



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)

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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.

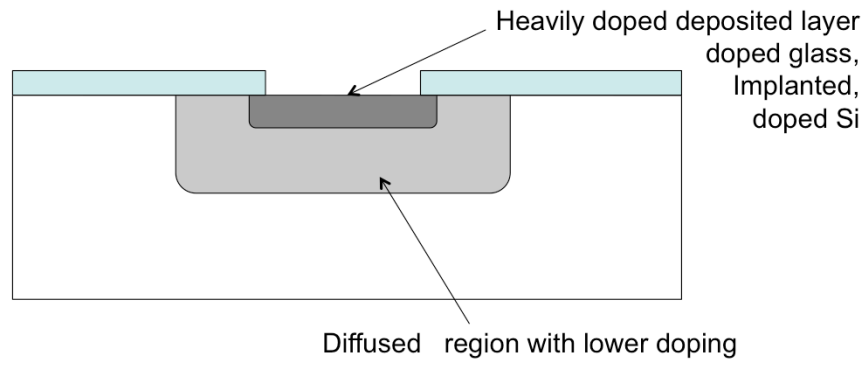
For modern VLSI device applications, ultra shallow junctions are required. The trend now is to do the anneal just for activation of the dopants and to remove implant damage without causing any diffusion. Diffusion in this case could increase junction depth which is undesirable in such applications. Junction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



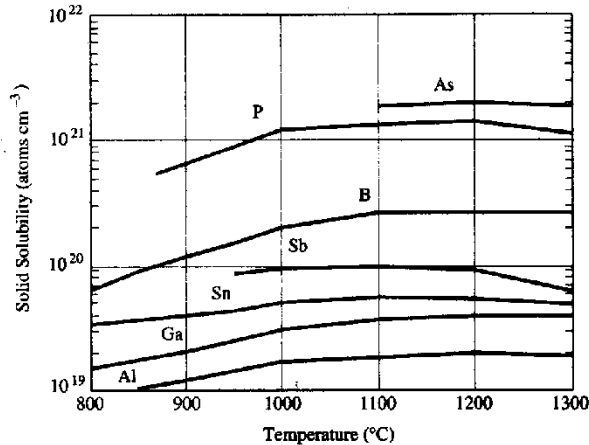
Generalized diffusion process





Solid solubility

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



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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 $2 \times 10^{21} \text{ cm}^{-3}$ 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 ($\sim 1000^\circ\text{C}$) is significantly higher than the device operating temperatures (room temperature to 100°C). 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.



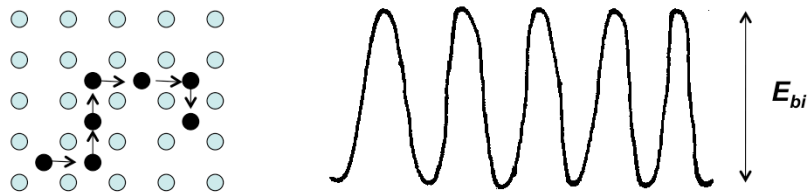
Diffusion process

- 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

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Concept of particle jump: Interstitial movement



$$v_I = 4v_0 \exp(-E_{bi}/kT)$$

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

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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.

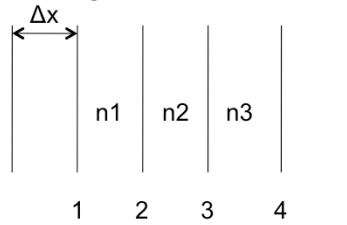
When the interstitial atom jumps from one site to the other, it has jump through a constriction that is present between lattice atoms. This can be thought of an energy barrier that the interstitial atom must overcome for a jump. We can also think of this in a different way by considering lattice vibrations. 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: $F_{1,L-R} = \frac{v}{2} n_1$
- Flux from the right to left of boundary 2: $F_{1,R-L} = \frac{v}{2} n_2$
- Net flux from left to right:

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

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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 $n_1, n_2, n_3, \dots$. The atoms from any slice can jump either left or right with equal probability.

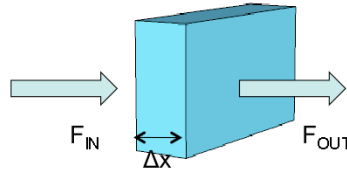
The flux from the left to right can be evaluated as shown. The jump frequency is the net of all jump mechanisms.

In the limit $\Delta x \rightarrow 0$, this reduces to Fick's first law of diffusion. The derivation also shows a thermal activation for the diffusion constant.



