Microfluidics
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Lecture - 23
Microfabrication Techniques (Continued...)

Okay, so let us continue our discussion on doping of silicon substrate, and as I was telling doping is necessary to modify the electrical conductivity of silicon substrate okay.

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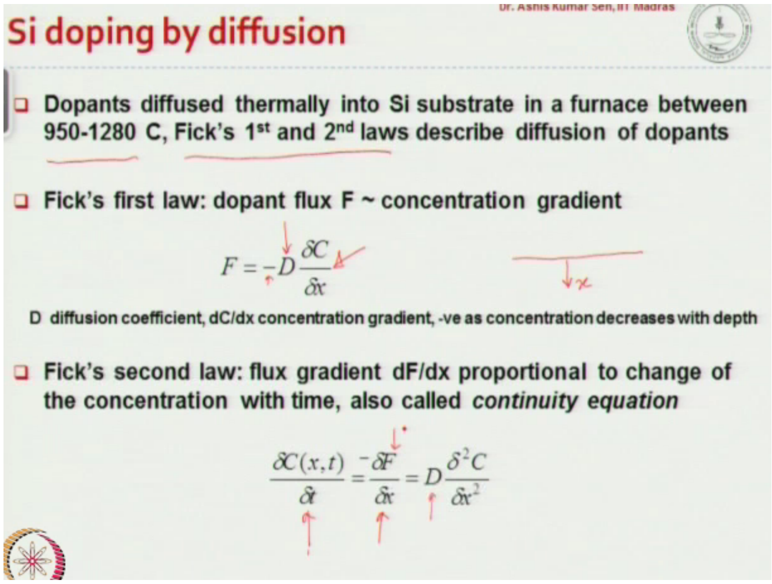

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Si doping by diffusion

- Dopants diffused thermally into Si substrate in a furnace between 950-1280 C, Fick's 1st and 2nd laws describe diffusion of dopants
- Fick's first law: dopant flux F ~ concentration gradient

$$F = -D\frac{\delta C}{\delta x}$$

D diffusion coefficient, dC/dx concentration gradient, -ve as concentration decreases with depth

- Fick's second law: flux gradient dF/dx proportional to change of the concentration with time, also called *continuity equation*

$$\frac{\delta C(x,t)}{\delta t} = \frac{-\delta F}{\delta x} = D\frac{\delta^2 C}{\delta x^2}$$

So let us look at here as we were discussing the dopants are diffused into silicon of substrate typically in a you know thermal furnace, where the temperature is between 950 to 1280 degree centigrade, and the diffusion of dopants is governed by the Fick's first and second laws okay. Fick's first class says that dopant flux is proportional to the concentration gradient and D is the diffusion coefficient okay.

And as we discuss the negative sign is because the concentration decreases along with depth okay, if this is the surface of the substrate x is into the substrate okay, so as the concentration produces with x there is a negative sign here okay. Fick's second law tells that the flux gradient del F/del x is proportional to the change of concentration with time okay, so del F/del x as you see here=del C/del t.

Now if you substitute the expression for F from Fick's first law, we can write it as D which is diffusion coefficient*del square C/del x square, so it is a second order differential second order in space and first order in time, so here we would need 2 boundary conditions.

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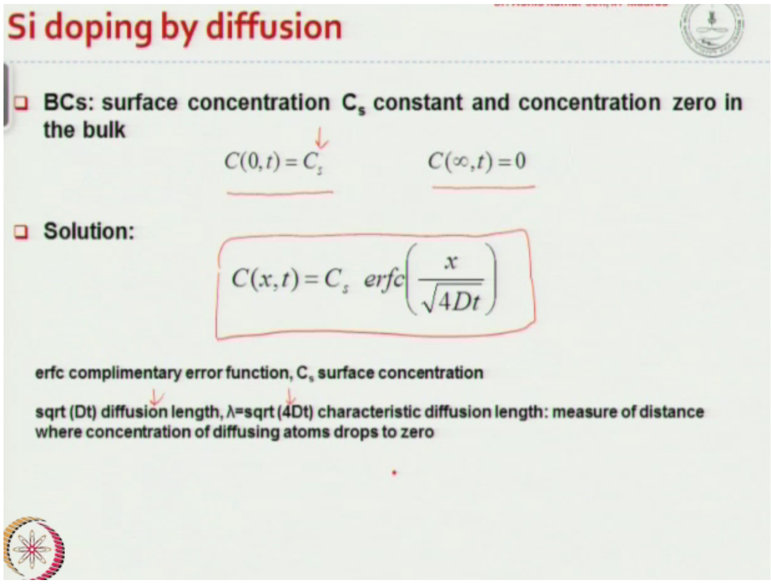

Si doping by diffusion

- BCs: surface concentration C_s constant and concentration zero in the bulk

$$\underline{C(0,t) = C_s} \qquad \underline{C(\infty,t) = 0}$$

- Solution:

$$\boxed{C(x,t) = C_s \; erfc\left(\frac{x}{\sqrt{4Dt}}\right)}$$

erfc complimentary error function, C_s surface concentration

sqrt (Dt) diffusion length, λ=sqrt (4Dt) characteristic diffusion length: measure of distance where concentration of diffusing atoms drops to zero

As you can see here, here we are assuming that in the first case we are assuming that the surface as the concentration of the dopant of the surface does not change with time okay, which means that there is an infinite supply of dopant at the surface okay, so what it means mathematically is that C at x=0 and anytime=Cs, so that is a constant value at the surface, and C at x=infinity for any time is 0 okay.

Because the concentration would reduce to 0 as you go away from the you know for away from the surface, with these 2 boundary conditions the equation can be solved, so this is the solution okay for C x, t, C x,t=Cs*complementary error function of x/square root of 4 Dt, and we said that the square root of Dt is the diffusion length, and we can define a parameter lambda which is the characteristic diffusion length as square root of 4 Dt okay.

And this characteristic diffusion length is the distance where the concentration will be reducing to 0 okay, so it is the distance from the surface where the concentration will reduce to 0 okay.

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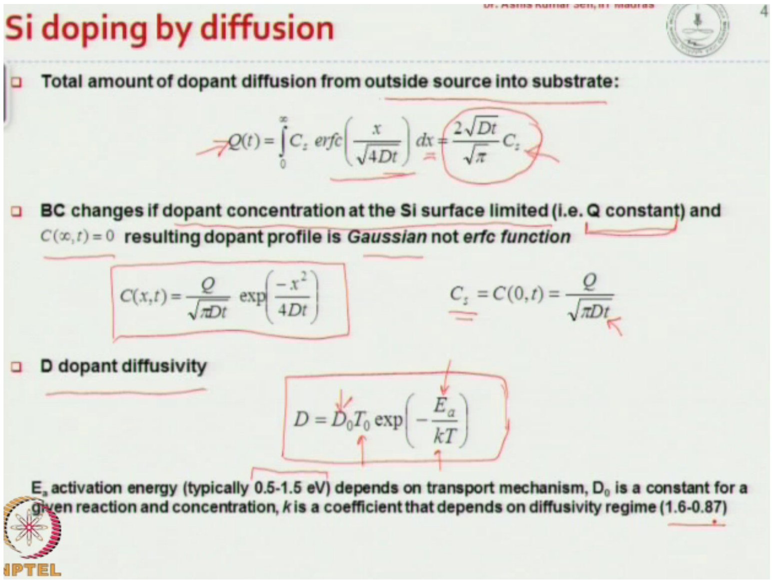

Si doping by diffusion

- Total amount of dopant diffusion from outside source into substrate:

$$Q(t)=\int_0^\infty C_s\,erfc\left(\frac{x}{\sqrt{4Dt}}\right)dx=\boxed{\frac{2\sqrt{Dt}}{\sqrt{\pi}}C_s}$$

- BC changes if dopant concentration at the Si surface limited (i.e. Q constant) and $C(\infty,t)=0$ resulting dopant profile is *Gaussian* not *erfc function*

$$\boxed{C(x,t)=\frac{Q}{\sqrt{\pi Dt}}\exp\left(\frac{-x^2}{4Dt}\right)}\qquad C_s=C(0,t)=\frac{Q}{\sqrt{\pi Dt}}$$

- D dopant diffusivity

$$\boxed{D=D_0T_0\exp\left(-\frac{E_a}{kT}\right)}$$

E_a activation energy (typically 0.5-1.5 eV) depends on transport mechanism, D_0 is a constant for a given reaction and concentration, k is a coefficient that depends on diffusivity regime (1.6-0.87)

Now knowing the variation of concentration with x and t we can find out the total amount of diffusion that occurs from outside source into the substrate, so you can find Q t=0 to infinity Cs complementary error function of x/square root of 4 Dt* dx okay, so we integrate throughout the depth, so if you do that we get an expression for the total dopant diffusion, so total doses is directly proportional to the concentration of the surface and is also directly proportional to square root of t okay which is time.

