

### FRAUNHOFER INSTITUTE FOR SOLAR ENERGY SYSTEMS ISE

## SOLAR ENERGY AND SYSTEMS RESEARCH

Florian Schindler

ELECTRICAL MATERIAL PROPERTIES AND EFFICIENCY LIMITS OF COMPENSATED AND MULTICRYSTALLINE SILICON FOR SOLAR CELLS



Fraunhofer Institute for Solar Energy Systems ISE

SOLARE ENERGIE- UND SYSTEMFORSCHUNG / SOLAR ENERGY AND SYSTEMS RESEARCH

# Electrical Material Properties and Efficiency Limits of Compensated and Multicrystalline Silicon for Solar Cells

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FRAUNHOFER VERLAG

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# Electrical Material Properties and Efficiency Limits of Compensated and Multicrystalline Silicon for Solar Cells

Dissertation

zur Erlangung des akademischen Grades des Doktors der Naturwissenschaften (Dr. rer. nat.) der Fakultät für Angewandte Wissenschaften der Albert-Ludwigs-Universität Freiburg im Breisgau

vorgelegt von

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"Ein Rabe geht im Feld spazieren. Da fällt der Weizen um."

Helge Schneider.

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# Abstract

The present work contributes to current research on compensated silicon and on multicrystalline silicon. The following summarizes the main achievements of this thesis:

- A unified model for charge carrier mobilities correctly predicting mobilities in compensated and uncompensated crystalline silicon is developed.
- The efficiency losses in multicrystalline *p*-type silicon due to impurities from the crucible system are quantified after different solar cell processes, the benefit from crystallizations in crucibles of higher purity is assessed, and the impact of interstitial iron on the solar cell parameters is elaborated.
- The efficiency potential of identically crystallized mc *n* and *p*-type silicon featuring a comparable impurity level is analyzed along the whole blocks after typical solar cell processing steps, the impact of the larger resistivity variation in the *n*-type block is examined, and the loss mechanisms in both materials are specified.
- The limitations in multicrystalline *n*-type silicon are investigated and the impact of specific metal impurities on recombination in mc *n*-type silicon is quantified.
- The material quality and lifetime limitations due to Fe<sub>i</sub> and Cr<sub>i</sub> in identically crystallized *n* and *p*-type high performance multicrystalline silicon are studied after different solar cell processes, the applicability of the high-efficiency TOP-Con cell concept to multicrystalline silicon is demonstrated, and a high efficiency potential of *n*-type HPM-Si after the TOPCon cell process is confirmed by ELBA analyses as well as on actual devices. The best multicrystalline *n*-type TOPCon solar cell features an efficiency of 19.6%, which is a record efficiency reported for a solar cell on multicrystalline *n*-type silicon substrate.

# Deutsche Zusammenfassung

Die vorliegende Dissertation liefert einen Beitrag zur aktuellen Forschung im Bereich von kompensiertem Silizium und multikristallinem Silizium. Die wesentlichen Ergebnisse dieser Arbeit sind im Folgenden zusammengefasst:

- Ein einheitliches Modell zur Vorhersage von Ladungsträgerbeweglichkeiten in kompensiertem und unkompensiertem kristallinen Silizium wird entwickelt.
- Wirkungsgradverluste in multikristallinem *p*-Typ Silizium nach unterschiedlichen Solarzellenprozessen aufgrund von Verunreinigungen aus dem Tiegelsystem werden quantifiziert, der Gewinn durch die Verwendung hochreiner Kristallisationstiegel wird analysiert, und der Einfluss von interstitiellem Eisen auf die Solarzellenparameter wird im Detail untersucht.
- Das Wirkungsgradpotential von identisch kristallisierten multikristallinen n- und p-Typ Siliziumblöcken mit vergleichbarem Verunreinigungsniveau wird in Abhängigkeit der Blockhöhe nach verschiedenen Solarzellenprozessen analysiert. Der Einfluss der stärkeren Variation des Basiswiderstands im n-Typ Material wird detailliert beleuchtet und die Verlustmechanismen in beiden Materialien werden spezifiziert.
- In multikristallinem *n*-Typ Silizium werden die Materiallimitierungen untersucht und die Auswirkung bestimmter metallischer Verunreinigung auf die Ladungsträgerrekombination quantifiziert.
- Die Materialqualität und Lebensdauerlimitierungen aufgrund interstitiellen Eisens und Chroms in identisch kristallisiertem n- und p-Typ "high performance" multikristallinen Silizium (HPM-Si) werden nach verschiedenen Solarzellenprozessen untersucht. Des Weiteren werden die Anwendbarkeit des Hocheffizienzzellkonzepts "TOPCon" auf multikristallinem Silizium nachgewiesen sowie ein hohes Wirkungsgradpotential von n-Typ HPM-Si in Kombination mit diesem Zellkonzept durch ELBA Analysen und auf Zellniveau bestätigt. Die beste multikristalline n-Typ TOPCon Solarzelle weist einen Wirkungsgrad von 19.6% auf, was einem Rekordwirkungsgrad für multikristalline n-Typ Siliziumsolarzellen entspricht.

# **1** Introduction

### **1.1** Thesis Motivation

The development of new technologies always relies on pioneering and innovative fundamental research, including experimental and theoretical studies. Therefore, I would not like to start my PhD thesis without mentioning two outstanding researchers who founded the experimental and theoretical basis for research on photovoltaics (PV). In the year 1839, Alexandre-Edmond Becquerel fabricated the first photovoltaic device [1]. His experiment demonstrated that it is principally possible to convert light directly into electric energy. In this perspective, he could be regarded as the experimental pioneer of PV. The thorough theoretical understanding of the photovoltaic effect is based on Albert Einstein's famous article on the mathematical description of the photoelectric effect caused by the absorption of light quanta [2], which he was rewarded for with the Nobel Prize in 1921. In the second half of the 20<sup>th</sup> century, starting with the invention of the silicon solar cell in the Bell laboratories [3], research on PV developed rapidly, and today PV is on its way to become a substantial constituent of the world's energy system. The major part of PV is based on crystalline silicon. For the fabrication of silicon crystals, costs and energy can be reduced significantly by avoiding the purification of metallurgical grade silicon in the gas phase and using alternative purification routes instead. Thereby, so called upgraded metallurgical grade (umg) silicon is obtained. Further, costs and energy can also be reduced during the crystallization process, if the costly Czochralski pulling process is replaced by directional solidification of silicon blocks in quartz crucibles, which delivers multicrystalline (mc) silicon. The drawback of both, umg-Si and mc-Si, is a larger defect density in the crystal, leading to inferior electrical material quality and, finally, lower solar cell efficiency.

This PhD thesis addresses the impact of defects limiting the charge carrier diffusion length in crystalline silicon from cheaper production routes, namely umg-Si and mc-Si. These defects can be classified into scattering centers, which affect the charge carrier mobility, and recombination centers, which influence the charge carrier lifetime.

Regarding umg-Si, the main issue is the removal of dopants. Typically, both acceptors and donors are present in significant amounts in umg-Si crystals, which is why it is denoted compensated silicon. The simultaneous presence of acceptors and donors acting as scattering centers in compensated silicon leads to strong reductions of the charge carrier mobility. Despite strong efforts in research of compensated silicon in the past years, the physical reasons for these mobility reductions are not yet understood and models for the prediction of charge carrier mobilities in compensated silicon are lacking. In this thesis, compensation effects and their influence on charge carrier mobility are investigated and a unified model for the prediction of charge carrier mobilities in uncompensated and compensated silicon is developed.

Multicrystalline silicon features structural crystal defects, such as grain boundaries and dislocations, as well as a larger amount of metal impurities incorporated from the crucible system into the silicon during crystallization. Although extensive research on defects in mc silicon was performed during the past decades, the complexity of this material and the development of new crystallization techniques for the fabrication of high performance multicrystalline silicon open new unexplored research fields. In this thesis, the origins of efficiency losses due to impurities from the crucible system are investigated, the role of the doping type is evaluated, and the efficiency limit for solar cells based on high performance multicrystalline silicon (HPM-Si) substrate is assessed.

### **1.2 Detailed Thesis Structure**

This thesis is structured in two fundamental chapters (2 and 3) and two result chapters (4 and 5), before a summary and outlook is given in chapter 6.

*Chapter 2* treats the general basics relevant for the topics of this thesis from the production of silicon feedstock and silicon crystals to the physics of charge carriers in crystalline silicon.

*Chapter 3* introduces the most important characterization techniques applied in this thesis.

*Chapter 4* is the first result chapter and deals with the impact of compensation on charge carrier mobility. After providing a theoretical and historical overview of models for charge carrier mobilities in crystalline silicon and research on mobility in compensated silicon, the development of a unified model for charge carrier mobilities in crystalline silicon, which is able to correctly predict mobilities both in compensated and uncompensated silicon, is presented.

Chapter 5 focuses on multicrystalline silicon. It consists of a historical overview of research relevant for this PhD thesis (chapter 5.1) and four result chapters (5.2-5.5). Chapter 5.2 deals with the origin of impurities in mc silicon, chapters 5.3-5.5 focus on mc n-type silicon. In chapter 5.3, identically crystallized mc p- and n-type silicon blocks are investigated in matters of their efficiency potential, chapter 5.4 assesses the main limitations in mc n-type silicon, before chapter 5.5 presents an approach for the fabrication of high efficiency multicrystalline silicon solar cells based on n-type HPM-Si substrate.

## 2 General Basics

This chapter introduces the fundamentals relevant for the topics of this thesis. First, section 2.1 treats the production of silicon feedstock and the crystallization of silicon blocks and ingots, before section 2.2 discusses the physics of charge carriers in crystalline silicon. Here, the focus is set on charge carrier mobility (section 2.2.1), which will be the main topic of chapter 4, and charge carrier lifetime (section 2.2.2), which will be important for the results of chapter 5. For further details on physics of semiconductors and silicon solar cells, the reader is referred to [4-7].

