EE669: VLSI Technology

Dopant Diffusion in Silicon

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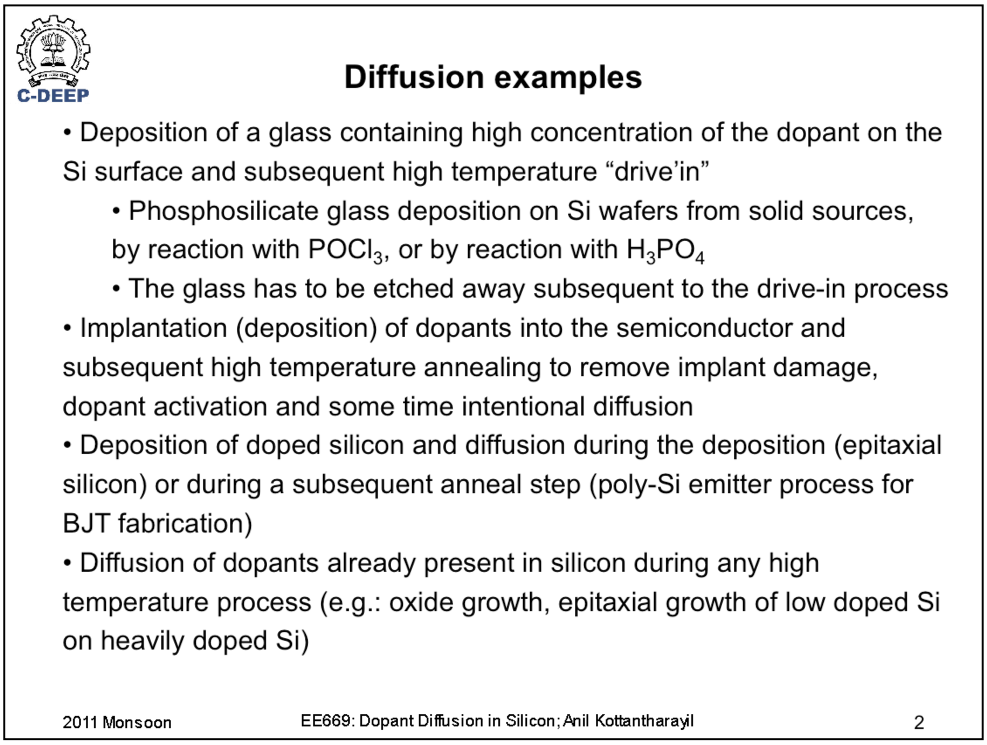
An important property of semiconductors is that the conductivity can be varied by several orders of magnitude by doping the semiconductor by small amounts of dopants. There are two types of charge carriers in semiconductors and the relative concentrations of these carriers under thermal equilibrium can be controlled by using appropriate dopants. Most of the semiconductor devices, especially in silicon, depends on the formation of junctions of differently doped, both in type and concentration, regions in the semiconductor.

We had seen in previous lectures that the dopant should be on a lattice site for it to be electrically active.

Dopants can be introduced into silicon by diffusion or ion implantation processes. Differently doped regions in silicon can be fabricated by epitaxial growth of films of differing doping types and concentrations.

Diffusion is the process by which dopants migrate from a region of higher concentration of the diffusing species to a region of lower concentration. Typical diffusion process may involve deposition of a film of a material which has a very high concentration of the dopant and subsequent high temperature treatment to transfer the dopants into the semiconductor or to redistribute the dopants within the semiconductor.



Diffusion examples

- Deposition of a glass containing high concentration of the dopant on the Si surface and subsequent high temperature “drive’in”
  - Phosphosilicate glass deposition on Si wafers from solid sources, by reaction with $POCl_3$, or by reaction with H_3PO_4
  - The glass has to be etched away subsequent to the drive-in process
- Implantation (deposition) of dopants into the semiconductor and subsequent high temperature annealing to remove implant damage, dopant activation and some time intentional diffusion
- Deposition of doped silicon and diffusion during the deposition (epitaxial silicon) or during a subsequent anneal step (poly-Si emitter process for BJT fabrication)
- Diffusion of dopants already present in silicon during any high temperature process (e.g.: oxide growth, epitaxial growth of low doped Si on heavily doped Si)

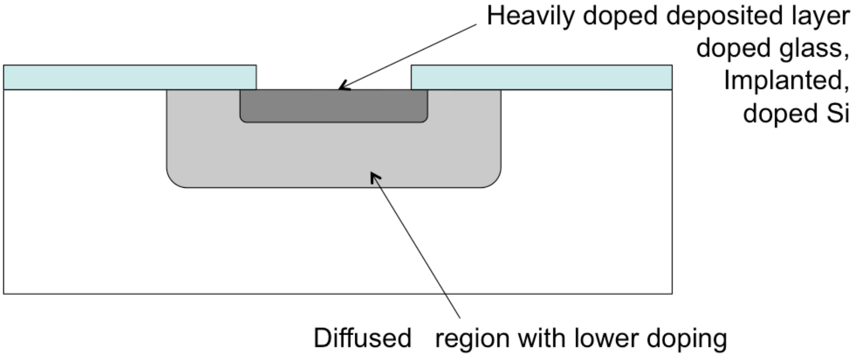
For VLSI applications where the dopant concentration and location have to be controlled precisely, ion implantation is the method of choice. However the implanted ions would be randomly placed in the semiconductor. For high dose implants, the crystal structure of the semiconductor can also be damaged in the region where the dopants are implanted.

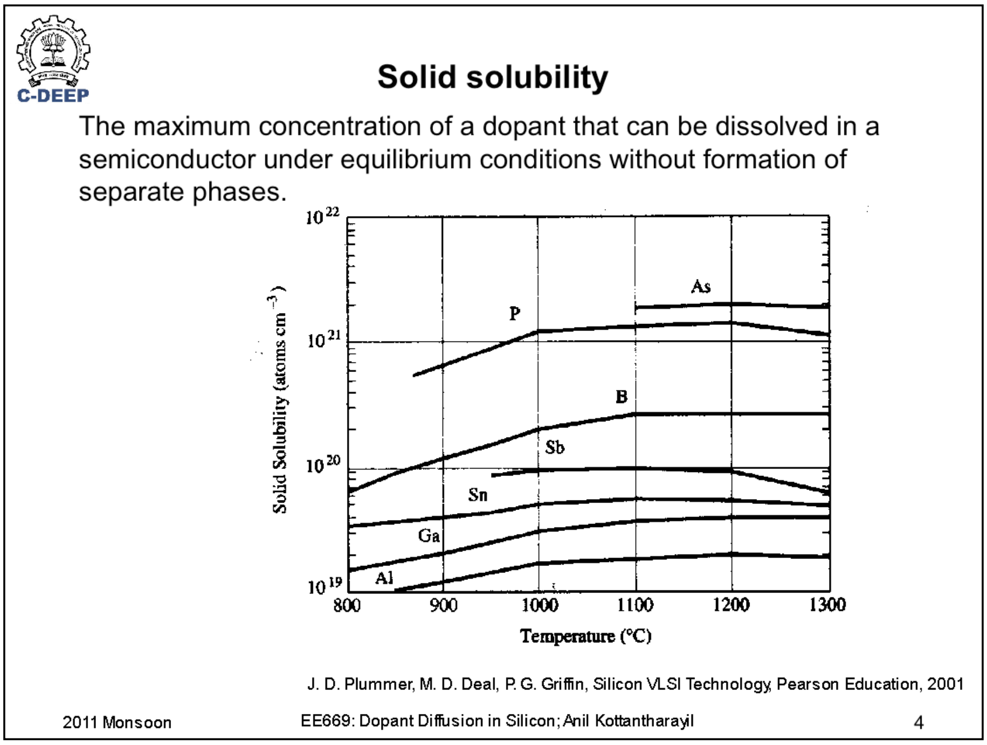
For modern VLSI device applications, ultra shallow junctions are required. The trend now is to do the anneal just for activation of the dopants and to remove implant damage without causing any diffusion. Diffusion in this case could increase junction depth which is undesirable in such applications. Junction depths we discuss are in the range of 20 nm.

Ion implantation is an expensive process. Solar cell manufacturing (presently) uses cheaper techniques for junction formation. Both $POCl_3$ and phosphoric acid based diffusion processes are widely used for commercial silicon solar cells. In these processes, a glass containing large concentration of phosphorous is deposited on the wafer surface. This is subsequently diffused into the substrate by high temperature annealing. Subsequent to this the glass is etched away in a HF solution.

In short, diffusion of dopants is a key process for fabrication of all kinds of devices in silicon, except in MEMS and optical applications. Dopant diffusion can be desirable in some cases and undesirable in some other cases.

Generalized diffusion process





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Solid solubility

The maximum concentration of a dopant that can be dissolved in a semiconductor under equilibrium conditions without formation of separate phases.

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

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Solid solubility is the maximum concentration that can be dissolved at a given temperature. However not all of the dopants thus dissolved need be in substitutional sites and hence electrically active. The highest solid solubility among dopants in Si is achieved in the case of Arsenic as the misfit factor of As in Si lattice is zero. The highest chemically dissolvable concentration is 2 x 10^{21} cm^{-3} whereas the highest concentration that can be electrically activated by conventional near equilibrium processes is about one order of magnitude smaller.

An important consideration here is that the solid solubility at silicon processing temperatures (~ 1000C) is significantly higher than the device operating temperatures (room temperature to 100C). So the excess dopants may form neutral complexes which are electrically inactive as the sample is cooled. However if the cooling carried out rapidly, it is possible to retain high concentrations of electrically active dopants. Any subsequent high temperature anneals are likely to relax such a meta stable state, reducing the active concentration. Such situations may arise in milli second annealing processes like laser anneal.

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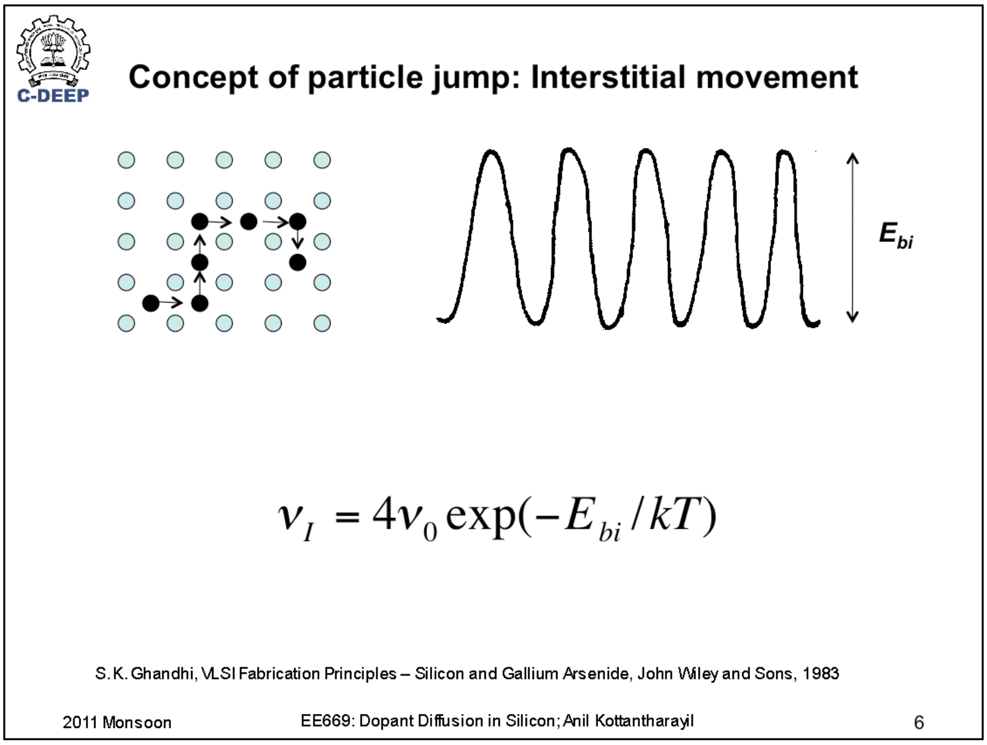
Diffusion process

- We had previous seen how the diffusion process proceeds when we discussed oxidation
- Diffusion is a consequence of random motion of particles in a system
- In a solid, however the lattice structure and defects can modify the details of the description

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001



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Concept of particle jump: Interstitial movement

$$\nu_I = 4\nu_0 \exp(-E_{bi}/kT)$$

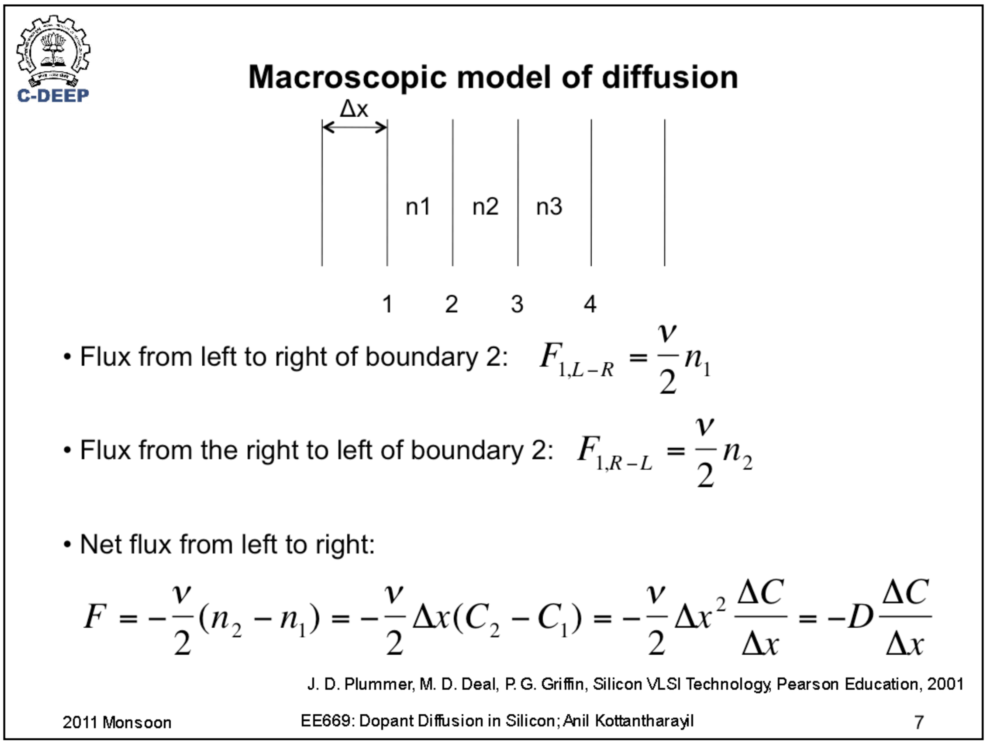
S.K. Ghandhi, VLSI Fabrication Principles – Silicon and Gallium Arsenide, John Wiley and Sons, 1983

Let us consider the movement of interstitial atoms in a diamond lattice. The perfect diamond lattice has 8 interstitial sites. One interstitial site has 4 interstitial sites in the immediate neighborhood. An atom in interstitial site in an otherwise perfect lattice can jump to any one of the 4 neighboring interstitial sites.

