Chapter 1

Introduction

High-purity silicon is an important resource in our modern world. Products based on silicon permeate our daily life, from integrated circuits in desktop computers, laptops, and mobile devices, to sensors in our cars, homes, and industrial production facilities, to photovoltaic systems on our roofs. Since the beginning of mass production of integrated circuits in the 1970s, research on the properties of defects in silicon has been a key to the evolution of present-day applications.

Electrically active defects which create deep levels in the electronic band gap of silicon fundamentally influence device performance. These defects can increase the recombination activity of electron-hole pairs and reduce minority carrier lifetimes. This effects, for example, a reduction of solar cell efficiencies [1] and an increase in device leakage currents [2].

There are three main sources of contamination which can lead to electrically active defects: (i) contamination of the bulk silicon crystal due to contaminated feedstock or crystal growth equipment, (ii) contamination of the wafer surface during wafer preparation (e.g. cutting, polishing), and (iii) contamination during device processing. The first two contamination pathways were tackled systematically in the 1980s and 1990s. Contamination levels of metals, which are the main impurities in device processing, are below 10^{11} cm^{-3} in the material used today in microelectronics.[3] Process contamination, however, is still a viable threat in microelectronic device production.

Besides the expensive nearly metal-free silicon used for microelectronics, cheaper and less refined material is often used in the solar cell industry, so-called solar grade silicon.[4–8] In contrast to microelectronic devices, defects in solar cells do not lead to a complete breakdown of their functionality. However, the resulting decrease in efficiency has to be weighed against the reduction in material cost.

Transition metals (TM) are common impurities in the silicon feedstock and are often electrically active.[9–12] Among the TMs, copper, nickel, and cobalt are the three fastest

diffusing species in silicon.[11] They diffuse in the interstitial species, but are electrically active in the substitutional species.[12] From a technological point of view, their high diffusivity increases the danger of contamination even at moderate temperatures and also leads to a high likelihood of precipitation. The electrical and structural properties of copper and its interaction with hydrogen have recently been well established.[13–17] Those of cobalt and nickel are discussed in this thesis. In contrast to copper, nickel, and cobalt, titanium is one of the slowest diffusing TMs in silicon.[12] It is electrically active in the interstitial site.[12] While the low diffusivity of titanium makes a contamination, for example during processing, less likely, it is also very hard to remove by annealing processes. For example, annealing a titanium containing silicon sample at 950 °C for nearly 3 h does not fully remove the electrically active titanium (see Chap. 6).

In addition to creating deep levels in the band gap by themselves, the TMs can form complexes with other impurities. A very common and reactive impurity in silicon is hydrogen. Its reactivity is often actively used in industry processes. For example, antireflection coatings on solar cells are used to introduce hydrogen into the top layer of the cell to passivate possible defects.[18] However, hydrogen is also inevitably introduced into the silicon lattice by wet-chemical etching [19, 20] and can even be found in as-grown and prepared wafers [21].

Hydrogen reacts easily with other defects, passivating surface states [22–24] and shallow donors and acceptors [25]. It reacts with the TMs, forming both electrically active and passive TM-H complexes.[26–34] Hydrogen can also activate formerly inactive defects like carbon [21, 35–38] or form other active centers [39, 40], dissolve precipitates [41], and enhance the formation of thermal donors [42, 43]. Furthermore, hydrogen itself has electric levels in the band gap of silicon [44–46]. In high concentrations, it can form extended structures in the lattice like platelets [39, 47–49] or form H_2 molecules [50, 51]. The complexity of possible reactions of hydrogen in the silicon lattice together with its technological use warrant further scientific investigations into the behavior of hydrogen in silicon and its reactions with other defects.

In this work, the properties of the TMs cobalt, nickel, and titanium in silicon, and their interaction with hydrogen are studied by deep level transient spectroscopy (DLTS) and minority carrier transient spectroscopy (MCTS). Investigation of the complexes of these metals with hydrogen started in the 1990s.[29–34] With the access to new techniques, open questions and inconsistencies can now be resolved. A natural starting point for this study is to investigate which hydrogen-related defects are created in metal-free silicon samples after hydrogenation.

This thesis is structured as follows: chapter 2 discusses the theory of deep traps in semi-conductors. Chapter 3 contains details about the measurement techniques used, while chap-

ter 4 presents the used samples and preparation techniques. In chapter 5, the results of hydrogenation of metal-free silicon and the influence of the hydrogen isotope on the electrical properties are discussed. The results on cobalt, titanium, and nickel are presented in the chapters 7-8. Each results chapter contains an introduction into the specific topic, the presentation of the results themselves, the discussion of these results, and a short summary. This thesis ends by comparing the studied metals with each other and with those adjacent in the periodic table.

