

Diffusion of dopants in silicon

Diffusion shows up in a number of different circumstances :

- Heat through a solid material
- Odors traveling through the air
- Tea moving from a tea bag into the surrounding hot water
- An ink stain moving through a piece of cloth
- Injected electrons or holes diffusing from the edge of depletion region in the neutral regions of a p-n diode
- Impurity atoms moving in a semiconductor lattice

Diffusion is the “smoothing out” that occurs in any situation where a high concentration of particles exists in one place and the particles can undergo random motion. The natural tendency is for particles to move towards regions of lower concentration.

Fick's law

The idea of particle movement created by non-uniformities can be expressed mathematically in the form of Fick's First Law, which relates particle flux to concentration gradients:

$$\mathcal{F} = -D \frac{\partial N}{\partial x}$$

where D is the diffusion coefficient or diffusivity, with units of m^2/s (or cm^2/s).

Basically, Fick's law states that if particles in some collection can move (i.e. $D \neq 0$), they will move in a way that tends to even out the distribution.

Continuity relation

To get to the diffusion equation, we must combine Fick's law with a basic continuity relation.

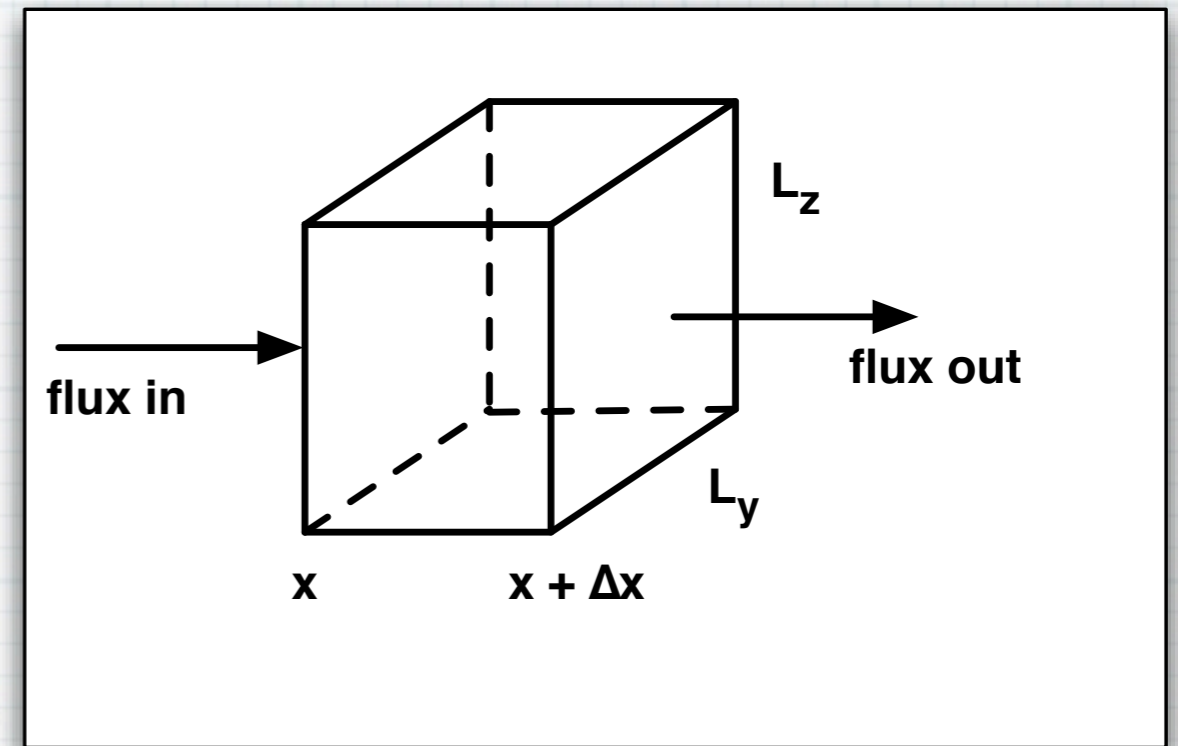
N - concentration of particles

$N(L_y L_z \Delta x)$ - number of particles in the box

ΔN - change in concentration within a given time Δt

$\Delta N(L_y L_z \Delta x)$ - change in number of particles in the box in the time span Δt .

