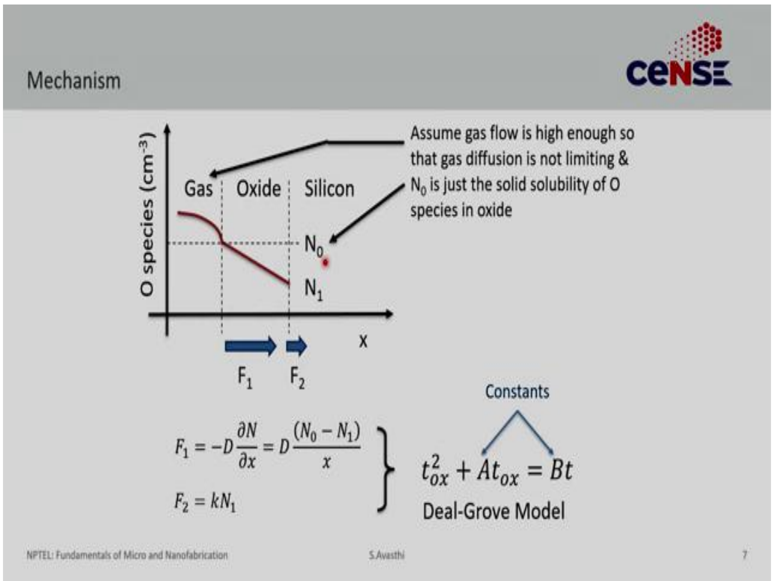

Mechanism

Assume gas flow is high enough so that gas diffusion is not limiting & N_0 is just the solid solubility of O species in oxide

$$F_1 = -D\frac{\partial N}{\partial x} = D\frac{(N_0 - N_1)}{x}$$

$$F_2 = kN_1$$

Constants

$$t_{ox}^2 + At_{ox} = Bt$$

Deal-Grove Model

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This kinetic model is called the Deal - Grove model. In the first paper, Deal and Grove wrote about this. Grove went on to be one of the founders of Intel. Let's assume a few things. Assume the gas flow is high enough so, the gas diffusion is not a limiting step and the concentration profile of oxygen in the gas is very shallow. Assume N_o to be the solid solubility of the oxygen in the oxide. How much diffusant can get inside the material is proportional to what is the solid solubility. As this is diffusion, Fick's model applies. The flux F_1 can be given by the first law: $F_1 = -D\frac{\partial N}{\partial x}$, where D is diffusivity of oxygen inside oxide. Assuming it to be linear, $F_1 = D\frac{N_0 - N_1}{x}$ where N_o is the solid solubility and N_1 is the concentration at the interface.

The second flux is related to a chemical reaction. Let's assume a first-order chemical reaction. This assumes that the rate of the reaction is completely decided by the oxygen concentration, which is not a bad approximation because we have a plethora of silicon, literally 10^{22} silicon atom/cm^3. The problem is not the availability of silicon but the availability of oxygen. So, the reaction rate depends on the concentration of oxygen. So, this flux $F_2 = kN_1$. As we have discussed, under equilibrium, these have to be the same. So, you equalize them and get rid of the N_1 as an unknown. N_o is known as it is solid solubility. If you solve this, you get: $t_{ox}^2 + At_{ox} = Bt$. Where t_{ox} is the thickness of the oxide. To calculate the thickness of the oxide at a given time, you have to solve this second-order equation.

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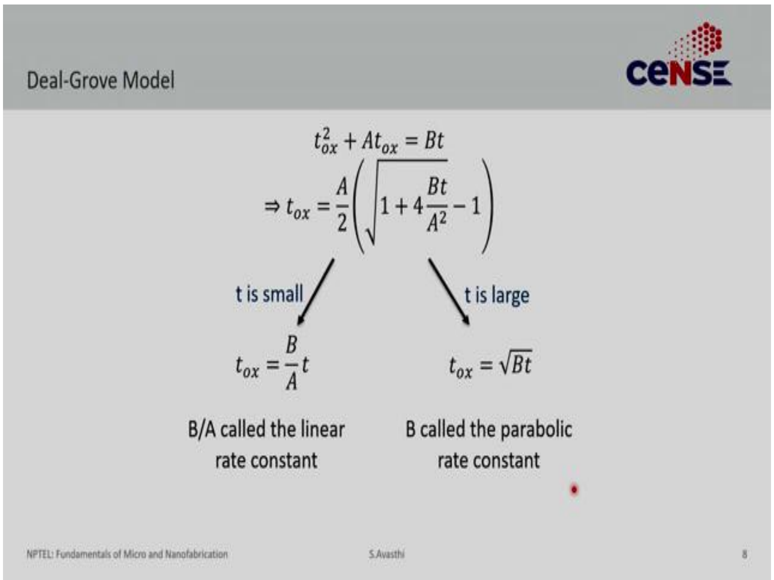