### 2.1 Silicon as Base Material for Solar Cells

With a market share of around 90%, crystalline silicon based photovoltaic (PV) modules are dominating the global PV module production [8]. The reason for this extraordinary success of crystalline silicon as base material for solar cells is a combination of its relatively low costs and its appropriate physical properties for the conversion of sunlight into electrical energy. The conversion efficiency of a silicon solar cell strongly depends on the recombination characteristics of the silicon bulk material. The theoretical upper efficiency limit for *p*-*n* junction solar cells was determined by Shockley and Queisser in 1961 [9] based on a detailed balance calculation. With the AM1.5 spectrum (spectrum after penetration of the 1.5-fold air mass compared with perpendicular irradiation) and without light concentration, this leads to a limit of 33% for a single junction solar cell [10]. The main losses are attributed to photons with energies smaller than the bandgap, which are not absorbed, and to thermalization of hot carriers generated by photons with energies larger than the bandgap. Due to these losses, the theoretical efficiency limit is a function of the bandgap, with its maximum at an optimal bandgap close to the bandgap of crystalline silicon. In the calculation by Shockley and Queisser, it is "radiative recombination that determines the detailed balance limit for efficiency. If radiative recombination is only a fraction  $f_c$  of all the recombination, then the efficiency is substantially reduced below the detailed balance limit." [9]. In crystalline silicon, non-radiative Auger recombination is the dominant intrinsic recombination channel, whereas radiative recombination is a quite improbable process in an indirect semiconductor, as it also involves a phonon. This reduces the upper efficiency limit for crystalline silicon solar cells to 29.4% [11]. In reality, further recombination at contacts or in the bulk, and optical and resistive losses lead to solar cell conversion efficiencies well below this theoretical limit. Today, the world record efficiency for crystalline silicon solar cells is 25.6% [12-14], achieved by Panasonic on a monocrystalline *n*-type rear junction solar cell. Compared with monocrystalline silicon, multicrystalline (mc) silicon features a higher concentration of impurities as well as additional structural crystal defects, such as dislocation clusters and grain boundaries, at which recombination of charge carriers can occur. This additional bulk recombination leads to lower conversion efficiencies of mc-Si solar cells. Currently, the world record efficiency on mc-Si solar cells is 21.25% [13, 15, 16]. In order to increase the solar cell efficiency of mc-Si solar cells, the loss mechanisms in the bulk have to be understood in detail. This topic is examined in this thesis in chapter 5. Besides enhanced bulk recombination in mc silicon, the simultaneous presence of acceptors and donors in socalled "compensated silicon" has a strong impact on charge carrier mobility, which is also a key parameter for solar cell efficiencies. This aspect will be discussed in chapter 4 in this thesis. In the following, the necessary basics for comprehension of these topics are introduced. This section focuses on the production of silicon feedstock (2.1.1) and the crystallization techniques (2.1.2), before the next section introduces the basic physics of charge carriers in crystalline silicon (2.2), with the focus on charge carrier mobility (2.2.1) and lifetime (2.2.2).

#### 2.1.1 Silicon feedstock

The content of this section is based on [17, 18]. For the production of silicon crystals, elemental silicon is obtained from quartz (SiO<sub>2</sub>). In an arc furnace, carbon reduces quartz in an endothermic reaction to metallurgical silicon:

$$\mathrm{SiO}_2 + 2\mathrm{C} \to \mathrm{Si} + 2\mathrm{CO} \tag{2.1}$$

Metallurgical silicon features an impurity concentration of approximately 1-2% [19]. These impurities are dopants (P, B, As, Sb, Al), which affect the resistivity, light elements (O, C, N) forming inclusions, as well as metal impurities (Fe, Cr, Cu, Ni, Ti, Co, etc.) reducing charge carrier lifetime. However, a feedstock purity of at least 99.999% (often referred to as "5N" for five nines) is inevitable for the fabrication of highly efficient silicon solar cells [20]. As shown in [20], the material quality after a complete solar cell process is highly sensitive to the feedstock quality, such that a switch from 5N to 4N feedstock would lower the efficiency potential by  $2\%_{abs}$ . Therefore, in a first step before crystallization in a clean environment, the metallurgical silicon has to be refined.

#### Siemens process

The standard process for purification of metallurgical silicon is the Siemens process, which is described in detail in [17, 21]. This process makes use of a transition of silicon to the gas phase and converts metallurgical-grade silicon into silanes, which can be trichlorosilane (TCS) or monosilane. In the TCS synthesis, the following reaction takes place in a fluidized bed reactor:

$$\text{Si} + 3\text{HCl} \rightarrow \text{SiHCl}_3 + \text{H}_2$$
 (2.2)

After a subsequent filtration and distillation, the purified TCS gas is reduced to elemental silicon by deposition at heated monocrystalline silicon seed rods, which are crushed and used as silicon feedstock for crystallization. This gas phase purification efficiently removes dopants, light elements and metals to concentrations below 1 part per million, which corresponds to a feedstock purity of 6N [17]. Other publications even report on purity levels of 10N [22]. The drawback of the Siemens process is the large heating energy loss during deposition of silicon from the TCS gas, which makes it energy consumptive and inefficient [21]. Therefore, alternative routes for the purification of metallurgical feedstock have been developed, some of which are discussed in the following.

#### Alternative purification routes

Alternative purification routes for the fabrication of silicon feedstock avoid the gas phase transition, as this is the most energy consumptive step. Refining of silicon in the liquid phase results in so-called "upgraded metallurgical-grade" (umg) silicon. Typical purification sequences include at least one of the following processes [17, 19]:

- Removal of boron by oxidation or reaction with water vapor
- Removal of phosphorus by vacuum treatment (evaporation of phosphorus)
- Refining by directional solidification (segregation of metal impurities, *cf.* section 2.1.2)
- Solvent refining (solidification of a Al-Si melt, alloying of silicon with aluminum [23, 24])
- Removal of impurities by acid leaching (dissolution of metal clusters)
- Removal of inclusions by settling or filtration
- Reduction of silica by carbon in specially designed arc furnaces of higher purity
- Gas blowing through the silicon melt (formation of volatile compounds which evaporate from the melt)
- Melting and refining of silicon with a reactive plasma (formation of volatile compounds, removal of metals and dopants)
- Slagging or calcium leaching (mixing silicon with a chemical that has a high affinity to undesirable impurities and subsequent separation by deposition on the crucible walls, filtering or acid and solvent leaching)

Further purification steps are discussed in [18, 25]. While the concentration of metal impurities can be effectively reduced by solidification due to their very small segregation coefficient, the removal of dopants by evaporation (phosphorus) and oxidation (boron) is more challenging. Consequently, in umg silicon typically both types of dopants are present, which is called compensation. This leads to some peculiar effects, one of which is the drastic impact on charge carrier mobility, which is discussed in chapter 4.

#### 2.1.2 Crystallization

A variety of crystallization techniques exist for the production of silicon crystals from the silicon feedstock. One can distinguish between *monocrystalline silicon* featuring only one orientation of the silicon lattice, and *multicrystalline silicon* featuring different areas with different crystal orientations ("grains"). The following introduces the most important aspects of crystallization relevant for this thesis.

#### Monocrystalline silicon

The most important crystallization techniques for monocrystalline silicon are the floating zone (FZ) process and the Czochralski (Cz) process.

In the *FZ process*, one end of a polycrystalline silicon rod is molten by an induction coil and brought in contact with a monocrystalline silicon seed crystal, which defines the crystal orientation. The molten zone is moved along the rod by moving the rod through a narrow heating zone, leading to the formation of a monocrystalline silicon ingot and a simultaneous refinement of the silicon due to segregation effects. Highest purity wafers from the FZ process are used as references for process control in this thesis. Due to their high costs, they are typically not used in industrial solar cell production. For further details on this crystallization technique, the reader is referred to[26].

The *Cz process* is a widespread crystallization technique for the production of monocrystalline silicon crystals used for the fabrication of silicon solar cells. It is explained in detail in [27]. In this technique, the silicon feedstock is molten in a quartz crucible. A rotating monocrystalline seed crystal is dipped into the melt, and, subsequently, slowly pulled upwards, which leads to the growth of a monocrystalline silicon ingot. Due to the contact of the melt with the quartz crucible, Cz crystals feature a high concentration of oxygen impurities, which is the main drawback of this technique compared with the FZ process. Together with the dopant boron, oxygen can form the boron-oxygen complex, which strongly affects charge carrier lifetime [28]. However, by using *n*-type Cz silicon, this defect can be avoided [29] and record solar cell efficiencies can be achieved [30]. In this thesis, the impact of compensation on charge

carrier mobility is studied on Cz wafers produced from compensated silicon feedstock (*cf.* chapter 4).

In recent years, a new technique for crystallization of so-called "mono-like" or "quasi-mono" silicon was developed [31]. This method combines the directional solidification in a crucible, as applied for multicrystalline silicon, with monocrystalline silicon seed wafers in the crucible bottom, which defines the crystal orientation of the resulting silicon block. The idea behind this approach is to combine the low costs of directional solidification in a crucible with the advantageous properties of monocrys-talline silicon wafers, which are in particular their defined crystal orientation enabling a better surface texture, and their lower concentration of structural crystal defects. However, the latter still is an issue in the production of mono-like silicon [31, 32], as thermal stress of the silicon block during crystallization is released by the formation of dislocation clusters, which are usually strongly recombination active.

A further novel approach for the crystallization of single bulk crystals inside silicon melts, which tries to avoid the formation and multiplication of dislocation clusters, is the Noncontact Crucible Method developed by Nakajima *et al.* [33, 34].

#### Multicrystalline silicon

An easy technique for the crystallization of silicon is the directional solidification of silicon blocks in quartz crucibles [35], also referred to as vertical gradient freeze (VGF) or block-casting. In the strict sense, the latter expression only describes the process, in which the silicon feedstock in molten in a separate crucible, from which it is cast into the crystallization crucible [36]. However, it is commonly, although misleadingly, used as a synonym for any block crystallization. Apart from the real blockcasting, the silicon feedstock can be molten and crystallized in the same crucible, as applied in the Bridgman Solidification or the Heat Exchange Method [36]. Today, these are the widely spread crystallization techniques for the fabrication of multicrystalline silicon. Figure 2.1 shows a sketch of block crystallization by directional solidification. The feedstock is molten in a quartz crucible coated with an anti-adhesion silicon-nitride layer, which is stabilized by a graphite cup. By controlled heat dissipation, the directional solidification starts at the crucible bottom, and the interface of planar and liquid silicon moves towards the top with a growth rate in the range of 10 mm/h. Thus, multicrystalline silicon blocks of different sizes and weights in the range of some kilograms (small lab-scale) to ~1200 kg (large industrial scale, "G7", cf. presentation of [37]) are obtained. Block sizes are usually denoted as "G1", "G2", ..., "G7", standing for "generation 1", "generation 2", etc., and indicating the number of  $156 \times 156$  mm<sup>2</sup> ingots per row that can be cut out from the entire block. For instance, 49  $156 \times 156$  mm<sup>2</sup> ingots are obtained from a G7 size block. The mc silicon material



Figure 2.1: Directional solidification of a silicon block in a quartz crucible. Figure adapted from [38].

investigated in this thesis (*cf.* chapters 5.2 - 5.5) was grown in a laboratory crystallization furnace adapted for the crystallization of G1 ( $\sim$ 14 kg) and G2 ( $\sim$ 65 kg) size silicon blocks at Fraunhofer ISE. Details on the applied crucibles and the crystallization conditions can be found in the corresponding subsections.