Chapter 2

Theory

This chapter discusses the physics of the phenomena investigated in this thesis. It will start with an analysis of the carrier capture and emission process of deep traps, describing how these processes depend on temperature, carrier concentration, and intrinsic properties of the trap. Next, the time dependence of the carrier capture and emission is considered. These parts follows closely Chap. 7 in P. BLOOD AND J.W. ORTON *The Electrical Characterization of Semiconductors: Majority Carriers and Electron States*.[52] In the third section, the influence of an electric field on the emission process is discussed in dependence of the charge state of the trap. It will outline the basics of the POOLE-FRENKEL theory and of tunneling processes. This chapter ends with a consideration of the penetration behavior of hydrogen during wet-chemical etching and the subsequent formation of hydrogen complexes. A method to determine the number of hydrogen atoms in a defect structure, as proposed by FEKLISOVA AND YARYKIN, is presented.[53]

2.1   Deep traps – capture and emission

The characteristic property of a semiconductor is the separation of two electronic bands, the so-called conduction and valence band. At temperature $T = 0$ K, the valence band is filled with electrons, whereas the conduction band is empty of electrons. The energy region between these bands is called the band gap, in which no allowed electronic states exist. If defects are introduced into the crystal lattice, they can create localized states which lie inside the band gap. These are either called shallow or deep, depending on their distance to the band edges.

Four types of interaction with the bands are possible for any deep (and shallow) level: electron capture from the conduction band, hole capture from the valence band, electron emission into the conduction band, and hole emission into the valence band. These inter-
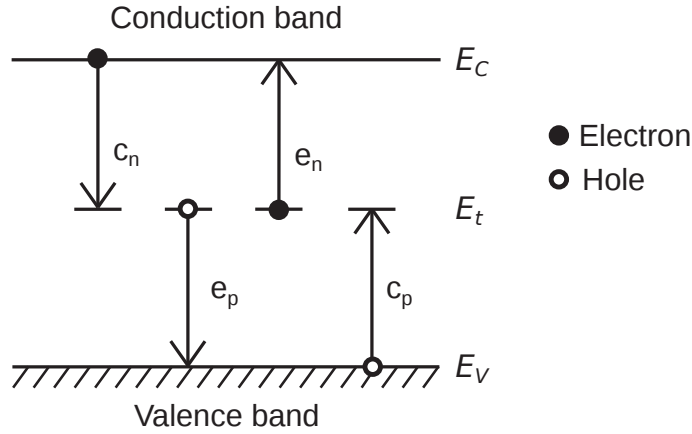
Figure 2.1: Energy diagram of a semiconductor with a deep trap in its band gap. The four possible interactions of the trap with the bands are shown, which are electron/hole capture/emission.

actions are governed by the corresponding capture and emission rates c_n, c_p, e_n, and e_p. Here, n stands for electron processes and p for hole processes. A schematic overview of these processes is given in Fig. 2.1. With these emission and capture rates, the time dependence of the concentration of traps filled with electrons n_t can be written as

$$\frac{\mathrm{d}n_t}{\mathrm{d}t} = (c_n + e_p)(N_t - n_t) - (e_n + c_p)n_t \tag{2.1}$$

with the total trap concentration N_t.

The capture process is characterized by the capture cross section σ, which is an intrinsic property of the defect. Furthermore, it depends on the number of carriers available for capture per unit time. For free carriers, this is the product of the concentration n (p) and the root mean square thermal velocity $\langle v_n \rangle$ ($\langle v_p \rangle$). The capture rate for electrons is then

$$c_n = \sigma_n \langle v_n \rangle n \tag{2.2a}$$

and for holes

$$c_p = \sigma_p \langle v_p \rangle p. \tag{2.2b}$$

To describe the emission process, the balance of emission and capture processes in thermal equilibrium is considered, that is, Eq. 2.1 is equal to zero. The principle of detailed balance holds, that is, both the emission and capture of electrons and of holes have to be in balance separately. Therefore both

$$e_n n_t = c_n (N_t - n_t) \tag{2.3a}$$

and

$$e_p (N_t - n_t) = c_p n_t \tag{2.3b}$$

have to be fulfilled.

From these equations it follows that in thermal equilibrium the occupancy of the trap is given by

$$\frac{n_t}{N_t} = \frac{c_n}{c_n + e_n} = \frac{e_p}{e_p + c_p}. \tag{2.4}$$

Another description of the thermal equilibrium occupancy can be obtained by using the Fermi-Dirac distribution, which yields

$$\frac{n_t}{N_t} = \left\{ 1 + \frac{g_0}{g_1} \exp\left(\frac{E_t - E_F}{kT}\right) \right\}^{-1} \tag{2.5}$$

for a trap with an energy level at E_t, degeneracy g_0 when empty of electrons and g_1 when filled with electrons, and with the Fermi energy E_F of the system. k denotes the Boltzmann constant.