Consider a rectangular volume as shown above. Suppose that particles are moving through the box as indicated by the incoming and outgoing fluxes. If the concentration of particles within the box is changing with time, it must happen because there is a difference in the fluxes coming in and going out.



If particles are not created or destroyed within the box, then any change in the number must be due to particles moving in and out. If the flux in is higher than the flux out, then number inside increases. If the flux outward is higher than the flux inward, then the number inside decreases.

number of particles entering the box at x within the time span Δt

$$= \mathcal{F}(x) L_y L_z \Delta t$$

number of particles leaving the box at $x+\Delta x$ within the time span Δt

$$= \mathcal{F}(x + \Delta x) L_y L_z \Delta t$$

Keeping track of the change in the concentration in the box, ΔN , during some time interval Δt :

$$\Delta N L_y L_z \Delta x = \mathcal{F}(x) L_y L_z \Delta t - \mathcal{F}(x + \Delta x) L_y L_z \Delta t$$

Rearranging

$$\frac{\Delta N}{\Delta t} = -\frac{\mathcal{F}(x + \Delta x) - \mathcal{F}(x)}{\Delta x}$$

and then taking the limit, we obtain the continuity relation

$$\frac{\partial N}{\partial t} = -\frac{\partial \mathcal{F}}{\partial x}$$

This type of continuity relation shows up in many different physical situations besides particle diffusion, including heat flow, electromagnetics and quantum mechanics.

Fick's second law - the diffusion equation

Inserting Fick's first equation into the continuity relation, we obtain Fick's second law:

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial N}{\partial x} \right)$$

This is the general diffusion equation. It is a partial differential equation for $N(x,t)$. To find a particular solution, we will need to specify an initial condition, $N(x,t=0)$, and two boundary conditions like $N(x=0, t)$ and $N(x=5\mu m, t)$, for example.

The above form of the diffusion equation is the most general, allowing for the possibility that D is a function of position. (D may be a function of position implicitly by being a function of concentration explicitly.) Of course, we also expect D to have an Arrhenius-type dependence on temperature.

If we assume that D does not depend on position, then we can write a slightly simpler form of the diffusion equation:

$$\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2}$$

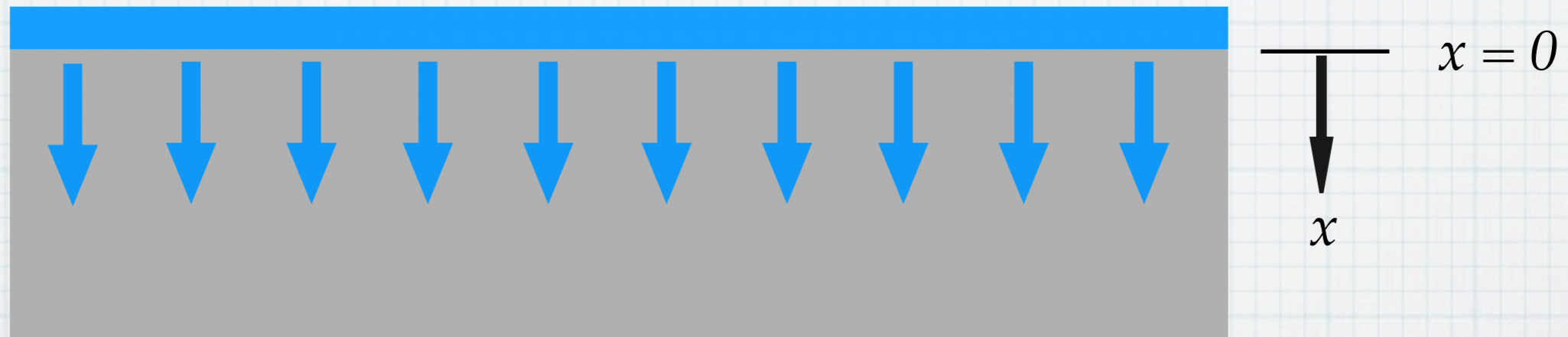
There are relatively straight-forward analytic solutions to the simpler form of the diffusion equation. However, we must note that the approximation used — that D is not a function of concentration — is not always valid. If so, then the analytic solutions obtained from the above equation may not even be good approximations. Some of the dopants that diffuse in silicon do not fall into the simple category. For example, boron can be described reasonably well with the simple theory, but phosphorus cannot.