Now instead of assuming that the concentration remains fixed at the surface, if you assume that there is a definite amount of dopant available okay Q, which is the total amount of dopant available and which reduces with the time, so there is not an infinite supply of dopant then the solution is going to change okay. So that is the second case that we will be looking at where we assume that the dopant concentration at the silicon surface is limited okay.

So we have a fixed amount of dopant that is present at the surface, but the condition that C at x=infinity, t=0 will be valid and the second boundary condition is that Q is constant at the surface, now if we use these 2 boundary condition then the resulting dopant profile okay the variation of the concentration of the dopant with x and t will be Gaussian in nature okay, whereas in the previous case it was a complementary error function.

So C x, t will vary as Q/square root of pi Dt* exponential –x square/4 Dt, now here if you plug in x=0, which is as the surface then you get the surface consideration which is not constant but a function of time okay, so that is the difference between the first case and the second case here the surface concentration is not constant but a function of time, so it reduces with time as 1/square root of t, D is the dopant diffusivity as I was telling, and you can express the dopant diffusivity in this from thermodynamics.

So D=D0 T0*exponential –Ea/KT, where Ea is the activation energy and that depends on the transport mechanism and the typical value is between 0.5 to 1.5 electron hole, and D0 is a constant for you know a given reaction and concentration, T0 is the temperature and the K is the coefficient that depends on the diffusivity regime, and typically it has a value between 1.6 to 0.87 okay.

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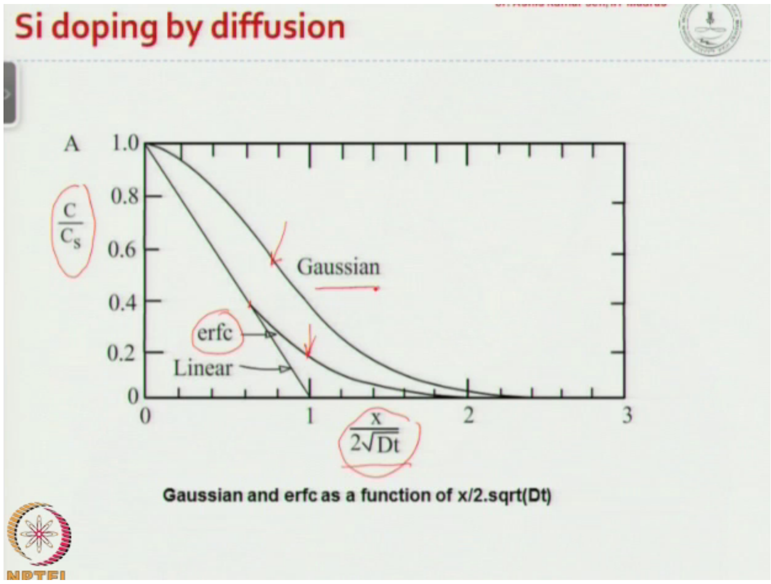

Si doping by diffusion

Gaussian and erfc as a function of x/2.sqrt(Dt)

So this is where we see you know 2 different cases that we just discussed, we are plotting you know the variation of the concentration with x okay, how the concentration is changing with x and as well as t, so here on the x-axis we have x/2 square root of Dt okay, and y-axis we have C/Cs. For the first case the solution is the complementary error function, so that is the nature of the curve as you see here.

And for small distance from the surface when x is of the order of let us say square root of Dt, then we can see that the curve is linear that means the concentration varies linearly with the depth okay, and this is the curve when the dopant concentration is not fixed at the surface but there is a definite amount of dopant present okay, so the curve is Gaussian in nature.

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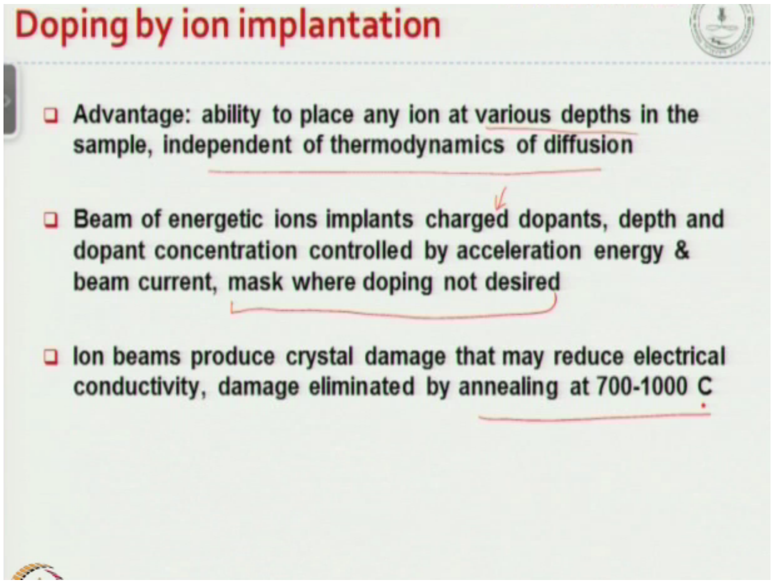

Doping by ion implantation

- Advantage: ability to place any ion at various depths in the sample, independent of thermodynamics of diffusion
- Beam of energetic ions implants charged dopants, depth and dopant concentration controlled by acceleration energy & beam current, mask where doping not desired
- Ion beams produce crystal damage that may reduce electrical conductivity, damage eliminated by annealing at 700-1000 C

Now the another approach to do you know doping is by ion implantation okay, so by you know diffusion based doping always the concentration of the dopant reduces with x okay, and if you want to dope at a particular depth it is not possible it has to always start from the surface go into the depth. However, if you can use ion implantation method it is possible to dope a particular section of the wafer at a particular depth okay.

And that is possible because you are using high energetic you know dopant ion which can be which can penetrate the depth of the wafer and locate at a particular depth okay, so you know the advantage of doping by ion implantation is shown here, it has the ability to place you know any dopant ion at any depth that we want, so it is not dependent on the thermodynamics of diffusion that we had seen in the previous cases.

So in this case in ion implantation the beam of energetic ions are implanted you know and these beam of energetic ions would implant the charged dopants and at a particular depth, and the depth and the dopant concentration will be controlled by the acceleration energy and the beam current okay. So the you know acceleration energy and the beam current of this beam of energetic ions would control the dopant concentration and the depth.

And we can selectively dope different areas by using mask okay. The one downside of ion implantation is that since we are talking about highly energetic ions okay that would create crystal damage in the wafer okay, so you know we are using high energetic ions to dope a particular type of you know dopant at a particular depth, but we are talking about high energetic ions, so they will they may create crystal damage.

But it is possible to reduce the crystal you know damage to take care of the crystal damage by annealing okay, so if you can anneal the substrate after the ion implantation at 700 to 1000 degree centigrade you can overcome the crystal damage.