While the advantage of directional solidification in crucibles are the lower costs, higher throughput, and lower energy consumption [27], its disadvantages are the development of structural crystal defects such as grain boundaries and dislocation clusters during solidification [39], the incorporation of larger amounts of impurities from the crucible system [40], as well as the variation in crystal orientation of the wafer surfaces, which poses a greater challenge for good surface texturing. As mentioned before, the development of quasi-mono silicon tries to address the latter issue by combining a directional solidification in a crucible with monocrystalline seed-wafers in the crucible bottom for a defined crystal orientation. However, it still seems to be complicated to avoid multiplication of dislocations along the block height during crystal growth [31, 32], leading to the development of strongly recombination active dislocation clusters.

The formation and multiplication of dislocation clusters is mainly driven by thermal stress, which could also be relaxed by certain grain boundaries [41, 42]. Therefore, a different approach was successfully put forward in the past years, which follows a converse idea: By introducing a seed layer with a large variety of different crystal orientations in the crucible bottom, a material featuring a large amount of small grains and random-angle grain boundaries can be crystallized. This has led to the development of so-called *"high-performance multicrystalline silicon"* (HPM-Si) [43]: By intentionally creating a larger amount of grain boundaries, the multiplication of dislocations along the block height can be avoided, leading to a material with a large



Figure 2.2: Dislocation mappings of wafers from different heights of a block with decreasing grain size (a) and a block with increasing grain size (b). The multiplication of dislocations with increasing block height (left to right) is efficiently suppressed in the latter case (b). Figure reprinted from [39].

amount of small high-quality grains and a low density of dislocation clusters, which are typically the areas of highest recombination activity in an mc silicon wafer.

In this context, an increasing grain size with block height seems to be important for reducing the growth rate of dislocations [39], as exemplarily shown in Figure 2.2. The multiplication of dislocations is significantly reduced in the block featuring an increasing grain size with increasing block height (*cf.* Figure 2.2a) compared to a block with decreasing grain size along the block height (*cf.* Figure 2.2b) [39].

The development of high-performance mc silicon has led to a significant increase in the conversion efficiencies of mc silicon solar cells [43], which is not least reflected by the new world record for an mc silicon solar cell presented recently [13, 15, 16]. The advantages of such a material for the fabrication of highly efficient multicrystalline silicon are discussed in this thesis in chapter 5.5.

Besides harmful structural crystal defects, which can be reduced by this advanced crystallization technique, the second major drawback of mc silicon is the incorporation of larger amounts of impurities from the crucible system [40]. This topic will be addressed in detail in sections 5.1.1 and 5.2 of this thesis. In the following, the relevant basics are elucidated.



Figure 2.3: Sketch of crucible and coating during crystallization, and  $\mu$ W-PCD measurement of charge carrier lifetime after crystallization. The arrows indicate the different mechanisms of incorporation of impurities from the crucible system: Indiffusion from the coating (1) and the crucible (2) into the liquid silicon, and solidstate diffusion from the coating (3) and the crucible (4) into the silicon crystal. Figure reprinted from [48].

#### Incorporation and redistribution of impurities during crystallization

The impurities in mc silicon stem from the feedstock, the quartz crucible, its coating, as well as from the crystallization environment (for instance, carbon can be incorporated from the graphite cup through the gas phase [44]). The focus of this thesis is on impurities stemming from the crucible and its coating (*cf.* sections 5.1.1 and 5.2), which are the dominant source for impurities in mc silicon [45-47].

Besides incorporation of whole particles by abrasion of the crucible coating, the dominant process is diffusion of metal impurities from the crucible system into the silicon. In this context, several processes have to be distinguished. As indicated by the arrows in Figure 2.3, impurities from the coating (1) and the crucible (2) can diffuse into the liquid silicon. Furthermore, they can also be incorporated into the solid part of the crystal by solid-state diffusion (3, 4). The impurities diffused into the liquid silicon mainly determine their concentrations in the center part of the block. The variation along block height is determined by the segregation coefficient  $k_{I,seg}$ , which describes the ratio of the solubility of an impurity in the solid phase and the liquid phase of silicon and is typically much smaller than one for metal impurities (e.g., reported segregation coefficients for Fe are  $k_{Fe,seg} = (5 - 7) \cdot 10^{-6}$  [49, 50] for monocrystal-line Si and  $k_{Fe,seg} = 2.2 \cdot 10^{-5}$  for intentionally contaminated mc-Si [51]). This means that metal impurities accumulate in the silicon metal and are concentrated in the

top part of the silicon block. A contrary behavior is found for oxygen, which features a segregation coefficient larger than one [52] and is therefore found in larger concentrations close to the block bottom. The typical dopants boron and phosphorus feature segregation coefficients of  $k_{B,seg} = 0.8$  and  $k_{P,seg} = 0.35$  [53]. Scheil's equation allows for a simple calculation of the impurity or doping concentrations in the crystal  $N_{I,crystal}(z)$  as a function of relative ingot height z from the starting concentration in the melt  $N_{I,0}$  due to segregation [54]:

$$N_{I,crystal}(z) = k_{I,seg} N_{I,0} (1-z)^{k_{I,seg}-1}$$
(2.3)

The different segregation coefficients of boron and phosphorus lead to a different behavior of dopant concentrations in p- and n-type silicon along a block. While the concentration of boron in *p*-type silicon features a weak dependence on block height, the concentration of phosphorus in *n*-type silicon shows a stronger increase towards the block top due to the lower segregation coefficient. This is the reason for the stronger resistivity variation in *n*-type silicon compared with *p*-type silicon. In compensated silicon, the different segregation coefficients lead to a peculiar behavior of the net doping concentration and resistivity: assuming a boron and phosphorus doped block with a higher concentration of boron incorporated at the block bottom, the block will be *p*-type first. With increasing block height, the concentration of phosphorus in the crystal increases more strongly than the concentration of boron, which leads to a decreasing net doping concentration and an increasing resistivity. Eventually, this can even result in a point of equal boron and phosphorus concentrations, where the net doping concentration decreases to virtually intrinsic conditions and the resistivity diverges. After this point, the phosphorus concentration exceeds the boron concentration and the material becomes *n*-type, which is why this block position is also called "point of type-changeover".

While Scheil's equation is a good approximation for the concentration of dopants along the block height, the description of the concentration of metal impurities is more complex, as their concentration is dominated by the in-diffusion from the crucible system into the liquid silicon during the crystallization. Thus, the concentration  $N_{I,crystal}(z)$  is not only determined by the initial concentration in the melt in combination with segregation according to equation (2.3), but the additional amount of metal impurities diffused into the remaining liquid silicon during crystallization has to be taken into account. This is treated in detail on the example of iron in [40].

The regions of a silicon block close to the crucible bottom and the crucible walls are additionally affected by solid-state diffusion of impurities from the crucible system into the silicon crystal. This leads to a region with a width of several centimeters of high impurity concentrations and low charge carrier lifetimes, visible as the blue area in the  $\mu$ W-PCD measurement of Figure 2.3. The width of the edge region depends on the impurity concentration in the crucible system, the diffusivity of the impurity dominating the edge region (which is typically iron [40, 48], see also sections 5.1.1 and 5.2) and, thus, the temperature profile during crystallization, as well as the crystallization time. As the block crystallizes first at the bottom, the edge region is widest there and decreases towards the block top (*cf.* Figure 2.3). The low lifetime region at the very top of the block is attributed to a back-diffusion of segregated impurities [55].

For further details on transition-metal profiles in mc silicon blocks, the reader is referred to [55]. A detailed discussion and literature review about the impact of crucible and coating on impurities in mc silicon is included in this thesis in section 5.1.1.

### 2.2 Charge Carriers in Crystalline Silicon

The fundamental working principle of a solar cell is the separation and selective transport of charge carriers, namely electrons and holes, to different terminals of the device [6, 56]. A solar cell can be mathematically described by

- the equations for the electron and hole currents, which are driven by a gradient in the electrochemical potentials,
- the continuity equations, which allow a calculation of electron and hole concentrations from generation and recombination processes
- Gauss's law, which links the electrical potential to the charge carrier concentrations.

Details on the calculations can be found in [6]. The focus of this thesis is the silicon bulk, where electron-hole pairs are created by the absorption of photons with energies larger than the band-gap. Away from the junctions of a solar cell, the created electrons and holes diffuse randomly through the silicon matrix. The diffusion is described by the charge carriers' diffusion length  $L_k$ , where k stands for electrons (subscript e) or holes (subscript h). The charge carrier diffusion length depends on the charge carrier's diffusion coefficient  $D_k$ , which is linked to the charge carrier's mobility  $\mu_k$  by the Einstein relation (2.10), and the charge carriers' lifetime  $\tau_k$  according to the following equation

$$L_k = \sqrt{D_k \tau_k} = \sqrt{\frac{k_B T}{e} \mu_k \tau_k}$$
(2.4)

where e is the elementary charge. Only if the minority charge carrier diffusion length is large enough, minority charge carriers will reach the junction of the solar cell, where they can be separated from majority charge carriers, thus create a potential, and contribute to the current of the device. This highlights the key role of charge carrier mobility and charge carrier lifetime in the silicon bulk. This PhD thesis focuses on the impact of defects in crystalline silicon on these two parameters. Therefore, section 2.2.1 introduces charge carrier mobility within the context of charge carrier transport in silicon. Section 2.2.2 then focuses on charge carrier lifetime. The descriptions are based on [4-7], for further details, the reader is referred to these references.