Lastly, we should note the diffusion can occur in all three dimensions, so the general 3-D form of the simple diffusion eq. is

$$\frac{\partial N}{\partial t} = D \nabla^2 N$$

Simplified geometry

The general approach to using diffusion for getting dopants into a semiconductor crystal is to introduce a large amount of the dopant material at the surface of a wafer (create a concentration gradient) and then turn up the temperature (increase D to a reasonable value) and let nature take its course.



We can treat the problem in a 1-D fashion. Also, we generally assume that initially there is no dopant within the bulk of the wafer [i.e. $N(x \neq 0, t=0) = 0$] and the wafer is so thick that no dopant will ever diffuse to the back surface (i.e. that the wafer is effectively infinitely thick).

Constant-source diffusion

One particular instance of this basic approach is the constant-source diffusion, in which a source of the dopant is applied to the surface and we assume that this has the effect of holding the surface concentration at some high, constant value. The initial and boundary conditions are:

$$N(x > 0, t = 0) = 0 \quad (\text{no dopant in the wafer before the diffusion})$$

$$N(x = 0, t) = N_s \quad (\text{surface concentration is held constant})$$

$$N(x \rightarrow \infty, t) = 0 \quad (\text{nothing gets to backside})$$

The solution to the simple diffusion equation with these conditions is in the form of the *error function*, which is well known in the field of statistics, but it is a bit unwieldy.

$$N(x, t) = N_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right]$$

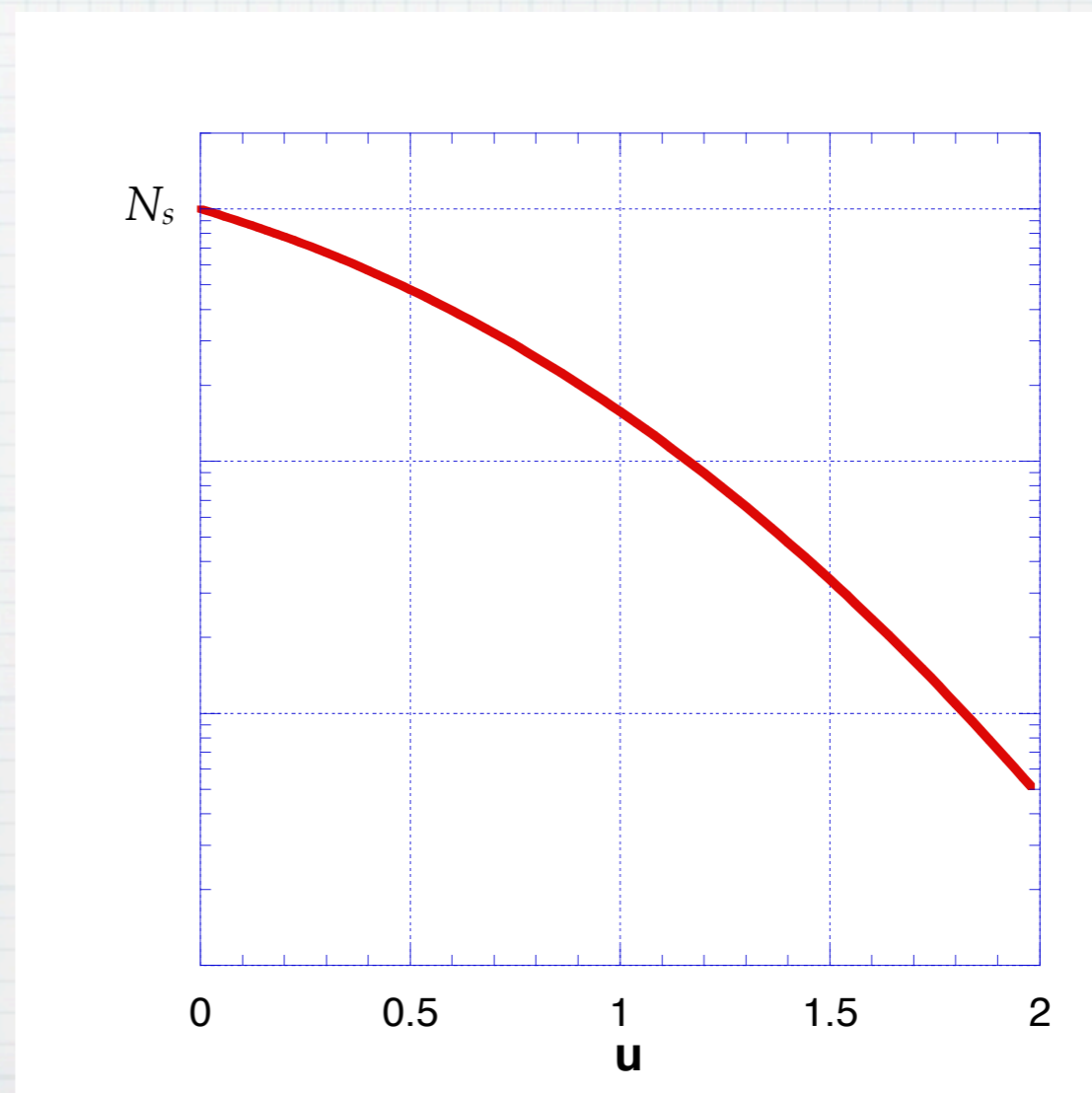
The error function is the integral of a gaussian. As such, there is no simple form of the expression,