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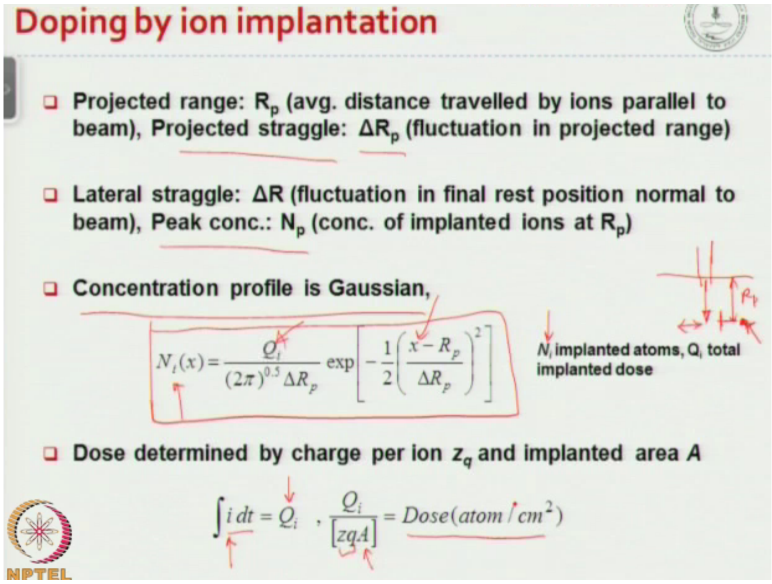

Doping by ion implantation

- Projected range: R_p (avg. distance travelled by ions parallel to beam), Projected straggle: ΔR_p (fluctuation in projected range)
- Lateral straggle: ΔR (fluctuation in final rest position normal to beam), Peak conc.: N_p (conc. of implanted ions at R_p)
- Concentration profile is Gaussian,

$$\boxed{N_i(x) = \frac{Q_i}{(2\pi)^{0.5}\Delta R_p} \exp\left[-\frac{1}{2}\left(\frac{x-R_p}{\Delta R_p}\right)^2\right]}$$

N_i implanted atoms, Q_i total implanted dose

- Dose determined by charge per ion z_q and implanted area A

$$\int i\,dt = Q_i \quad , \frac{Q_i}{[zqA]} = Dose(atom/cm^2)$$

So in the context of ion implantation there are few terms that need to be defined, the first term is the projected range, so the projected range is the distance the average distance travelled by the ions parallel to the beam okay, so if you have a you know substrate surface here, how much distance the ion is penetrating into the wafer parallel to the beam is called as the projected range. And the second term is projected straggle, so it is the fluctuation in the projected range.

So if you target let us say this as your Rp and there is some variation around Rp that is known as the projected straggle, the lateral straggle is the fluctuation in the final rest position normal to the beam, so how much variation you get in a direction normal to the beam direction is known as lateral straggle. And peak concentration Np is the concentration of the implanted ion at the projected range, so if this is the projected ranges the peak concentration would occur at the projected range okay.

So here in this case it has been found that the concentration profile is Gaussian in nature okay, so this is the equation by which you can express the concentration, how the concentration of the doping varies, so this is the formula here ni is the implanted atoms, so this is the number of atoms that are implanted number of dopant atoms that are implanted, and Qi is the total dose and we already have defined Rp and delta Rp which are the projected range and the lateral the projected straggle and x is the depth.

Now we can know Qi, so Qi would be so it is basically the total current total ion that you are depositing you know doping into the surface into the substrate, if you integrate with the time that will give you the total dose that is being implanted into the substrate. Now if you divide that with the charge for ion which is zq and the area over which this implantation is being done then that is known as the dose, so it is expressed in the form of atom per centimeter square.

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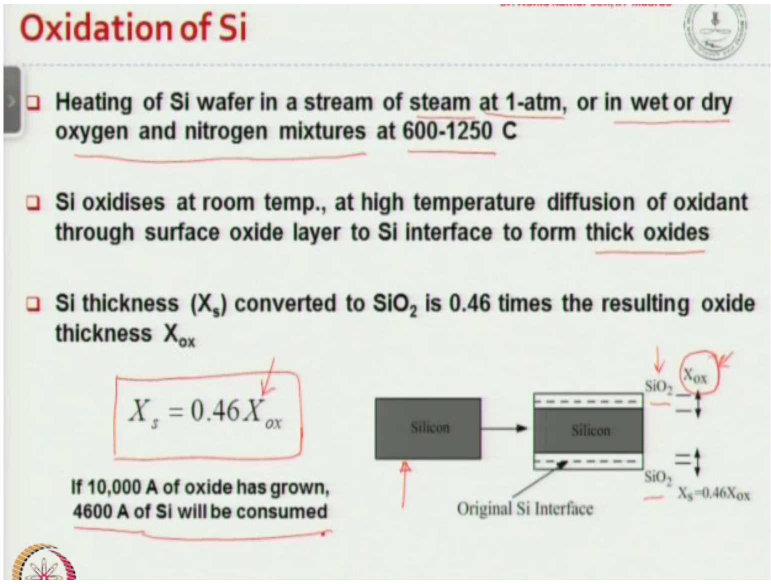

Oxidation of Si

- ☐ Heating of Si wafer in a stream of steam at 1-atm, or in wet or dry oxygen and nitrogen mixtures at 600-1250 C
- ☐ Si oxidises at room temp., at high temperature diffusion of oxidant through surface oxide layer to Si interface to form thick oxides
- ☐ Si thickness (X_s) converted to SiO_2 is 0.46 times the resulting oxide thickness X_{ox}

$$\boxed{X_s = 0.46 X_{ox}}$$

If 10,000 A of oxide has grown, 4600 A of Si will be consumed

So with that let us move on and talk about oxidation of the silicon okay, so we clean the wafer then we dope the wafer if it is required it is relevant for electrical application where we are relying on the conductivity of the substrate. And then the next step would be to grow an oxide layer on silicon okay, and this oxidation is typically done in the oven the furnace the oxidation furnace.

And there are different techniques it can be either wet oxidation, it can be dry oxidation or it can be pyrogenic oxidation okay. So typically the oxidation would involve you know heating of the wafer in a steam of stream, in case of stream of steam, in case of wet oxidation that is typically done at 1 atmosphere, or in wet or dry oxygen and nitrogen mixture at about 600 to 1250 centigrade okay. So this is the typical process that is done in a oxidation furnace.

So the silicon if you expose a typical silicon substrate to air, it would always have an oxidation layer on the surface it would oxidize okay. However, if you subject it to high temperature then it can grow thicker oxide layer okay, so if you want to grow thicker oxide layer you have to subject the wafer to high temperature okay. So silicon oxidizes at room temperature and at high temperature the diffusion of oxidant through the surface oxide layer will happen to create the thick oxide layer that is required.

Now if you start with a silicon wafer as you can see here, let us say this is the silicon wafer and you put it in an oxidation furnace, now let us say you have silicon dioxide layer going on both sides of the wafer, let us consider only one side let us say the total oxide thickness is specified by x okay. Now if the total thickness is x about 0.46 of 46% of the total oxide layer will be the consumed silicon okay.

So the silicon dioxide so the oxidation occurs both into the silicon substrate as well as above the silicon substrate, so if you have grown let us say 1000 micron of silicon dioxide on a silicon wafer, then 400 let us say 1000 nanometer of silicon dioxide and let us say silicon wafer 460 nanometer of silicon thickness of silicon has been consumed okay, and you have 500 and the 540 nanometers has been grown on the surface okay.

So you can see here in the oxidation process the thickness of the silicone that is consumed is 0.46 time the total oxide thickness okay, so if you have 10000 angstrom of oxide has grown 4600 angstrom of silicon will be consumed in the process.

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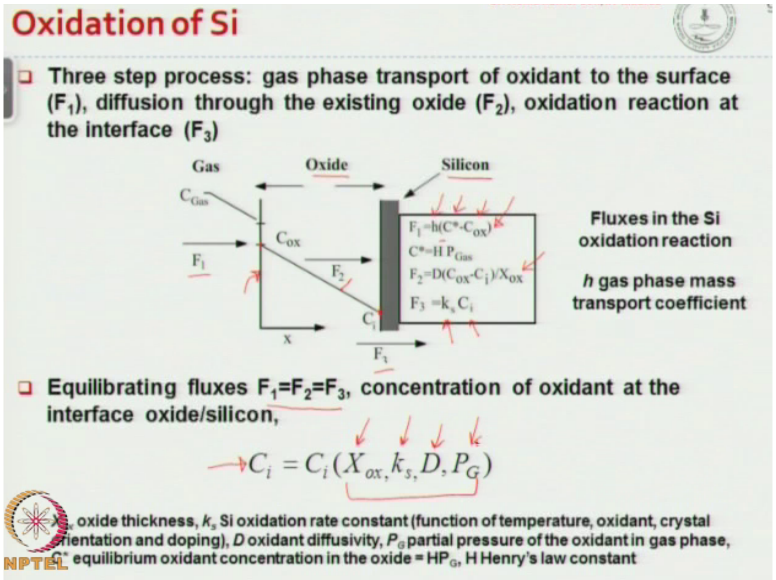

Oxidation of Si

- Three step process: gas phase transport of oxidant to the surface (F_1), diffusion through the existing oxide (F_2), oxidation reaction at the interface (F_3)

$F_1 = h(C^* - C_{ox})$
$C^* = H\,P_{Gas}$
$F_2 = D(C_{ox} - C_i)/X_{ox}$
$F_3 = k_s C_i$

Fluxes in the Si oxidation reaction

h gas phase mass transport coefficient

- Equilibrating fluxes $F_1 = F_2 = F_3$, concentration of oxidant at the interface oxide/silicon,

$$\rightarrow C_i = C_i(\underbrace{X_{ox}, k_s, D, P_G})$$

X_{ox} oxide thickness, k_s Si oxidation rate constant (function of temperature, oxidant, crystal rientation and doping), D oxidant diffusivity, P_G partial pressure of the oxidant in gas phase, C^* equilibrium oxidant concentration in the oxide = HP_G, H Henry's law constant

Now the oxidation is typically a 3 step process, as you can see here this is the silicon substrate, so as you can see here this is the silicon substrate and this is the oxide layer which is the next to the silicon substrate, and here is the gas that is exposed either it is gas or steam depending on the type of oxidation furnace you have. And the 3 step process are shown here F1, F2 and F3, the first step is the gas phase transferred of oxidant to the surface.