Deal-Grove Model

$$t_{ox}^2 + At_{ox} = Bt$$

$$\Rightarrow t_{ox} = \frac{A}{2}\left(\sqrt{1+4\frac{Bt}{A^2}}-1\right)$$

t is small

$$t_{ox} = \frac{B}{A}t$$

B/A called the linear rate constant

t is large

$$t_{ox} = \sqrt{Bt}$$

B called the parabolic rate constant

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Let's look at the quadratic solution of this equation. If the t is small; when you are looking at a very small time after the beginning of this oxidation process, you can approximate $t_{ox} \approx \frac{B}{A}t$ by using Taylor series expansion of the square root term. So, for very small times, the oxidation rate is linear and the film thickness will linearly increase with time. Which is why B/A is often called a linear rate constant. If we take the other extreme, after a long time, you can ignore both the ones and $t_{ox} \approx \sqrt{Bt}$, which now is a parabolic function of time. B is called the parabolic rate constant.

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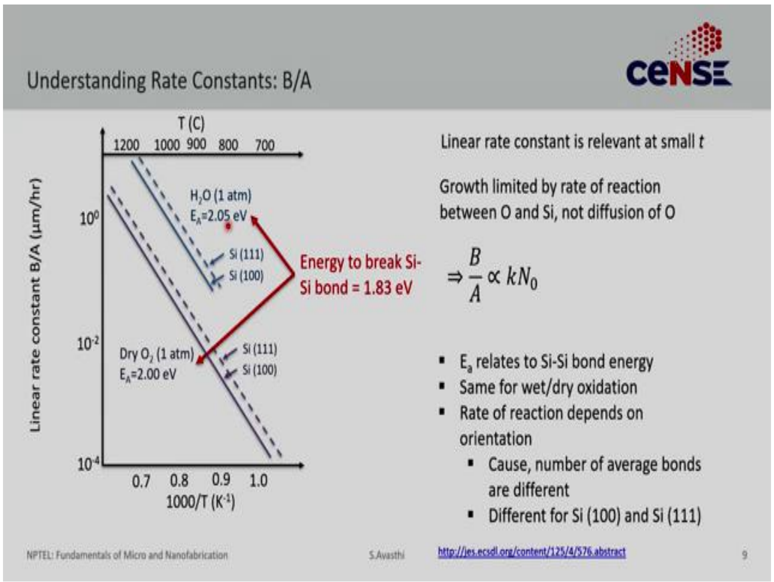

Understanding Rate Constants: B/A

Linear rate constant is relevant at small *t*

Growth limited by rate of reaction between O and Si, not diffusion of O

$$\Rightarrow \frac{B}{A} \propto kN_0$$

- E_a relates to Si-Si bond energy
- Same for wet/dry oxidation
- Rate of reaction depends on orientation
  - Cause, number of average bonds are different
  - Different for Si (100) and Si (111)

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Let’s look at the linear rate constant which is relevant at small t. Here is the linear rate constant as a function of temperature. The graph that you are seeing is called an Arrhenius plot that is often used in a lot of mechanism-based studies. For ease, these plots are often plotted as a function of 1000/T, where T is in Kelvin unit. On the top, we also have a temperature axis, which is more easy to visualize. So, 0.7 on 1000/T refers to ~ 1200^{o}C, 1 refers to ~ 700^{o}C. As 1000/T increases, T decreases. You get linear curves for the logarithm of the rate constant as a function of 1/T. Let’s look at this linear relation for wet oxidation and dry oxidation. Notice that the activation energy E_A, which is the slope of these curves is roughly the same and ~ 2 eV. Also, notice a difference in the absolute value between silicon (111) and (100).