#### 2.2.1 Transport of charge carriers: mobility, conductivity, doping

Transport of charge carriers in crystalline silicon is determined by electric fields (drift) and gradients in charge carrier densities (diffusion). This transport strongly depends on charge carrier mobility  $\mu$ , which is defined as the proportionality constant between the drift velocity  $\vec{v_d}$  and the electric field strength  $\vec{E}$  at low electric field [4]:

$$\overrightarrow{v_d} = \mu \vec{E} \tag{2.5}$$

Charge carrier mobility is determined by scattering at phonons, ionized impurities and free charge carriers. Calculations of mobility due to these scattering mechanisms will be discussed in section 4.1. Scattering mechanisms can be quantified by the mean scattering time  $\tau_s$  between two collisions of a charge carrier with a scattering center. Using the mobility definition of equation (2.5) allows for deriving the relation between mobility and mean scattering time, which is needed for theoretical mobility calculations. This derivation shall be sketched here: In a classical picture, the force  $\vec{F}$  on a moving charged particle of mass m, charge q and velocity  $\vec{v}$  in an electric field  $\vec{E}$  can be written as:

$$\vec{F} = m \frac{d\vec{v}}{dt} = q\vec{E}$$
(2.6)

By introducing the effective mass  $m^*$ , electrons in a semiconductor can be treated as a classical "electron gas". With the velocity change being  $\overrightarrow{v_d}$  in the mean scattering time  $\tau_s$  between two collisions, equation (2.6) can now be transferred to charge carriers of mass  $m^*$  and elementary charge e in a semiconductor:

$$m^* \frac{\overline{v_d}}{\tau_s} = e\vec{E}$$
(2.7)

Comparing equation (2.7) and (2.5) delivers the relation between charge carrier mobility and mean scattering time:

$$\mu = \frac{e\tau_s}{m^*} \tag{2.8}$$

Let us now come back to general transport properties. To completely describe distribution and transport of charge carriers, charge current densities  $\vec{J}_k$  for electrons (subscript *e*) and holes (subscript *h*) are regarded:

$$\vec{J_k} = e\mu_k n_k \vec{E} - z_k e D_k \operatorname{grad} n_k \tag{2.9}$$

Here,  $z_e = -1$  for electrons,  $z_h = 1$  for holes, *e* stands for the elementary charge,  $n_k$  denotes the density of electrons or holes,  $\mu_k$  their mobilities and  $D_k$  their diffusion coefficients, which can be related to mobilities by the Einstein relation

$$D_k = \frac{k_B T}{e} \mu_k \tag{2.10}$$

where  $k_B$  is the Boltzmann constant and T the temperature. The proportionality constant between electric field and charge current density  $\vec{J_k}$  is defined as the electron or hole conductivity:

$$\sigma_k = e\mu_k n_k \tag{2.11}$$

The total conductivity is the sum of electron and hole conductivity, and its reciprocal is the material's resistivity  $\rho = \sigma^{-1}$ .

By replacing the electric field with the gradient of the electric potential,  $\vec{E} = -\text{grad}\varphi$ , introducing the chemical potential  $\Phi_{\text{chem},k}$  [6, 56], and making use of the definition of conductivity, equation (2.9) can be rewritten as

$$\vec{J}_{k} = -\frac{\sigma_{k}}{z_{k}e} \operatorname{grad}(z_{k}e\varphi + \Phi_{\operatorname{chem},k}) = -\frac{\sigma_{k}}{z_{k}e} \operatorname{grad}\eta_{k}$$
(2.12)

where  $\eta_k$  denotes the electrochemical potential [6, 56].

In a last step, the electrochemical potential of electrons in the conduction band can be identified with their (quasi-) Fermi energy  $\varepsilon_{FC}$ , which describes the occupation of states in the conduction band with electrons:

$$\eta_e = \varepsilon_{FC} \tag{2.13}$$

Identically, the electrochemical potential of holes in the valence band can be identified with their (quasi-) Fermi energy  $\varepsilon_{FV}$ , which describes the occupation of states in the valence band:

$$\eta_h = -\varepsilon_{FV} \tag{2.14}$$

Thus, the electron current density can be expressed as a function of electron conductivity and their (quasi-) Fermi energy

$$\vec{J_e} = \frac{\sigma_e}{e} \operatorname{grad} \varepsilon_{FC}$$
(2.15)

and in the same manner, the hole current density can be expressed as a function of hole conductivity and their (quasi-) Fermi energy

$$\vec{J_h} = \frac{\sigma_h}{e} \operatorname{grad} \varepsilon_{FV} \tag{2.16}$$

These are the only existent currents of electrons and holes in a semiconductor in steady state conditions, in contrast to the widely spread assumption of the simultaneous and independent existence of a field current and a diffusion current [56].

Considering generation  $G_k$  and recombination  $R_k$  of electrons and holes, the charge carrier distribution can now be expressed by the continuity equation:

$$\frac{\partial n_k}{\partial t} = G_k - R_k - \frac{1}{z_k e} \operatorname{div} \vec{J_k}$$
(2.17)

The direct dependence of charge current density on charge carrier mobility highlights the paramount importance of charge carrier mobility for transport properties of silicon. As the properties of charge carrier mobility will be an essential part of this PhD thesis, some more remarks shall be made at this stage. Up to now, charge carrier mobilities were discussed independently of the doping of the material. In thermal equilibrium and without generation of excess charge carriers, the electron concentration in the conduction band  $n_{e0}$  and the hole concentration in the valence band  $n_{h0}$  can be expressed as:

$$n_{e0} = N_C exp(-\frac{\varepsilon_C - \varepsilon_F}{k_B T})$$
(2.18)

$$n_{h0} = N_V exp(-\frac{\varepsilon_F - \varepsilon_V}{k_B T})$$
(2.19)

Here,  $N_C$  is the effective density of states of the conduction band,  $N_V$  the effective density of states of the valence band,  $\varepsilon_C$  the lower edge of the conduction band,  $\varepsilon_V$  the upper edge of the valence band, and  $\varepsilon_F$  the Fermi energy. For intrinsic silicon, the electron concentration in the conduction band equals the hole concentration in the valence band,  $n_{e0} = n_{h0}$ , and their concentration is called the intrinsic density  $n_i$ . In the following, the role of doping for the electrical material properties is introduced [6]. The product of electron and hole concentration is independent of the position of the Fermi level. That means that is does not depend on the individual densities of electrons and holes and is thus unaffected by doping:

$$n_{e0}n_{h0} = n_i^2 = N_C N_V exp(-\frac{\varepsilon_C - \varepsilon_V}{k_B T})$$
(2.20)

Typically, doping atoms replace silicon atoms at their lattice position and are thus substitutional impurities. Here, we regard donors with five and acceptors with three valence electrons. If silicon is doped with such donors, typically phosphorus, four of the donors' valence electrons are used for chemical bonding with the neighboring silicon atoms. The fifth valence electron is now only weakly bound to the positively charged donor in the silicon lattice by Coulomb attraction. This means that its energy is only slightly smaller than the lower edge of the conduction band, the lowest energy of free electrons within the silicon, such that it can be donated easily to the conduction band. Silicon only doped with donors is called (uncompensated) *n*-type silicon, due to the higher concentration of electrons in the conduction band compared with holes in the valence band. At room temperature, typical ionized doping concentrations in silicon for PV applications are several orders of magnitude larger than the intrinsic carrier concentration. In that case, the electron density in *n*-type Si can be approximated by the density of ionized donors  $N_D^+$ :

$$n_{e0} \approx N_D^+ \tag{2.21}$$

In combination with equation (2.20), the hole density in *n*-type silicon reads:

$$n_{h0} \approx \frac{n_i^2}{N_D^+} \tag{2.22}$$

In analogy, if silicon is doped with acceptors with three valence electrons, typically boron or gallium, one electron for chemical bonding with the neighboring silicon atoms misses. An electron filling the hole for chemical bonding is not bound as strongly as an electron in the valence band, due to the lack of Coulomb attraction to the acceptor atom. However, as the missing Coulomb bond is only a weak bond, the energy of the electron at the acceptor is only slightly larger than the upper edge of the valence band. Therefore, acceptors can easily accept an electron from the valence band, or, in the hole picture, donate a free hole to the valence band. Silicon only doped with acceptors is called (uncompensated) p-type silicon. As discussed for the case of n-type, at typical dopant concentrations orders of magnitudes larger than the intrinsic carrier concentration the hole and electron densities in p-type read:

$$n_{h0} \approx N_A^- \tag{2.23}$$

$$n_{e0} \approx \frac{n_i^2}{N_A^-} \tag{2.24}$$

Here,  $N_A^-$  denotes the concentrations of ionized acceptors.

As doping leads to different concentrations of electrons and holes, charge carriers can now be classified as *majority* and *minority charge carriers*. In *n*-type silicon, the concentration of electrons is larger than the concentration of holes, which is why electrons are the majority charge carriers and holes the minority charge carriers. In *p*-type silicon it is the other way round, here electrons are the minority charge carriers and holes the minority charge carriers and holes the majority charge carriers. This defines four different types of charge carriers in silicon, which are summarized in Table 2.1.

Thus, also charge carrier mobility can be classified in majority electron mobility  $\mu_{maj,e}$  and minority hole mobility  $\mu_{min,h}$  in *n*-type as well as majority hole mobility  $\mu_{maj,h}$  and minority electron mobility  $\mu_{min,e}$  in *p*-type.

Silicon doped with both types of dopants, acceptors and donors, is called *compensated*. In this case and for typical dopant concentrations orders of magnitudes larger than the intrinsic density, the electron concentration in compensated *n*-type silicon  $(N_D > N_A)$  is given by the difference of ionized donors and ionized acceptors:

$$n_{e0} \approx N_D^+ - N_A^-$$
 (2.25)

The hole concentration can be deduced from the intrinsic density and the electron concentration:

$$n_{h0} \approx \frac{n_i^2}{n_e} \tag{2.26}$$

In the same way, the hole concentration in compensated *p*-type silicon  $(N_A > N_D)$  is given by

$$n_{h0} \approx N_A^- - N_D^+ \tag{2.27}$$

and the electron concentration reads:

$$n_{e0} \approx \frac{n_i^2}{n_h} \tag{2.28}$$

This means that in compensated silicon at a given majority dopant concentration, the majority carrier concentration is reduced due to the presence of compensating minority dopants. While in uncompensated silicon the majority carrier concentration equals the

			-
	<i>n</i> -type	<i>p</i> -type	
Majority charge carriers	electrons	holes	
Minority charge carriers	holes	electrons	

Table 2.1: Majority and minority charge carriers in n- and p-type silicon.

doping concentration, their difference can be huge in compensated silicon. For the characterization of compensated silicon, it is therefore convenient to define a compensation level, which quantifies the difference between ionized dopants and majority carrier concentration. In this PhD thesis, the formulation suggested by Libal *et al.* [57] is used, who define the compensation level  $C_l$  as ration of total amount of ionized dopants and majority charge carrier concentration

$$C_l = \frac{N_A^- + N_D^+}{n_{maj}} = \frac{N_A^- + N_D^+}{|N_A^- - N_D^+|}$$
(2.29)

The second equal sign holds for the case without injection of excess charge carriers, where the majority charge carrier concentration can be approximated by the net doping concentration  $n_{net}$ , which is determined by the difference of ionized majority and minority dopants. These definitions are relevant for the discussion of charge carrier mobility in compensated silicon in chapter 4. Mobilities introduced so far are *conductivity mobilities*  $\mu_c$ , as they directly refer to the charge carrier conductivity via equation (2.11). However, majority carrier mobilities are often obtained from Hall effect measurements. Such mobilities are called *Hall mobilities*  $\mu_H$  and are related to conductivity mobilities by the Hall scattering factor  $r_H$  [7]:

$$\mu_H = r_H \cdot \mu_C \tag{2.30}$$

Here,  $\mu_c$  stands for  $\mu_{maj,e}$  in *n*-type or  $\mu_{maj,h}$  in *p*-type silicon. The Hall scattering factor is defined as  $\langle \tau^2 \rangle / \langle \tau \rangle^2$ , where  $\tau$  is the mean time between collisions of carriers, and accounts for the dependence of scattering mechanisms on magnetic field and temperature. The presence of a magnetic field during Hall effect measurements thus leads to the difference between Hall and conductivity mobility. Details on Hall effect measurements are given in section 3.1 and on Hall scattering factors in section 4.2.