$$\text{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u \exp(-v^2) dv$$

We are forced to deal with the messiness of the integral form. Generally, we use a table of values or numerical means. (Excel or Matlab both can be used to calculate values for erf(u). Note that erf(0) = 0 and erf(1) = 1, so we use these that the error function does satisfy the boundary conditions of the constant source diffusion.

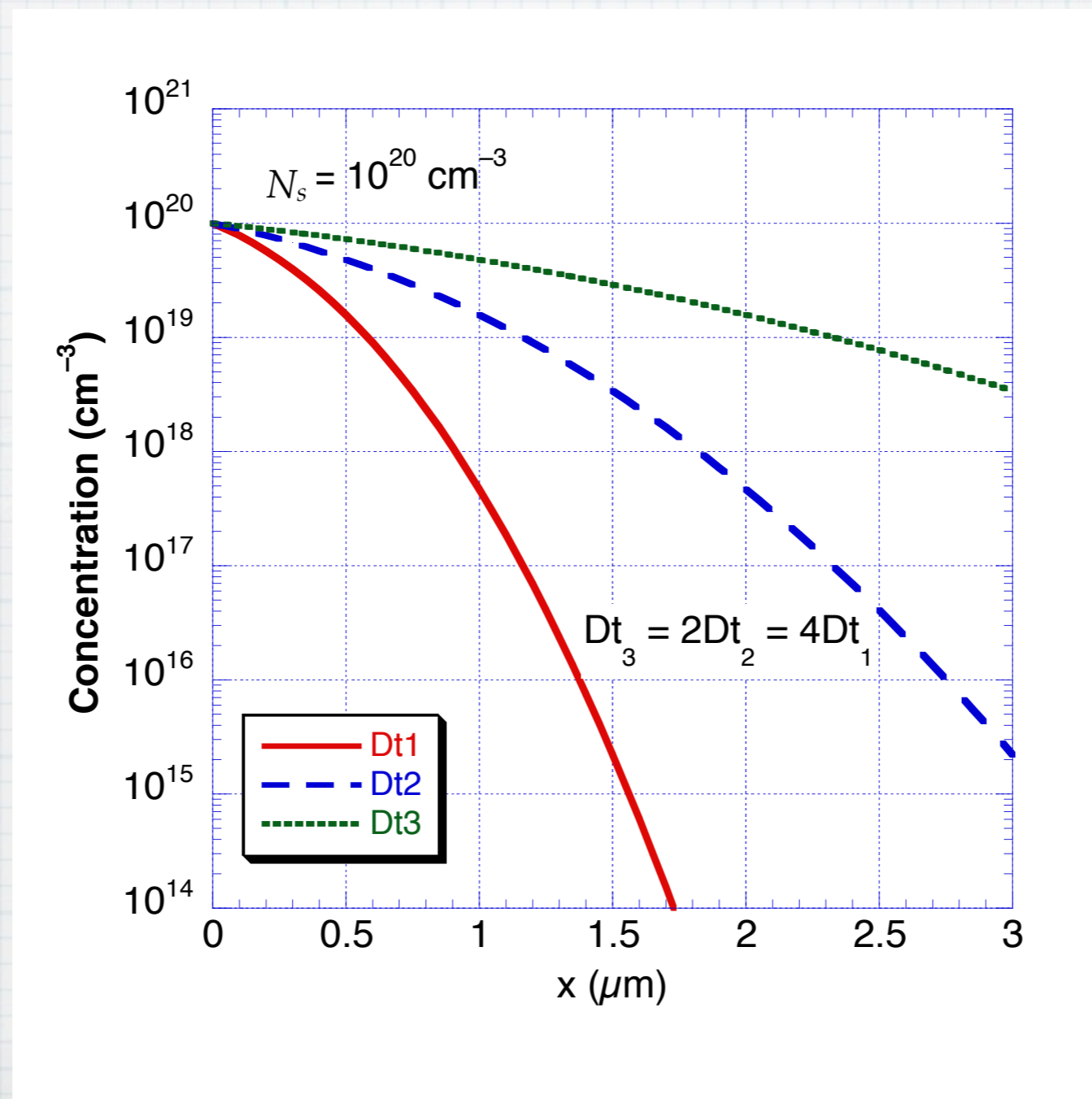
Plot of an erf-function diffusion profile.