So you have the gas phase here the oxidant has to be transported from the gas medium to the surface of the top surface of the oxide layer okay that is the first step. Then the second step the oxidant has to diffuse through the existing oxide layer okay, say this is the concentration of oxidant on the top surface okay, and it will reduce to the oxidant concentration will reduce to Ci on the top of the silicon, so the oxidant has to diffuse through the existing oxide layer.

And the third step is the oxidation reaction at the interface, so the oxidation reaction always happens at the silicon-silicon dioxide interface okay, so the oxidant has to come to the top of the silicon dioxide surface, they have to diffuse to the existing silicon dioxide layer and then the oxidation reaction have to start at the silicon-silicon dioxide interface okay.

So you know F1 the diffuse you know the transport of the oxidant to the surface is governed by this equation h*C star-Cox where h is the gas phase mass transport coefficient okay and C star is the equilibrium oxidant concentration in the oxide, and Cox is the concentration of the oxidant on the oxide layer okay, C star is can be thermodynamically expressed as H*partial pressure of the gas phase and H is called the Henry constant okay.

F2 since it is diffusion through the existing oxide layer it will be governed by the Fick's first law of the diffusion and that is given by D*the concentration gradient which is Cox-Ci/Xox the thickness of the oxide layer. And F3 which is the oxidation reaction at the interface that would depend on Ks, Ks is the oxidation rate constant and Ci is the concentration of the oxidant on the silicon and silicon dioxide interface okay at that very interface there.

So those 3 are the 3 different steps in a typical oxidation process, now if you, you know equilibrate all these 3 fluxes F1=F2=F3 then you can find the expression for the concentration of the oxidant at the silicon and oxide interface. So the concentration of the oxidant of the silicon oxide interface is dependent on these parameters okay, it depends on the oxidation thickness, the oxide layer thickness, it depends on the rate constant, it depends on the diffusion coefficient, and the partial pressure of the oxidant in the gas phase.

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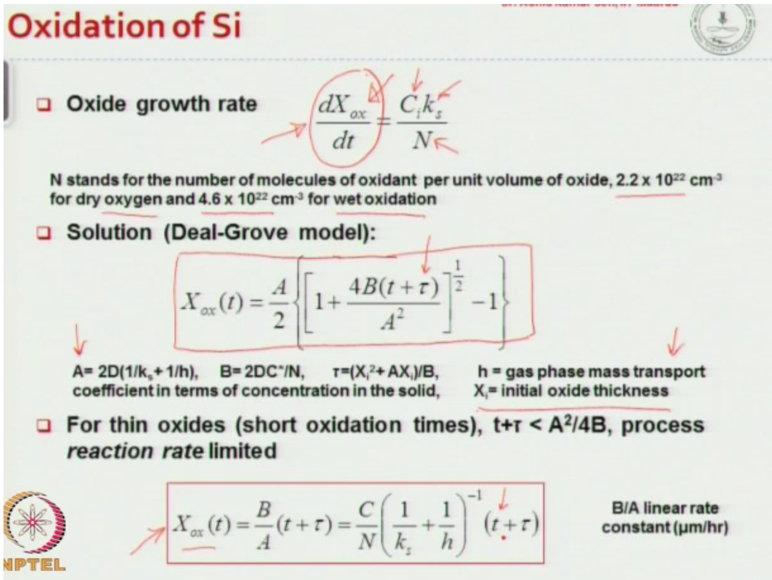

Oxidation of Si

- Oxide growth rate $$\frac{dX_{ox}}{dt} = \frac{C_i k_s}{N}$$

N stands for the number of molecules of oxidant per unit volume of oxide, 2.2×10^{22} cm^{-3} for dry oxygen and 4.6×10^{22} cm^{-3} for wet oxidation

- Solution (Deal-Grove model):

$$\boxed{X_{ox}(t) = \frac{A}{2}\left\{\left[1 + \frac{4B(t+\tau)}{A^2}\right]^{\frac{1}{2}} - 1\right\}}$$

$A = 2D(1/k_s + 1/h)$, $B = 2DC^*/N$, $\tau = (X_i^2 + AX_i)/B$, h = gas phase mass transport coefficient in terms of concentration in the solid, X_i = initial oxide thickness

- For thin oxides (short oxidation times), $t + \tau < A^2/4B$, process *reaction rate* limited

$$\boxed{X_{ox}(t) = \frac{B}{A}(t+\tau) = \frac{C}{N}\left(\frac{1}{k_s} + \frac{1}{h}\right)^{-1}(t+\tau)}$$

B/A linear rate constant (μm/hr)

So you know the oxide growth rate how the oxidation thickness changes with time, it has been found that the oxidation growth rate can be expressed as Ci which is the concentration of the oxidant at the silicon oxide interface*the rate constant/N, where N is the number of molecules of oxidant per unit volume of oxide okay, and typically it has a value of 2.2 into 10 to the power 22 centimeter cube for dry oxygen.

And it is a value which is about you know twice 2 times for wet oxidation say about 4.6 into 10 to the power 22 centimeter cube for wet oxidation. Now if you seek a solution to this equation here there are different models available, and once this model is the Deal-Grove model, and using deal-grove model the expression for the oxide thickness with time can be found, so this is the expression for how the thickness of the oxide layer changes with the time.

So it is A/2*1+4 B*t+ tau/A square 1/2-1, where A is given by 2*diffusion coefficient*1/rate constant+1/the mass transfer coefficient h, and B=2*diffusion coefficient C star/N, and tau is the time constant which is given by Xi square so initial oxide layer thickness square +A*Xi is the initial oxide layer thickness/B, and h is the we have already defined is the mass transfer coefficient, Xi as I said is the initial oxide thickness.

Now if you consider that the oxide layer is very thin that means we are talking about the beginning of the oxidation, then we can say that here as you see here for the oxidation time when it is small then t+tau in this equation t+tau will be small compared to A square/4 B, and if that is the case then we can use you know expand this we can bring 1/2 as a coefficient here, so you can find the oxide layer thickness as a function of time which will be B/A*t+tau.

And if you plug in the values for B and A, we would get C/N*1/Ks+1/h -1*t+tau, so you know what you see here is that the oxide layer thickness is linearly varying with the time okay, and that is at when the oxide layer thickness is small okay. And here you know B/A the ratio B/A as you see here is a linear rate constant which has unit as micrometer per hour.

