3.1.2 Diffusion

General Remarks

- If you are not very familiar with diffusion in general, it would be wise to consult some other Hyperscripts:
  - Basic diffusion in "Introduction to Materials Science I" *(at present in German)*
  - Point defects and diffusion in "Defects in Crystals"
- The diffusion of dopants is of course one of the major topics in all process and device considerations. For any modern **Si** technology you must be able to have exactly the right concentration of the right dopant at the right place - with tolerances as small as **1%** in critical cases.
  - And it is not good enough to assure the proper doping *right after* the doping process - what counts is only the dopant distribution in the *finished* device.
  - Annoyingly, every time a high temperature process is executed after one of the doping steps, *all* dopants already put in place will diffuse again, and this must be taken into consideration.
  - Even more annoying, the diffusion of the dopants may depend on the process - it may, e.g., be different if other dopants are present.
  - A well-known example is the so-called emitter-dip or **emitter-push effect** which makes it difficult to achieve very thin base regions in bipolar transistors. The effect is due to a changed diffusion coefficient of **B** in the presence of **P**.
- The only way to master diffusion in making devices is an extensive simulation of the concentration profiles as a function of all parameters involved - always in conjunction with feed-back from measurements. This requires a mathematical framework that can be based on three qualitatively different approaches:
  - Use equations that describe typical solutions to diffusion problems and determine a sufficient number of free parameters experimentally. Observed but poorly understood phenomena may simply be included by adding higher order terms with properly adjusted parameters. This will always work for problems within a certain range of the experimental parameters for which the fit has been made - but not necessarily for other regions in parameter space.
  - Solve macroscopic diffusion equations matched to the problem; i.e. equations of the type expressed in Ficks **1st** and **2nd** law. The input are the diffusion coefficients together with the relevant boundary conditions. This works fine if you know the the dependence of the diffusion coefficients on everything else (which you usually don't).
  - Base the math on the proper atomic mechanisms. If all mechanisms and interactions are fully known, they will contain all informations and the results will be correct by necessity. Unfortunately, all mechanisms and interactions are not fully known - neither in **Si**, nor in all the other semiconductors.
- So none of theses approaches works satisfactorily by itself - what is needed is a combination.
  - In the eighties, e.g., it proved necessary to include diffusion mechanisms mediated by **Si** self-interstitials; a diffusion mechanisms not observed in most other materials.
  - This would be not necessary for "simple" diffusion as expressed in Ficks laws with a constant diffusion coefficients - regular vacancy or interstitial mechanisms are not distinguishable at this level.
  - Special effects, however, may occur and it is far easier to include these effects if the additional mathematical terms reflect the atomic mechanisms - the alternative is to add correction terms with adjustable parameters.
- In any case, diffusion in **Si** (and the other semiconductors) is complicated and an issue of much research and debate. It has become extremely important to include all possible "classical" effects usually neglected because very high precision is needed for very short diffusion times (or penetration depth), but the atomic mechanisms of diffusion in **Si** are still not entirely clear.
  - In what follows a few basic facts and data will be given; in due time some advanced modules with more specific items may follow.
- Basic equations are the two phenomenological laws known as "**Ficks laws**" which connect the (vector) flux $\boldsymbol{j}$ of diffusion particles to the driving force and describe the local change in particle density, $\rho\,(\boldsymbol{x,y,z,t})$ and the **Einstein-Smoluchowski relations** which connect Ficks laws with the atomic mechanisms of diffusion. Ficks first and second law are
- *First law*:

$$\boldsymbol{j} = -\boldsymbol{D} \cdot \nabla \boldsymbol{c}$$

  - With $\boldsymbol{c}$ = concentration of the diffusing particles, $\boldsymbol{D}$ = diffusion constant and ∇ = Napla operator. We have

$$\nabla c = \text{vector} = \left(\frac{\partial c}{\partial x}, \frac{\partial c}{\partial y}, \frac{\partial c}{\partial y} \right)$$