Combining equations 2.4 and 2.5 results in

$$\frac{e_n}{c_n} = \frac{g_0}{g_1} \exp\left(\frac{E_t - E_F}{kT}\right) \tag{2.6}$$

for the case of electron emission. Since the processes for electrons and holes are decoupled, the equations are from here on derived for electron processes only. Analogue descriptions are valid for the hole processes.

The carrier concentration in a non-degenerate semiconductor can be described by the well-known equation

$$n = N_c \exp\left(-\frac{E_c - E_F}{kT}\right) \tag{2.7}$$

with the effective density of states in the conduction band N_c. Then, n is substituted in Eq. 2.2a and c_n in Eq. 2.6 to derive the general formula for the emission rate

$$e_n(T) = \sigma_n \langle v_n \rangle \frac{g_0}{g_1} N_c \exp\left(-\frac{E_c - E_t}{kT}\right). \tag{2.8}$$

To obtain the temperature dependence of the emission process, one substitutes

$$N_c = 2 M_c \left(\frac{2\pi m^* kT}{h^2}\right)^{\frac{3}{2}} \tag{2.9}$$

and

$$\langle v_n \rangle = \sqrt{\frac{3kT}{m^*}} \tag{2.10}$$

with M_c being the number of conduction band minima, m^* the effective electron mass, and h the Planck constant. The capture cross section can also be temperature dependent. When the energy the electron gains during capture is dissipated by the emission of multiple phonons, the temperature dependence takes the form

$$\sigma(T) = \sigma_\infty \exp\left(-\frac{\Delta E_\sigma}{kT}\right) \tag{2.11}$$

with an energy barrier for capture ΔE_σ. For more information about the multiphonon emission process, refer to Refs. [54–57].

Including the aforementioned substitutions, the emission rate can be written as

$$e_n(T) = \gamma T^2 \sigma_{na} \exp\left(-\frac{E_{na}}{kT}\right) \tag{2.12}$$

with the material constant $\gamma = 2\sqrt{3}M_c(2\pi)^{\frac{3}{2}}k^2 m^* h^{-3}$, the apparent capture cross section $\sigma_{na} = \frac{g_0}{g_1}\sigma_\infty$ and the activation energy $E_{na} = E_c - E_t + \Delta E_\sigma$. For n- and p-type silicon, $\gamma = 7.03 \times 10^{21}\ 1/\mathrm{s\,cm^2\,K^2}$ and $\gamma = 2.64 \times 10^{21}\ 1/\mathrm{s\,cm^2\,K^2}$, respectively.

Equation 2.12 is the final result on the behavior of carrier emission from a deep trap. The two characteristic parameters of a trap follow from this formula, namely the activation energy E_{na} and the apparent capture cross section σ_{na}. Both can be determined by measurements of the emission rate versus temperature.

It should be mentioned that the activation energy E_{na} determined by electrical measurements with variable temperature is, thermodynamically speaking, not exactly equal to the energy level of the trap. This is due to the fact that the size of the band gap is also temperature dependent. The emission of a carrier can be interpreted as the change in chemical potential for the formation of a free carrier and an ionized defect. Then, the activation energy can be described by the change in Gibbs free energy $\Delta G(T)$, which is itself temperature dependent. With the thermodynamical identity

$$\Delta G(T) = \Delta H - T\Delta S \tag{2.13}$$

the Gibbs free energy can be described by the enthalpy H and the entropy S. Substituting Eq. 2.13 for E_{na} in Eq. 2.12, the emission rate has a temperature dependence of the form

$$e_n(T) \propto T^2 \exp\left(-\frac{\Delta H}{kT}\right). \tag{2.14}$$

Therefore, the activation energy determined by the electrical measurements is strictly speaking an enthalpy. For more detailed information, see Chap. 8 of Ref. [52] and references therein.

2.2   Deep traps – transients

The time dependence of the occupancy of a trap is given by Eq. 2.1. Solving this differential equation with the initial concentration $n_t = n_t(0)$ at $t = 0$ yields

$$n_t(t) = \frac{a}{a+b}N_t - \left(\frac{a}{a+b}N_t - n_t(0)\right)\exp[-(a+b)t] \tag{2.15}$$

with the rates increasing the electron population on the deep level

$$a = c_n + e_p \tag{2.16}$$

and those reducing the electron population

$$b = e_n + c_p. \tag{2.17}$$

The steady state at $t = \infty$ is then

$$n_t(\infty) = \frac{a}{a+b} N_t. \tag{2.18}$$

This is a similar result to Eq. 2.4, where the principle of detailed balance was additionally considered.

