2.3. Point Defects in Semiconductors like Silicon

2.3.1 General Remarks

- In all semiconductors, lattice defects change the electronic properties of the material locally, and this may result in electronic energy states in the band gap of the semiconductor and this is true for all kinds of lattice defects
  - Semiconductor technology actually depends completely on this fact. **Doping** a semiconductor, after all, mostly means the incorporation of (usually) substitutional **extrinsic point defects** in defined concentrations in defined regions of the crystal - we have **B**, **As** and **P** for **Si**.
  - Our extrinsic point defects now exist in two states: we have some concentration $[P]^0$ of e.g. a neutral donor like **P** and some concentration $[P]^+$ of ionized donors; and $[P]^0 + [P]^+ = [P_0]$, the total concentration of **P** holds at all conditions.
  - The concentration $[P]^+$ is simply given by the the total concentration times the probability that the electronic state associated with the **P** impurity atom is *not* occupied by an electron.
  - If this electrons state is at an energy E_D in the band gap, basic semiconductor physics tells us that for a given E_F and temperature T the concentration of ionized impurity atoms is given by

$$[P^+] = [P^0] \cdot \{1 - f(E_D, E_F; T)\}$$

$$\approx [P^0] \cdot \exp \frac{E_F - E_D}{kT}$$

- There is no reason whatsoever that a vacancy (or any other point defect you care to come up with) should not have a energy level (or even more than one) in the band gap of its host semiconductor. This level then will be occupied or not occupied by electrons exactly like the extrinsic point defect.
  - If the vacancy is mobile at the temperature considered, it will diffuse around - exactly like an extrinsic mobile defect.
  - If the temperature changes, the intrinsic point defects concentration changes to the extent that it can establish equilibrium - *in pronounced contrast to the extrinsic point defects*.
- It should be clear form this, that intrinsic point defects in semiconductors are not all that simple. Charge states must be considered that depend on primary doping with extrinsic point defects and temperature. If things get really messy, the intrinsic point defects change the actual doping and their mobility (or diffusion coefficient) depends on their charge state.
- Looking at jus at few topics in the case of **Si**, we obtain a bunch of complex relations, which shall only be touched upon:
  - Once again, the equilibrium concentration of charged point defects depends on the **Fermi energy** E_F (which is the chemical potential of the electrons). As an example, for a negatively charged vacancy we obtain

$$c(V^-) = c(V) \cdot \exp \frac{E_F - E_A}{kT}$$

  - With E_F = Fermi energy, and E_A = *acceptor level of the vacancy* in the band gap.
  - This tells us that besides the formation energies and entropies, we now also must know the **energy levels** of the defects in the band gap!
  - The dependence of the concentration of arbitrarily charged point defects on the carrier concentration (i.e. on doping) is given by

$$\frac{c_{Vx}(n)}{c_{Vx}(n_i)} = \left(\frac{n}{n_i}\right)^{-x}$$

  - With n_i, n = (intrinsic) carrier density, x = charge state of point defect.
- As a ***Si** special*, we also must consider **self-interstitials** (which, if you remember, we always can safely neglect for just about any other elemental crystal)
  - Local equilibrium between vacancies and interstitials follows this relation:

$$c_V(\text{loc}) \cdot c_i(\text{loc}) \approx c_V(\text{equ}) \cdot c_i(\text{equ})$$

- Considering that carrier densities and the Fermi energy depend on the temperature, too, things obviously get complicated!
- It thus should not be a big surprise that the scientific community still has not come up with reliable, or least undisputed numbers for the basic properties of intrinsic point defects in **Si**, not to mention the more complicated semiconductors.
  - But do not let yourself be deceived by this: While *you* might have problems coming up with numbers for e.g. the vacancy concentration in **Si** at some temperature and so on, the ***Si*** *crystal* has no problems whatsoever to "produce" the concentration that is just right for this condition.

- Here are two relevant articles that can be read as a *pdf file*:
  - **The Engineering of Intrinsic Point Defects in Silicon Wafers and Crystals**
    R. **Falster** and V.V. **Voronkov**
  - **Defects in Monocrystalline Silicon**
    Wilfried von Ammon, Andreas Sattler, Gudrun Kissinger; in: Springer Handbook of Electronic and Photonic Materials, Safa Kasap, PeterCapper (Eds.), 2017