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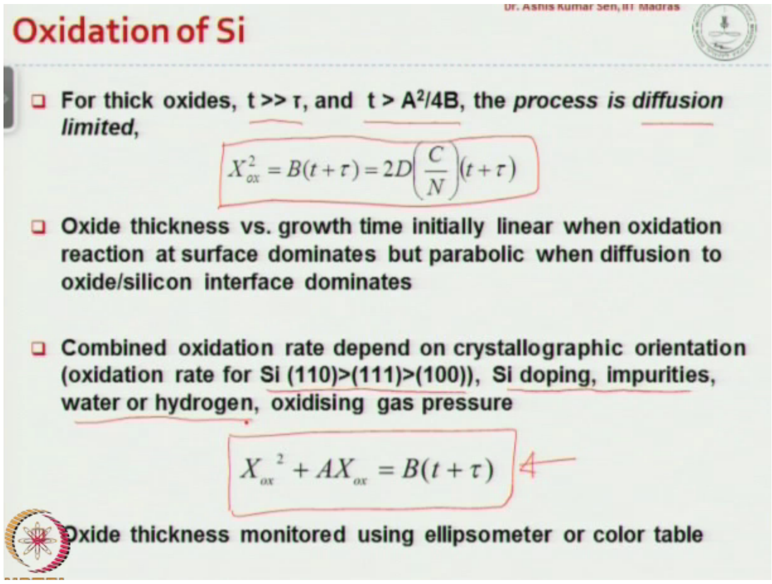

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Oxidation of Si

- For thick oxides, $t >> \tau$, and $t > A^2/4B$, the *process is diffusion limited*,

$$\boxed{X_{ox}^2 = B(t+\tau) = 2D\left(\frac{C}{N}\right)(t+\tau)}$$

- Oxide thickness vs. growth time initially linear when oxidation reaction at surface dominates but parabolic when diffusion to oxide/silicon interface dominates

- Combined oxidation rate depend on crystallographic orientation (oxidation rate for Si (110)>(111)>(100)), Si doping, impurities, water or hydrogen, oxidising gas pressure

$$\boxed{X_{ox}^2 + AX_{ox} = B(t+\tau)} \leftarrow 4$$

- Oxide thickness monitored using ellipsometer or color table

On the other hand, if the oxide layer thickness is a large where you know t will be>> the time constant tau, and so t will be>A square/4 B, then you can work on that equation to show that you can reduce the equation as into this form, so square of the oxide layer thickness with the time will be B*t+tau, and if you use the expression for B you can show that=2 D*C/N*t+tau. So what do we see here is that you know the oxide layer thickness would increase linearly with the time at the small times, and at a larger time it is going to be parabolic in nature okay.

So the oxide layer thickness will increase parabolically okay, and this is what we see here at you know at small timescales okay at thinner oxidation layer thickness the oxidation would depend on the rate constant okay, the rate constant at the silicon oxide interface, at large timescales for thicker oxide layer because you would have already built thicker oxide layers for large times, the oxidation will depend on the diffusion okay.

So first oxidant has to diffuse through thicker oxide layer okay, so that is what we see here. And the combined oxidation rates the case where it is you know the reaction rate are limited, and the case where it is diffusion limited we can combine the 2 to find an expression generic expression that can be applied for anytime. So this is a generic expression which is square of oxide layer thickness +A*oxide layer thickness=B*t+tau.

So the combined oxidation rate would depend on the crystallographic orientation okay, so depending on the orientation of the oxide the silicon substrate the oxidation rate will vary, so typically it has been found that the oxidation for a 1 1 0 wafer >1 1 1 and that is >1 0 0 wafer. And the oxidation is also going to be affected by the doping, how we are dropping the wafer, the impurities that are present on the substrate water or hydrogen you know depending on how you are going to you know oxidize the wafer and the gas pressure.

So these are different parameters that would affect the oxidation rate, so typically you know this is one model that you can use to predict the thickness of the oxidation layer. Alternatively, you can use tools like ellipsometer to predict how the let us say an optical technique that can be used to measure the thickness of an oxidized wafer okay. And you can also use color table to get an approximate idea of how thick the oxide layer is.

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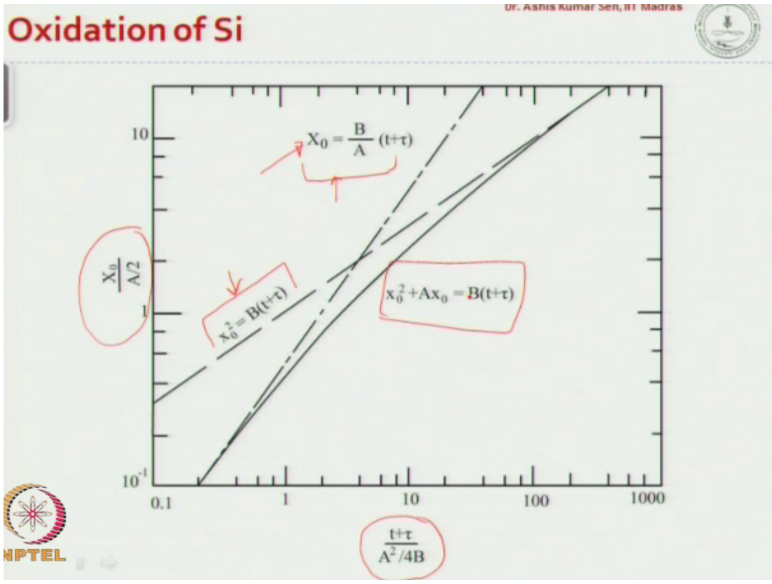

Oxidation of Si

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So here is what we have discussed you can see you know we are talking about how the oxidation thickness is varying, and on x-axis we have time, and this is a case where this is valid for a smaller oxide you know thinner oxide layer or when the time is less okay, so small times this equation is valid. And at a large times when the oxidation is diffusion dependent, this equation is going to be valid okay, and this is the rate constant dependent. Now this gives a combined you know equation which can be valid for any time scale okay.

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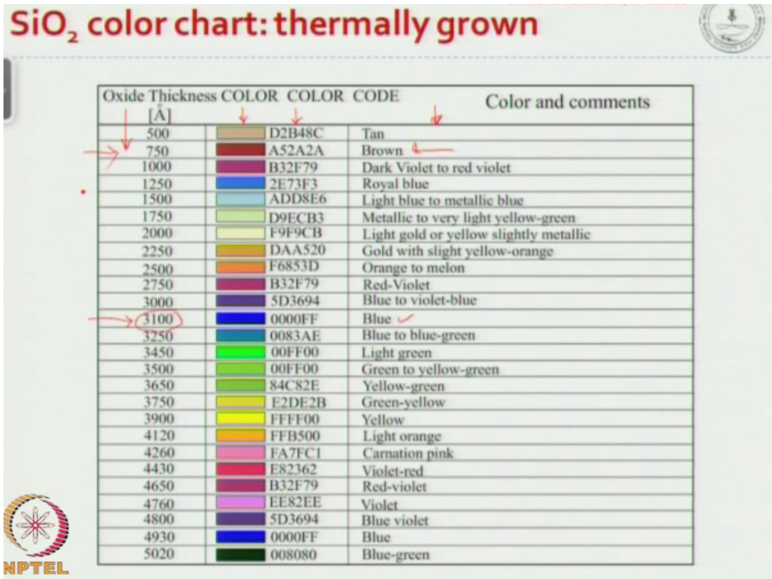

SiO_2 color chart: thermally grown

Oxide Thickness [Å]	COLOR	COLOR CODE	Color and comments
500	🟫	D2B48C	Tan
750	🟥	A52A2A	Brown
1000	🟪	B32F79	Dark Violet to red violet
1250	🟦	2E73F3	Royal blue
1500	🟦	ADD8E6	Light blue to metallic blue
1750	🟩	D9ECB3	Metallic to very light yellow-green
2000	🟨	F9F9CB	Light gold or yellow slightly metallic
2250	🟧	DAA520	Gold with slight yellow-orange
2500	🟧	F6853D	Orange to melon
2750	🟪	B32F79	Red-Violet
3000	🟪	5D3694	Blue to violet-blue
3100	🟦	0000FF	Blue ✓
3250	🟦	0083AE	Blue to blue-green
3450	🟩	00FF00	Light green
3500	🟩	00FF00	Green to yellow-green
3650	🟩	84C82E	Yellow-green
3750	🟨	E2DE2B	Green-yellow
3900	🟨	FFFF00	Yellow
4120	🟧	FFB500	Light orange
4260	🟪	FA7FC1	Carnation pink
4430	🟥	E82362	Violet-red
4650	🟪	B32F79	Red-violet
4760	🟪	EE82EE	Violet
4800	🟪	5D3694	Blue violet
4930	🟦	0000FF	Blue
5020	⬛	008080	Blue-green

Now here you see a color chart you know depending on here you know here you have the oxide thickness in angstrom, and here you have you know different colors that are shown, and for each color there is a color code associated, and here you know you have this is the description of what color that you see. So typically you know in oxidation wafer take out of the oxidation furnace and you can have a look there will be a color chart available depending on you know how we can judge the color you can predict the thickness of the oxidation layer okay.

So as you can see in the table for example you know take out the wafer from the oxidation furnace, and you find that the surface looks blue okay, so if the surface looks blue you know you can say that the oxidation thickness is about 3100 angstrom. And for example if the surface is looking brown you can say that the thickness is 750 angstrom, so this is an approximate but it is a quick approach to measure the oxidation thickness okay.