Note that the plot is semi-log, as is the custom with the dependent variable ranges over several orders of magnitude.



The quantity Dt determines the shape of the profile. The units of Dt are m^2 . $(Dt)^{1/2}$ has dimension of length, and it represents the characteristic scale of the diffusion. If $(Dt)^{1/2}$ is small, the diffusion is shallow, and if $(Dt)^{1/2}$ is big the diffusion is deeper.

Of course, $(Dt)^{1/2}$ is determined by the temperature and time of the diffusion. So a diffusion can be characterized in terms of a time and a temperature.



Dose

We can define a quantity called the dose, which is the total amount of a dopant diffused into a wafer. Mathematically,

$$Q = \int_0^{\infty} N(x) dx$$

Clearly, the units of dose are m^{-2} (or cm^{-2} or μm^{-2} , etc.) Physically, it means that, if you mapped out a square on the surface of the wafer and then stood within the square on the surface and looked down, the dose would represent all of the dopant that you could see below your feet and within the square, irrespective of distance from the surface.

Surprisingly, the dose of a constant-source diffusion has a simple analytic form, even though the error function itself is unfriendly.

$$\begin{aligned} Q &= \int_0^{\infty} N_s \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] dx \\ &= \frac{2N_s}{\sqrt{\pi}} \sqrt{Dt} \end{aligned}$$

Solid-solubility limit

In principle, the surface concentration that shows up in the diffusion expression could be controlled by changing the flow of a gaseous source of the dopant. (More about this later.)

In practice, however, N_s will be determined by the “solid solubility limit” of the dopant in the silicon. This is the thermodynamic limit of the amount of dopant that can be held by the silicon. Trying to shove in more dopant would require a phase change of some sort. This approach works because we use a process that deposits a glassy layer of dopant on the surface of the wafer. The glassy layer provides an essentially infinite source of dopant available for diffusion. This is how we will do diffusion in EE 432/532 lab.

For some of the dopants, the amount of electrically active dopant is less than the solubility limit. For example, at 1000°C, the solubility limit of As is about 10^{21} cm^{-3} . However, less than half (about $4 \times 10^{20} \text{ cm}^{-3}$) of the available As donors are providing free electrons.

Solid-solubility limits in silicon

All values in cm^{-3} .

	800°C	900°C	1000°C	1100°C	1200°C
Boron	7.00×10^{19}	1.20×10^{20}	2.00×10^{20}	2.70×10^{20}	2.70×10^{20}
Phosphorus		7.00×10^{20}	1.20×10^{21}	1.30×10^{21}	1.50×10^{21}
Arsenic				2.00×10^{21}	2.00×10^{21}
Antimony			1.00×10^{20}	1.00×10^{20}	9.00×10^{20}

(Values taken from "Silicon VLSI Technology" by Plummer, Deal, & Griffin, Fig. 7-4, page 376.)