- *Second law*:

$$\frac{\partial c}{\partial t} = D \cdot \Delta c$$

  - With Δ = Delta operator (= ∇^2), and Δc given by

$$\Delta c = \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}$$

- An atomic view of diffusion considering the elementary jumps of diffusing atoms (or vacancies) over a distance a (closely related to the lattice constant) yields not only a justification of Ficks laws, but the relations

$$D = g \cdot a^2 \cdot \nu$$

$$\nu = \nu_0 \cdot \exp - \frac{E^M}{kT}$$

  - With g = geometry factor describing the symmetry of the situation, i.e. essentially the symmetry of the lattice, and ν = jump frequency of the diffusion particle, E^M = activation enthalpies of migration.
- If the diffusion mechanisms involves intrinsic point defects as vacancies (**V**) or self-interstitials (**i**), their concentration is given by

$$n^{V,i} = \exp - \frac{E^F}{kT}$$

  - With E^F = formation enthalpy of the point defect under consideration.
- The problem may get complicated if more than one atomic mechanism is involved. A relevant example for **Si** is the so-called **"kick-out" mechanism** for extrinsic point defects (= impurities):
  - A foreign atom (most prominent is **Au**) diffuses rather fast as interstitial impurity, but on occasion "kicks out" a lattice atom and then becomes substitutional and diffuses very slowly. However, the substitutional **Au** atom may also be kicked out by **Si** interstitials and then diffuses fast again. An animation of this process can be seen in the link.
  - The "kick-out" process is *not* adequately described by the simple version of the Fick equation given above.
- Since even the simple Fick equations are notoriously difficult to solve even for simple cases, not to mention complications by more involved atomic mechanisms, only the two most simple standard solutions shall be briefly discussed.

Diffusion from an Unlimited Surface Source

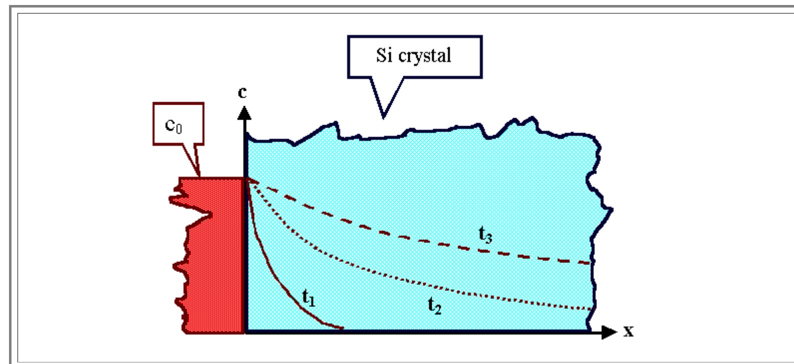
- Consider the following situation:
  - On the surface of a **Si** crystal the concentration c_0 of some dopant species is kept constant - e.g. by immersing the **Si** in a suitable gas with constant pressure or by depositing a thick layer of the substance on the surface.
  - The dopant will then diffuse into the **Si** and since the source of dopant atoms is the surface, there will be a drop in concentration of the dopant from the value c_0 at the surface to zero deep in the crystal.
  - Independent of the dopant concentrations outside the **Si**, the maximum concentration in the **Si** next to surface cannot be larger than the solubility of the dopant atom an the temperature considered; we take c_0 than as solubility limit.
- The general one-dimensional solution of the differential equations of Ficks laws for this boundary condition of an *inexhaustible source* then is given by

$$c(x,t) = c_0 \cdot \mathrm{erfc}\,\frac{x}{L}$$

  - With $L = 2(D \cdot t)^{1/2}$ = diffusion length, and **erfc(*x*)** = complementary errorfunction = **1 – erf(*x*)** and **erf (*z*)** = **errorfunction** given by

$$\mathrm{erf}\,(z) = \frac{2}{\pi^{1/2}} \cdot \int_0^z \exp - a^2 \cdot \mathrm{d}a$$

  - The errorfunction can not be written in closed form; its values, however are tabulated. A typical solution of the diffusion problem may look like this:



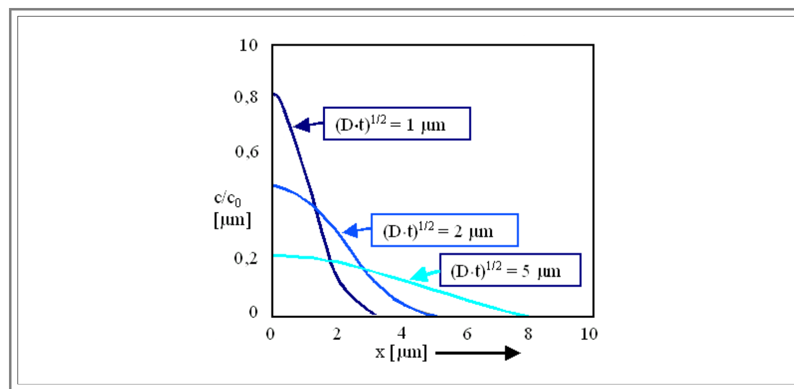
- The interesting quantity is the diffusion length L which is a direct measure of how far the diffusion particles have penetrated into the **Si**. At a distance L from the surface, the concentration of the dopant is about **1/2** c_0 or, to be exact **0,4795 · c_0**.
  - This *diffusion length for dopants* or any other kind of atoms is not to be confused with the diffusion length of minority carriers as introduced before. Of course, the physics is exactly the same - the diffusion length for electron and holes as introduced before could just as well be obtained from solving the Fick equations for these particles.
  - Note in passing that while all definitions of diffusion lengths contain the $(D \cdot t)^{1/2}$ term, the factor **2** (or on occasion $2^{1/2}$) may or may not be there, depending on the exact solution - but this is of little consequence for qualitative discussions.
- The total quantity of dopant atoms now in the **Si** expressed as a concentration c_{total} can be obtained by integrating the "**diffusion profile**", i.e. the curve of the concentration versus depth. This is analytically possible if the integration runs from **0** to ∞ - a very good approximation for slowly diffusing atoms and thick wafers. The result is

$$c_{total} = \frac{L \cdot c_0}{\pi^{1/2}} = 0{,}56 \cdot L \cdot c_0$$

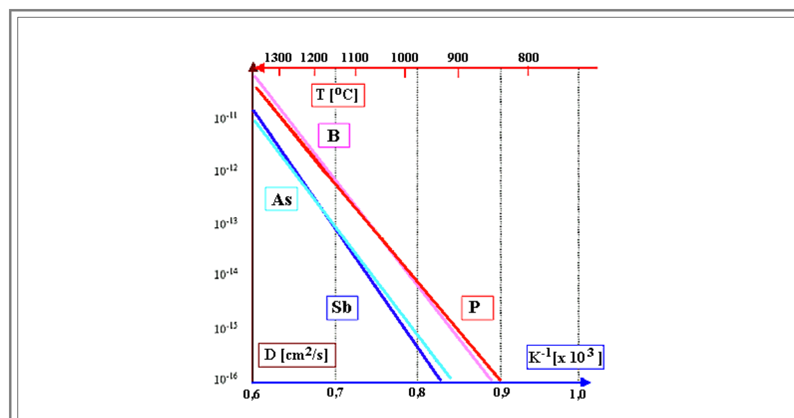
- The other standard solution for diffusion problems deals with the case of a *finite source*; i.e. only a limited amount of diffusion particles is available.
  - This is the standard case for, e.g. **ion implantation**, where a precisely measured number of dopant atoms is implanted into a surface near area.
  - For simplifying the math, we may assume that these dopants are all contained in one atomic layer - a delta function type distribution at the surface.
  - This is of course not true for a real ion implantation, where there is some depth distribution of the concentration below the implanted surface, but as long as the diffusion length obtained in this case is much larger than the distribution width after implantation, this is a good approximation.
- It is more convenient to resort from *volume concentrations* ***c*** of atoms to *areal densities* ***C*** because that is what an ion implantation measures: the total number of **P**-, **As**- or **B**-atoms shot into the wafer per **cm**^{2} called the **dose = atoms/cm**^{2}. With C_0 = implanted dose and $C(x, t)$ the area density in the **Si**, the following solution is obtained:

$$C(x,t) = \left(\frac{C_0}{\pi \cdot D \cdot t}\right)^{1/2} \cdot \exp - \frac{x^2}{4D\,t}$$

  - This is simply one half of a Gaussian distribution (the "–" sign in front of x^2 takes care of this) with a "half-width" of $(Dt)^{1/2}$; what it looks like is shown in the picture.