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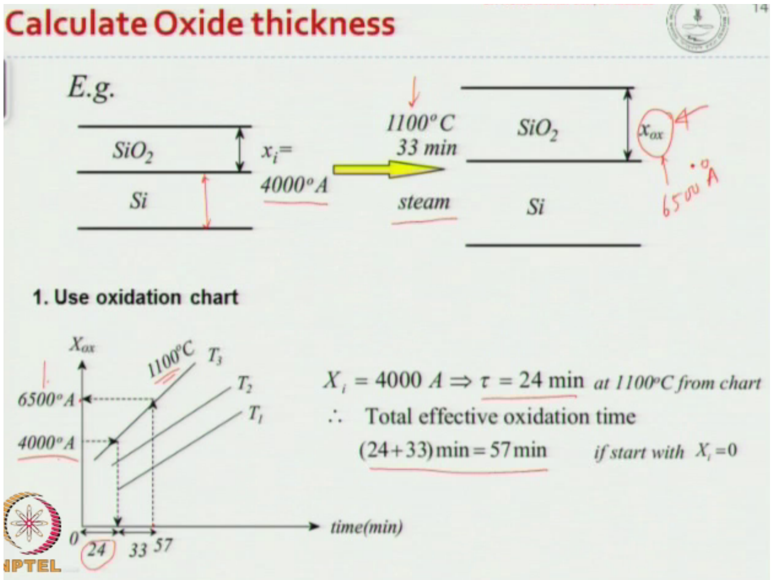

Calculate Oxide thickness

E.g.

1. Use oxidation chart

$X_i = 4000\ A \Rightarrow \tau = 24\ \text{min}$ at 1100°C from chart

$\therefore$ Total effective oxidation time

$(24+33)\,\text{min} = 57\,\text{min}$ if start with $X_i = 0$

Now here we take an example of how to predict the thickness of silicon dioxide layer, as you can see you know here we have a silicon substrate, and on the silicon substrate initially we have an existing silicon dioxide layer which is 4000 angstrom, and we put this pre-oxidized silicon wafer for steam oxidation or wet oxidation in a furnace at 1100 degree centigrade for 33 minute, and we get some oxide thickness.

And we are going to predict what is going to be the thickness of the oxidation layer after 33 minutes. So there are 2 approaches to do that, one is there are oxidation charts available, second approach is to use the equation that using the deal-grove model okay.

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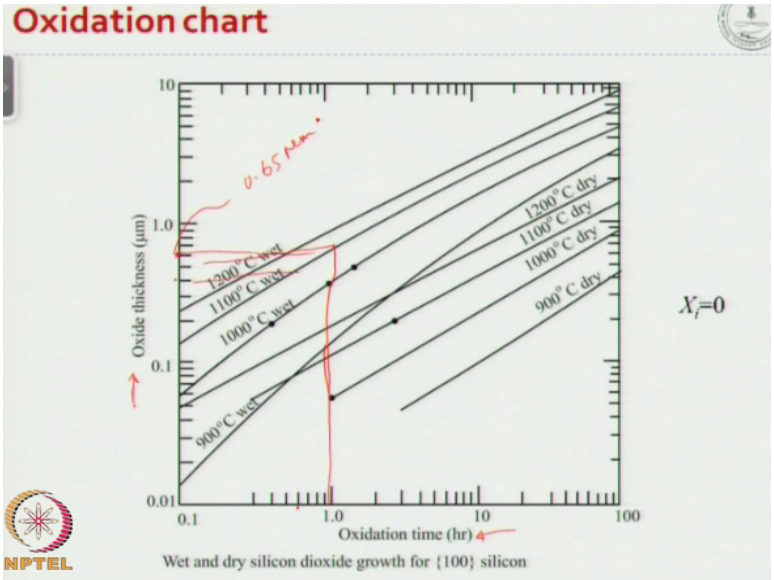

Oxidation chart

Wet and dry silicon dioxide growth for {100} silicon

$X_i = 0$

Now if you use oxidation chart which is here that you see, and this chart is valid for Xi=0 that means there is no existing oxidized layer on the surface, and based on that condition on the x-axis we have oxidation time in hour, and y-axis we have oxide thickness in micron. So in our problem we say that there is an existing oxide layer at 4000 angstrom, so for the initial oxide layer thickness if you look at the oxidation chart.

So this is an extract from the oxidation chart that I just showed you 4000 angstrom and temperature being 1100 degree centigrade okay, so this temperature is what we are going to use for the existing oxide layer thickness, but for the existing oxide layer thickness if that were grown at 1100 degree centigrade assuming that it was grown at 1100 degree centigrade, what would have been the time, so the temperature is 1100 degrees centigrade thickness is 4000 angstrom.

So we can say that on the x-axis the time is going to be 24 minute. So similar thing that you can observe in the chat, so if you say that you know your oxide thickness is about 0.4 micron, so this is 0.1 this is about 0.4 and 1100 degree if you draw a horizontal line here, and you draw a vertical line is going to intersect at the 0.4 hour okay so somewhere here okay, so 0.4 hour so that will be about 24 minute.

So you get the initial time assuming that the temperature was 1100 degree centigrade would be 24 minute, now you are oxidizing it for additional 33 minutes, so the total time that you are giving is 57 minute. Now if you again go to the oxidation chart for 57 minutes 1100 degree centigrade you can draw a horizontal line and this value you can read from the table, so that will be about 6500 angstrom, so the final thickness of the oxidation layer would be 6500 angstrom okay.

So that is something that we can also see from the oxidation table that we have here, so we found out that the time is about 0.5 sorry 57 minute, so it is about you know 0.95 hour, so if you draw a vertical line somewhere here and to the 1100 degree centigrade, and you draw a horizontal line from there so you will get about 0.65 so here this value you will read it as 0.65 micron okay.

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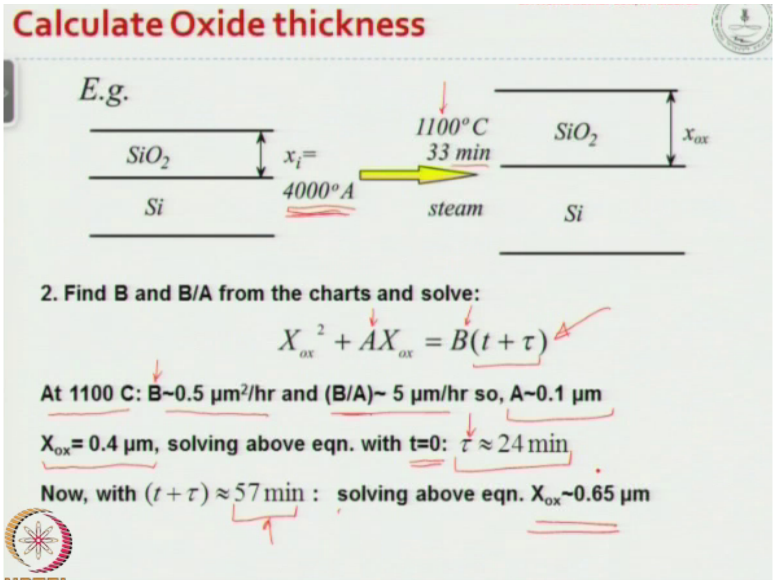

Calculate Oxide thickness

2. Find B and B/A from the charts and solve:

$$X_{ox}^{2} + AX_{ox} = B(t+\tau)$$

At 1100 C: B~0.5 µm²/hr and (B/A)~ 5 µm/hr so, A~0.1 µm

X_{ox}= 0.4 µm, solving above eqn. with t=0: $\tau \approx 24\,\text{min}$

Now, with $(t+\tau) \approx 57\,\text{min}$ **: solving above eqn. X_{ox}~0.65 µm**

Now so that is one approach, the second approach would be to you know predict the thickness from the deal-grove model, so you have this equation okay. Now at 1100 degree centigrade you can also there are tables available to give you the values of B and the ratio of B/A, so 2 such tables I will show you here.