#### 2.2.2 Charge carrier lifetime

If a semiconductor is subjected to an external excitation source, e.g. a light source, featuring a generation rate G, additional free electrons in the conduction band with a concentration of  $\Delta n_e$  and free holes in the valence band featuring a concentration of  $\Delta n_h = \Delta n_e$ , can be created. In the following, this excess charge carrier density is denoted  $\Delta n$ , regardless the type of charge carrier. If  $\Delta n$  serves for the description of measurement conditions at a specified concentration of excess charge carriers, it is also called injection level. According to the continuity equation (2.17), the excess charge carrier density  $\Delta n$  can be expressed by

$$\frac{\partial \Delta n_k}{\partial t} = G_k - R_k - \frac{1}{z_k e} \operatorname{div} \vec{J_k}$$
(2.31)

where k stands for electrons (subscript e) or holes (subscript h). If the charge current density  $\vec{J_k}$  is divergence free and the excitation source is turned off, the decay of  $\Delta n_k$  is determined by the recombination rate  $R_k$ :

$$\frac{\partial \Delta n_k}{\partial t} = -R_k \tag{2.32}$$

The time constant of this exponential decay defines the charge carrier lifetime  $\tau_k$ :

$$\tau_k = \frac{\Delta n_k}{R_k} \tag{2.33}$$

In presence of an external excitation source and for a divergence free charge current density, this leads to the general definition of charge carrier lifetime:

$$\tau_k = \frac{\Delta n_k}{G_k - \frac{\partial \Delta n_k}{\partial t}}$$
(2.34)

If several recombination channels are present simultaneously, their recombination rates add up to a total recombination rate, and, correspondingly, the total lifetime can be derived from the sum of the inverse lifetimes related to each recombination mechanism *i*:

$$\tau_{tot}^{-1} = \sum_{i} \tau_i^{-1} \tag{2.35}$$

#### 2.2.2.1 Recombination mechanisms

Recombination of charge carriers occurs due to intrinsic recombination mechanisms and extrinsic recombination mechanisms. Intrinsic recombination mechanisms in a silicon crystal are *radiative recombination* as well as *Auger recombination*, extrinsic recombination occurs at crystal defects such as point defects, structural crystal defects (grain boundaries, dislocations) and impurity precipitates. Recombination at defects featuring a defined defect level in the band gap, e.g. point defects, can be described by a theory of Shockley, Read [58], and Hall [59], and is therefore also called *Shockley-Read-Hall-recombination*, or simply SRH-recombination.

#### Radiative recombination

Due to the indirect band gap in silicon, radiative recombination represents only a small fraction of recombination compared with recombination via defects and Auger recombination. However, the radiative band-band recombination can be exploited to measure the excess charge carrier density, which is determined by other recombination channels (*cf.* section 3.2.1). The radiative recombination rate is proportional to the density of free electrons and holes:

$$R_{rad} = Bn_e n_h \tag{2.36}$$

Here, *B* denotes the radiative recombination coefficient. Several values for *B* can be found in literature, Kerr *et al.* published a value of  $9.5 \times 10^{-15}$  cm<sup>3</sup> s<sup>-1</sup> according to Schlangenotto *et al.* [60]. Trupke *et al.* [61] published temperature dependent radiative recombination coefficients, with a value of  $4.73 \times 10^{-15}$  cm<sup>3</sup> s<sup>-1</sup> at 300 K.

#### Auger recombination

The major fraction of intrinsic recombination in crystalline silicon is attributed to Auger recombination. In this process, an electron-hole pair recombines by transferring the excess energy to a third charge carrier, either an electron ("eeh" process) or a hole ("ehh" process). Thus, the recombination rates of both processes are proportional to the concentrations of the involved charge carriers

$$R_{eeh} = C_n n_e^2 n_h; \quad R_{ehh} = C_p n_e n_h^2 \tag{2.37}$$

with the Auger coefficients  $C_n$  and  $C_p$ . Dziewior and Schmid published values of  $C_n = 2.8 \times 10^{-31}$  cm<sup>6</sup> s<sup>-1</sup> and  $C_p = 9.9 \times 10^{-32}$  cm<sup>6</sup> s<sup>-1</sup> [62]. The total Auger recombination rate is then obtained as the sum of  $R_{eeh}$  and  $R_{ehh}$ . While this traditional Auger theory can explain lifetimes measured in highly doped silicon ( $N_{dop} > 5 \times 10^{18}$  cm<sup>-3</sup>), a more complex description is needed for lower doping concentrations [63]. Hangleiter and Häcker included Coulomb interactions [64], and further parameterizations for Coulomb-enhanced Auger recombination were developed by Altermatt *et al.* [65] and Glunz *et al.* [66]. A general parameterization of Auger recombination in crystalline silicon was proposed by Kerr and Cuevas [67], and, very recently, Richter *et al.* [63] developed a general parameterization for intrinsic recombination in crystalline silicon at 300 K, which is consistent with the theory of Coulomb-enhanced Auger and radiative recombination. Calculations of intrinsic recombination in this thesis are based on the latter parameterization.

#### Shockley-Read-Hall-recombination

While intrinsic recombination gets important in crystalline silicon featuring a very low density of crystal defects as well as for high charge carrier densities, extrinsic recombination typically dominates lifetime in multicrystalline silicon. If an electron-hole pair recombines via a trap with an energy level  $\varepsilon_t$  in the bandgap, it can be described by the SRH-theory. The recombination rate is determined by the energy level of the trap  $\varepsilon_t$ , the trap density  $N_t$ , as well as the capture cross sections for electrons  $\sigma_n$  and holes  $\sigma_p$ . A detailed deduction can be found e.g. in [68]. The SRH-recombination rate  $R_{SRH}$  reads:

$$R_{SRH} = \frac{n_e n_h - n_i^2}{\tau_{n0}(n_h + n_{h1}) + \tau_{p0}(n_e + n_{e1})}$$
(2.38)

Here,  $n_{e1}$  and  $n_{h1}$  can be derived from equations (2.18) and (2.19) by replacing the Fermi energy  $\varepsilon_F$  with the energy level of the trap  $\varepsilon_t$ . These concentrations are also called SRH-densities. Inserting  $n_e = n_{e0} + \Delta n$  and  $n_h = n_{h0} + \Delta n$  and making use of equations (2.20) and (2.33) leads to the expression for the SRH-lifetime  $\tau_{SRH}$ :

$$\tau_{SRH} = \frac{\tau_{n0}(n_{h0} + n_{h1} + \Delta n) + \tau_{p0}(n_{e0} + n_{e1} + \Delta n)}{n_{h0} + n_{e0} + \Delta n}$$
(2.39)

 $\tau_{n0}$  and  $\tau_{p0}$  are defined as

$$\tau_{k0} = \frac{1}{N_t \sigma_k v_{th}} \tag{2.40}$$

where  $v_{th}$  is the thermal velocity. In low-level injection,  $\tau_{n0}$  and  $\tau_{p0}$  correspond to the minority charge carrier lifetimes in *p*- or *n*-type silicon.

#### Recombination at precipitates

Within the SRH-theory, only recombination at defects featuring a defined trap level in the bandgap can be described, e.g. recombination at point defects. However, especially in mc silicon, a significant amount of impurities can be agglomerated in precipitates, which do not introduce defined trap levels into the band gap. Metallic precipitates can rather be regarded as an internal Schottky contact between the metal cluster and the surrounding silicon [69]. Plekhanov and Tan [70] suggested an approach to estimate the impact of an internal Schottky contact between precipitate and semiconductor on charge carrier recombination. Recently, Kwapil *et al.* [69] suggested a model for charge carrier recombination at Fe precipitates based on realistic Fe precipitate distributions. This model accounts for the parameters that affect the electric field around the precipitates and, according to the thermionic emission theory [71], have a strong impact on charge carrier recombination. Thus, the doping concentration, the precipitate size, the Schottky barrier height, and the injection level are taken into account in the calculation of recombination at iron precipitates [69]. Further technical details on the precipitate recombination model from [69] can be found in section 5.4.2.2.

#### Surface recombination

Without a proper surface passivation, the discontinuity of the crystal lattice at the wafer surface introduces a large number of unsaturated atomic bindings, so called dangling bonds, which introduce many energy levels in the bandgap and thus strongly increase charge carrier recombination. In this thesis, lifetime samples were surface passivated with an adequate passivation layer, as described in the corresponding subsections of chapters 5.2-5.5.

#### 2.2.2.2 Defects and recombination centers

As mentioned in the previous section, the major part of recombination in mc silicon is attributed to recombination at crystal defects, which can be of different nature. In general, a crystal defect is a region in the silicon lattice, where the arrangement of atoms differs significantly from that of a perfect silicon crystal. The following summarizes briefly the most important types of crystal defects, before the change in distribution and recombination activity of crystal defects during solar cell processing is discussed in the last subsection.

#### Point defects

Point defects can be separated in *intrinsic point defects* and *extrinsic point defects*. If a silicon atom leaves its lattice position due to thermal excitation, it creates a vacancy in the silicon lattice and can diffuse through the crystal as a *self-interstitial*. Both, the vacancy and the self-interstitial, are intrinsic point defects that occur even in perfect crystals at temperatures larger than 0 K [72]. In terms of recombination in mc silicon, intrinsic point defects play only a minor role. Extrinsic point defects are any atoms other than Si or atom complexes consisting of a few atoms only that are present in the silicon crystal. These extrinsic point defects can occur as *substitutional point defects*, substituting a Si atom at its lattice position, or *interstitial point defects*, occupying a place between the Si lattice positions. Examples for typical substitutional point defects are dopants such as boron and phosphorus. Due to their shallow defect levels, their impact on recombination is usually negligible. However, as the major part of the dopants is ionized at room temperature and typical concentrations are orders of magnitudes larger than metal impurity concentrations, they play an important role as charged scattering centers. Metal point defects with deep trap levels are important in terms of recombination. They can exist as interstitial point defects, such as interstitial Fe, Cr or Ti, or substitutional point defects, such as Cu, Zn or Au [73, 74]. Further, metal point defects can introduce single or multiple defect levels, and can exist in an acceptor state or donor state. A good overview of metal impurities in silicon and their properties can be found in [74]. In the context of this thesis, it is important to mention that the majority of common metal point defects in silicon feature larger capture cross sections for electrons than for holes, which leads to a stronger recombination activity in *p*-type silicon compared to *n*-type silicon. This is exemplarily shown in Figure 2.4, which plots the ratio of electron and hole capture cross sections for a selection of common metal impurities in mc silicon [73]. Ratios larger than one in the upper half of the graph feature a larger capture cross section for electrons and, therefore, lead to a stronger recombination rate in *p*-type silicon, where electrons are the minority charge carriers.



