

3. Silicon: General Properties and Technologies

3.1 General Properties

3.1.1 Conductivity, Lifetime and Lattice Defects

General Remarks

This Module is unfinished

- ▶ Silicon is by far the most common semiconductor used for all kinds of products; it accounts for more than **90%** (my estimate) of semiconductor products (measured in **kg** or **\$**; whatever).
 - It is also by far the most perfect semiconductor in terms of crystalline perfection, the cheapest in its field of applications if you consider value for money, and perhaps the best understood.
 - There are, however, plenty of questions concerning the properties of **Si** that are *not* well understood and thus there is plenty of research opportunity and enough room for new uses of the good old **Si**.
- ▶ Most of the basic properties of **Si** were already covered in the illustrations to the preceding chapter. Here only a short summary will be given.
- ▶ The **intrinsic conductivity** is governed by the band gap which determines the carrier density. The resistivity, in turn, is given by *carrier density times mobility*. It should thus be possible to give precise values.
 - However, upon closer inspection it turns out that not only carrier mobilities are temperature dependent, but the band gap, and the effective masses, too. That makes precise calculations difficult. We have, e.g.
 $E_g(300\text{ K})=1,1242\text{ eV}$
 $E_g(0\text{ K})=1,1700\text{ eV}$.
 - Measurements, while always possible, must allow for non-perfection - there is no such thing as an perfect intrinsic semiconductor. With lots of precautions, it is possible to grow crystals with a resistivity (at room temperature) of about **1 000 Ωcm** - still far lower than the intrinsic value.
- ▶ This should motivate a little exercise:

Exercise 3.1.1

What is perfection?

- ▶ All in all, the precise temperature dependence of truly intrinsic **Si** is not so interesting anyway - because we never encounter it.
 - What is interesting are some basic numerical values:

Bandgap (indirect)	$E_g(300\text{ K})=1,1242\text{ eV}$
Effective density of states (conduction band)	$3,22 \cdot 10^{19}\text{ cm}^{-3}$
Effective density of states (valence band)	$1,83 \cdot 10^{19}\text{ cm}^{-3}$
Intrinsic carrier density n_i (300K)	$1,3 \cdot 10^{10}\text{ cm}^{-3}$
Intrinsic mobility of electrons (300K)	ca. $1400\text{ cm}^2/\text{Vs}$
Intrinsic mobility of holes (300K)	ca. $500\text{ cm}^2/\text{Vs}$
Lifetime (max).	1 ms (für $\approx 100\ \Omega\text{cm}$)
Density	$2.33\text{ g/cm}^{-3} \approx 5 \cdot 10^{22}\text{ atoms/cm}^{-3}$
Surface density	$\begin{matrix} 11.8 \\ 9.6 \\ 6.8 \end{matrix} \left. \vphantom{\begin{matrix} 11.8 \\ 9.6 \\ 6.8 \end{matrix}} \right) \times 10^{14} \frac{\text{atoms}}{\text{cm}^2} \left(\begin{matrix} \text{on } \{111\} \\ \text{on } \{110\} \\ \text{on } \{100\} \end{matrix} \right)$

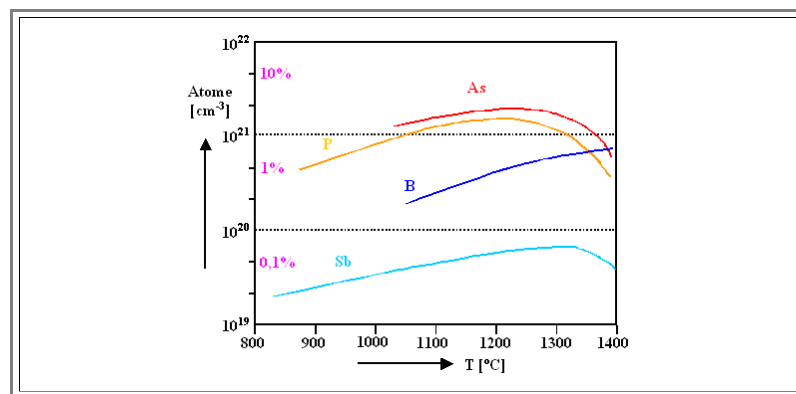
Conductivity and Initial Doping

As stated above, it is not easy to produce **Si** with a conductivity close to the intrinsic limit.