When the interstitial atom jumps from one site to the other, it has jump through a constriction that is present between lattice atoms. This can be thought of an energy barrier that the interstitial atom must overcome for a jump. We can also think of this in a different way by considering lattice vibrations. During the random lattice vibrations, there are chances that the constriction between lattice atoms would reduce. Higher the temperature (higher the thermal energy), higher the probability. As the constriction reduces, higher is the jump probability.

v_I is the jump frequency, v_0 is the frequency of lattice vibrations, E_{bi} is the energy barrier.

Similarly atoms in substitutional sites can jump to vacancies or the jump can be mediated by vacancies. It is also possible for Frenkel pairs (vacancy – interstitial pair) to be involved in such jumps.



Macroscopic model of diffusion

- Flux from left to right of boundary 2: $F_{1,L-R} = \frac{\nu}{2} n_1$
- Flux from the right to left of boundary 2: $F_{1,R-L} = \frac{\nu}{2} n_2$
- Net flux from left to right:

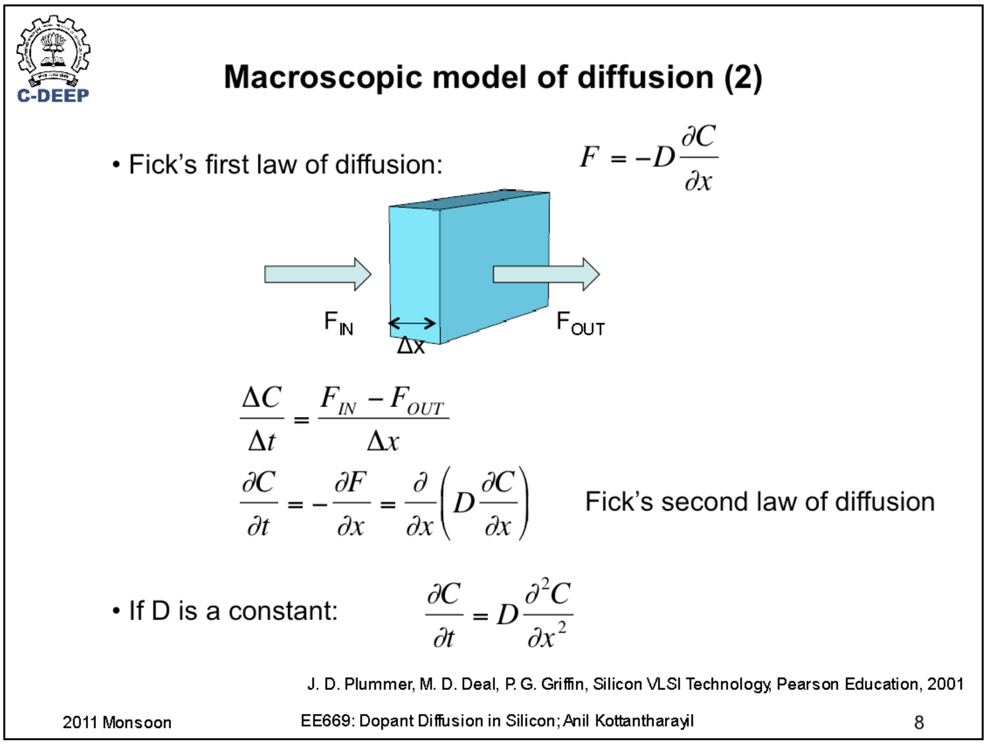
$$F = -\frac{\nu}{2}(n_2 - n_1) = -\frac{\nu}{2}\Delta x (C_2 - C_1) = -\frac{\nu}{2}\Delta x^2 \frac{\Delta C}{\Delta x} = -D\frac{\Delta C}{\Delta x}$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

Let us assume that the crystal can be split up into parallel slices bounded by 1, 2, 3, 4,…. separated by Δx. Let the areal density of dopant atoms in different slices be n_1, n_2, n_3, ….. The atoms from any slice can jump either left or right with equal probability.

The flux from the left to right can be evaluated as shown. The jump frequency is the net of all jump mechanisms.

In the limit Δx ➔ 0, this reduces to Fick's first law of diffusion. The derivation also shows a thermal activation for the diffusion constant.



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Macroscopic model of diffusion (2)

- Fick's first law of diffusion: $F = -D\frac{\partial C}{\partial x}$

$$\frac{\Delta C}{\Delta t} = \frac{F_{IN} - F_{OUT}}{\Delta x}$$

$$\frac{\partial C}{\partial t} = -\frac{\partial F}{\partial x} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$ Fick's second law of diffusion

- If D is a constant: $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$

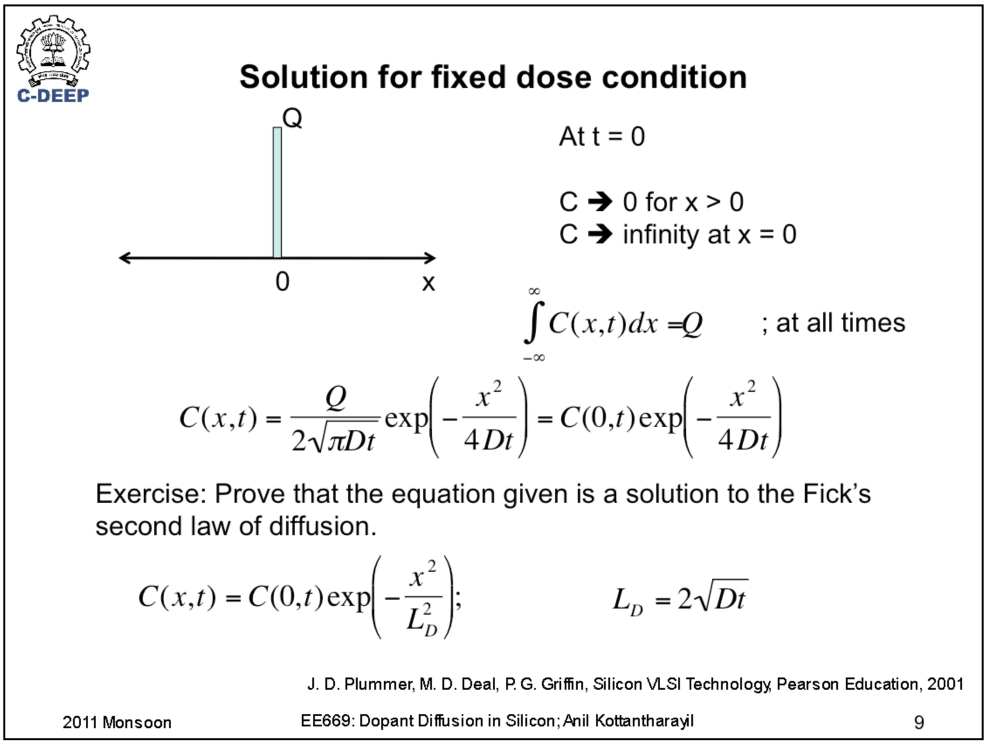
J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

The first law gives the flux as a function of concentration gradient. However in a diffusion problem we would be interested to know the distribution of dopants after carrying out the diffusion for some time. This can be obtained by solving the Fick's second law of diffusion.

The law of conservation of matter can be applied to the diffusion process to derive the Fick's second law of diffusion.

Consider an incremental volume of the crystal. We would consider one dimensional diffusion which can be easily generalized to 3D. The rate of build up of dopants in the volume with unity cross section would be equal to the difference in the fluxes that enter the volume from the left boundary and that goes out from the right boundary. The corresponding rate of build in concentration is given by the difference in flux divided by the thickness of the slice along the direction of diffusion.

In 3D the second law can be stated as follows: the rate of increase of concentration in an incremental volume is equal to the divergence of the dopant flux.



Solution for fixed dose condition

At t = 0

C ➔ 0 for x > 0
C ➔ infinity at x = 0

$$\int_{-\infty}^{\infty} C(x,t)\,dx = Q \qquad \text{; at all times}$$

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

Exercise: Prove that the equation given is a solution to the Fick’s second law of diffusion.

$$C(x,t) = C(0,t)\exp\left(-\frac{x^2}{L_D^2}\right); \qquad L_D = 2\sqrt{Dt}$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

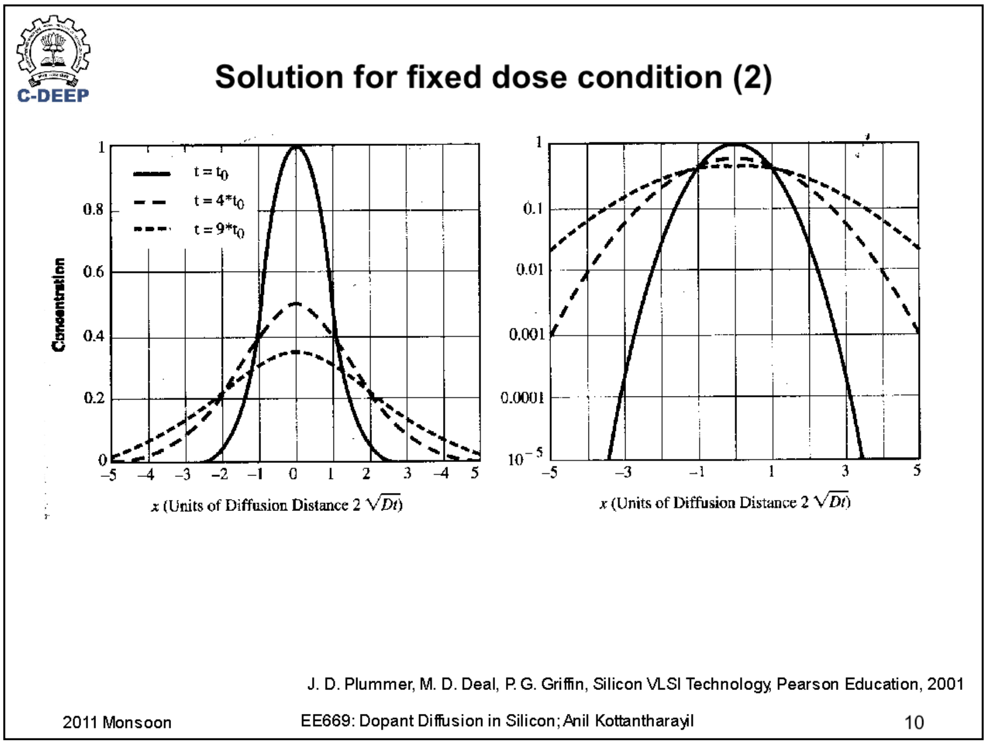
Suppose we place a fixed number of dopants in a narrow box shaped profile within an infinite piece of semiconductor. This can be achieved by low temperature molecular beam epitaxial (MBE) process as described in A. Stadler, et al., Solid-State Electronics, 44 (5), 2000, pp. 831-835.

The doping profile can be approximated by a delta function with an area of Q. The unit of Q is number of dopants per cm^2. Now the material is heated so that the dopants diffuse. The time evolution of the dopant profile can be calculated by solving the Fick’s second law of diffusion with the boundary conditions shown.

The solution is a Gaussian profile. The profile is also symmetric with respect to the origin.

A convenient “diffusion length” can be defined as shown. We would discuss the use of this concept soon.

We may also define the concept of “thermal budget” based on this solution. Thermal budget is a concept used for quick comparison of diffusion under two temperature conditions for different times. Dt is a measure of the thermal budget. D is a strong function of temperature. If Dt is maintained the same in two difference diffusion processes carried out at two different temperatures for two different times, then starting from the same initial profile, the diffused profiles would be identical. The two processes have same thermal budget.



Solution for fixed dose condition (2)

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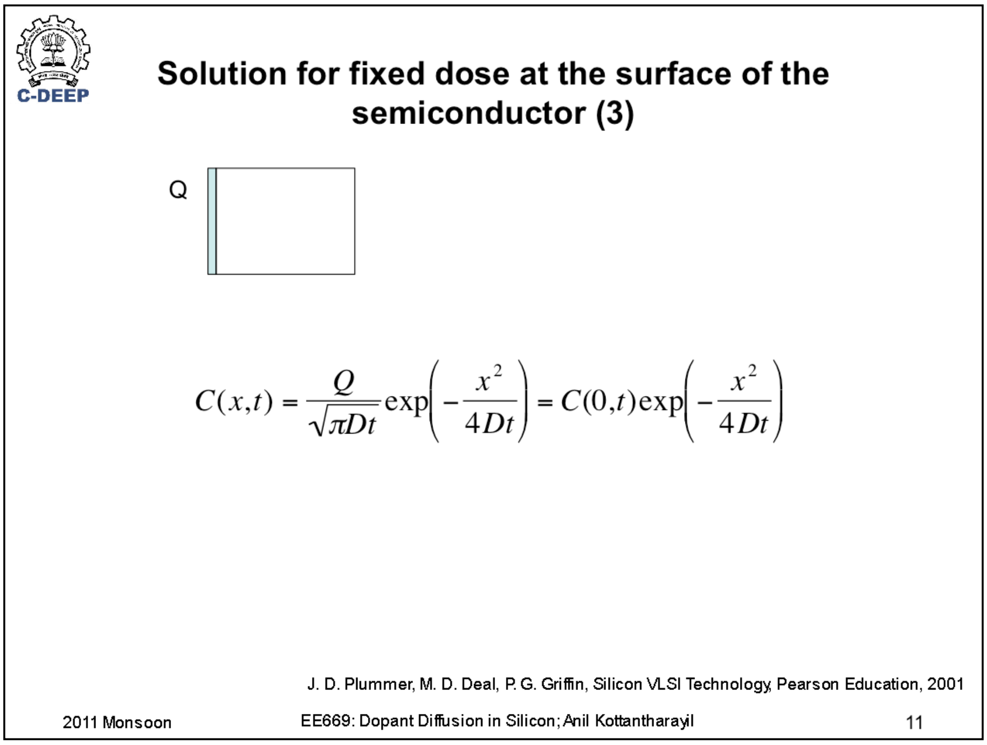
The normalized dopant profiles are shown on this slide. The peak concentration used for normalization is the concentration obtained after an initial time t_0. The peak concentration decrease by a factor 1/sqrt(t) with time.

The space coordinate is scaled to the diffusion length. The concentration at one diffusion length from the origin (the position of the peak) would be 1/e times the peak value at any time.

Even though the initial profile at t=o for which C (0,0) ➔ infinity is not shown, the profile evolution can be of practical interest where we start the diffusion with a fixed dose Gaussian profile also.