Macroscopic model of diffusion (2)

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



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

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

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

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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.

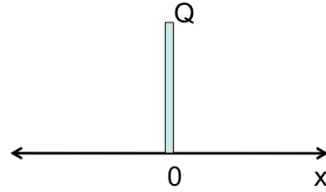
The law of conservation of matter can be applied to the diffusion process to derive the Fick's second law of diffusion.

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 $t = 0$

$C \rightarrow 0$ for $x > 0$

$C \rightarrow \text{infinity}$ at $x = 0$

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

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

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

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

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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.

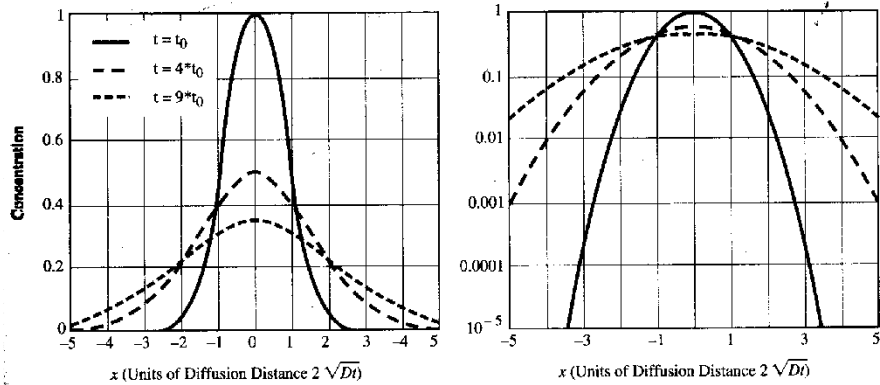
The solution is a Gaussian profile. The profile is also symmetric with respect to the origin.

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 different 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 $t=0$ for which $C(0,0) \rightarrow \infty$ 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)



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

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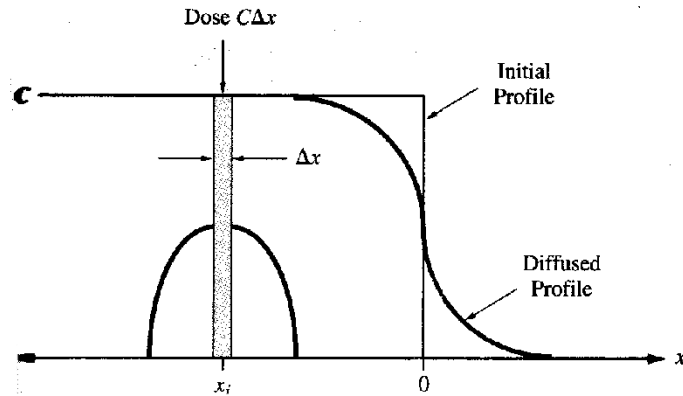
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In this case a dopant source is deposited on the wafer surface as shown. Examples include poly-Si emitter in BJT fabrication, pre-deposition of doped glasses like phospho silicate glass and subsequent diffusion by drive-in anneal, low energy ion implantation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



Solution for diffusion from an infinite source



Boundary condition:

$$C = 0 \text{ at } t = 0 \text{ for } x > 0$$

$$C = C \text{ at } t = 0 \text{ for } x < 0$$

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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)

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

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

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

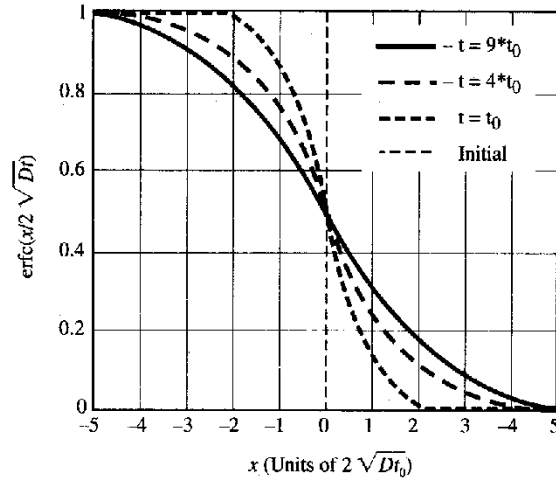
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In the limit, the sum can be replaced by the integral. erfc is the complementary error function and the values of this function are available in tabular form.