- **Si** wafers commercially available therefore have resistivities $\rho \leq 100 \Omega\text{cm}$ (at room temperature); if you want something better than that you have to negotiate with the supplier.
- An [example for what is on the market](#) can be found in the link.

At the other end, large conductivities, obtained by heavy doping, are limited by the maximum **solubility** of the dopants. The term "solubility" refers to the (temperature dependent) equilibrium concentration of impurity atoms that can be incorporated into a crystal as single atoms.

- For concentrations higher than the **solubility limit**, the surplus impurity atoms would tend to precipitate - and precipitates of **As**, **B**, or **P**, while possibly introducing defect levels in the band gap, are *not* active as dopants.
- The highest achievable meaningful doping levels are thus given by the highest solubility of a doping element (always at a high temperature) - provided it can be kept in **solid solution**. This means that precipitation must be suppressed because at room temperature the solubility is usually low.
- The picture below shows solubility data for the common **Si** dopants. In all cases the solubility is rather large (with a maximum between **1200 °C** and **1400 °C**), and may surpass the **1%** level.



- If the maximum concentration *could* be kept in solid solution while the crystal is grown, the resistivity *could* be lower than what has been listed above. However, this is neither feasible nor sensible. Making devices always involves some heating, and if dopants are present in a high supersaturation, precipitation may start during processing, leading to all kinds of unwanted effects besides the unavoidable change in conductivity.
- There is, however, no particular need for high doping levels *and* a high precision of doping. Making devices always means that *local* doping is optimized - e.g. while making a source/drain area - and this requires medium to low doping levels of the substrate which are easily achieved.
- High doping is only important if the wafers are used as substrate for epitaxial layers, and then the exact doping level is not crucially important.
- The real importance of the solubility curves thus is in specifying how much doping can be achieved on top of the initial doping by e.g. diffusion or ion-implantation. This will of course depend on the temperature!
- Ion implantation done at room temperature thus always needs an **annealing** step to "**activate**" the dopants, i.e. to dissolve them in the **Si** up to the solubility limit at the chosen temperature. At the same time, this high temperature process also (hopefully) "anneals" the lattice defects produced by ion implantation.
- There are limits to **defect annealing**, too: High doping levels change the average lattice constant - especially the small **B** ion reduces this parameter. Heavily **B**-doped layers thus want to contract, and since this is not possible on top of a solid substrate, mechanical stress is introduced which may lead to the formation of so-called "misfit dislocations" - [the link](#) shows an example.

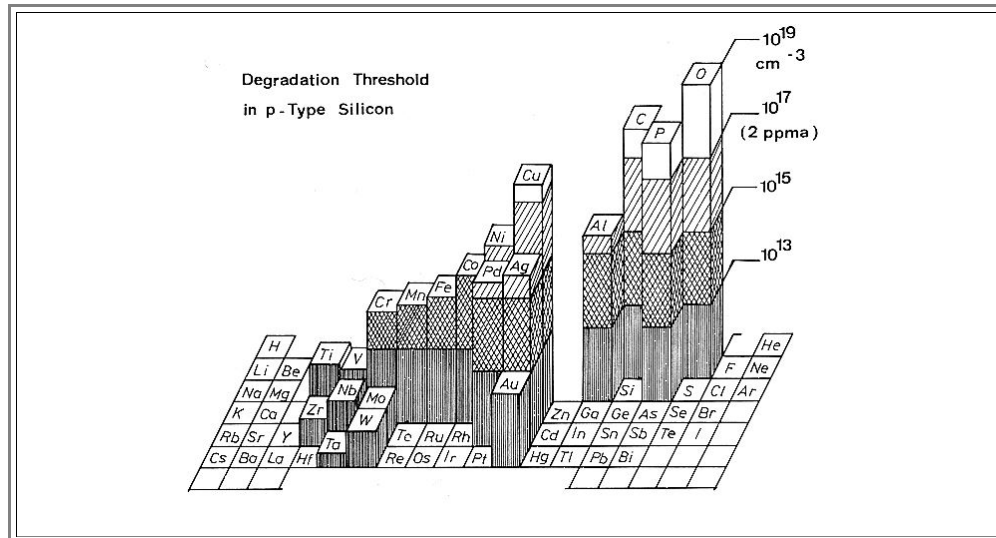
Lifetime and Diffusion Length

Silicon is an indirect semiconductor, [we expect](#) relatively large lifetimes and diffusion lengths.