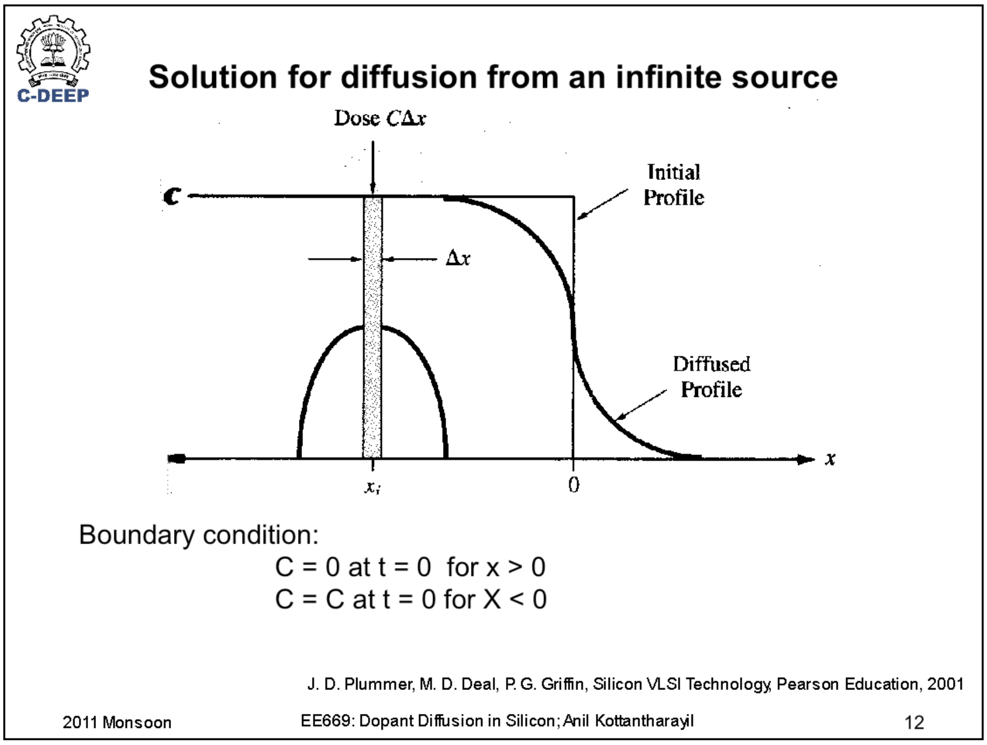
Solution for fixed dose at the surface of the semiconductor (3)

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

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

In this case a dopant source is deposited on the wafer surface as shown. Examples include poly-Si emitter in BJT fabrication, pre-deposition of doped glasses like phospho silicate glass and subsequent diffusion by drive-in anneal, low energy ion implantation on the surface, doped epitaxial layers on low doped substrates etc.

This case can be treated like in the previous discussion by observing that the Gaussian profile is symmetric about the point of the initial delta doping. However in this case the dose is half on the surface and half on the imaginary material on the left of the left boundary shown.



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Solution for diffusion from an infinite source

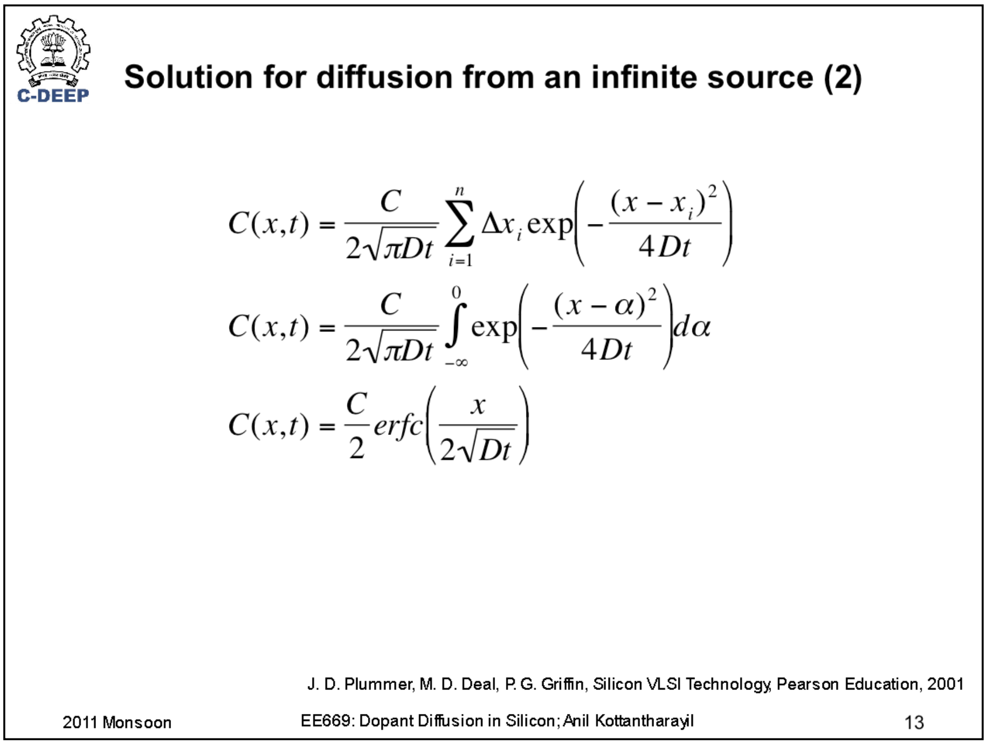
Boundary condition:

C = 0 at t = 0 for x > 0
C = C at t = 0 for X < 0

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

One notable example is the diffusion from an epitaxial layer during the deposition of the epitaxial layer. The epitaxial process is designed such that the concentration of dopants in the deposited layer does not vary with time. However at the interface between the epitaxial layer and the low doped substrate significant diffusion can happen leading to a gradual profile at the interface.

The problem can be solved by slicing the initial box profile into equal interval Δx. Then the diffusion from each slice would develop into Gaussian profiles. The solution in the present case can be obtained by adding up all the resultant Gaussian profiles.



Solution for diffusion from an infinite source (2)

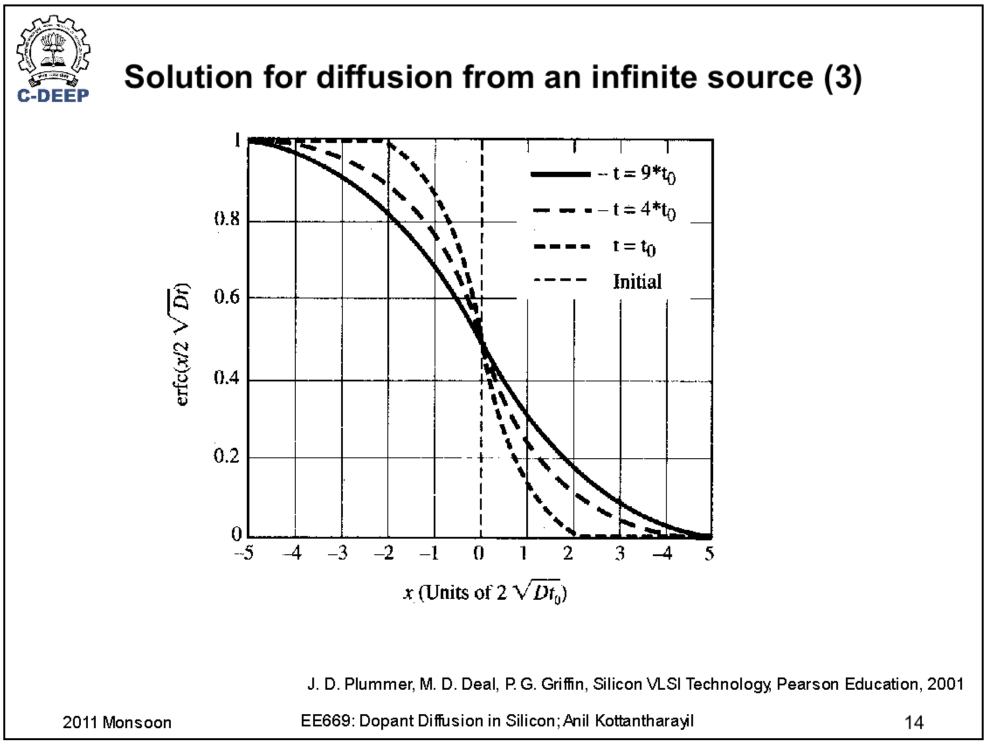
$$C(x,t) = \frac{C}{2\sqrt{\pi D t}} \sum_{i=1}^{n} \Delta x_i \exp\left(-\frac{(x - x_i)^2}{4Dt} \right)$$

$$C(x,t) = \frac{C}{2\sqrt{\pi D t}} \int_{-\infty}^{0} \exp\left(-\frac{(x - \alpha)^2}{4Dt} \right) d\alpha$$

$$C(x,t) = \frac{C}{2} erfc\left(\frac{x}{2\sqrt{Dt}} \right)$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

In the limit, the sum can be replaced by the integral. erfc is the complementary error function and the values of this function are available in tabular form.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Solution for diffusion from an infinite source (3)

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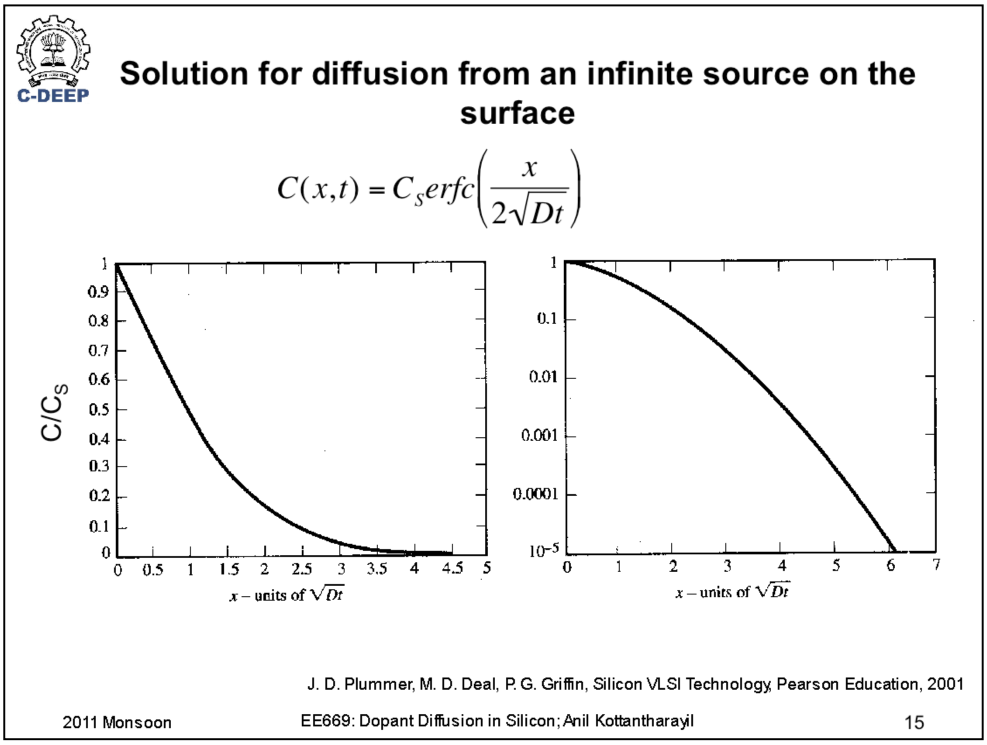
The figure shows the dopant profile as a function of the “diffusion length”. A key point to note is that the dopant concentration at the interface (x = 0) is half of the original concentration for all times.

The solution on either side of x = 0 are sort of symmetric. In this respect the profile is similar to the Fermi – Dirac function about the fermi level. This symmetry can be extended to obtain the diffusion profile on the surface a semiconductor to which dopants are diffused from a gaseous source in a furnace.



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Solution for diffusion from an infinite source on the surface

$$C(x,t) = C_S erfc\left(\frac{x}{2\sqrt{Dt}}\right)$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

The solution would be an error function solution with the surface concentration being constant at all times.

Analytical solutions for more complex cases of diffusion are not possible. Further we have not accounted for several other factors that can influence diffusion process. The analysis we have discussed so far could be a good approximation when the dopant concentrations involved are low so that at the processing temperature the semiconductor can be considered intrinsic.

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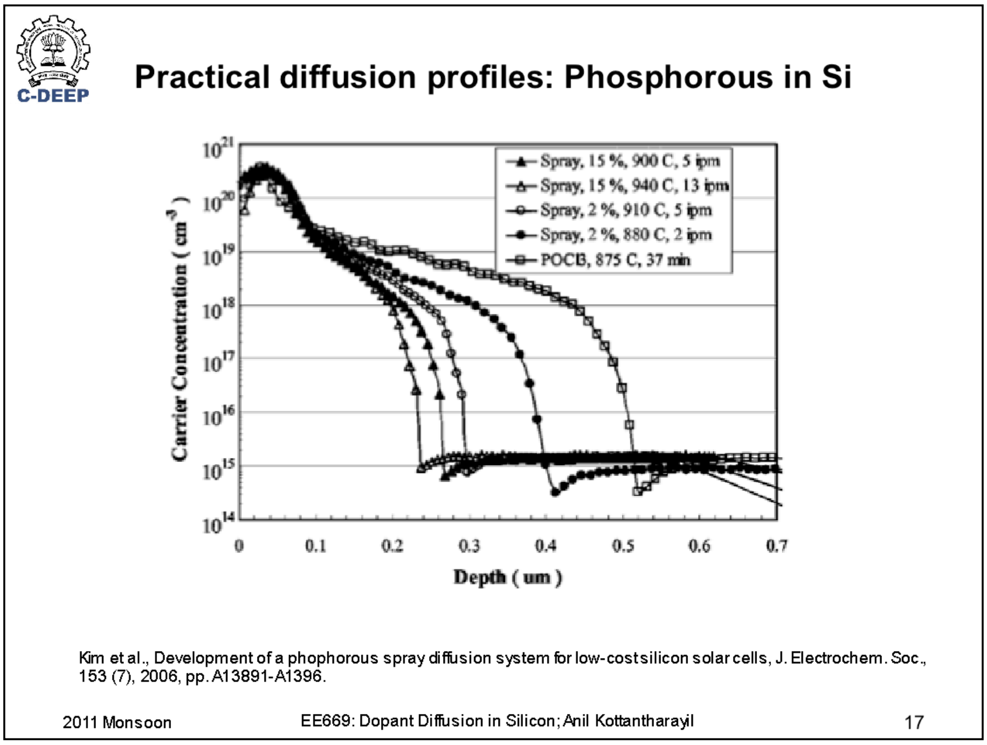
Intrinsic diffusivities in Si

$$D = D_0 \exp\left(-\frac{E_A}{kT}\right)$$

	Si	B	In	As	Sb	P	Units
D_0	560	1.0	1.2	9.17	4.58	4.7	$cm^2\ s^{-1}$
E_A	4.76	3.5	3.5	3.99	3.88	3.68	eV

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

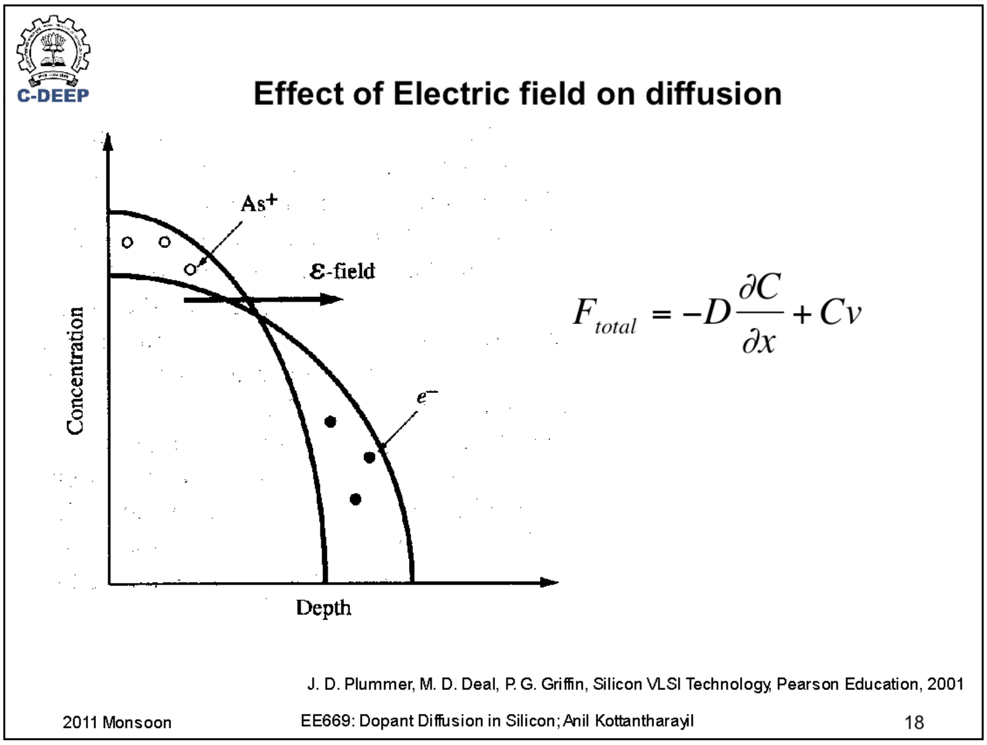


Practical diffusion profiles: Phosphorous in Si

Kim et al., Development of a phophorous spray diffusion system for low-cost silicon solar cells, J. Electrochem. Soc., 153 (7), 2006, pp. A13891-A1396.

