

3.3 Experimental Approaches to Diffusion Phenomena

3.3.1 Determination of Diffusion Profiles

General Remarks

- ▶ In a typical diffusion experiment, some impurity atoms are introduced into a host by first putting them (ideally) with δ - distribution at the surface.
 - After annealing for a specified time at a specified temperatures, some diffusion of the impurity atoms will have produced a **diffusion profile**, i.e. a smooth curve of the concentration c vs. depth x in the sample (usually plotted as $\lg(c) - x$ curve).
 - Some experimental care is necessary. Simply depositing the impurity atoms on the surface of the host crystal may not lead to any results, because e.g. an impenetrable oxide layer may prevent any diffusion of the impurity atoms into the crystal. "Shooting" the impurity atoms into a surface-near area via ion implantation will overcome that problem, but may create its own problems by generating point defects which change the regular diffusion behavior.
 - There are some well established standard methods for measuring the diffusion profiles after a successful diffusion experiment (see below). Fitting the profile to the applicable solution of Ficks law will provide two results:
 1. The numerical value of the diffusion coefficient D for the set of parameters considered.
 2. The validity of Ficks law for this case as evidenced by the quality of the fit.
 - Of course, any "macroscopic" method for measuring profiles relies on having a profile on a, lets say, **10 μm** scale in the first place, i.e. each impurity atom must have made *many* individual jumps.
 - This will in most cases only happen at sufficiently high temperatures. Waiting a long time is not very effective; this is immediately clear if looking at diffusion phenomena in a [slightly different way](#).
- ▶ How then do we get experimental data at small concentrations or small numbers of jumps? The answer is: use radioactive **tracer atoms** as the diffusing atoms, that can be found and identified in extreme small concentrations!

Tracer Techniques

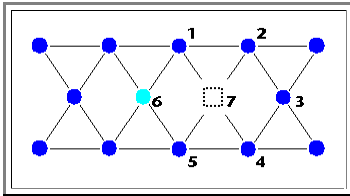
- ▶ Radioactive tracer atoms can be easily detected whenever they decay, emitting some high energy radiation.
 - If the half-life time of the tracer used is relatively small (but still large enough to allow an experiment before the tracer has vanished), a large percentage of the tracer atoms can be detected by their decay products - typically α , β , or γ -rays. We thus may have an extremely high detection efficiency, many orders of magnitude below the detection limits of standard methods.
- ▶ Lets consider the general way a tracer experiment is done:
 - Deposit a thin layer of the atoms that are to diffuse on the (very clean) host crystal. Some of those atoms should be a suitable radioactive isotope of the species investigated. Use any deposition technique that works for you (evaporation, sputtering techniques, sol-gel techniques ("painting it on")...), but make sure that the deposition technique does not alter your substrate (sputtering, e.g., may produce point defects) and that you have no "barrier layer" between the substrate and the thin layer.
 - Anneal for a suitable time at a specific temperature.
 - Remove thin layers from the surface (ideally one atomic layer after the other) by, e.g. sputtering techniques, anodic oxidation and chemical stripping, ultramicrotomes, chemical dissolution, ...).
 - Measure the radioactivity of each layer.
 - With the known half-life of the tracer and the time since the deposition of the layer, calculate how many tracer atoms are in your layer. From the measurement of many layers a concentration profile of the tracer atoms results.
- ▶ The rest is conventional: Fit the profile against a standard solution of Ficks law or against your own solution and extract the diffusion coefficient for the *one* temperature used. This gives *one* data point. And then:
 - Repeat the experiment for several other temperatures, collecting data points for different temperatures.
 - From an Arrhenius representation of the measured diffusion coefficients you obtain D_0 *and* an activation energy for the tracer diffusion if your data are on a (halfway) straight line.
- ▶ If this sounds tedious, it's because it is! You appreciate why students doing a master or PhD thesis are so essential to research. Still, nothing beats tracer experiments when it comes to sensitivity and accuracy.
 - There is, however, a basic problem that we have to discuss if you want to extract information about the vehicle of the tracer diffusion, i.e. about the vacancies or, in some cases, interstitials from a tracer experiment. This is always the case when dealing with self-diffusion.

- The diffusion coefficient of the tracer atom is not necessarily identical with the diffusion coefficient for self-diffusion as defined for the vehicles - usually vacancies.

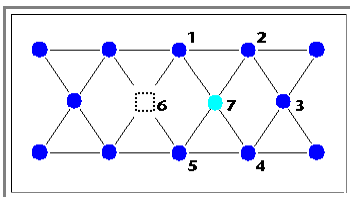
The reason for this is that the tracer is a *specific* atom, while we look at *many* vacancies that help it along - and we must not confuse the vehicle with the diffusing impurity (or tracer) atom, *as noted before*. In particular, the jumps of the tracer atom may be *correlated* with the jumps of the individual vacancy coming by.