Figure 2.4: Ratio of electron and hole capture cross section as a function of energy level depth. Figure reprinted from [73].

Point defects can also occur as metastable defects. For instance, in *p*-type silicon, positively charged interstitial iron can form pairs with negatively charged acceptor dopants. FeB-pairs feature different trap levels and different capture cross sections than  $Fe_i$ , thus changing the recombination properties. Further details on metastable defects are discussed in section 3.2.4 as well as in reference [75].

#### Multidimensional defects

Besides point defects, which are 0-dimensional, also multidimensional defects can introduce energy levels into the band gap and thus enhance recombination in silicon. In this thesis, *structural crystal defects*, comprising one-dimensional dislocation lines, two-dimensional grain boundaries, and agglomerations of dislocation lines, denoted dislocation clusters, are distinguished from *precipitates*, which are three-dimensional clusters of impurities. Further three-dimensional defects are inclusions of impurities. A detailed specification of defect types can be found in [76]. The recombination activity of structural crystal defects strongly depends on the specific type of dislocation or grain boundary and on the level of decoration with impurities. As discussed in [77], silicide precipitates are supposed to be the main cause for the recombination activity of grain boundaries, whereas the recombination activity of dislocations is attributed to precipitates as well as impurities trapped in the strain field around the core of the dislocation.

As discussed in further detail in section 3.3, in this thesis three categories for the physical origins of bulk-related efficiency losses are distinguished:

• *Homogeneously distributed recombination centers*, comprising all defects within grains of mc silicon wafers. Thus, this category comprises point de-

fects as well as a low density of homogeneously distributed "background" dislocations and precipitates distributed across the grains.

- *Recombination active structural crystal defects*, comprising recombination active grain boundaries, dislocations, and dislocation clusters that are visible in a photoluminescence image.
- *Edge region*, comprising all impurities that had diffused into the silicon crystal from the crucible system by solid-state diffusion during crystallization. As shown in chapters 5.2 and 5.4, recombination in the edge region is strongly related to interstitial iron (mc *p*-type Si) or FeSi<sub>2</sub>-precipitates (mc *n*-type Si).

# Change in distribution and recombination activity of crystal defects during solar cell processing

During high temperature solar cell process steps, the distribution and the recombination activity of crystal defects can be changed. The active use of such processes for enhancement of material quality is called defect engineering.

The most common process is *diffusion gettering*. This shall be explained on the example of a phosphorus diffusion. The elevated temperature of approximately 800°C leads to a higher diffusivity of metal impurities. Furthermore, their solubility is strongly increased in the P-doped layer compared with the silicon bulk, which leads to a diffusion of impurities to the diffused layer. Thus, the bulk material is purified, and the metal impurities agglomerate in the highly doped layer, where their impact on recombination is significantly smaller due to the limitation by Auger recombination [78]. Such gettering processes are called *external gettering*. The applied phosphorus diffusions in this thesis are typical P-diffusions developed for the fabrication of high efficiency solar cells, optimized in terms of emitter recombination and sheet resistance rather than in terms of their gettering efficacy. Nevertheless, a substantial impact of external gettering was observed also for these P-diffusions (*cf.* chapter 5).

The gettering efficacy of boron diffusions strongly depends on the process parameters [79]. While an optimized boron diffusion gettering can effectively getter metal impurities and, thus, increase the electrical quality of the bulk material, a standard boron diffusion can be virtually ineffective in terms of gettering at temperatures above 850°C. Boron diffusions applied for the fabrication of high efficiency solar cells require higher temperatures than P-diffusions. The B-diffusions investigated in this thesis were applied at 890°C. Especially in mc silicon, the higher temperature can even harm the material quality due to a stronger dissolution and redistribution of previously large metal precipitates to a higher density of smaller metal precipitates. Also, a potential cross-contamination of the material from the furnace tube at high temperatures was suggested in [79]. *Internal gettering* denotes the diffusion of dissolved impurities to regions within the bulk, where their solubility is increased, e.g. the strain fields around dislocations, and the precipitation of dissolved impurity atoms. Details are described in [78].

Finally, *passivation* of crystal defects can reduce their recombination activity. This is particularly important for the surface of silicon wafers, as mentioned in section 2.2.2.1. Additionally, also crystal defects in the bulk can be passivated, for example by hydrogen [80]. The exact mechanism behind this passivation and the type of defects and impurities that can be passivated by hydrogen are subject of current research [81]. Recently, Karzel *et al.* investigated the influence of hydrogen on interstitial iron in mc silicon [81] as well as the dependence of hydrogen passivation efficacy on grain boundary type in mc silicon [82].
# **3** Characterization Techniques

## 3.1 Mobility

A main topic of this thesis was the development of a unified model for charge carrier mobilities in crystalline silicon (*cf.* chapter 4) based on experimental mobility data in compensated silicon, which was gathered from literature as well as obtained from experiments by the author during his diploma thesis [38] and during this PhD thesis (*cf.* section 4.2). While details on data acquisition are given in section 4.2, the most relevant characterization techniques for charge carrier mobilities in crystalline silicon are described in the following.

Basically, there are two different methods for the determination of majority charge carrier mobilities used in the reviewed literature. One is to measure directly the conductivity mobility  $\mu_C = 1/(e \cdot \rho \cdot n_{net})$  via a measurement of the resistivity  $\rho$  and the net doping concentration  $n_{net}$  (where e is the elementary charge). Alternatively, the Hall mobility  $\mu_H$  can be determined by Hall effect measurements. To deduce the conductivity mobility from the Hall mobility, the Hall scattering factor  $r_H$  has to be known, which links both mobilities via  $\mu_C = \mu_H/r_H$ . Section 3.1.1 introduces the basic principles of Hall measurements, and section 3.1.2 describes the determination of majority carrier mobility via measurements of the resistivity and net doping concentration. Finally, the determination of minority charge carrier mobility is explained in section 3.1.3.

#### 3.1.1 Hall measurements

If electric current flows through a conductor or semiconductor placed in a stationary magnetic field with a perpendicular component to the current, a voltage difference is produced across the (semi)conductor. This effect was discovered by Edwin Hall in 1879 and is called Hall effect [83]. In the following, the determination of the Hall mobility from Hall effect measurements is explained.

Charge carriers of charge q that move with velocity v in a magnetic field of flux density B will experience a force

$$\vec{F_L} = q \cdot (\vec{v} \times \vec{B}) \tag{3.1}$$

which is called Lorentz force. If the charge carriers are not moving parallel to the magnetic field, their paths will be curved, leading to an asymmetric distribution of charge carriers across the Hall element. The separation of charge carriers produces an electric field  $\overrightarrow{E_H}$ . In steady state, the electric force balances the Lorentz force:



Figure 3.1: Hall effect setup. Figure reprinted from [38].

$$\overrightarrow{F_L} + q \cdot \overrightarrow{E_H} = 0 \tag{3.2}$$

If we express the drift velocity v as a function of current density J,

$$\vec{v} = \frac{\vec{J}}{q \cdot n} \tag{3.3}$$

where n denotes the charge carrier density, this results in the following expression:

$$\overrightarrow{E_H} = -(\vec{v} \times \vec{B}) = -\frac{1}{q \cdot n} (\vec{J} \times \vec{B})$$
(3.4)

The Hall coefficient  $R_H$  is defined as:

$$R_H = \frac{1}{q \cdot n} \tag{3.5}$$

and the voltage correlated with the electric field  $\overrightarrow{E_H}$  is called Hall voltage  $U_H$ , of which the value depends on the sample's geometry. Let us consider the simple case of a rectangular sample of edge lengths l and b, and thickness d as sketched in Figure 3.1, with a current flowing in longitudinal direction and a magnetic field perpendicular to it and the sample's surface. For this geometry, the Hall voltage can be calculated from equation (3.4) according to:

$$U_H = b \cdot E_y = \frac{b}{q \cdot n} (J_x \cdot B_z) = \frac{b}{q \cdot n} \cdot \frac{I_x \cdot B_z}{b \cdot d} = \frac{1}{q \cdot n} \cdot \frac{I_x \cdot B_z}{d} = R_H \cdot \frac{I_x \cdot B_z}{d} \quad (3.6)$$

Thus, the Hall coefficient  $R_H$  can be determined by measuring the Hall voltage for a known current, magnetic field and sample thickness.

Hall measurements conducted by the author were performed with a "Hall Profiler System HL5900PC" from BIORAD on square  $1 \times 1$  cm<sup>2</sup> samples with GaIn point contacts in the corners. This enables a determination of the base resistivity according



Figure 3.2: Hall measurement according to van der Pauw [84]. a) Determination of the resistivity without magnetic field. b) Measurement of the Hall voltage in a magnetic field perpendicular to the sample's surface. Figure reprinted from [38].

to the method of van der Pauw [84] and, in combination with measuring the Hall coefficient, a determination of the Hall mobility.

The resistivity is determined by measuring the voltage drop  $U_{43}$  between the contacts 3 and 4 for a given current  $I_{12}$  through contacts 1 and 2 and, subsequently, measuring the voltage drop  $U_{23}$  for a given current  $I_{14}$  (*cf.* Figure 3.2a). The resistivity can then be calculated by the following equation:

$$\rho = \frac{\pi \cdot d}{2\ln(2)} \cdot \left(\frac{U_{43}}{I_{12}} + \frac{U_{23}}{I_{14}}\right) \cdot F(Q)$$
(3.7)

where the correction factor F(Q) is a function of the symmetry factor Q, which is defined as

$$Q = \max\left\{\frac{U_{43}}{I_{12}} \cdot \frac{I_{14}}{U_{23}}, \frac{I_{12}}{U_{43}} \cdot \frac{U_{23}}{I_{14}}\right\}$$
(3.8)

For Q < 10, the correction factor F(Q) can be approximated by

$$F(Q) = 1 - 0.34657 \cdot \left(\frac{Q-1}{Q+1}\right)^2 - 0.09236 \cdot \left(\frac{Q-1}{Q+1}\right)^4$$
(3.9)

The correction factor is determined for all contact pairs with one mutual contact. The resistivity is determined by measuring all four permutations of contact pairs with one common contact in both directions. Each of these measurements delivers a value for the resistivity according to equation (3.7). The final value is then obtained by averaging these eight values.