Usually, one type of carriers (electrons or holes) dominates the system. These carriers are called majority carriers. Since $c \propto n$ and $n_{min} \ll n_{maj}$, $c_{min} \ll c_{maj}$. Then, capture of minority carriers can be neglected. In general, emission of minority carriers can also be neglected, since majority carrier traps are measured in the corresponding half of the band gap and $e \propto \exp(E_c - E_t)$.

Two specific boundary conditions will be analyzed in more detail. The first one corresponds to a pure capture process. In this situation, the initial concentration of filled traps is zero $n_t(0) = 0$. With the considerations from above, Eq. 2.15 becomes

$$n_t(t) = \frac{c_n}{c_n + e_n} N_t \left\{ 1 - \exp[-(c_n + e_n)t] \right\}. \tag{2.19}$$

At the temperature where the emission transients are measured, the capture process is usually much faster than the emission process. Therefore, one can often neglect the emission rate in this equation and thus receives the simplified formula

$$n_t(t) = N_t \left[1 - \exp(-c_n t) \right]. \tag{2.20}$$

The second boundary condition considered is $n_t(0) = N_t$, that is, all traps are filled with electrons. In addition, a situation is assumed in which no free carriers are available for capture and therefore $c_n = 0$. This is for example the case in the depletion region of a Schottky diode. Then, the emission transient can be described as

$$n_t(t) = N_t \exp(-e_n t). \tag{2.21}$$

2.3   Electric field dependence

The emission of carriers from a deep trap can be also influenced by the presence of an electric field. The carrier is trapped in the potential of the defect, the form of which depends on
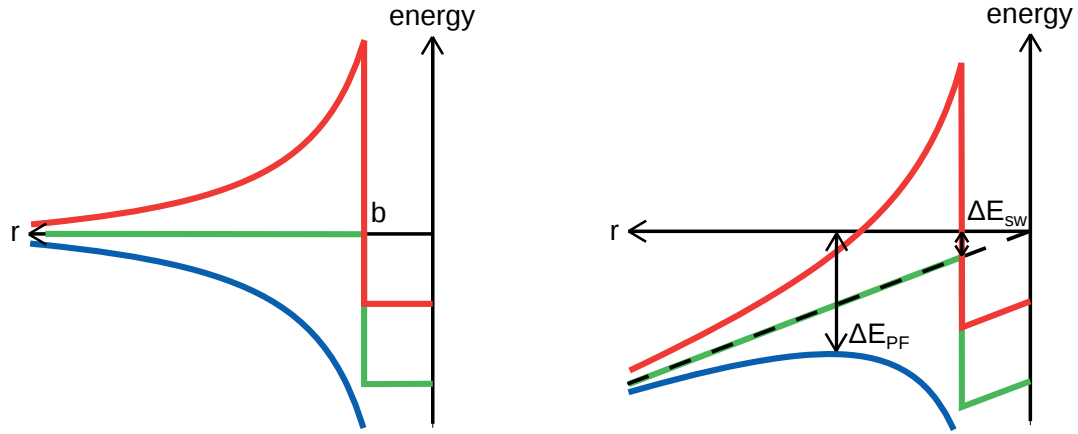
Figure 2.2: Defect potentials in real space for different charge states: attractive (blue), neutral (green), and repulsive (red). The left hand side shows the undisturbed potentials. On the right hand side, the deformation and corresponding barrier lowering by an applied electric field (black dashed line) is shown.

the charge state of the defect. The possible potentials are depicted in Fig. 2.2. If a donor level emits an electron, it is positively charged after the emission of the electron. Then, the potential would be an attractive Coulomb potential (blue line in Fig. 2.2). In the case of a single acceptor which is neutral after the emission, one can approximate the potential by a square well potential (green line in Fig. 2.2). For a double acceptor, the defect potential would be a combination of a square well potential close to the core of the defect with a repulsive Coulomb potential for larger distances (red line in Fig. 2.2).

It should be noted that the charge states associated to the potentials change when one considers hole emission instead of electron emission. Then, the attractive Coulomb potential corresponds to a single acceptor state, the square well potential to a single donor state, and the repulsive Coulomb potential to a double donor state.

In any case, an applied electric field has to be superimposed on the defect potential. This results in the reduction of the potential barrier in the direction of the field (ΔE_{PF} and ΔE_{SW} in Fig. 2.2). The field dependence of this reduction varies between the different possibilities, though.

In the case of the square well potential, the energy barrier is reduced at the edge of the potential well, which is at the distance b. Calculating the effect on the emission rate in three dimensions, one obtains [58]

$$\frac{e_n}{e_{n0}} = \left(\frac{kT}{2eEb} \right) \left[\exp\left(\frac{eEb}{kT} \right) - 1 \right] + \frac{1}{2} \tag{2.22}$$

with the electric field E and the elemental charge e. The emission rate without electric field is denoted with e_{n0}.