- In other words, whereas a particular vacancy may (and usually does) jump around in a perfect *random walk* pattern (i.e. each jump contributes to the mean square displacement of the vacancy), the *tracer atom* may *not* move randomly!

Lets look at a simple example for a two-dimensional vacancy diffusion mechanism.



The tracer atom is marked in light blue, it has a vacancy as a neighbor, a jump is possible.



Vacancy and tracer atom have exchanged their positions.

- Next, the vacancy will jump again - with equal probability on one of the **6** surrounding atom sites - so it is truly doing a random walk. And *one* of those jumps goes back to position **7**, with exactly the same probability as to the other available sites.
- The "viewpoint" of the tracer atom, however, is different. It will jump back to site **6** with a *higher probability* than to the sites **1 - 5** because a vacancy *is available on 6*, whereas for the other sites the passing of some *other* vacancy must be awaited. There is a *correlation between jump 1 and jump 2 - there is no random walk*. The jumps back will lead to wrong values of the mean square displacement, because this combination does not add anything and occurs more frequently as it would for a truly random walk.

The correlation effects between individual jumps of the tracer atom and the random jumps of vacancies can be calculated by a rigid theory of diffusion by individual jumps, but here I won't go into that.

- As a result, these **correlation effects** (in all dimensions and for all lattice types) can be dealt with by defining a **correlation factor f** that must be introduced into the equations coupling the tracer diffusion to the vacancy diffusion.

We define a correlation coefficient f_{1V} that allows to correlate the diffusion coefficient for the (vacancy driven) self-diffusion, $D_{SD}(T)$, *as measured by a tracer experiment*, to the diffusion coefficient for self-diffusion, $D_{SD}(\text{Theo})$ *as given by theory* via the equation

$$D_{SD}(T) = f_{1V} \cdot D_{SD}(\text{Theo})$$

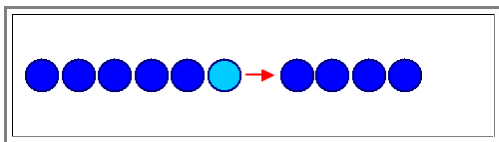
- As an example for a real correlation factor we look at $f_{1V}(\text{cub})$, the correlation factor for self-diffusion mediated by single vacancies in a cubic lattice. It is given in a good approximation by

$$f_{1V}(\text{cub}) \approx 1 - \frac{2}{z} = \begin{matrix} 5/6 & \text{fcc} \\ 3/4 & \text{bcc} \end{matrix}$$

- With z = number of nearest neighbors.

To illustrate the correlation phenomena, suppose that $f = 0$. In this case, even for wildly moving vacancies ($D_{SD} \gg 0$), the tracer atoms would not move - we would not observe any diffusion.

- This case is fully realized for *one-dimensional* diffusion, where it is also easy to see what happens - just consider a chain of atoms with one vacancy:



- The vacancy may move back and forth the chain like crazy - the tracer atom (light blue) at most moves between two position, because on the average there will be just as many vacancies coming from the right (tracer jumps to the left) than from the left (tracer jumps to the right).
- Correlation coefficients can be *calculated* - as long as the diffusion mechanism and the lattice structure are known. They are, however, very difficult to *measure* which is unfortunate, because they contain rather direct information about the mechanism of the diffusion. The calculations, however, are not necessarily easy.
- Impurity atoms, which may have some interaction with a vacancy, may show complicated correlation effects because in this case the vacancy, too, does no longer diffuse totally randomly, but shows some correlation to whatever the impurity atom does.
- If a kick-out mechanism is active, the tracer atom might quickly be found immobile on a lattice site, whereas another atom - which however will not be detected because it is not radioactive - now diffuses through the lattice. The correlation factor is very small.
- Some examples for correlation coefficients are given in the table for a simple vacancy mechanism (after **Seeger**). The correct value from extended calculations is contrasted to the value from the simple formula given above.

Lattice type	coordination number z	$f_{1V} \approx 1 - 2/z$	f_{1V} (correct)
One dim. lattice			
Chain	2	0	0
Two dim. lattices			
hex. close packed	6	0,6666	0,56006
square	4	0,5	0,46694
Three dim. lattice			
cub. primitive	6	0,6666	0,65311
Diamond	4	0,5	0,5
bcc	8	0,75	0,72722
fcc	12	0,83	0,78146

Other Methods for Measuring Diffusion Coefficients

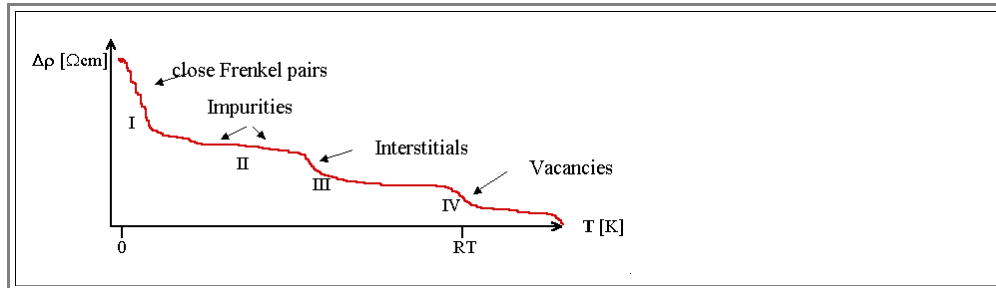
There is a *plethora* of methods, some are treated in other lecture courses. In what follows a few important methods are just mentioned.