After the resistivity measurement, the magnetic field is applied and the current conducted through the diagonal contacts, as indicated in Figure 3.2b. The Hall voltage is measured across both diagonals of the sample for varying directions of the current and the magnetic field. The final value is again obtained by averaging the single values. The Hall factor is then calculated according to equation (3.6).

As mentioned in section 2.2.1, the presence of a magnetic field during Hall effect measurements leads to a difference between the measured Hall mobility and the actual charge carrier conductivity mobility. The dependence of scattering mechanisms on magnetic field and temperature is accounted for by the Hall (scattering) factor  $r_H$ , which relates the conductivity mobility to the measured Hall mobility according to equation (2.30). The Hall factor also has to be applied to the Hall coefficient, which modifies equation (3.5) to

$$R_H = \frac{r_H}{q \cdot n} = \frac{1}{q \cdot n_H} \tag{3.10}$$

As Hall measurements are conducted without generation of electron hole pairs, the charge carrier density n equals the net doping concentration of the sample. In the evaluation software of the Hall setup, the Hall factor is not implemented (or, in other words, a Hall factor of 1 is assumed). Thus, the measured Hall net doping concentration  $n_H$  is linked to the actual net doping concentration by the Hall factor according to equation (3.10).

Finally, the Hall mobility can be derived from the measured Hall coefficient  $R_H$  and the measured resistivity according to

$$\mu_H = \frac{R_H}{\rho} = \frac{r_H}{\rho \cdot q \cdot n} = r_H \cdot \mu_C \tag{3.11}$$

and, for a known Hall scattering factor, the majority charge carrier conductivity mobility  $\mu_c$  can be calculated.

Hall measurements of the author were performed at room temperature, additional temperature-dependent Hall mobility measurements were carried out by Maxime Forster in the frame of his PhD-thesis [85], using an Ecopia HMS-5000 device equipped with a temperature control system cooled with liquid nitrogen [86]. Details on the applied Hall factors for the calculation of conductivity mobilities from Hall measurements are given in section 4.2.

#### **3.1.2** Deduction from resistivity and net doping concentration

Besides deriving the conductivity mobility from Hall measurements as explained in the previous section, it can also be determined by a measurement of the resistivity and the net doping concentration. From equation (2.11), the following expression can be derived for the majority carrier mobility (approximation for  $n_{net} \gg n_i$ ):

$$\mu_{maj} = \frac{1}{\rho \cdot e \cdot n_{net}} \tag{3.12}$$

Thus, the majority carrier mobility can be directly calculated from the *resistivity* and the *net doping concentration*, both measured without generation of electron hole pairs.

A typical method for determining the *resistivity* is a four-point probe measurement. The basic idea behind this method is to contact four in-line contact needles with the sample and measure the voltage drop across the inner two contacts for a given current through the outer two contacts. For further details, the reader is referred to [7]. Alternatively, the resistivity can be measured by contactless methods, of which the most frequently applied ones are inductive measurements [87], such as eddy current measurements [7].

A direct determination of the *net doping concentration* can be done by electrochemical capacitance-voltage (ECV) measurements [88], where an electrolyte on the silicon wafer surface forms a Schottky-contact. By varying the capacity of the spacecharge region with a modulated voltage, the free charge carrier concentration in the silicon sample can be measured. Without generation of electron hole pairs, this concentration corresponds to the net doping concentration. Another method for the determination of net doping concentrations is the FTIR-FCA method introduced in [89] and extended in [90], which is based on measurements of the free carrier absorption (FCA) by Fourier Transform Infrared Spectroscopy (FTIR). The free carrier absorption leads to an increase in the baseline of the absorption spectra in the wavelength range from 6 to 20  $\mu$ m. A quantitative description of the increase allows for a determination of the free carrier concentration. Since no external generation of electron hole pairs occurs during the FTIR-measurement in the investigated wavelength range, the measured free carrier concentration corresponds to the net doping concentration.

#### 3.1.3 Determination of minority charge carrier mobility

The minority charge carrier mobility data, which served as a basis for the model adaption presented in section 4.3.2.3, was extracted from minority charge carrier lifetime data [86, 91]. The data from Forster *et al.* [86] was obtained by using a combination of the techniques developed by Sproul *et al.* [92] and Stephens and Green [93], the data from Rougieux *et al.* [91] was obtained by the method of Sproul. The basic idea of this method is sketched in the following. For further details, the reader is referred to [92].

The effective lifetime of a sample with abraded surfaces, yielding very high surface recombination velocities, is limited by the diffusion of minority charge carriers to the surface in low injection. Assuming an infinite surface recombination velocity, the effective lifetime  $\tau_{eff}$  can be expressed by

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \left(\frac{\pi}{w}\right)^2 D_k \tag{3.13}$$

where  $\tau_{bulk}$  is the bulk lifetime of the sample, w the sample thickness and  $D_k$  the minority charge carrier diffusion coefficient. By measuring  $\tau_{eff}$  for different sample thicknesses, the minority carrier diffusion constant can be determined from the slope of

a plot of  $1/\tau_{eff}$  versus  $(\pi/w)^2$ . In combination with the Einstein relation (2.10), this allows for a determination of the minority charge carrier mobility.

An additional method for the characterization of minority charge carrier mobility was developed recently at Fraunhofer ISE by Giesecke *et al.* [94]. Like the technique developed by Sproul *et al.* [92], it infers minority charge carrier mobility via the Einstein relation from the minority charge carrier diffusion coefficient obtained from lifetime measurements (here: harmonically modulated photoluminescence, *cf.* section 3.2.2) on samples dominated by surface recombination. In contrast to Sproul's approach, this method is based on an asymmetrical surface passivation scheme. The illuminated side of the sample features an optimal surface passivation, whereas the opposite side is dominated by surface recombination. Thus, charge carrier recombination is dominated by minority charge carrier transport from the illuminated side to the opposite side, and, like in Sproul's method, effective charge carrier lifetime is affected predominantly by the minority charge carrier diffusion coefficient and the sample thickness.

Note that in order to avoid the measured mobility to be affected by ambipolar diffusion [6], it is important to measure under rigorous low level injection conditions [94]. While this is essential for the exact determination of minority charge carrier mobility by Sproul's method, the accurate knowledge of the injection level in Giesecke's approach enables to correct the measured mobility value for ambipolar diffusion effects [94].

## 3.2 Lifetime and Defect Characterization

A large part of the results presented in chapter 5 are based on state-of-the-art characterization by photoluminescence imaging (PLI) [95] of silicon wafers and solar cells. In this section, the most relevant aspects and applications of this technique are presented. For a more detailed discussion of the PL imaging setup used for characterization in this thesis and its recent enhancements, the reader is referred to [20]. Section 3.2.1 focuses on the basics of PL imaging and the used setup. Section 3.2.2 discusses the calibration of PL images to lifetime images. The next two sections introduce two applications of lifetime imaging applied in this thesis: injection-dependent lifetime imaging (section 3.2.3) and metastable defect imaging (section 3.2.4). To complete the chapter on defect characterization, a short description of inductively coupled plasma mass spectrometry is presented in section 3.2.5.

#### 3.2.1 Photoluminescence imaging

PL imaging [95] allows for depth-averaged, spatially resolved measurements of excess charge carrier density, charge carrier lifetime and diffusion length in crystalline silicon

wafers. The basic idea behind this technique is to make use of the band-band recombination radiation in crystalline silicon. A laser, in our case with a wavelength of 790 nm, provides a homogeneous, steady-state illumination source, which generates electron-hole pairs in the wafer. The radiative recombination rate is given by equation (2.36). Due to the indirect band gap in silicon, radiative recombination represents only a small fraction of recombination compared with recombination via defects and Augerrecombination. Nevertheless, a camera can detect the emitted photons, and the signal is large enough for quantitative measurements. This is of importance, as the detection of radiative band-band recombination is exploited to measure the excess carrier density, which is determined by other recombination channels. As the probability for radiative recombination is proportional to the product of the density of electrons and holes, the count rate of the detected photons serves as a measure for excess charge carrier density.

For each camera pixel *i*, the correlation of the local PL intensity  $\varphi_i$ , measured at a steady-state generation rate  $G_0$ , and the local excess charge carrier density  $\Delta n_i$  in a wafer featuring a net doping concentration of  $n_{net}$ , can be expressed by

$$\varphi_i = a \cdot \Delta n_i \cdot (\Delta n_i + n_{net}) \tag{3.14}$$

with a yet unknown proportionality factor a, which is affected by the coefficient for radiative recombination, the optical properties of the sample, as well as all relevant properties of the setup (geometry, filter stacks, quantum efficiency of the camera, etc.). According to equation (2.34), for steady-state conditions the local excess charge carrier density reads:

$$\Delta n_i = G_0 \cdot \tau_i \tag{3.15}$$

Thus, the local PL intensity from equation (3.14) can be expressed as a function of the local charge carrier lifetime  $\tau_i$ :

$$\varphi_i = a \cdot G_0 \cdot \tau_i \cdot (G_0 \cdot \tau_i + n_{net}) \tag{3.16}$$

The generation rate per volume  $G_0$  can be calculated from the incident photon flux density  $j_{\gamma}$ , the front reflection R(790 nm) of the wafer and the wafer thickness w:

$$G_0 = (1 - R(790 \text{ nm})) \cdot j_\gamma / w \tag{3.17}$$

The use of a 790 nm laser with a penetration depth in silicon of 10.8 µm at 300K [20] ensures that virtually all incident photons penetrating the wafer are absorbed for typical wafer thicknesses. As explained in detail in [20], a 1 sun equivalent of

$$j_{\gamma,1sun}(w = 200 \,\mu\text{m}, T = 300\text{K}) = 2.55 \cdot 10^{17} \text{cm}^{-2} \text{s}^{-1}$$
 (3.18)

is used for all evaluations of this thesis. With this definition, the monochromatic generation rate inside the sample is comparable with the generation rate of the AM1.5G spectrum (standardized irradiation spectrum representing the solar spectrum after penetration of the 1.5-fold air mass compared with perpendicular irradiation, accounting for direct and diffuse irradiation), if the reflectivity of the wafer at 790 nm is comparable with the weighted reflectivity, the wafer thickness is around 200  $\mu$ m, and enhanced absorption of photons due to internal reflectance is insignificant [20].

The incident photon flux density  $j_{\gamma}$  is determined with a reference cell of area *A* with a known external quantum efficiency (EQE) at 790 nm by measuring the voltage drop *V* over a resistance *R* 

$$j_{\gamma} = \frac{V}{A \cdot R \cdot \text{EQE}(790 \text{ nm}) \cdot e}$$
(3.19)

where *e* is the elementary charge. The resistance *R* is small, such that measuring the voltage drop corresponds to measuring the short-circuit current density of the solar cell  $J_{sc} = V/(A \cdot R)$ .