We can explain this observation based on the model we have made. A good way to understand the model is to compare it to something physical. This activation energy that is a fitting parameter right now can be related to the energy to break a silicon-silicon bond which is 1.83 eV, fairly close to 2 eV. Does the mechanism support this? If the time is small, the growth is not limited by diffusion as the silicon oxide has not grown to a large thickness. The diffusion of the oxygen-containing species through the dioxide will be fast and the bottleneck is the reaction with silicon. So, F_1 is large and F_2 is the bottleneck. In equilibrium, they must be equal, so, the concentration gradient changes such that $F_1 = F_2$. So, this linear rate constant $\frac{B}{A} \propto kN_o$, where k is the reaction rate. In that case, E_A for this process being related to silicon-silicon bond energy is no surprise. This energy barriers

1.83 and 2.05 eV are similar because, in order to do the oxidation, you need to break the silicon-silicon bonds and form the silicon-oxygen bond.

As the oxidation here is limited by the ability of silicon-silicon bonds to break, the oxidant does not matter. So, it is also no surprise that E_A is the same for the wet and dry oxidation. How can you explain that the rate of reaction is dependent upon the orientation? The average number of bonds that you see at the interface depends upon orientation, and because the number of average bonds in silicon (100) face and (111) face is different, there is a small difference in the absolute value of the linear rate constant. However, the temperature dependence will not change because it depends upon the activation energy. All of this observation can be explained by the model and that is the hallmark of a good model, where all the data is explained.

If you have not read this landmark paper, I would urge you to do so. It is a very old paper (1960?), but very convincing. Can we do a similar analysis for the parabolic rate constant?

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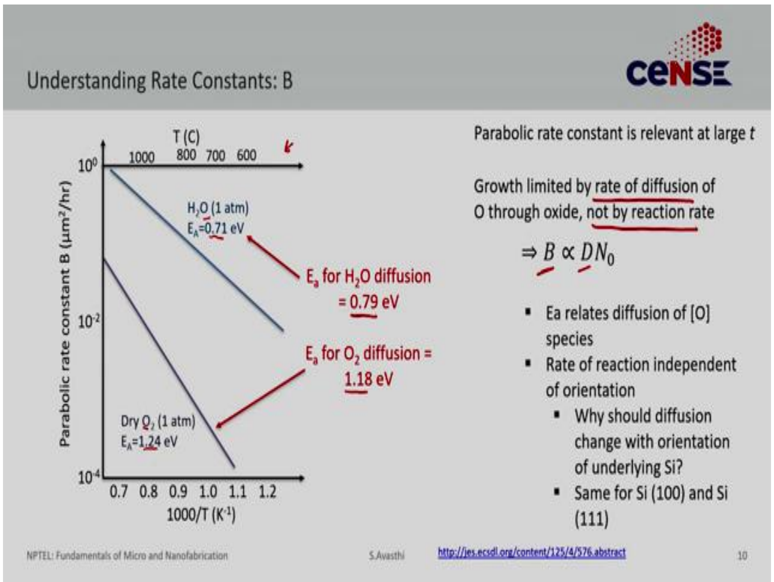

Understanding Rate Constants: B

E_a for H_2O diffusion = 0.79 eV

E_a for O_2 diffusion = 1.18 eV

Parabolic rate constant is relevant at large *t*

Growth limited by rate of diffusion of O through oxide, not by reaction rate

$\Rightarrow B \propto DN_0$

- Ea relates diffusion of [O] species
- Rate of reaction independent of orientation
  - Why should diffusion change with orientation of underlying Si?
  - Same for Si (100) and Si (111)

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Here is the Arrhenius plot for the parabolic rate constant (vs 1/T) for two different oxidation: wet (with water) and dry (with oxygen). Unlike the previous case, we see different activation energy; however, we don't see an orientation dependence. So, I have only plotted one curve because there is no difference for (111) and (100). Can we explain all of that data by comparing it with known values? Let's compare these activation energies with the diffusion of the oxidants. For water diffusion in silicon dioxide, that value is 0.79

eV, which is very close to what we measure for wet oxidation. Similarly, the activation energy for oxygen diffusion in silicon dioxide is 1.18 eV which is also very close to the value we measure for dry oxidation. This is giving us a hint about the mechanism. The parabolic rate constant is relevant for the large thickness of the silicon dioxide. So, the growth rate is not limited by the reaction rate but by the diffusion. It becomes difficult to get the oxygen species through very thick silicon dioxide and allow it to reach the interface. If you are limited by the rate of diffusion, it only makes sense that the activation energy that you measure must also be the activation energy for the diffusion of the oxidants.