Constant-dose diffusion

A second important diffusion configuration is the constant-dose diffusion. As the name implies, a constant dose of dopant is introduced into the semiconductor from some source. The source is removed and then diffusion proceeds with a fixed amount of dopant available. Generally, we assume that initial dose is located exactly at the surface of the wafer.

The constant-dose boundary condition is

$$Q = \int_0^{\infty} N(x) dx = \text{constant}$$

The other boundary condition and the initial condition are identical to the constant-source case:

$$N(x > 0, t = 0) = 0 \quad (\text{no dopant in the wafer prior to diffusion})$$

$$N(x \rightarrow \infty, t) = 0 \quad (\text{nothing gets to backside})$$

The diffusion equation solution under these conditions is a Gaussian function:

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

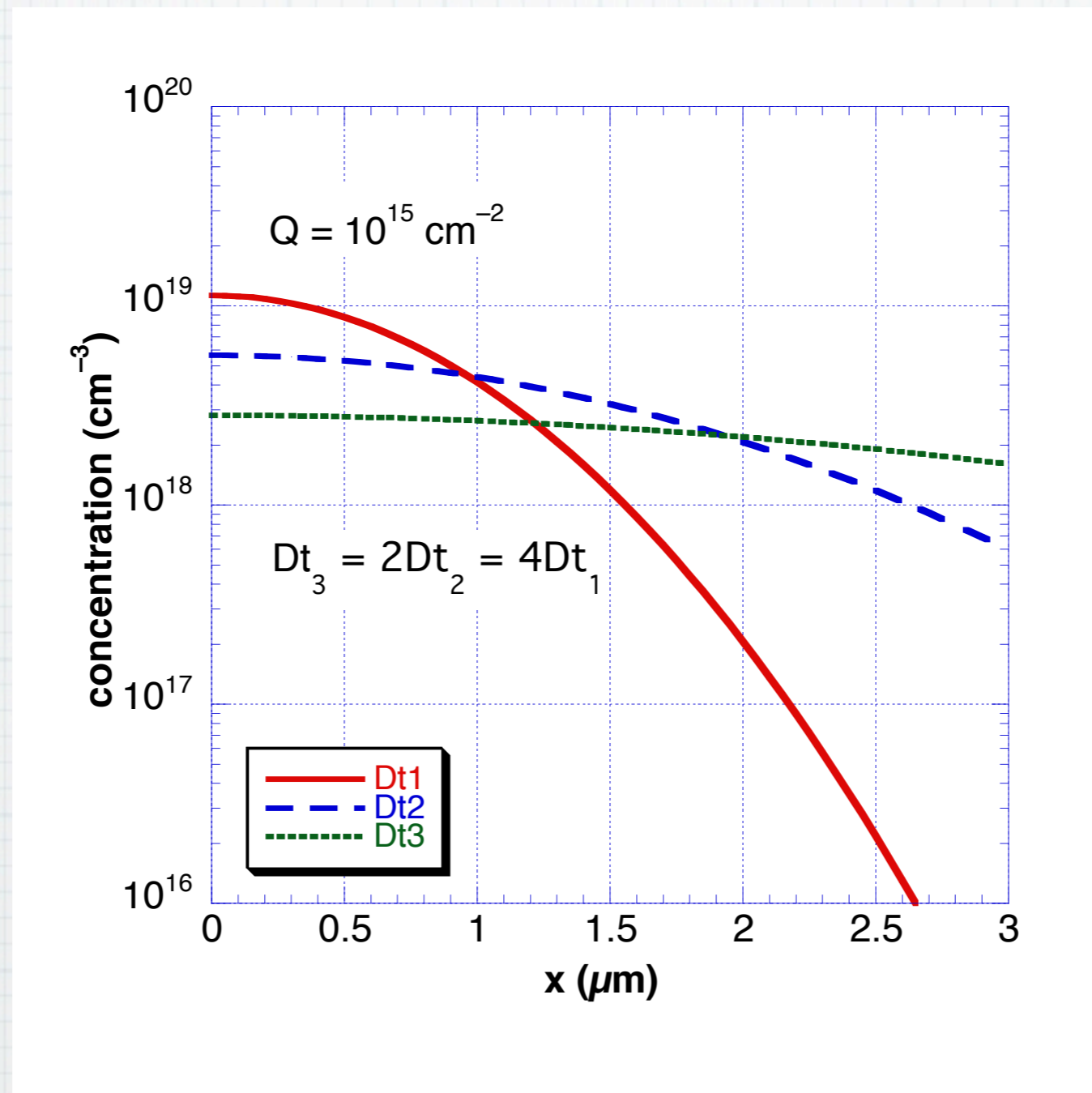
The surface concentration for the Gaussian profile is

$$N(0, t) = \frac{Q}{\sqrt{\pi Dt}}$$

Again, we see that the Dt -product determines the shape of the profile. With a bigger Dt (hotter or longer diffusion), more dopant moves deeper into the wafer.