This slide shows diffusion profile for phosphorous diffusion in Si. The sources in this case are $POCl_3$ and sprayed H_3PO_4. Both these processes are used in commercial silicon solar cell production. These processes involve a pre-deposition of P_2O_5 and subsequent drive-in in an oxygen ambient. Based on the previous discussions we may expect a Gaussian profile. However the experimentally obtained doping profile is not Gaussian.

This implies that the model we have described so far is inadequate for describing phosphorous diffusion in Si. This is also true for other dopants. We would consider other mechanisms that can influence diffusion on subsequent slides.



Effect of Electric field on diffusion

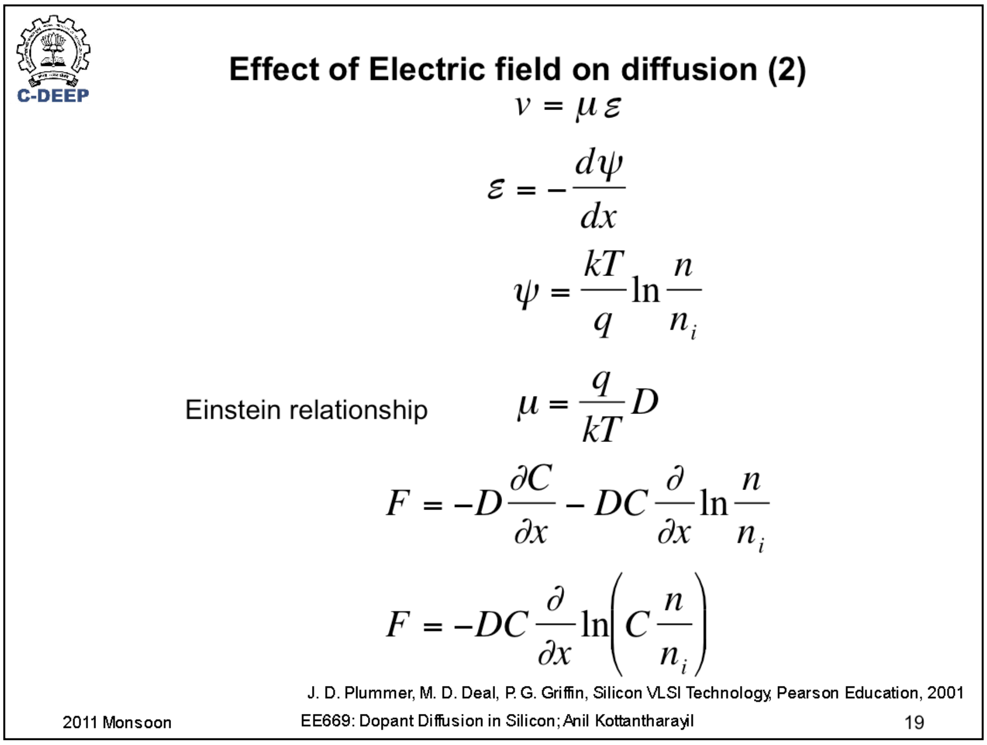
$$F_{total} = -D\frac{\partial C}{\partial x} + Cv$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

Presence of electric field can modify the dopant diffusion process in the following way. When a high concentration of the dopants are present and for temperatures below the intrinsic temperature, the charges in the material would be decided by the dopant concentration. Let us consider an n-type doped semiconductor with the doping profile shown. All the dopants would be ionized. Also the free electron concentration would be higher where the doping concentration is higher. Both the electrons and the positive ions would diffuse as shown. However the electrons being lighter than ions, can diffuse faster. The resulting charge separation would set up an electric field that would slow down the electrons and speed up the ions. This would result in faster diffusion.

The Fick's first law can be modified to include this additional dopant flux due to the electric field. v is the drift velocity.

Fick's second law can be modified accordingly by substituting for the flux.



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Effect of Electric field on diffusion (2)

$$v = \mu \varepsilon$$

$$\varepsilon = -\frac{d\psi}{dx}$$

$$\psi = \frac{kT}{q} \ln \frac{n}{n_i}$$

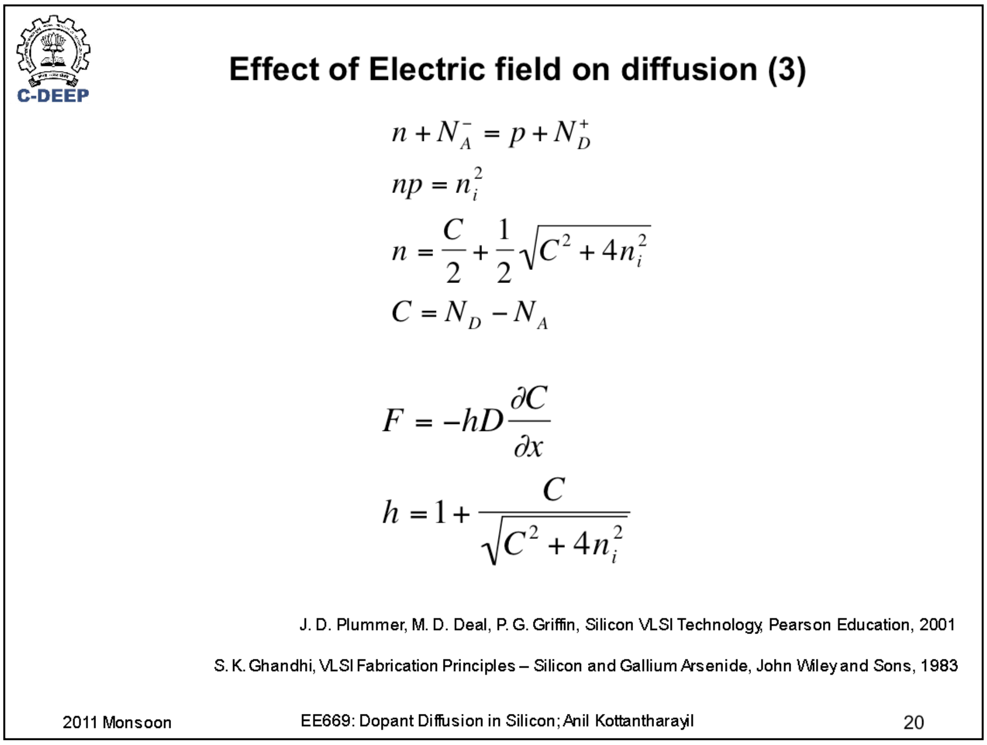
Einstein relationship $$\mu = \frac{q}{kT} D$$

$$F = -D \frac{\partial C}{\partial x} - DC \frac{\partial}{\partial x} \ln \frac{n}{n_i}$$

$$F = -DC \frac{\partial}{\partial x} \ln \left(C \frac{n}{n_i} \right)$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

Drift velocity is related to the electric field through mobility.



Effect of Electric field on diffusion (3)

$$n + N_A^- = p + N_D^+$$

$$np = n_i^2$$

$$n = \frac{C}{2} + \frac{1}{2}\sqrt{C^2 + 4n_i^2}$$

$$C = N_D - N_A$$

$$F = -hD\frac{\partial C}{\partial x}$$

$$h = 1 + \frac{C}{\sqrt{C^2 + 4n_i^2}}$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

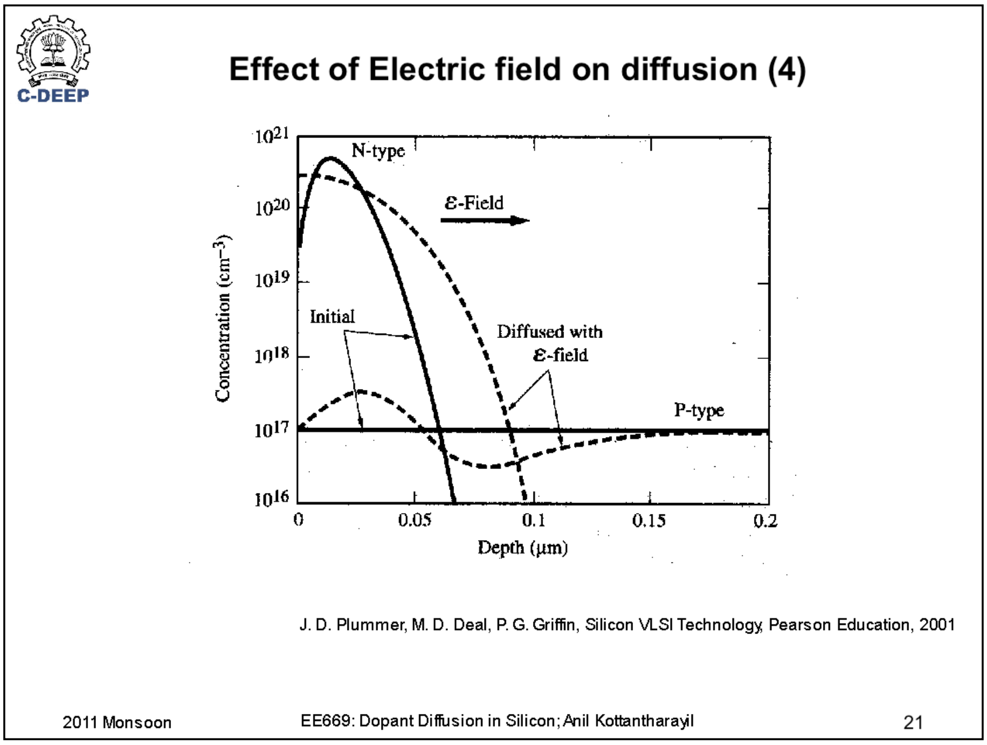
S. K. Ghandhi, VLSI Fabrication Principles – Silicon and Gallium Arsenide, John Wiley and Sons, 1983

Typically in a device, Silicon is doped with both n-type dopants and p-type dopants. The type of the semiconductor is decided by the dopant with higher concentration. Since at the processing temperature, all the dopants would be ionized and charge neutrality can be applied, the electron concentration can be expressed in terms of the net dopant concentration.

Exercise: derive the expression for the field enhancement factor, h.

It can be seen that when C >> n_i, h = 2. i.e. the diffusion flux can be doubled by the field effect.

Similar result can also be obtained for heavily p-type doped material.

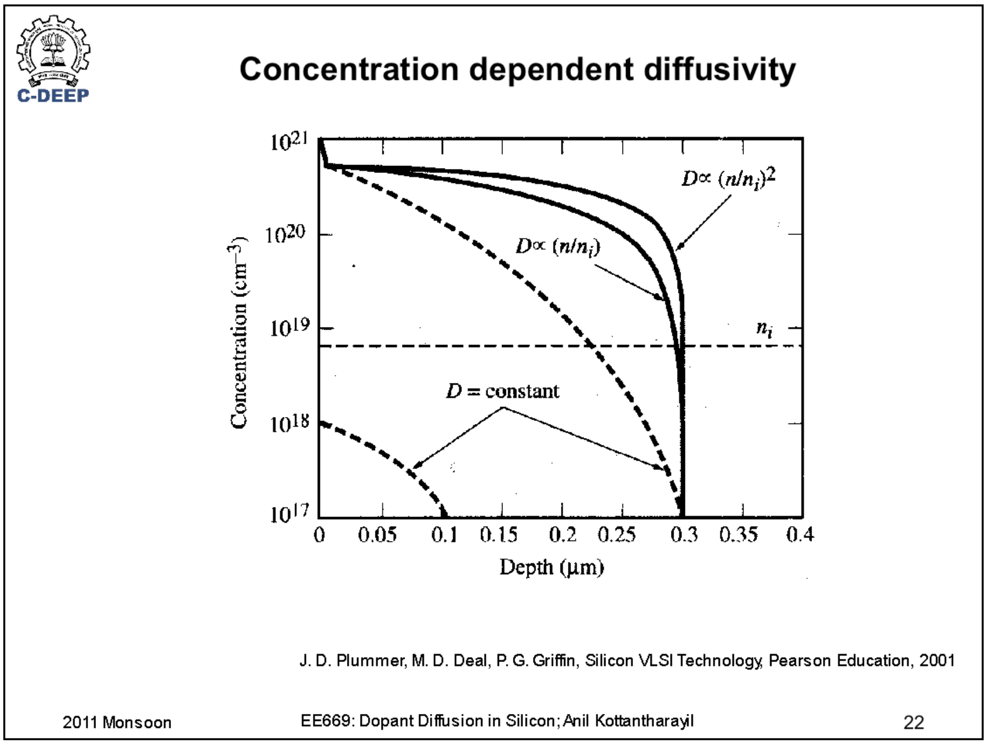


Effect of Electric field on diffusion (4)

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

The consequences of the electric field effect can be interesting. The figure shows a n-p junction in Silicon. The substrate is uniformly p-doped. Since the p-doping is uniform, we may not expect any diffusion of the p-type dopant as the diffuion flux due to the concentration gradient would be zero. However the profile in the n-type sets up an electric field during diffusion and this can set up a drift flux of the acceptor ions. The field would tend to pull the negatively charged acceptor ions away from the junction and towards the surface. So the acceptor concentration near the junction decreases. As a consequence the junction can be deeper than without the field effect.