So, the parabolic rate constant $B \propto DN_O$. It depends upon D, so, the activation energy of B must be the same as that of D. Whether you take silicon (111) or (100), the oxide on the top is amorphous, so, it stands to reason that independent of the substrate orientation, the diffusion will be the same in silicon dioxide as it is amorphous. It makes sense that there is no orientation effect; (111) has the same rate as (100). All of these things are consistent with the Deal-Grove model.

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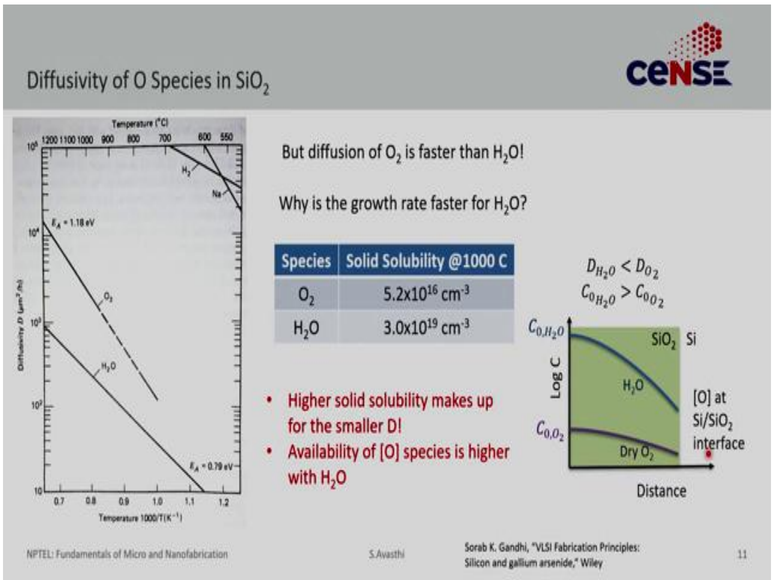

Diffusivity of O Species in SiO_2

But diffusion of O_2 is faster than H_2O!

Why is the growth rate faster for H_2O?

Species	Solid Solubility @1000 C
O_2	5.2×10^{16} cm^{-3}
H_2O	3.0×10^{19} cm^{-3}

- Higher solid solubility makes up for the smaller D!
- Availability of [O] species is higher with H_2O

$D_{H_2O} < D_{O_2}$

$C_{O_{H_2O}} > C_{O_{O_2}}$

Sorab K. Gandhi, "VLSI Fabrication Principles: Silicon and gallium arsenide," Wiley

There is one problem here. It turns out that oxygen diffuses faster in silicon dioxide than water molecules. If that is the case, how is wet oxidation faster than dry oxidation? If the bottleneck is diffusion and the diffusivity of the oxygen is higher, the rate of oxidation with oxygen should also be higher, but that is not the case. With dry oxidation, the parabolic rate constant is lower, and so is the growth. How is that possible?

Here is a chart of the diffusivity of oxygen and water as a function of 1/T. So, this is also an Arrhenius plot. The absolute value of D for oxygen is higher. The concentration of oxygen species in the gas that does not change, but you have certain solid solubility of the oxidant in the oxide and depending upon that, you have a gradient of oxygen species across the oxide. For the flux F_1, two things matter; Diffusion coefficient and the concentration gradient or the change from high concentration to low concentration $-\frac{\partial N}{\partial x}$. It turns out that the diffusivity of oxygen is higher in silicon dioxide, but not the solid solubility, which is only 5×10^{16}/ cm^3 but the solid solubility of water inside silicon dioxide is $\sim 10^{19}$/cm^3; a 1000 times higher.

Hence, the concentration gradient is much higher with water (blue curve) than oxygen (violet curve). Even though the oxygen diffusivity is higher, flux is lower. The profile of oxygen species is much shallower with dry oxygen than it is with water. As this is the bottleneck, the availability of the oxygen species at the interface is higher with water than with dry oxide and that explains higher growth rate.

A good theory is one that explains all the data and is consistent with all the data. The growth model of silicon dioxide is a very good example of a good theory that has been backed by data. Whoever of you wants to do the mechanism type of studies of growth should read and understand the oxide growth because, in my opinion, it is a beautifully written paper that captures everything in a very consistent and elegant fashion.

With that, we come to the end of this lecture. In the next lecture, we will go into a little more detail of silicon oxide growth, look at some equipment, some advance concepts like ultra-thin oxides, and look at defects.