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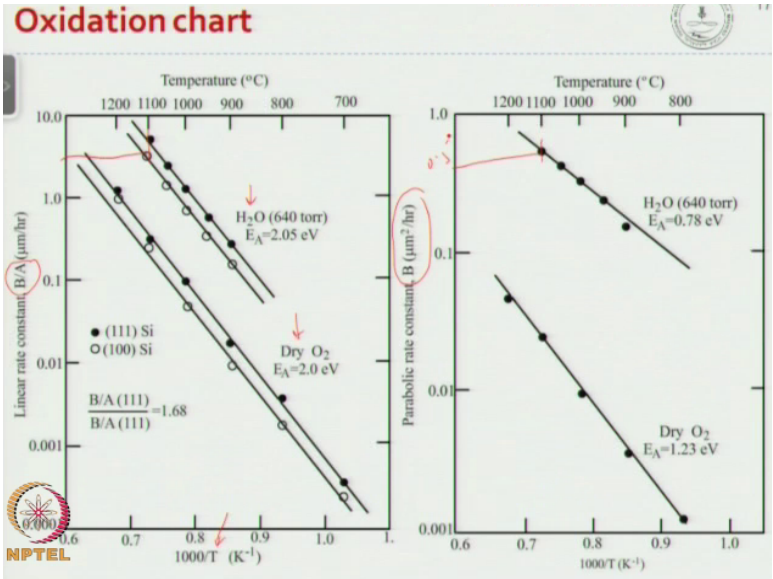
Oxidation chart



So depending on you know the crystal silicon here in this case we are talking about 1 0 0 wafer, so depending on the temperature okay depending on the temperature and what type of oxidation you are talking about either you are talking about wet oxidation or dry oxidation, you would have the value for B/A and the unit is micrometer micron per hour, and you have a value for B which is micrometer square/hour micron square/hour.

So you can find what is the value of A right, so in this case for 1100 degree centigrade if you, you know draw a line there okay and onto the 1 0 0 silicon wafer and draw a horizontal line there, so you will get about 5 micron per hour is the B/A. And similarly if you do that to find the value of B you draw a vertical line there, and then you draw a horizontal line there let us say this is about 0.5 or 0.6.

So from these values you can using these 2 values you can apply to this equation, so B will be let us say 0.5 microns square per hour and B/A is 5 micron per hour, so from there you can calculate what is A? A is 0.1 micron. Now knowing the value of A and B the initial oxide layer thickness is 0.4 micron that is given, and so to calculate the time so for you know for pre-oxidized wafer t=0 okay, so we have not started oxide you know doing the oxidation process.

So in that case you have to find what is the time scale that you need to do it the to grow this oxidation layer, so you can solve this with the t=0 in this equation, so you can find tau is about 24 minute. Now we are putting again 33 minute you are doing oxidation for 33 minutes, so t+tau will be 57 minute, now if you go back to the same equation and you put t+tau as 57 minute, and plug in the values for B and A.

Because they are only dependent on the temperature and the wafer and the dry or steam oxidation, so they are not changing so you can use the same values of B and A, now if you use t+tau as 57 minute and you solve that equation, you can find the final oxidation layer is about 0.65 micron which is 6500 angstrom. So there are 2 approaches that you can use to predict the oxide layer thickness, one is by using the oxidation chart. The second one is by using the chart where you can find the value of B and B/A, and use deal-grove model okay.

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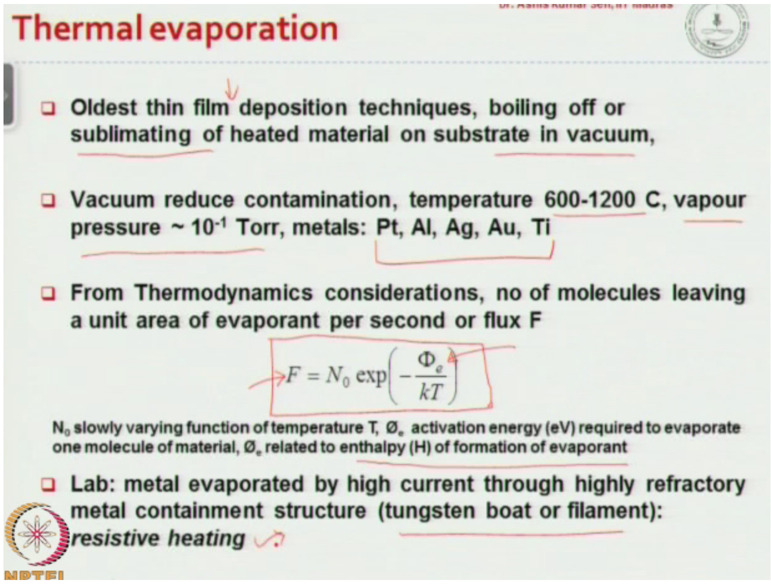

Thermal evaporation

- Oldest thin film deposition techniques, boiling off or sublimating of heated material on substrate in vacuum,
- Vacuum reduce contamination, temperature 600-1200 C, vapour pressure ~ 10^{-1} Torr, metals: Pt, Al, Ag, Au, Ti
- From Thermodynamics considerations, no of molecules leaving a unit area of evaporant per second or flux F

$$\boxed{F = N_0 \exp\left(-\frac{\Phi_e}{kT}\right)}$$

N_0 slowly varying function of temperature T, $Ø_e$ activation energy (eV) required to evaporate one molecule of material, $Ø_e$ related to enthalpy (H) of formation of evaporant

- Lab: metal evaporated by high current through highly refractory metal containment structure (tungsten boat or filament): *resistive heating*

Now let us look at thermal evaporation okay, so many times you need to metalize the surface of a substrate with some electrode patterns to build microfluidic devices or other micro devices. The one of the you know widely used technique for metalized wafer is thermal evaporation, it is one of the old technique that has been used in semiconductor industry, and it is also used to fabricate micro devices okay.

So you know thermal evaporation as I said it is the oldest thin film deposition technique, and which relies on you know boiling of a sublimating of heated material, if you heat solid at certain condition at certain temperature at certain way it will directly go and become wafer okay, instead of going to liquid and going to gas it will directly become wafer, so that is called so the sublimation process.

And it is possible to achieve you know boiling of sublimation of you know metals easily if you create vacuum condition okay. So typically in a thermal evaporation furnace the temperature that you required is 600 to 1200 degree centigrade, and the vapour pressure would be around 0.1 Torr, and these are some of the metals that are typically used for thermal evaporation platinum, aluminum, silver, gold and titanium.

Now from thermodynamics the number of molecules that will leave a certain area of the evaporant per second is given by the flux okay, so you know the flux is representative of how many molecules are leaving a particular target and going and falling on to the substrate. So F=N0*exponential-phi/kT, where N0 is a slowly varying function of temperature, and phi is activation energy okay that is intrinsic of the metal that we are trying to evaporate.

And so it is related to the enthalpy of formation of a evaporant, T is the temperature and k is the Boltzmann constant okay. So typically in labs metal is evaporated bypassing high current through a highly refractive metal containment structure typically a tungsten boat or a filament, and this process is called resistive heating.

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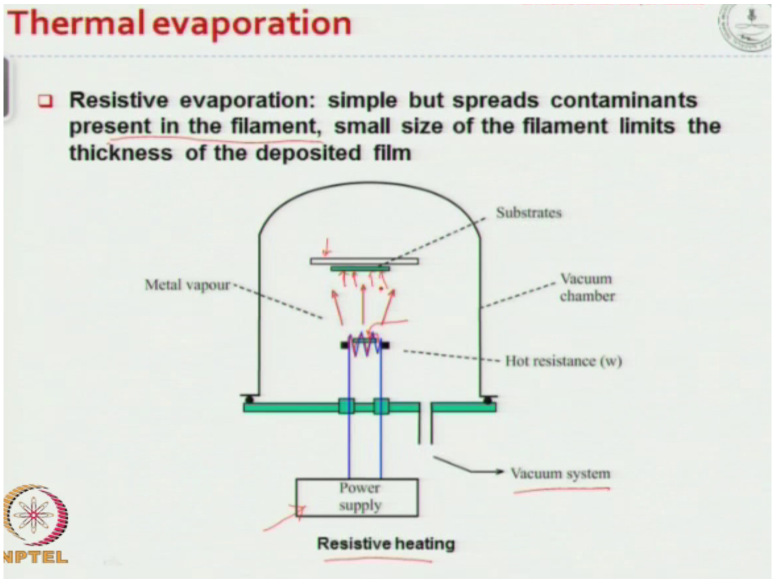

Thermal evaporation

- Resistive evaporation: simple but spreads contaminants present in the filament, small size of the filament limits the thickness of the deposited film

Resistive heating

So as you see here the metal that we want to evaporate will be present here, so this is the metal that we are trying to evaporate, and you have a highly resistance wire here, and you apply a high voltage using a power supply, and when you do so this metal will evaporate okay, and you know everything is enclosed in a chamber connected to a vacuum system, and here you have a platform that will support the substrate on which you are trying to evaporate and deposit this metal.