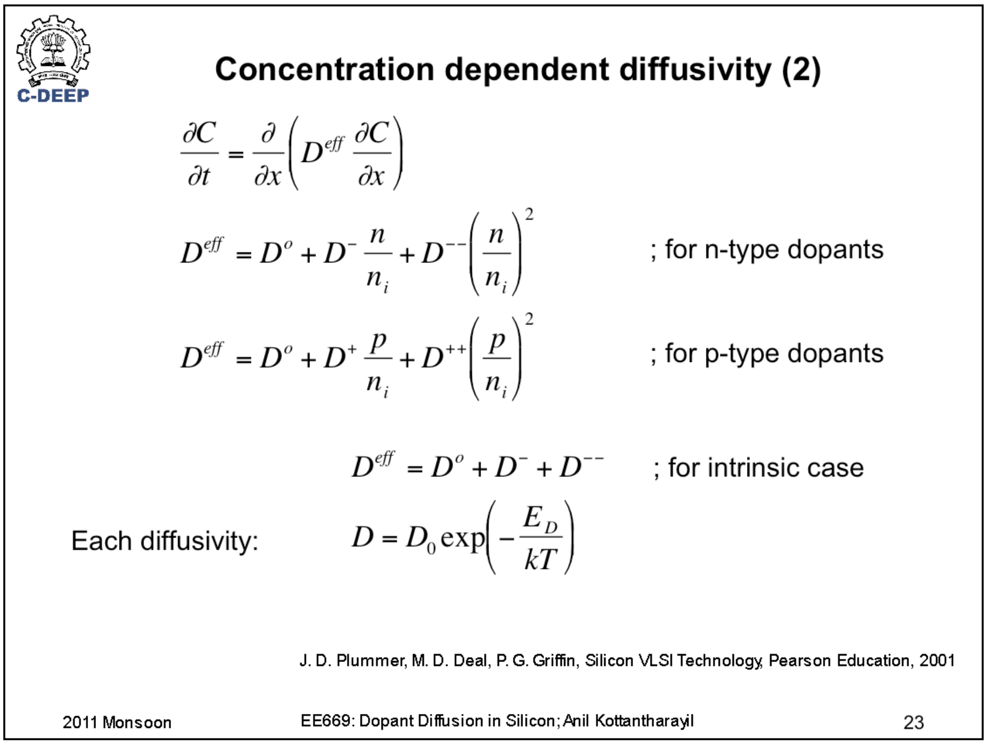
This can have interesting consequences in a 2D structure like a MOSFET. It can be inferred that source – drain diffusion can result in depletion of acceptor dopants from the channel region, reducing the threshold voltage and increasing the short channel effects.



Concentration dependent diffusivity

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

Experimentally it is observed that for high doping concentrations, the error function or Gaussian solutions do not match with experimental data for the diffusion of most dopants in Si. The figure shows the comparisons. The dashed lines are erf profiles corresponding to two different surface concentrations. For low surface concentration, the erf solution would reproduce the experimental data with good accuracy. However for higher doping concentration, the experimental profiles are more box like than what is predicted by the erf profile. It is seen that a solution with concentration dependent diffusivity is closer to the experimental observations. This effect is modeled using a diffusivity that depends on the free carrier concentration in the material.



Concentration dependent diffusivity (2)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D^{eff}\frac{\partial C}{\partial x}\right)$$

$$D^{eff} = D^{o} + D^{-}\frac{n}{n_i} + D^{--}\left(\frac{n}{n_i}\right)^2$$; for n-type dopants

$$D^{eff} = D^{o} + D^{+}\frac{p}{n_i} + D^{++}\left(\frac{p}{n_i}\right)^2$$; for p-type dopants

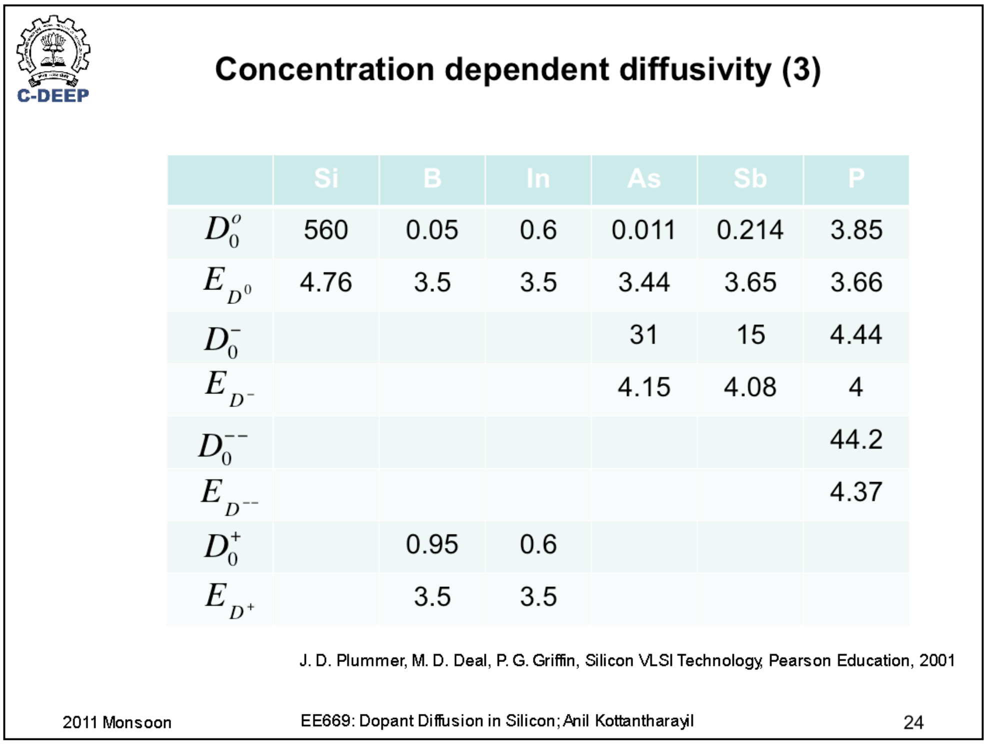
$$D^{eff} = D^{o} + D^{-} + D^{--}$$; for intrinsic case

Each diffusivity: $$D = D_0 \exp\left(-\frac{E_D}{kT}\right)$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

Fick’s second law of diffusion can be rewritten to take concentration dependence into account.

The dependence is thought to come arise from the interact of the dopants with neutral and charged point defects (vacancies and interstitials).



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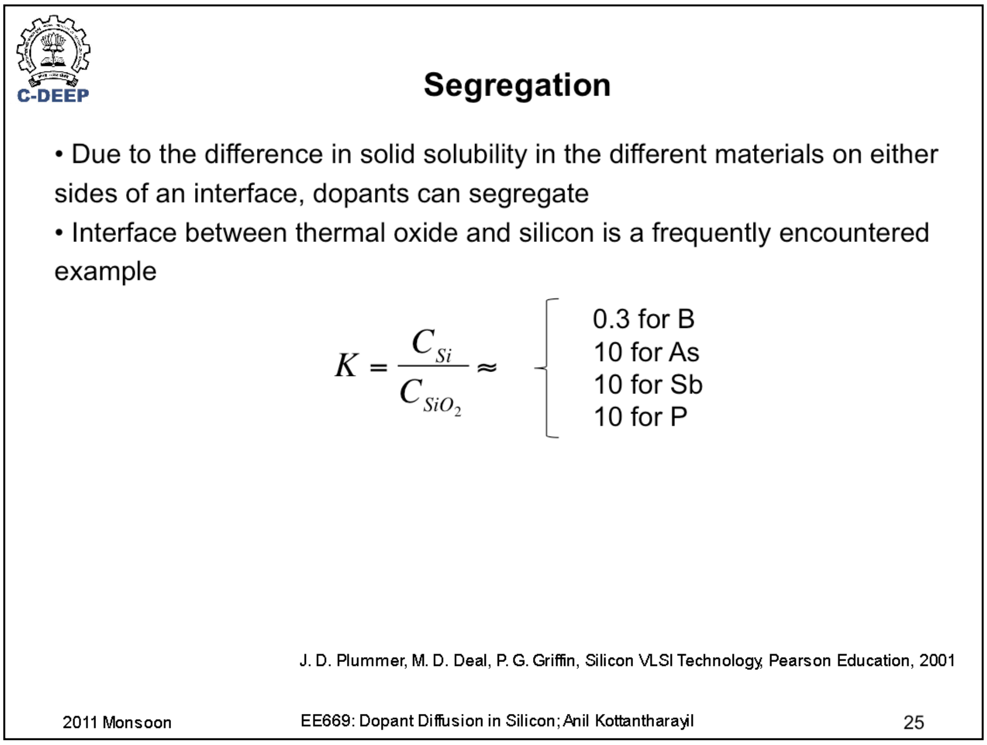
Concentration dependent diffusivity (3)

	Si	B	In	As	Sb	P
D_0^o	560	0.05	0.6	0.011	0.214	3.85
E_{D^0}	4.76	3.5	3.5	3.44	3.65	3.66
D_0^-				31	15	4.44
E_{D^-}				4.15	4.08	4
D_0^{--}						44.2
$E_{D^{--}}$						4.37
D_0^+		0.95	0.6			
E_{D^+}		3.5	3.5			

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

Fick’s second law of diffusion can be rewritten to take concentration dependence into account.

The dependence is thought to come arise from the interact of the dopants with neutral and charged point defects (vacancies and interstitials).



C-DEEP

Segregation

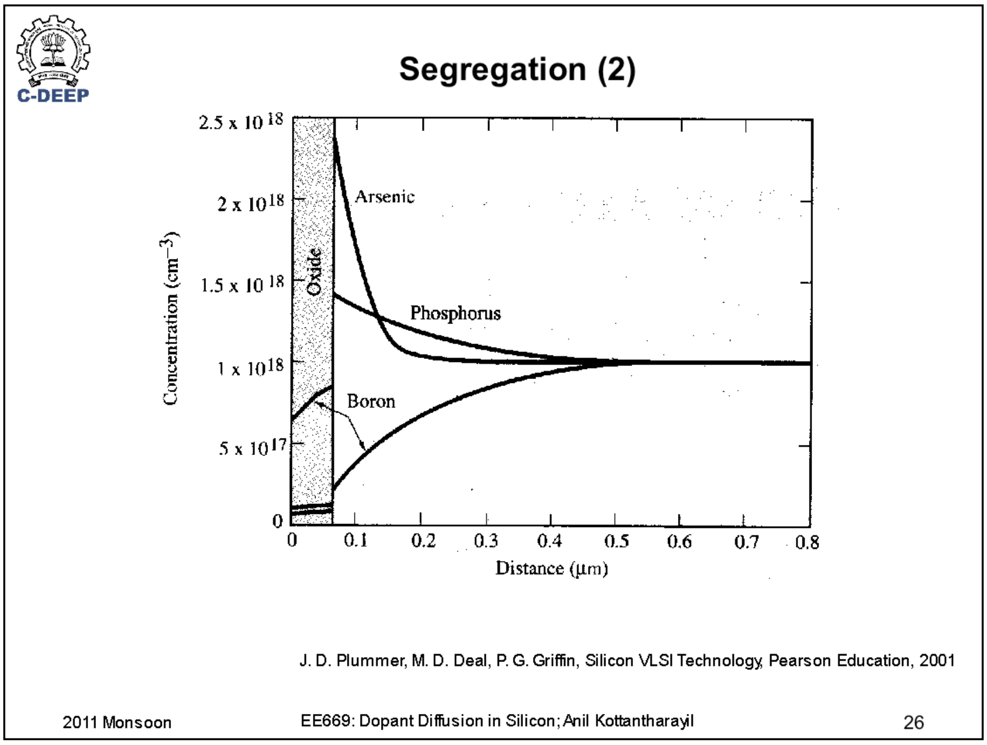
- Due to the difference in solid solubility in the different materials on either sides of an interface, dopants can segregate
- Interface between thermal oxide and silicon is a frequently encountered example

$$K = \frac{C_{Si}}{C_{SiO_2}} \approx \begin{cases} 0.3 \text{ for B} \\ 10 \text{ for As} \\ 10 \text{ for Sb} \\ 10 \text{ for P} \end{cases}$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

Segregation is an issue we had discussed in the module on crystal growth.

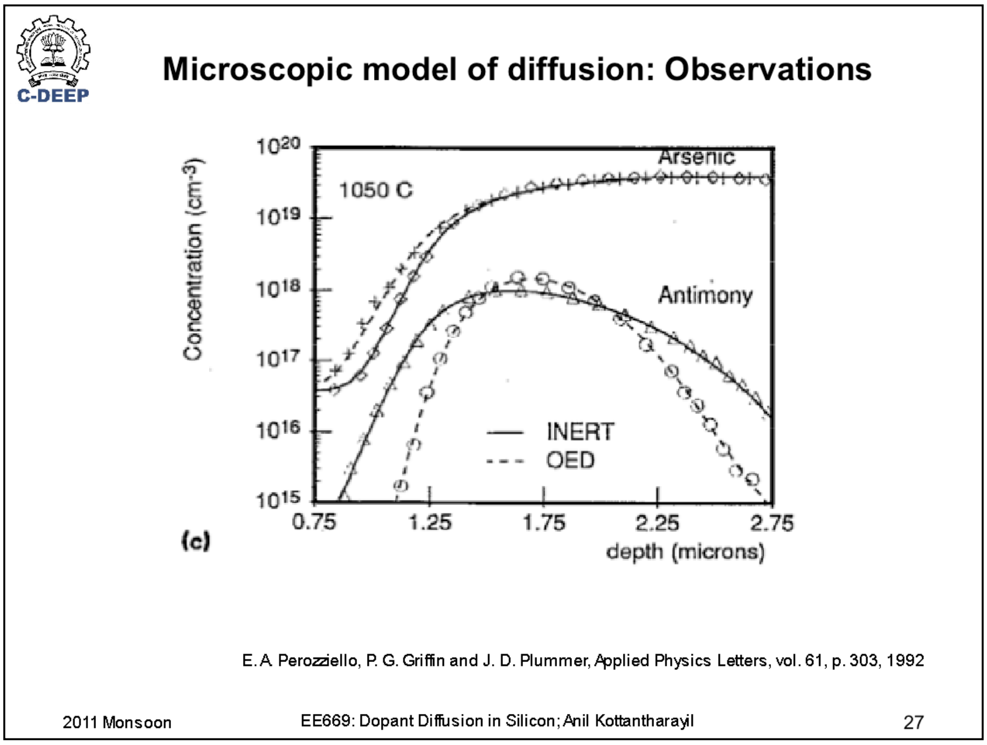
Thermal SiO_2 – Si system is an important example compared to other interfaces in Si because thermal oxidation is carried out at temperatures at which the dopant diffusivity can be significant.



Segregation (2)

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

The slide shows the dopant distribution after oxidation of a substrate with the same initial uniform doping concentration of 10^{18} cm^{-3}.