Solution for diffusion from an infinite source (3)



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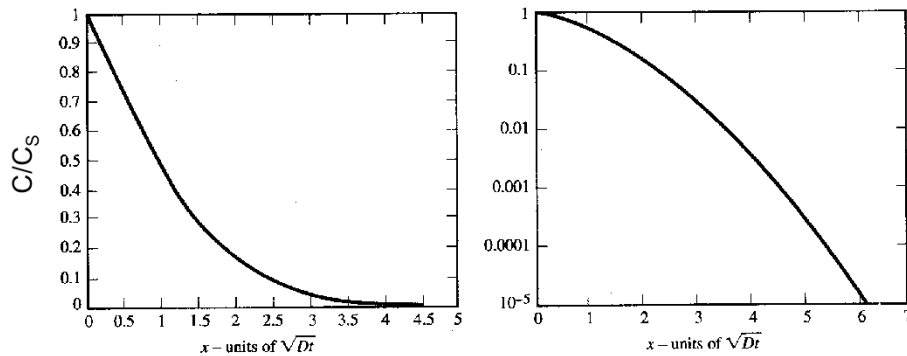
The figure shows the dopant profile as a function of the “diffusion length”. A key point to note is that the dopant concentration at the interface ($x = 0$) is half of the original concentration for all times.

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.



Solution for diffusion from an infinite source on the surface

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



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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.



Intrinsic diffusivities in Si

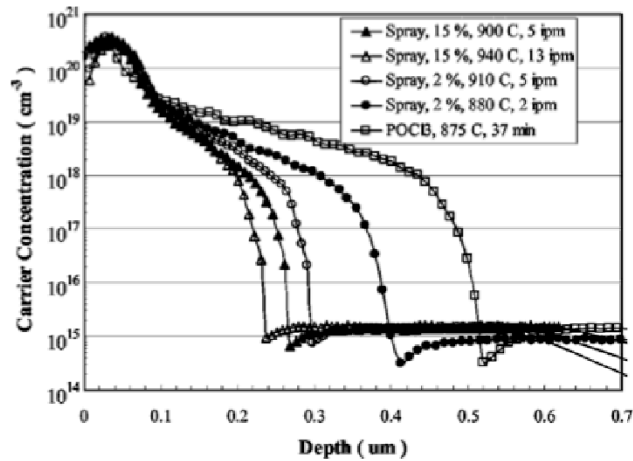
$$D = D_0 \exp\left(-\frac{E_A}{kT}\right)$$

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

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Practical diffusion profiles: Phosphorous in Si

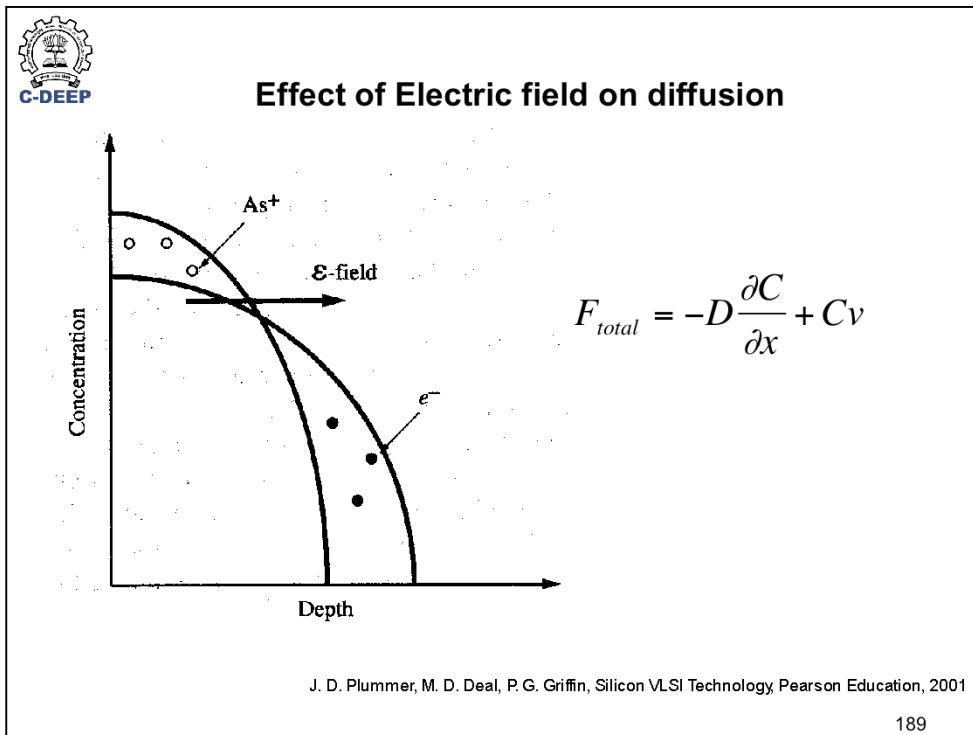


Kim et al., Development of a phosphorous spray diffusion system for low-cost silicon solar cells, J. Electrochem. Soc., 153 (7), 2006, pp. A13891-A1396.