Since there is a fixed dose of dopant, as more atoms move deeper into the wafer, the surface concentration must decrease. The expression for $N(0)$ confirms that expectation – as Dt increases, the surface concentration decreases.

A graph comparing constant-dose (Gaussian) diffusion with differing values of Dt shows the basic behavior.



Two-step diffusion

A constant-dose diffusion seems to provide more flexibility since we would be able to design the diffusion to get a particular surface concentration. But that begs the question of how to get the initial dose at the surface of the wafer. One method would be to use ion implantation (to be discussed later). Another approach is to use a constant-source (error function) diffusion to introduce the dose. We know that the dose of a constant-source diffusion is given by

$$Q = \frac{2N_s}{\sqrt{\pi}} \sqrt{Dt}$$

If the time is kept short and the temperature kept low, (so that the Dt -product is small), none of the dopant will have diffused far from the surface. As an approximation, we can assume that all of the dopant is right at the surface.

Then we can remove the dopant source (thus fixing the dose) and follow up with constant-dose diffusion step.

Inserting the dose from the constant-source step into the equation for the Gaussian diffusion profile, we obtain the two-step diffusion equation.

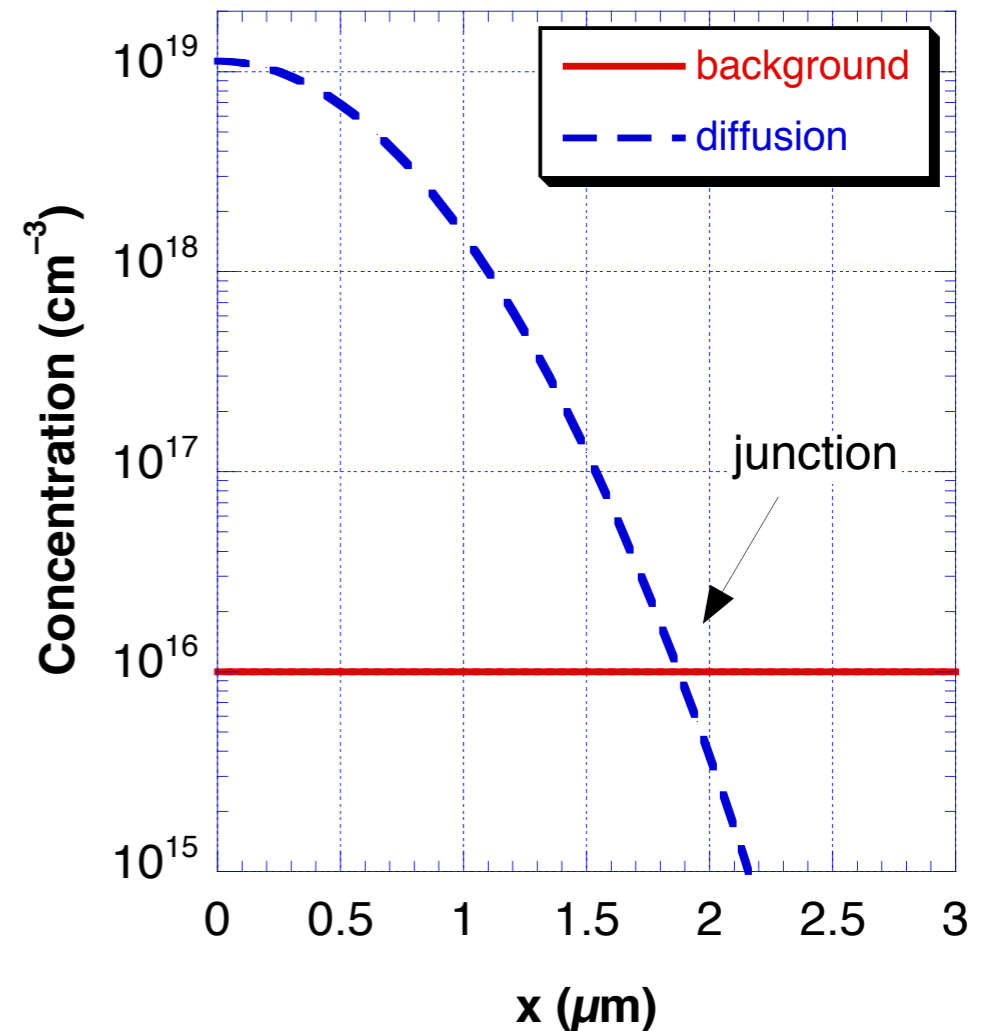
$$N(x, t) = \frac{2N_s}{\pi} \sqrt{\frac{D_1 t_1}{D_2 t_2}} \exp\left(-\frac{x^2}{4D_2 t_2}\right)$$