C-DEEP

Microscopic model of diffusion: Observations

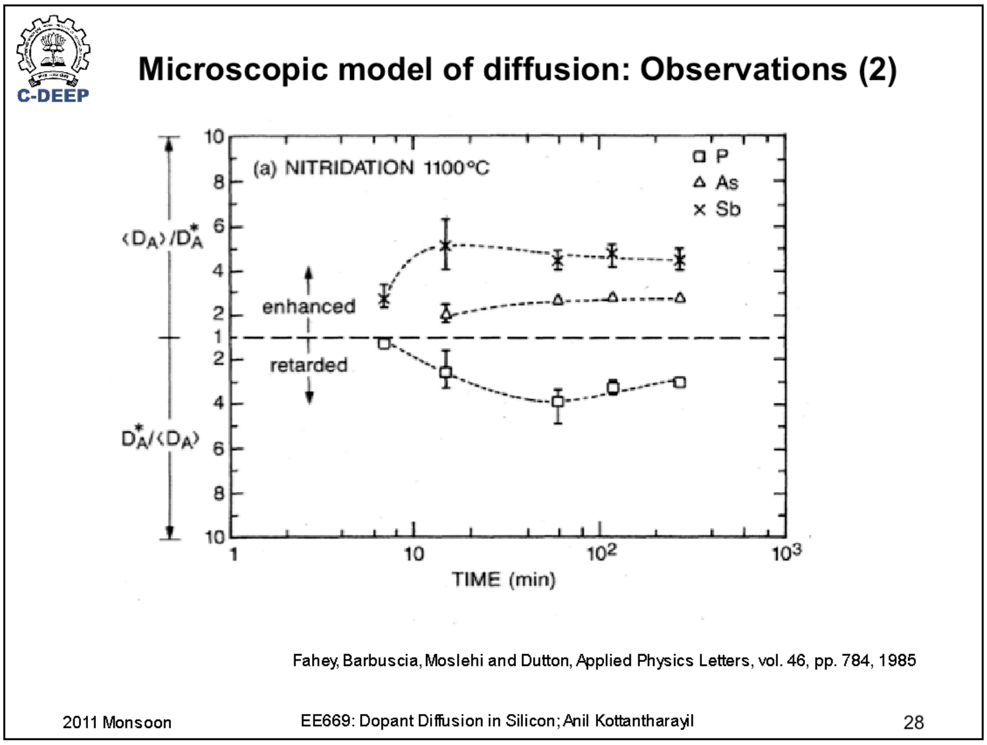
E. A. Perozziello, P. G. Griffin and J. D. Plummer, Applied Physics Letters, vol. 61, p. 303, 1992

In this particular example, the sample was prepared by implanting 10^{16} cm^{-2} of Asat an energy of 50 keV into silicon and annealed at 1150 C for 12 hours. This resulted in a uniform As doping of 4 x 10^{19} cm^{-3} for several micro meters. Subsequently a Sb implant of 5 x 10^{13} cm^{-2} at an energy of 180 keV resulting in a peak concentration of 2 x 10^{18} cm^{-3} followed by a rapid thermal anneal for activation. Subsequently a 1 micron thick Si was epitaxially grown at low temperature. The wafers were then annealed at different temperatures (850C, 950C and 1050C) for different times (6h, 24h and 41h respectively). The samples were then analyzed using secondary ion mass spectroscopy.

Anneals were carried out under two ambient conditions (i) inert ambient – most likely Ar (ii) dry oxygen.

It is seen that the Antimony diffusion is retarded under an oxidizing ambient whereas the Arsenic diffusion is enhanced under an oxidizing ambient. The symbols represent simulation data and can be ignored in this discussion.

Note that both As and Sb are n-type dopants. So whatever mechanisms we have discussed so far cannot explain the different diffusion behavior.



Microscopic model of diffusion: Observations (2)

Fahey, Barbuscia, Moslehi and Dutton, Applied Physics Letters, vol. 46, pp. 784, 1985

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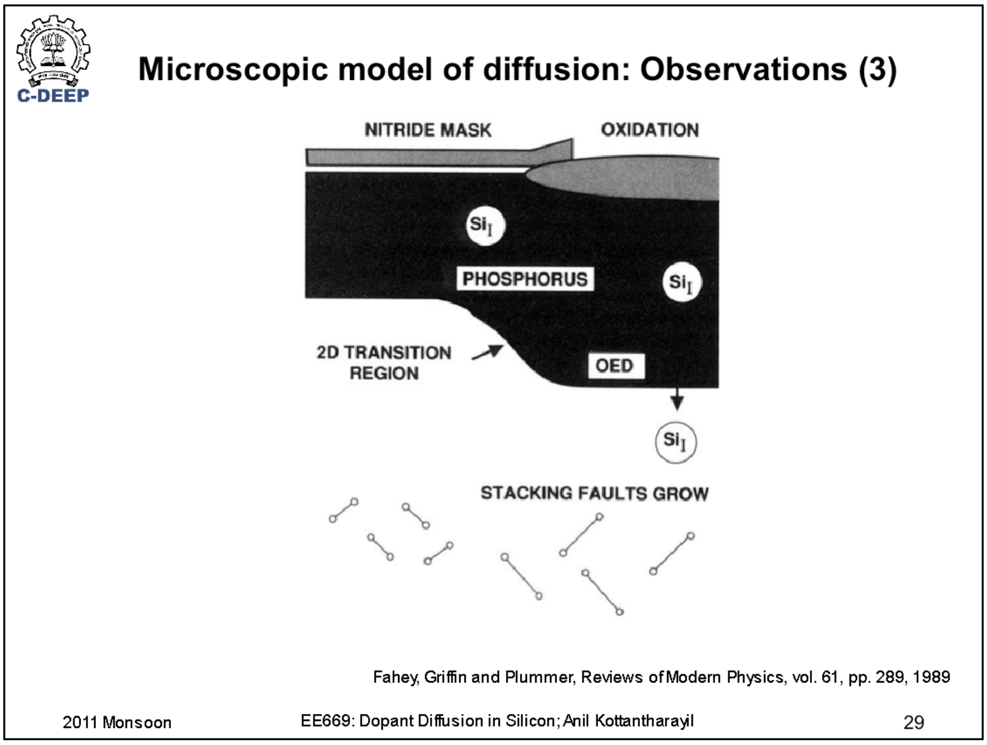
A complementary set of data was also reported for nitridation. Nitridation was carried out under NH_3 ambient for three different kinds of dopants. The diffusivities extracted (D_A) were compared with the diffusivities estimated for inert diffusion (D^*_A). The plot shows the the enhancement (retardation) of diffusivity extracted as the processes evolves.

Contrary to what is seen under oxidation conditions, the diffusion of Antimony is seen to be enhanced. The diffusion of As is enhanced as before. The diffusion of phosphorus is retarded. All of these are n-type dopants.



C-DEEP

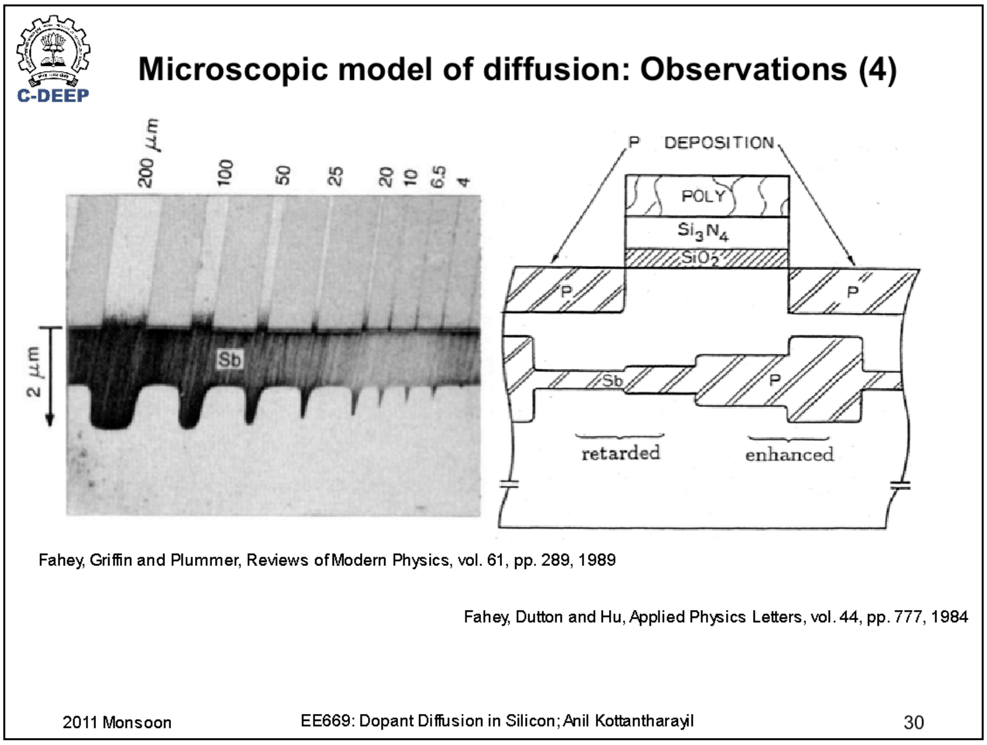
Microscopic model of diffusion: Observations (3)

Fahey, Griffin and Plummer, Reviews of Modern Physics, vol. 61, pp. 289, 1989

An interesting observation that is of significance is that thermal oxidation of silicon also leads to growth of stacking faults deep in silicon. Stacking faults as we had seen before are extra planes of Si atoms in the regular crystalline structure.

These two observations have been consolidated to suggest that the fundamental mechanisms that result in creation of stacking faults are the same or similar to those which cause oxidation enhanced or retarded diffusion.

Stacking faults can be generated if extra Si is injected into the bulk of the material.



Microscopic model of diffusion: Observations (4)

Fahey, Griffin and Plummer, Reviews of Modern Physics, vol. 61, pp. 289, 1989

Fahey, Dutton and Hu, Applied Physics Letters, vol. 44, pp. 777, 1984

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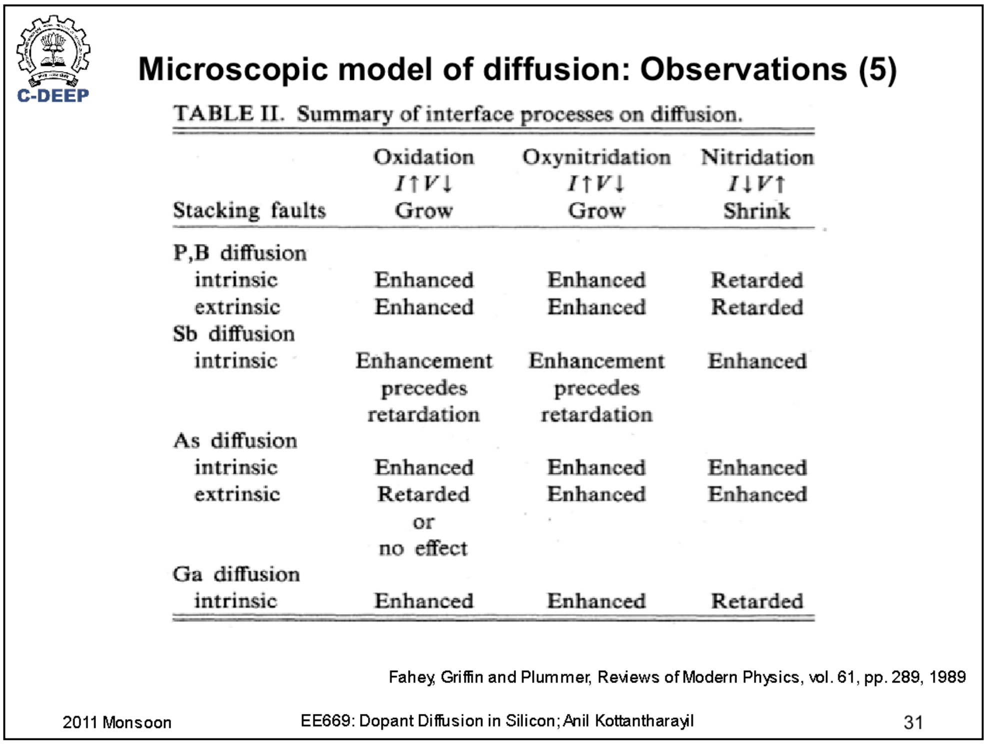
Some of the other observations from carefully designed test structures are shown in the figures on this slide.

On the left side figure enhancement of Sb diffusion under NH_3 ambient is illustrated. Windows are opened at the top of the wafer which is covered with SiO_2. Subsequently anneal was carried out in NH_3 ambient. Larger the size of the window in which the nitridation is done, higher is the diffusion of antimony.

On the right side figure, silicon substrate is implanted with Sb and P with appropriate masks. Subsequently the wafer was annealed. Epitaxial layer of Si was subsequently grown at low temperature and MOSFET structures were fabricated as shown. Subsequently the wafer was annealed. It is seen that the diffusion of the buried phosphorous doped layer is enhanced when it lies below the phosphorous doped regions at the top. Similarly the diffusion of the Sb underlayer is retarded when it lies below the phosphorous overlayer. Such situations can arise in devices, though not exactly as shown.



Microscopic model of diffusion: Observations (5)

TABLE II. Summary of interface processes on diffusion.

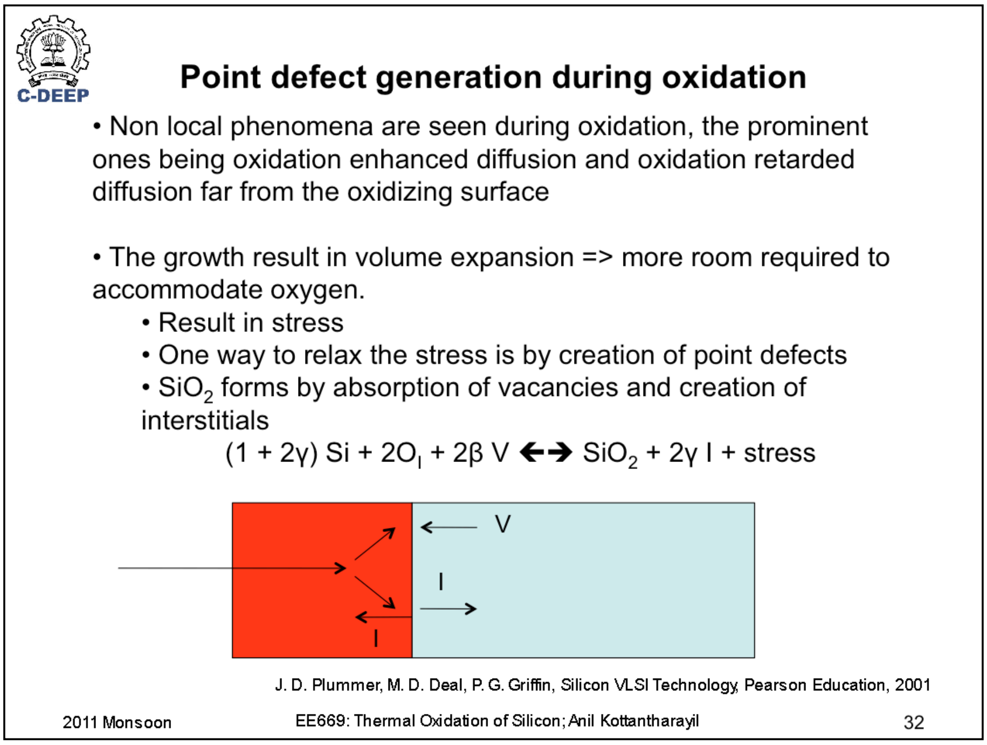
	Oxidation	Oxynitridation	Nitridation
	$I\uparrow V\downarrow$	$I\uparrow V\downarrow$	$I\downarrow V\uparrow$
Stacking faults	Grow	Grow	Shrink
P,B diffusion			
intrinsic	Enhanced	Enhanced	Retarded
extrinsic	Enhanced	Enhanced	Retarded
Sb diffusion			
intrinsic	Enhancement precedes retardation	Enhancement precedes retardation	Enhanced
As diffusion			
intrinsic	Enhanced	Enhanced	Enhanced
extrinsic	Retarded or no effect	Enhanced	Enhanced
Ga diffusion			
intrinsic	Enhanced	Enhanced	Retarded

Fahey, Griffin and Plummer, Reviews of Modern Physics, vol. 61, pp. 289, 1989

The oxidation enhanced or retarded diffusion and stacking fault growth process under various conditions are summarized in this table.