Concentration Profile Measurements

- **Secondary Ion Mass Spectrometry (SIMS)** for direct measurements of atom concentrations. This is the most important method for measuring diffusion profiles of dopants in Si (and other semiconductors).
- **Rutherford Backscattering (RBS)** for direct measurements of atom concentrations.
- Various methods for measuring the *conductivity* as a function of depth for semiconductors which corresponds more or less directly to the concentration of doping atoms. In particular:
 - Capacity as a function of the applied voltage (" $C(U)$ ") for **MOS** and junction structures)
 - Spreading resistance measurements
 - Microwave absorption.
- Local **growth kinetics** of defects, e.g. the precipitation of an impurity, contain information about the diffusion, e.g.
 - Growth of **oxidation induced stacking faults** in **Si**
 - Impurity -"free" regions around grain boundaries (because the impurities diffused into the grain boundary where they are trapped).
- An example for a "diffusion denuded" zone along grain boundaries can be seen in the [illustration](#)

Annealing experiments (See also [chapter 4.2.1](#))

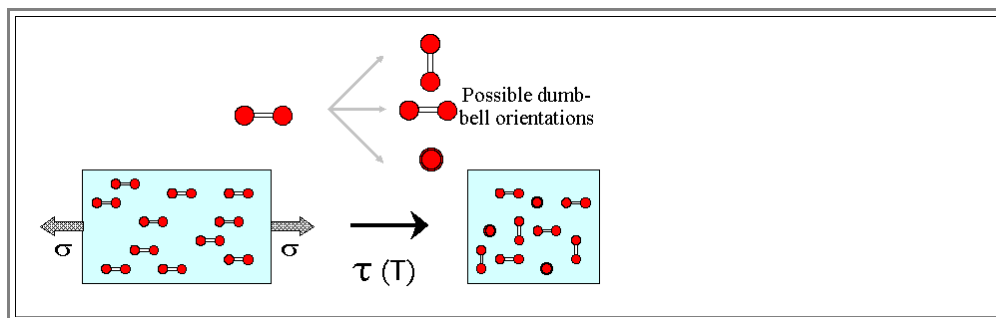
- These experiments are in a class of their own. In this case point defects which have been rendered immobile in a large *supersaturation*, e.g. by rapid cooling from high temperatures, are made mobile again by controlled annealing at specified temperatures. Since they tend to disappear - by precipitation or outdiffusion - measuring a parameter that is sensitive to point defects - e.g. the residual resistivity - will give kinetic data.
- A classical experiment produces supersaturated point defects by irradiation at low temperatures with high-energy electrons (**a few MeV**). The energy of the electrons must be large enough to displace single atoms - Frenkel pairs may be formed - but not large enough to produce extended damage "cascades".
- Annealing for a defined time at a specified temperature will remove some point defects which is monitored by measuring the residual resistivity - always at the same very low temperature (**usually 4K**). Repeating the sequence many times at increasing temperatures gives an annealing curve. A typical annealing curve may look like this:



- What "impurities" means in this context is left open. They may form small complexes, interact with nearby vacancies or interstitials, or whatever.
- The interpretation of the steps in the annealing curves as shown above is not uncontested. The "Stuttgart school" around **A. Seeger** has a completely different interpretation, invoking the "crowdion", than the (more or less) rest of the world.

Methods measuring single atomic jumps

- This ultimate tool can be used if the point defects have rather low symmetry. The best example is the dumbbell configuration of the interstitial or interstitial carbon in **Fe**
- In the classical experiment the crystal is uniaxially deformed at not too low temperatures. The dumbbells will, given enough time, orient themselves in the direction of tensile deformation (there is more space available, so the energy is lower) and thus carry some of the strain. We have more dumbbells in one of the three possible orientations than in the two other ones (see below)



- The tensile stress is now suddenly relieved. Besides the purely and instantaneous elastic relaxation, we will now see a slow and temperature dependent additional relaxation because the dumbbells will randomize again. The time constant of this process directly contains the jump frequency for dumbbells. This effect, which exists in many variants, is called "**Snoek effect**".
- If you do not use a static stress, but a periodic variation with a certain frequency ω , you have a whole new world of experimental techniques!

Last, there are methods which monitor the *destruction (or generation) of some internal order* in the material. The prime technique is **Nuclear Magnetic Resonance (NMR)**, which monitors the decay of nuclear magnetic moments which were first oriented in a magnetic field and then disordered by atomic jumps, i.e. diffusion. The **Mößbauer effect** may be used in this connection, too.