- This is indeed the case, lifetimes as large as **1 ms** can be observed in extreme cases (This is an exceedingly long time for an electron!)
- The corresponding diffusion length approach **mm**; again a very large distance for an atomic particle.
- Some [numerical values](#) linking lifetime and diffusion length for Silicon can be found via the link

Lifetime and diffusion length are direct measures of the cleanliness of **Si** with respect to "deep level" impurities which act as life time killers as directly evident from the [Shockley-Read-Hall theory](#).

- There are many ways to measure the life time. A particularly unconventional approach giving the most precise data for the diffusion length is the ["ELYMAT" technique](#), which is discussed in an advanced module.
- The ELYMAT and other tools like it have been used extensively in the nineties to "clean up" **Si** production and processing lines because even minute traces of contamination show up in a reduced diffusion length.
- While it is generally important to maintain large diffusion lengths as a measure of cleanliness (and for some electronic properties) in integrated circuits, it is particularly important for **solar cells**.
- Any carrier generated by light that recombines in the bulk of the solar cell is lost for the external current that the solar cell is supposed to produce. Diffusion lengths thus must be larger than the absorption depth for solar light, otherwise the light generated carriers will not be able to diffuse to the the surface junction and produce current. What this means in practical (rather relaxed) terms is shown in the graph:



- For **CMOS** grade **Si** the requirements are much more stringent: Allowed levels of "life time killing" metals are much lower and specified at $< 5 \cdot 10^{10} \text{ cm}^{-3}$, i.e. at **<1ppt** (introducing now for the first time the **ppqt** - "parts per quadrillion" range).
- This is not so much because large lifetimes are so important, but because the metals killing the lifetime tend to precipitate - and even extremely low densities (say **1 precipitate /cm²**) of extremely small precipitates (say **10 nm**), if contained in a critical part of a device - e.g. at the **Si** - gate oxide interface - will kill a transistor and such the whole device. [An example](#) is given in the link.

Lattice Defects

- Lattice defects in microelectronic **Si** are easy to deal with: *They are simply not allowed!*
- While it is indeed possible to avoid "larger" defects like grain boundaries, dislocations and sizeable precipitates in **Si** crystals (cf. the relevant chapters of the ["Electronic Materials"](#) and ["Defects in Crystals"](#) Hyperscripts), there is no way to avoid point defects or small agglomerates of point defects, also known as **"BMD"s (bulk microdefects)** or **"COP"s (crystal originated particles or pits)**, or **LLS** (sometimes also abbreviated **LPDs**): [Localized Light Scattering Defect](#).
- Why? Simply because point defects (vacancies and self interstitials) will be present in thermal equilibrium during crystal growth - and they cannot disappear at internal sinks like grain boundaries and dislocations because there aren't any; and the surface as an external sink is simply too far away for all but the surface-near point defects. The equilibrium point defects thus will be either "frozen-in" during cooling or form agglomerates which constitute the **BMDs**.
- Usually, these microdefects are few and small - it is not easy to detect them and often they are below the detection limits of the most advanced methods. Historically, however, they are periodically rediscovered because devices are becoming steadily smaller and more sensitive and their (always negative) influence on device properties is felt at some point.
- As a curiosity, it shall be noted in passing that point defect equilibria in **Si** are much more complicated than in other elemental crystals and not very well understood up to this day.
- In particular, **Si** seems to be the only elemental crystal so far where self-interstitials are present in thermal equilibrium in concentrations that are comparable to vacancies (otherwise their concentration is always much lower). This implies that both vacancies and self-interstitials are involved in the formation of **BMDs** and that the diffusion of substitutional impurities (including all dopants) might be more complicated than usual.
- Some more details can be found in the ["Defects in Crystals"](#) Hyperscript.