It is seen that P and B diffusion is enhanced by oxidation and retarded by nitridation. Oxynitridation, a process in which a SiO_2 already grown is nitrided in a NH_3 ambient also result in enhancement. On a related note it is observed that stacking faults grow during oxidation and shrink during nitridation. There is a close correlation between the growth of stacking fault and enhancement of diffusion of P and B.

The correlation is important. It is recognized for a long time that point defects play an important role in diffusion processes. However it was believed till late 1970s that vacancies were responsible for the enhanced diffusion of P and B. This view was challenged in 1974 when S. M. Hu of IBM pointed out the correlation between growth of stacking faults and enhanced diffusion during oxidation. If just one type of native point defect is responsible for enhancement of diffusion, all kinds of diffusion should be enhanced similarly. However as we have seen before, that is not the case.



Point defect generation during oxidation

- Non local phenomena are seen during oxidation, the prominent ones being oxidation enhanced diffusion and oxidation retarded diffusion far from the oxidizing surface

- The growth result in volume expansion => more room required to accommodate oxygen.
  - Result in stress
  - One way to relax the stress is by creation of point defects
  - SiO_2 forms by absorption of vacancies and creation of interstitials

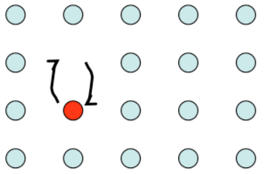
$$(1 + 2\gamma)\,\mathrm{Si} + 2\mathrm{O}_I + 2\beta\,\mathrm{V} \leftrightarrow \mathrm{SiO}_2 + 2\gamma\,\mathrm{I} + \text{stress}$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

This is just to recap what happens during oxidation of the surface of Silicon. To accommodate the large volume expansion during oxidation, the interface would consume vacancies diffused from the bulk of silicon. We also discussed that interstitials can be injected into silicon from the interface of Si and SiO_2. We had also seen equations for the equilibrium concentration of vacancies and interstitials in silicon as a function of temperature. One consequence of interstitial injection into silicon from the oxidizing interface would be that the interstitial concentration in the silicon bulk would increase over and above the equilibrium condition. This is called interstitial supersaturation.

C-DEEP

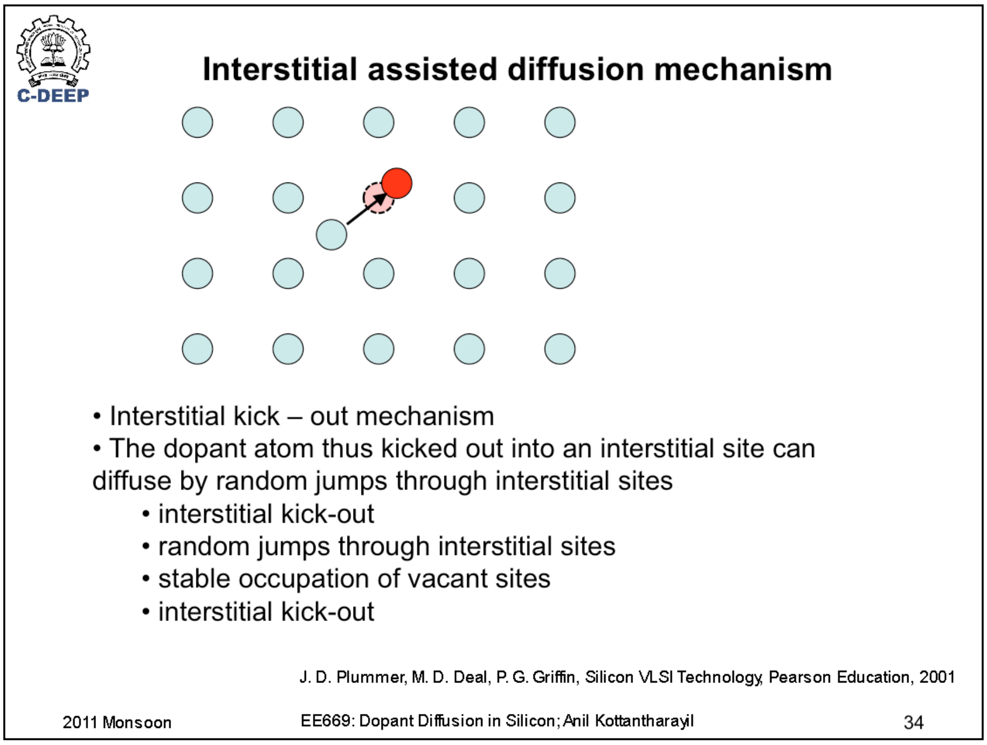
Vacancy assisted diffusion mechanism



- Jump of an impurity from the substitutional site it occupy would be easier to a vacancy than to an occupied lattice site.
- The diffusion can be thought of a sequence of random hops of this kind where in the following processes occur
  - vacancy in the vicinity of a dopant atom
  - hop of the dopant atom to the vacancy
  - dopant atom stable in the substitutional site
  - vacancy mediated hop

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

We had seen that vacancies are consumed at the interface during oxidation. So the vacancy concentration in the bulk of the silicon would decrease during an oxidation process. If a diffusion process happens by vacancy assisted process, this would be retarded during oxidation. That is likely to be the case for antimony diffusion.



Interstitial assisted diffusion mechanism

- Interstitial kick – out mechanism
- The dopant atom thus kicked out into an interstitial site can diffuse by random jumps through interstitial sites
    - interstitial kick-out
    - random jumps through interstitial sites
    - stable occupation of vacant sites
    - interstitial kick-out

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

In addition to the process described above, it is also possible to have the interstitial – dopant pair diffusing together. This is likely especially if the dopant is smaller than the Si atom. The pair would have lower energy than a pair of silicon interstitial – and silicon at lattice site.

If a particular dopant diffusion is enhanced in an oxidizing ambient, it is likely that the particular dopant diffuses with assistance from interstitials.

Interstitial injection into silicon from an oxidizing ambient also can lead to creation of stacking faults as the interstitials nucleate deeper in the silicon forming additional planes in an otherwise perfect lattice.

Interstitial and vacancy assisted diffusion

- In general, a diffusion process can be thought to have a vacancy assisted component and an interstitial assisted component
- Suppose a fraction, f_v of the mobile dopants diffuse by vacancy mechanism and f_I by the interstitial mechanism

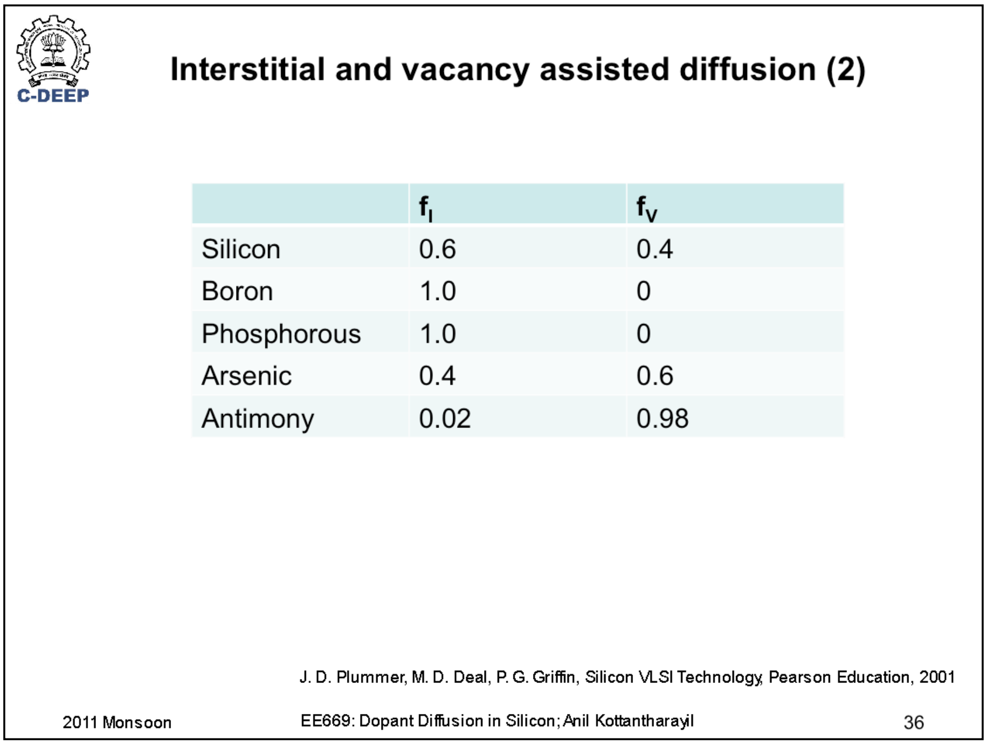
$$f_v + f_I = 1$$

- The effective diffusivity can be expressed as follows:

$$D_{A\_eff} = D_{A0}\left(f_I \frac{C_I}{C_{I0}} + f_V \frac{C_V}{C_{V0}} \right)$$

$D_{A\text{-}eff}$ is the effective diffusivity, C_{I0} and C_{V0} are the interstitial and vacancy concentration respectively at equilibrium and, C_I and C_V are the interstitial and vacancy concentration respectively under the processing condition.

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

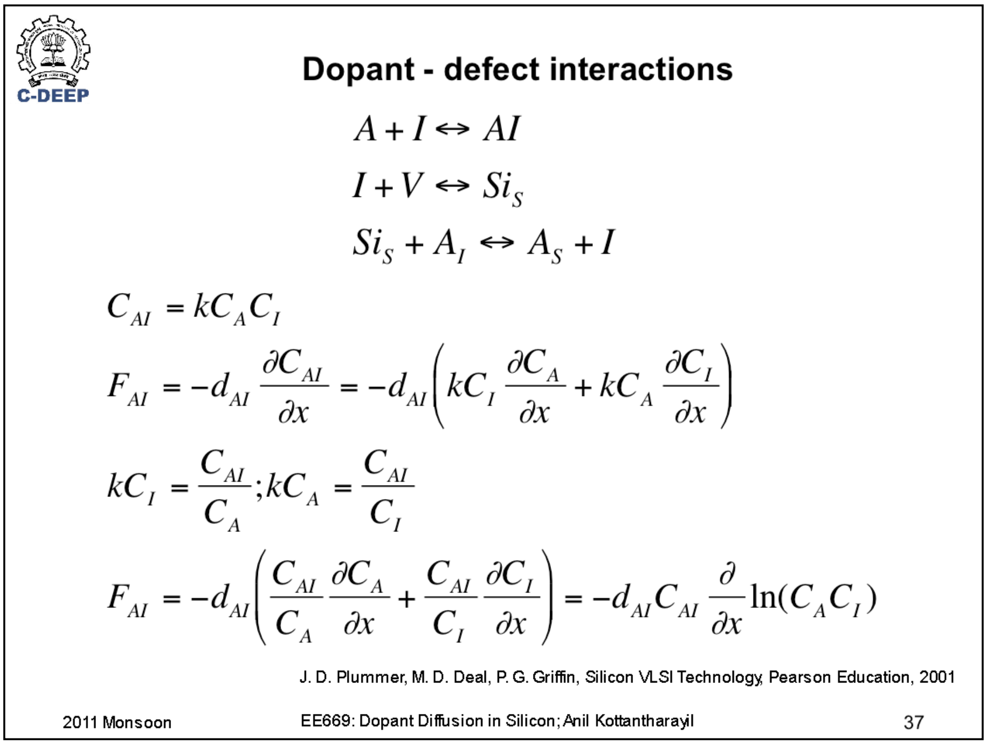


Interstitial and vacancy assisted diffusion (2)

	f_I	f_V
Silicon	0.6	0.4
Boron	1.0	0
Phosphorous	1.0	0
Arsenic	0.4	0.6
Antimony	0.02	0.98

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

The typical values of f_I and f_V determined for various dopants and silicon self diffusion are given in the table. Note that there is no way to directly measure the vacancy and interstitial concentrations in silicon. These numbers are obtained by careful modeling of the diffusion process on an atomic scale and using the models to fit data obtained from specially designed test structures.



C-DEEP

Dopant - defect interactions

$$A + I \leftrightarrow AI$$

$$I + V \leftrightarrow Si_S$$

$$Si_S + A_I \leftrightarrow A_S + I$$

$$C_{AI} = kC_A C_I$$

$$F_{AI} = -d_{AI}\frac{\partial C_{AI}}{\partial x} = -d_{AI}\left(kC_I\frac{\partial C_A}{\partial x} + kC_A\frac{\partial C_I}{\partial x}\right)$$

$$kC_I = \frac{C_{AI}}{C_A}; kC_A = \frac{C_{AI}}{C_I}$$

$$F_{AI} = -d_{AI}\left(\frac{C_{AI}}{C_A}\frac{\partial C_A}{\partial x} + \frac{C_{AI}}{C_I}\frac{\partial C_I}{\partial x}\right) = -d_{AI}C_{AI}\frac{\partial}{\partial x}\ln(C_A C_I)$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

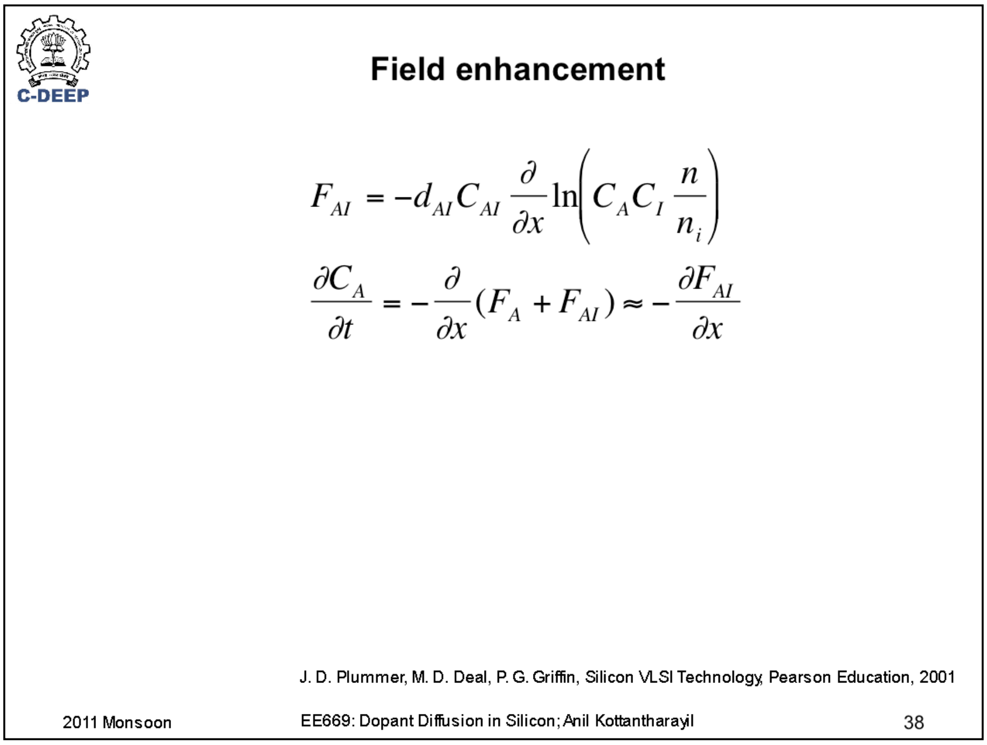
In these expressions, A stands for the dopant atom. AI is the mobile species generated by the interaction between the dopant atom and silicon interstitial. It should be noted that the dopant atom by itself sitting in a substitutional site may not be mobile.