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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.



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.



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

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

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

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Drift velocity is related to the electric field through mobility.



Effect of Electric field on diffusion (3)

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

$$np = n_i^2$$

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

$$C = N_D - N_A$$

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

$$h = 1 + \frac{1}{2} \left(1 + \left(1 + \frac{4n_i^2}{C^2} \right)^{-1/2} \right)$$

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

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

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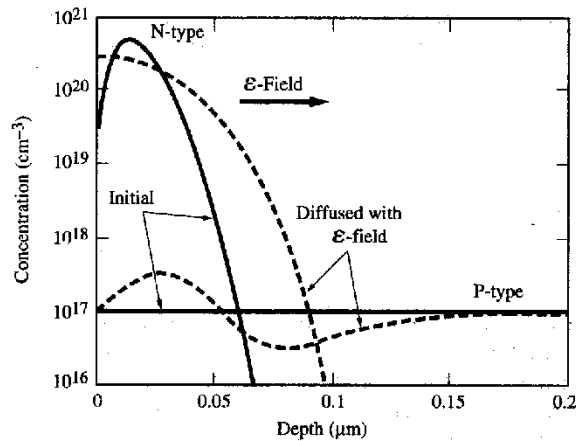
Typically in a device, Silicon is doped with both n-type dopants and p-type dopants. The type of the semiconductor is decided by the dopant with higher concentration. Since at the processing temperature, all the dopants would be ionized and charge neutrality can be applied, the electron concentration 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 $C \gg n_i$, $h = 2$. 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)



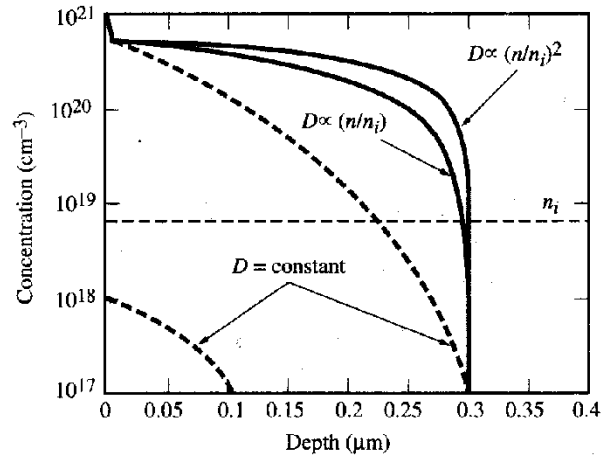
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The consequences of the electric field effect can be interesting. The figure shows a n-p junction in Silicon. The substrate is uniformly p-doped. Since the p-doping is uniform, we may not expect any diffusion of the p-type dopant as the diffusion flux 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



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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)

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

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

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

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

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

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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).



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			

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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

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

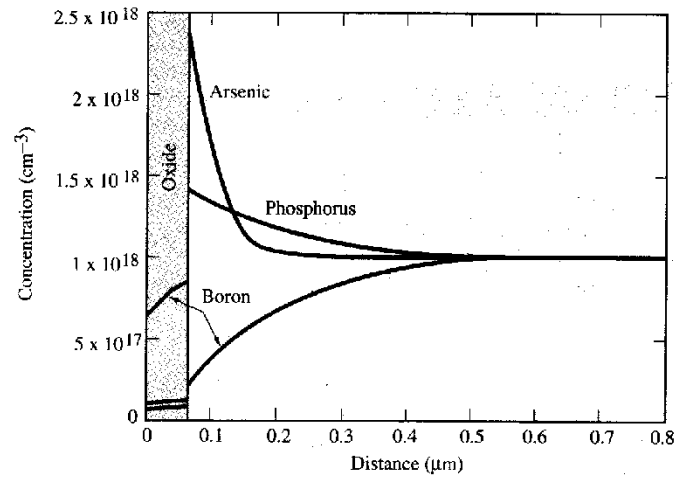
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Segregation is an issue we had discussed in the module on crystal growth.

Thermal SiO₂ – 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)



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