  - The curves can be characterized by a $(Dt)^{1/2}$ product, which again gives a typical *diffusion length*.
- The quantity of prime importance is always the diffusion coefficient of the diffusing particle. Only for "simple" mechanisms it is a simple function of the prime parameters of the point defect involved as implicitly stated above.
  - $D(T)$ then follows a simple Arrhenius kind of behavior; examples for the common dopants are shown in the figure:



  - The lines shown are perfect straight lines over more than **8** orders of magnitude - provided there are no complications.
- The example of an ion-implanted layer as the source for diffusion, however, provides a good example for some of the complications that may be encountered in real **Si** diffusion:
  - *First* of all, if the distribution of implanted dopant atoms cannot be treated as a delta function, but must be taken into account as it is. Solutions then can only be obtained numerically - with some effort.
  - *Second*, if only a small area has been implanted through a mask, at least a two-dimensional problem must be solved - which is much more complicated.
  - *Third*, some dopant atoms will reach the surface after some random walk. The idealized solution assumes that they will go back into the bulk, i.e. the surface does not act as sink for diffusion atoms. This is, however, not always true and will lead to complications.

- *Fourth*, while all of the above still only amounts to a mathematical exercise in solving Ficks differential equations, there are physical problems, too: Ion implantation produces lots of surplus vacancies and interstitials which will become mobile during the diffusion procedure. The point defect concentration at the diffusion temperature thus is *not* identical to the equilibrium concentration (at least for some time), and the diffusion coefficient which always reflects the underlying atomic mechanism for equilibrium conditions, will be changed and become time dependent - a very messy situation!

In fact, the usual goal after ion implantation is to keep the implanted profile in place as much as possible - no diffusion would just be great. But you must get rid of the crystal lattice defects produced by the implantation and for that you must anneal at elevated temperatures for some time - and diffusion will take place!

- What is better: Long anneals at low temperatures or short anneals at high temperatures to remove the defects but keep your dopants in place. Not an easy question; the answer must depend on the kinetics of the defect annealing and the diffusion peculiarities of the atom under consideration.
- However, the second case is usually preferred, and a whole industry has developed around this point under the catch phrase "**rapid thermal annealing** or **rapid thermal processing** (***RTA*** or ***RTP***, respectively).

But there are more complications yet:

- The diffusion of an atom may be changed if there are noticeable concentrations of other foreign atoms around - and this includes the own species. **P**, as an example, diffuses faster in large concentrations and also enhances the diffusivity of **B** (a key word is: "emitter push effect").
- Some processes (notably thermal oxidation) produces non-equilibrium point defects (oxidation produces **Si** interstitials) which will be felt by atoms diffusing via these point defects - their diffusivity will be different if the **Si** is oxidized compared to an inert surface.
- Some atoms, as already mentioned above, diffuse by more complicated mechanisms, e.g. the kick-out mechanism. In a treatment with Ficks equations, this calls for two superimposed mechanisms, each with its own diffusion constant and some boundary conditions to assure particle conservation etc.
- A review from **1988** (which almost certainly will have been contested in the meantime in some points) covering just fast diffusing elements in Si and discussing some of the complications mentioned above, is provided in the link.
- Some prominent cases of deviations from simple diffusion behavior can be found in an advanced module

It should come as no surprise than that diffusion in **Si**, as far as the application to devices is concerned, is an active area of research and development, and that no process engineer will ever believe the results of a simulation for diffusion under a new set of conditions without experimental verification.

This leaves us with the question how diffusion profiles are measured - a large issue in its own right. We will deal with this only cursory, by giving catch words. You must look it up yourself if you want to know more.

- **Sheet resistance measurements**
  This is the easiest method, but it only gives the average resistance of the doped layer (always assuming that it sits on top of something pretty insulating).
- **Spreading resistance measurements**
  Here the resistance is measured as a function of depth by bevelling the sample. Cheap and easy in principle, but error prone and tricky for shallow profiles (say for diffusion length smaller than a few µm).
- **Direct doping concentration measurements by SIMS**
  Very expensive and slow - but the ultimate method.