An interstitial and vacancy can interact to form a substitutional Silicon.

A substitutional silicon and a dopant at an interstitial site can interact to form a dopant occupying a substitutional site and a silicon interstitial.

If we consider the case where the interstitial assisted diffusion is dominant, we may consider the first and third reactions to be dominant.

In such a scenario, the concentration of the mobile species, AI can be written in terms of a reaction constant.



Field enhancement

$$F_{AI} = -d_{AI} C_{AI} \frac{\partial}{\partial x} \ln\left(C_A C_I \frac{n}{n_i} \right)$$

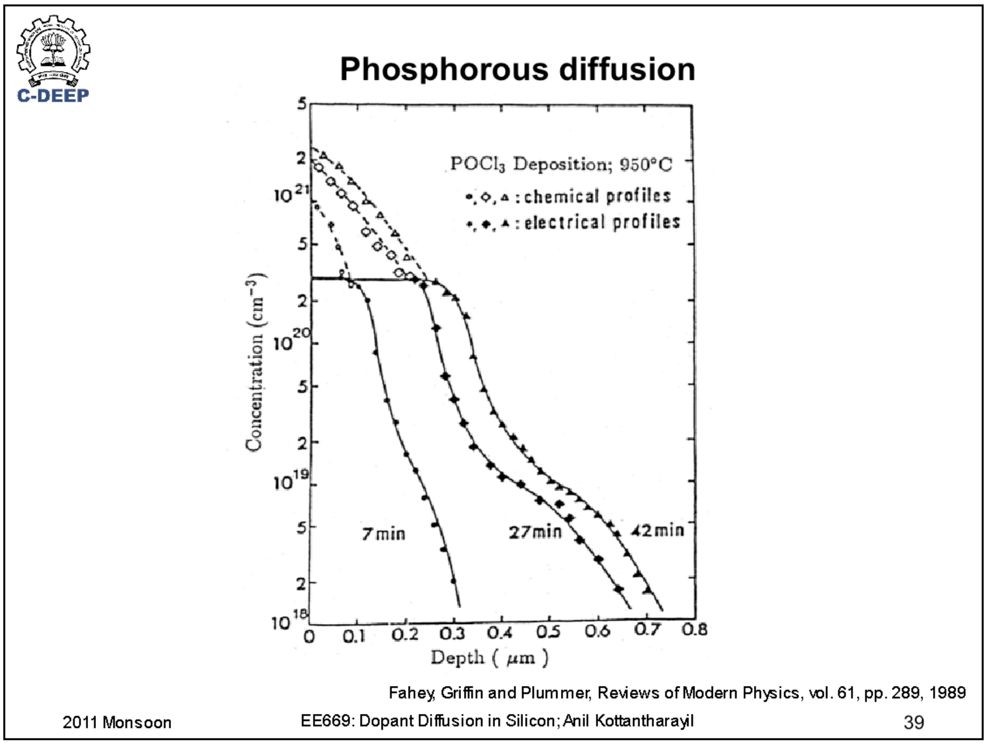
$$\frac{\partial C_A}{\partial t} = -\frac{\partial}{\partial x}(F_A + F_{AI}) \approx -\frac{\partial F_{AI}}{\partial x}$$

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

The field enhancement can be included as we had discussed bfore. In this particular case we have assumed that the field enhancement is due to a heavily n-type doped profile.

The Fick's second law of diffusion can be written down by noting that the dopant atom in a substitutional site is not mobile.

This is the equation that is solved in process simulators. The equation can be developed further for various special conditions and also considering the charged states of the interstitials. We would not discuss those advanced topics here. Interested students may refer to Fahey, Griffin and Plummer, Reviews of Modern Physics, vol. 61, pp. 289, 1989.



C-DEEP

Phosphorous diffusion

Fahey, Griffin and Plummer, Reviews of Modern Physics, vol. 61, pp. 289, 1989

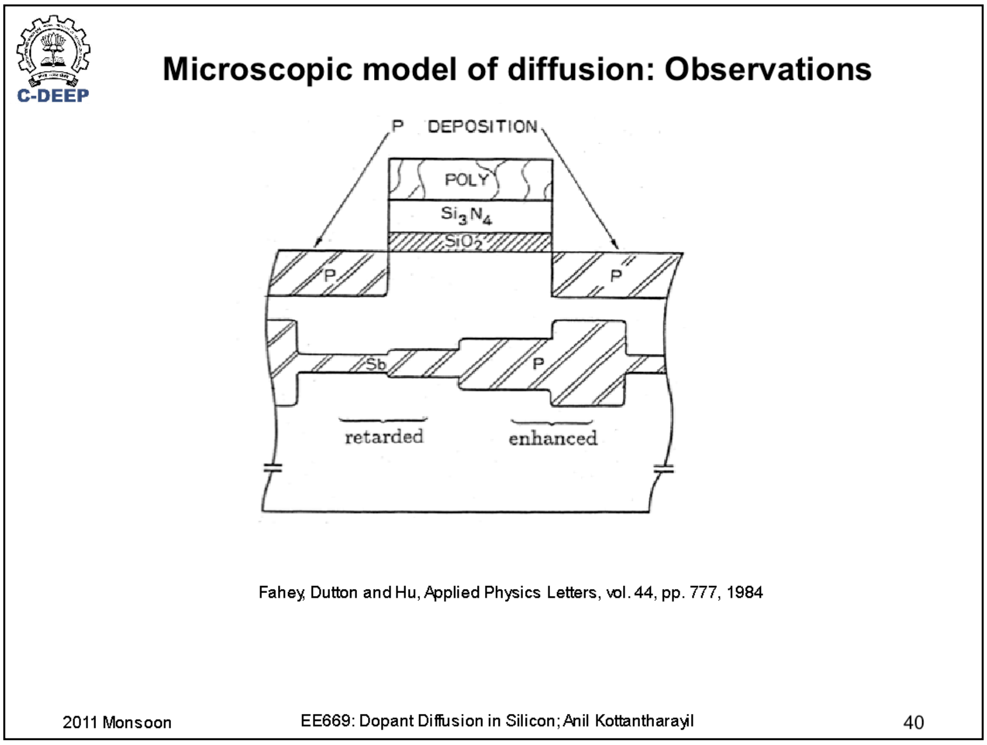
Now we would consider some examples of practical importance.

Phosphorous diffusion is an important process for fabrication of several devices. Modern VLSI device fabrication may use phosphorous only for well implants or anti punch through implants. We would discuss these in later sessions. However phosphorous diffusion is a very important process for the fabrication of crystalline silicon solar cells. POCl3 based diffusion is an important process for phosphorous diffusion. Other processes of importance are those using phosphoric acid sprays and solid source diffusion.

For low concentration intrinsic diffusion of phosphorous profiles in Silicon is not very complicated in the sense that an initial Gaussian profile would result in a broader Gaussian profile. However if the doping concentration is very high in which case intrinsic diffusion is no more valid, some anomalous behavior is observed. This is the case for all the phosphorous sources discussed above.

What is observed is shown on the graph. The open symbols represent chemical concentration and the filled symbols represent electrically active concentration. Concentrations above ~ 3×10^{20} cm^{-3} are not electrically active suggesting that a significant part of the dopants in the top layer are not incorporated in substitutional sites. They are incorporated as SiP complexes and phosphorous precipitates.

The initial part of the profile can be adequately explained by field enhanced diffusion. However a kink is observed as the concentration reaches around 10^{19} cm^{-3}. The diffusion is seen to be significantly enhanced beyond this point. The present understanding is that from the highly defective surface layer P-Si complexes diffuse together into the bulk. However as the dopant finds substitutional sites deeper in Silicon, the interstitials are released resulting in a high concentration of Silicon interstitials away from the surface. This would enhance the diffusion of phosphorous deeper in Silicon.



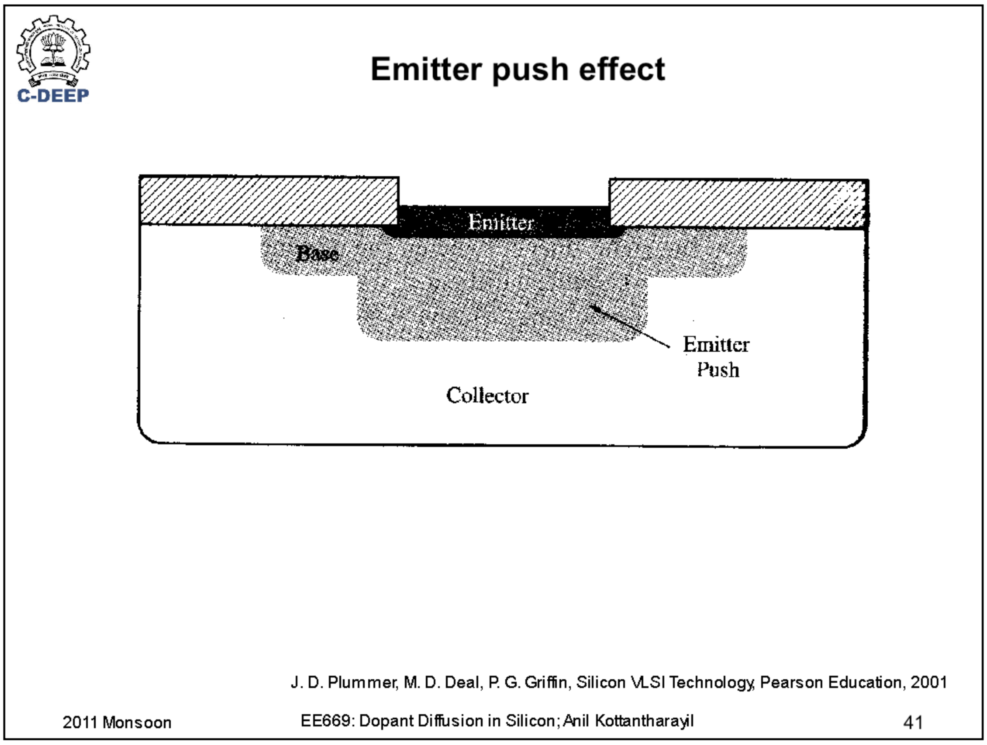
Microscopic model of diffusion: Observations

Fahey, Dutton and Hu, Applied Physics Letters, vol. 44, pp. 777, 1984

In previous discussions we had seen that phosphorous diffusion on the surface layer of Si can impact the diffusion of underlying dopant distributions as shown.

Based on the previous slide, it is possible to explain these observations. Diffusion of the heavily phosphorous doped surface layer would result in the injection of Si interstitials into the bulk. This would subsequently enhance the diffusion of phosphorous in the underlayer.

On the other hand the injection of larger number of interstitials would result in reduction of vacancies in the bulk due to vacancy – interstitial recombination. Since antimony diffuses by the vacancy assisted process, antimony diffusion would retard.



Emitter push effect

J. D. Plummer, M. D. Deal, P. G. Griffin, Silicon VLSI Technology, Pearson Education, 2001

In the previous examples, the observations were made on specially designed test samples which may not have much practical interest.

What you see here is a practical example. A bipolar junction transistor is fabricated by first diffusing boron into a n-type doped substrate through a window as shown. Subsequently phosphorous is diffused to form the emitter. It is seen that in the region immediately under the emitter, base to collector junction becomes deeper. This would result in an increase in the base width which would in turn reduce the base transport factor and hence the current gain of the transistor.

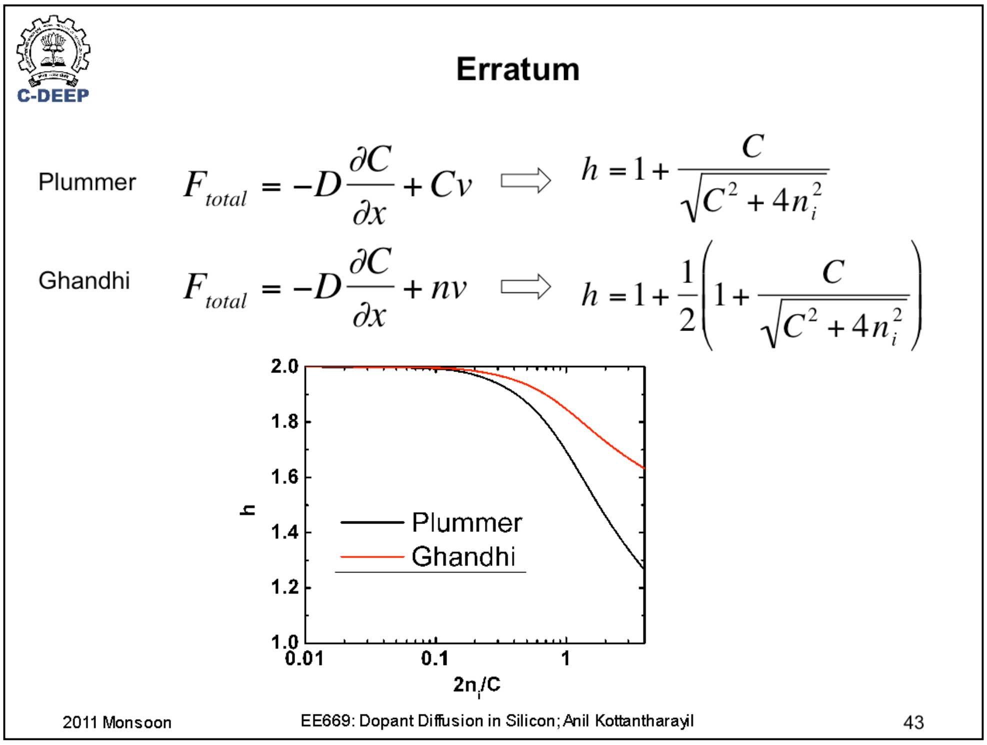
The explanation is the same as in the previous slide. The phosphorous diffusion would result in the injection of large number of interstitials into the silicon which enhances boron diffusion.

One way to reduce this is by using diffusion from a heavily doped poly-Si. The poly-Si grain boundaries can provide a sink for the interstitials.

Point defects can be created on the surface of the wafers by a variety of other mechanisms like ion implantation or radiation damage, physical grinding of the surface etc.

Self study

Reverse short channel effects in MOSFETs: C. S. Rafferty et al., IEDM Technical Digest, 1993, p. 311.



Erratum

Plummer $$F_{total} = -D\frac{\partial C}{\partial x} + Cv \Longrightarrow h = 1 + \frac{C}{\sqrt{C^2 + 4n_i^2}}$$

Ghandhi $$F_{total} = -D\frac{\partial C}{\partial x} + nv \Longrightarrow h = 1 + \frac{1}{2}\left(1 + \frac{C}{\sqrt{C^2 + 4n_i^2}}\right)$$

In the previous lecture we had derived an expression for the field enhancement factor and the result was from S. K. Ghandhi. However it is seen that Ghandhi had assumed the field term in the flux to be nv, whereas we are interested in the drift of the ions and not of electrons. This is correctly expressed in the book written by Plummer et al. So the equations describing the field enhancement factor are different in the two cases. Plummer’s derivation is correct.