where $D_1 t_1$ refers to the constant-source step and $D_2 t_2$ are the parameters for the constant-dose step.

With the two-step process, we can control all aspects of the diffusion.

Junction depth

When we perform a diffusion, the new dopant is generally diffusing into a region where some dopant (probably of the opposite type) already exists. The old dopant may be the constant background of the starting wafer or it may be from a previous diffusion. So the new dopant is probably compensating the old dopant in the regions near the surface. Farther down, there will be a junction. In general, we will want to know where that junction occurs. In designing a diffusion, we may want to design for a specific junction location.



Mathematically, we can determine the junction depth in a straightforward manner. If the junction is formed with the background doping of the wafer, simply set the doping profile equal to the background doping at the junction,

$$N(x_j) = N_B$$

and solve for x_j .

Doing this for the constant-source (error function) diffusion:

$$N_B = N_s \left[1 - \operatorname{erf} \left(\frac{x_j}{2\sqrt{Dt}} \right) \right]$$

$$x_j = 2\sqrt{Dt} \left[\operatorname{erf}^{-1} \left(1 - \frac{N_B}{N_s} \right) \right]$$

And for the constant-dose (Gaussian) diffusion:

$$N_B = \frac{Q}{\sqrt{\pi Dt}} \exp\left(-\frac{x_j^2}{4Dt}\right)$$

$$\begin{aligned} x_j &= \sqrt{4Dt \ln\left(\frac{Q}{N_B \sqrt{\pi Dt}}\right)} \\ &= \sqrt{4Dt \ln\left(\frac{N(0)}{N_B}\right)} \end{aligned}$$

Note that the two-step diffusion profile is a special of a constant-dose diffusion.

If the junction is formed by diffusion profiles, the same idea applies, except that you will not use the constant background doping. Instead,

$$N_1(x_j) = N_2(x_j)$$

where $N_1(x)$ and $N_2(x)$ are both doping profiles. (See the homework.)

Diffusion coefficients

	$D_0(\text{cm}^2/\text{s})$	E_A (eV)
boron	1.0	3.50
phosphorus	4.70	3.68
arsenic	9.17	3.99
antimony	4.58	3.88
indium	1.20	3.50

These diffusion coefficients should be viewed as being very approximate. (More on this later.)

study questions

1. Try to think of other examples of diffusion in everyday life.
2. Flux implies a direction of flow, so properly it should be treated as a vector quantity. Determine the vector form of Fick's law.
3. Similarly, write the vector form the continuity relation.
4. Suppose that for some reason, the diffusion coefficient depended on position, such that $D(x)=D_0\exp(-bx)$, where D_0 and b are constants. Starting with the general diffusion equation on slide 5 find the diffusion equation under this particular condition.
5. Confirm the 3-D (vector) form of the diffusion equation.
6. Confirm the erfc-type function solution by inserting it into the diffusion equation and showing that it works. (Or better yet, look up the details of this particular solution and work through it yourself.)

study questions

7. Confirm the Gaussian function solution by inserting into the diffusion equation and showing that it works. (Or better yet, look up the details of this particular solution and work through it yourself.)
8. Confirm the two junction depth equations on slide 22.
9. Do a variety of the web-based diffusion problems.