So the metal evaporates and coats the surface of the wafer here, so the metal will evaporate and in wafer form it will come and get deposited on to the top surface of the substrate. So you know the resistive evaporation process using you know resistive heating is relatively simple as compared to other techniques that we will see. But one downside of this is, it would spread the contaminants that are present in the filament.

Since the metal will evaporate and it may interfere with the filament itself, while it evaporates that may bring in contaminants that are already present in the filament okay, so that is one issue that we see in the thermal evaporation. And the second issue is the filament that we typically used are smaller in size, so the resistance so that the resistance is higher, but this small size of the filament would limit the thickness of the film that we can bring in on the surface of the substrate okay.

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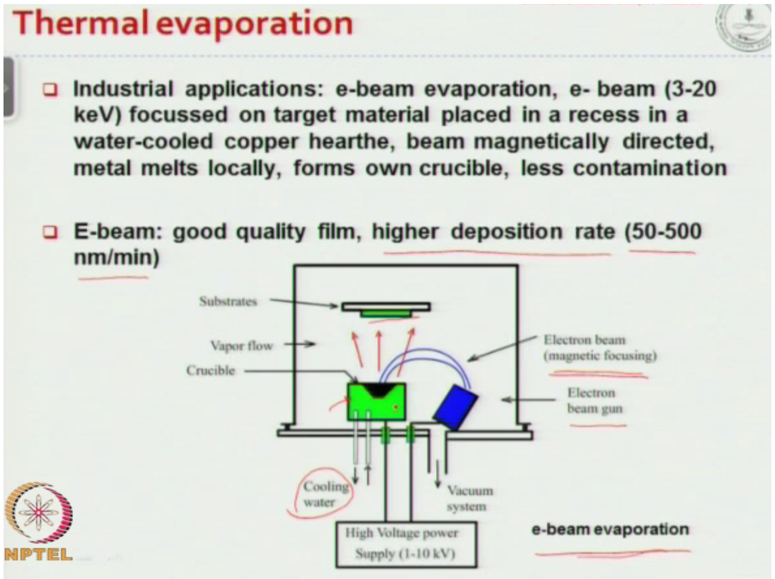

Thermal evaporation

- Industrial applications: e-beam evaporation, e- beam (3-20 keV) focussed on target material placed in a recess in a water-cooled copper hearthe, beam magnetically directed, metal melts locally, forms own crucible, less contamination
- E-beam: good quality film, higher deposition rate (50-500 nm/min)

e-beam evaporation

So the thermal evaporation is used in the lab setting, and whereas an industrial application what we use is called E-beam evaporation okay, so in E-beam evaporation if you look at the set up here typically we would have the metal that we want to evaporate or deposit on to a substrate in a crucible okay, so this is the crucible made out of you know ceramic materials, and we would be constantly calling this crucible.

And here we would have a high voltage power supply connecting to the crucible as well as to an electron beam gun, so high energy electron beam gun will be generated using high power high voltage, and these electron beams can be you know projected directed towards the metal present on the crucible using a magnetic field, so that is called magnetic focusing. So when these high energetic electrons will fall on to the metal, the metal will get vaporized and it will coat on the substrate so that is the principle.

And the electron beam based thermal evaporation it results in good quality film, because we are not talking about any filament here, the metal just evaporates, and in fact the metal itself part of the metal where the electron beam is coming and heating the metal there itself it evaporates and the other part of the metal form the crucible, so there is no contaminant that is present in this E-beam evaporation method.

And the other advantage is that the deposition rate of E-beam evaporation is between 50 to 500 nanometer per minute which is you know higher as compared to thermal evaporation. But the downside of evaporation is the setup is expensive, and you would need you know sophisticated arrangement of you know a magnetic focusing of the electron beam on to the metal.

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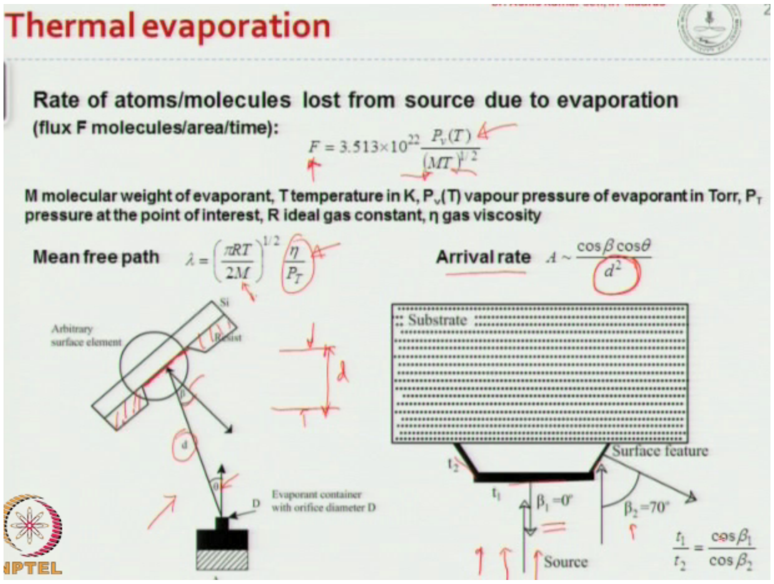

Thermal evaporation

Rate of atoms/molecules lost from source due to evaporation

(flux F molecules/area/time):

$$F = 3.513\times10^{22}\frac{P_v(T)}{(MT)^{1/2}}$$

M molecular weight of evaporant, T temperature in K, $P_v(T)$ vapour pressure of evaporant in Torr, P_T pressure at the point of interest, R ideal gas constant, η gas viscosity

Mean free path $\lambda = \left(\frac{\pi RT}{2M}\right)^{1/2}\frac{\eta}{P_T}$

Arrival rate $A \sim \frac{\cos\beta\cos\theta}{d^2}$

$$\frac{t_1}{t_2} = \frac{\cos\beta_1}{\cos\beta_2}$$

So if you look at the thermal evaporation when we look at how the process works, so the rate of at which the atoms or the molecules are you know lost from the source or the metal source due to evaporation, the flux F is represented in this way, which is dependent on the vapour pressure of the evaporant Pv T, and it is also dependent on the temperature okay. So these are 2 parameters which affect the flux, the rate at which the molecules or the atoms of the metal are lost from the source and they fall onto the substrate.

It also depends on the molecular weight of the evaporant okay, so the flux is directly proportional to the vapour pressure and inversely proportional to the square root of the molecular weight and the temperature. We can define a mean free path of these atoms how they are removed and how they go and fall onto the substrate, the mean free path is expressed in this way, it is dependent on the gas constant, temperature, molecular weight, the viscosity of the gas and partial pressure.

Now let us say in this example if you see here let us say this is the surface of the substrate, and here you have photoresist patterns, so these areas you do not want to evaporate and you want to put the metal evaporated metal on these areas, and here is the source okay and they are at an angle okay. Now how do we determine the arrival rate okay, the evaporated metal coming out of the source and reaching here, the arrival rate will depend on the angles okay.

The angle between the vertical to the line connecting the source and the substrate okay, so it would depend on the cosine of that angle cos theta, and would also depend on the angle between the connecting line and normal to the wafer beta cosine of beta, so the arrival rate is proportional to cos beta and cos theta, and inversely proportional to the square of the distance between the 2 the source and the substrate.

And imagine if they are facing each other like parallel, where this is the source and this is the substrate beta and theta will be 0, so the arrival rate will be inversely proportional to the square of the separation distance. Here, you see you know the source is somewhere here the source the metals are directed towards the substrate in this way, and on the surface you know the surface have different topology okay.

So one surface is normal to the source that you know source of ions that are coming, but it also has other surfaces which are at an angle okay, let us say beta 2 is an angle of that those 2 inclined surfaces, and for this surface the beta 1 is 0. So the thickness of the metal layer evaporated metal layer that we end up with t1/t2 will be cos beta 1/cos beta 2 okay, so the thickness depends on the orientation of the substrate with respect to the metal source okay. So with that let us stop here.