With these considerations, the local charge carrier lifetime at a specific local excess charge carrier density can be determined from the measured local PL intensity according to equations (3.14) and (3.16), if the proportionality factor a is known. Therefore, a calibration of the image is necessary, which will be discussed in the next section. Prior to that, to complete the section on PL imaging, a short overview of the used setup is given.

#### PLI setup

A sketch of the setup is shown in Figure 3.3. The silicon wafer is irradiated homogeneously by the laser with a wavelength of 790 nm. A stable sample temperature during the measurement is ensured by the temperature control of the chuck, which was set to 298K for all measurements of this thesis. The spatial homogeneity of the laser intensity on the illuminated area of approximately  $20 \times 24$  cm<sup>2</sup>, provided by a beam shaper at the end of the optical fiber of the laser. is approximately  $(j_{\gamma,max} - j_{\gamma,min})/(j_{\gamma,max} + j_{\gamma,min}) \approx 7.5\%$  [96, 97]. These inhomogeneities are considered in the measurement of the photon flux density with the reference cell, such that the applied generation rate in the evaluations refers to the generation rate in the central part of the sample for each measurement.



Figure 3.3:PL imaging setup. A 790 nm laser, equipped with a beam-shaper and a short-pass filter in the beam path, homogeneously illuminates the silicon wafer. The radiative emission of photons (photoluminescence) is detected by a CCD-camera. In front of the camera, two long-pass filters and an optional short-pass filter are installed. Figure adapted from [97].

The silicon CCD camera features a resolution of  $1024 \times 1024$  pixels, which corresponds to a pixel size of  $122 \times 122 \ \mu\text{m}^2$  for a typical image side length of 125 mm. In order to assure detection of band-band luminescence and avoid undesired detection of laser light, a short-pass filter is installed in the beam path of the laser. This filter blocks fractions of the illuminating light in the long wavelength range. Additionally, a stack of long-pass filters is installed in front of the camera, which blocks the reflected laser light from the chuck and the wafer. Still, a small fraction of undesired laser light is detected by the camera. This is corrected for by an appropriate background subtraction, as described in the next subsection. Optionally, in addition to the two long-pass filters, a short-pass filter can be installed in front of the camera. This reduces blurring of PL images due to long wavelength photons detected by the camera. Long wavelength photons with energies close to the silicon band gap feature a low absorption coefficient and can travel long distances in the range of centimeters, both in the silicon wafer as well as in the silicon CCD chip of the camera. This leads to an artificially enhanced count rate in low lifetime regions by photons originally emitted in high lifetime regions of the wafer. By inserting an additional short-pass filter, only photons with wavelengths smaller than 1000 nm will be detected. These photons feature a much smaller absorption length (about 160 µm at 300 K for 1000 nm [20]). Thereby, optical blurring in the wafer is efficiently suppressed, as this absorption length is in the range of the

spatial image resolution. Still, blurring in the silicon CCD chip of the camera is harder to suppress, as the pixel size of the camera chip is only  $13 \times 13 \ \mu\text{m}^2$  and the absorption length is larger at a chip temperature of -50°C as phonons are required for the absorption [20]. A deconvolution of the images with a point-spread function could be a solution for this issue [98, 99]. As shown in [98], the use of a 1000 nm short-pass filter is the best method to reduce image blurring without further deconvolution calculations. Unfortunately, the use of a short-pass filter also comes along with the drawback of increased integration times of approximately a factor of 10. This is why it cannot be applied in all of our characterization methods. For instance, for metastable defect imaging (*cf.* section 3.2.4) long integration times have to be avoided due to the rearrangement of metastable defects during the measurement. Therefore, in this thesis the short-pass filter was applied for standard lifetime and diffusion length measurements, for lifetime spectroscopy (*cf.* section 3.2.3) and for ELBA analyses (*cf.* section 3.3), but not for metastable defect imaging.

#### Background

Several terms contribute to the background signal of the measured PL images. One is the dark noise of the camera, which depends on the integration time. This term is accounted for by a parameterization obtained from dark image measurements for different integration times. Also, as mentioned before, a small fraction of reflected laser light is detected by the camera, which contributes to the background signal. This background term depends on the integration time and on the laser intensity and can be accounted for by a parameterization as described in [20].

#### 3.2.2 Harmonically modulated photoluminescence

In order to derive lifetime images from the measured PL images, the proportionality factor *a* from equations (3.14) and (3.16) has to be determined. This is done by harmonically modulated photoluminescence (HMPL) [100-102] in a separate setup, consisting of a 790 nm laser, which can be modulated harmonically, an InGaAs diode for the detection of the time-dependent PL signal  $\phi(t)$ , and a diode for the detection of the modulated generation rate G(t). A sketch of the setup is shown in Figure 3.4.



Figure 3.4: Harmonically modulated PL setup. A 790 nm laser with a harmonically modulated generation rate G(t), measured with a monitor diode, illuminates the silicon wafer. The time-dependent PL signal  $\phi(t)$  of the wafer is detected by an InGaAs diode. Figure reprinted from [100].

The time-dependent generation rate G(t) generates a time-dependent excess charge carrier density  $\Delta n(t)$  in the sample, which obeys the following continuity equation:

$$\frac{\partial \Delta n(t)}{\partial t} = G(t) - \frac{\Delta n(t)}{\tau(\Delta n(t))}$$
(3.20)

where  $\tau(\Delta n(t))$  is the injection-dependent effective charge carrier lifetime. As in steady-state (*cf.* equation (3.14)), the measured time-dependent PL intensity  $\phi(t)$  is related to the effective lifetime by

$$\phi(t) = A \cdot \Delta n(t) \cdot (\Delta n(t) + n_{net})$$
(3.21)

where the proportionality factor *A* again incorporates the coefficient for radiative recombination, the optical properties of the sample, as well as all relevant properties of the setup.

From equations (3.20) and (3.21), the injection dependent lifetime can be derived by the self-consistent approach as published by Trupke *et al* [103]. Given the measured functions G(t) and  $\phi(t)$  together with the net doping concentration  $n_{net}$ , the factor A in equation (3.21) can be derived by eliminating the hysteresis of the trajectory

$$\tau(\Delta n(t)) = \frac{\Delta n(t)}{G(t) - \partial \Delta n(t) / \partial t}$$
(3.22)

In this evaluation, knowledge of the net doping concentration is only required, if the measurement is not conducted under low level injection. For low injection conditions  $(\Delta n \ll n_{net})$ , equation (3.21) can be simplified to

$$\phi(t) = A \cdot \Delta n(t) \cdot n_{net} = A' \cdot \Delta n(t)$$
(3.23)

where  $A' = A \cdot n_{net}$  remains the only unkown.

#### Lifetime calibration of PL images

With the described method, we obtain an injection-dependent lifetime  $\tau_{\text{HMPL}}(\Delta n)$ . As the lateral resolution of the HMPL-measurement is larger than typical areas of homogeneous material quality of mc silicon wafers, it has to be addressed how these different areas contribute to the measured PL signal  $\phi(t)$  and finally to the resulting injection-dependent lifetime  $\tau_{\text{HMPL}}(\Delta n)$ . In the following,  $\tau_{\text{HMPL}}(G = G_0)$  denotes the measured lifetime at the generation rate corresponding to the steady-state generation rate  $G_0$ , at which the PL image was obtained. For the calibration of the PL image, it is important that the modulated generation rate G(t) of the HMPL-measurement covers this steady-state generation rate  $G_0$ . As shown in [100], the measured lifetime  $\tau_{HMPL}(G = G_0)$  is composed of the local lifetimes  $\tau_i$  corresponding to pixel *i* of the PL image  $\varphi_i$  in the area of the HMPL-measurement according to the following relation:

$$\tau_{HMPL}(G = G_0) = \frac{\sum_{HMPL \ measurement \ area} \tau_i S_i (2G_0^2 \tau_i^2 + G_0 \tau_i n_{net})}{\sum_{HMPL \ measurement \ area} S_i (2G_0^2 \tau_i^2 + G_0 \tau_i n_{net})}$$
(3.24)

Here,  $S_i$  is the relative sensitivity of the measurement setup at pixel *i*. Thus, the averaging procedure, which enables a lifetime calibration of the measured PL image, is defined by this equation. Given a PL image with a measured PL intensity  $\varphi_i$  for pixel *i*, equation (3.16) has to be solved for positive  $\tau_i$  and inserted in equation (3.24) for all pixels of the PL image contributing to the HMPL-measurement. Thereby, the calibration factor *a* in equation (3.16) is determined, which corresponds to a lifetime calibration of the PL image.

#### Conversion to diffusion length images

As discussed in chapter 5.3.2 of [20], the diffusion length is the better figure of merit for a comparison of material quality of *p*- and *n*-type silicon, as solar cell efficiency is determined by the diffusion length for equal dark resistivity  $\rho$ . As a large part of this thesis focuses on the differences between multicrystalline *p*- and *n*-type silicon, for these comparisons the lifetime images  $\tau_i$  obtained from PL imaging are converted to images of the minority charge carrier diffusion length according to

$$L_{min,i} = \sqrt{D_{min} \cdot \tau_i} \tag{3.25}$$

where  $D_{min}$  is the minority charge carrier diffusion coefficient, which relates to minority charge carrier mobility via the Einstein relation from equation (2.10). The diffusion coefficients for electrons and holes are calculated from the measured resistivity with the mobility model developed in this thesis (*cf.* chapter 4).

#### Image averaging

For many evaluations in this thesis, an adequate diffusion length or lifetime averaging for whole wafers or wafer parts is required. Therefore, we make use of the harmonic mean in the diffusion length, as suggested in [104], both for diffusion length and lifetime averaging. This leads to the following expression for the average diffusion length

$$\frac{1}{L_{min,avg.}} = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{L_{min,i}}$$
(3.26)

and to a corresponding expression for the average lifetime

$$\frac{1}{\sqrt{\tau_{1/L}}} = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{\sqrt{\tau_{bulk,i}}}$$
(3.27)

The latter average will be referred to as "square root harmonic mean" in this thesis. This averaging procedure accounts for the fact that the impact of low lifetime regions on solar cell efficiency is stronger compared with high lifetime regions, and low lifetime regions cannot be overcompensated with higher lifetimes [105]. This is discussed in very detail in chapter 3.1 of [20]. For an exact prediction of solar cell parameters, a more advanced procedure has to be applied, accounting for the injection dependence of lifetime as well as for the specific solar cell concept (*cf.* section 3.3). Nevertheless, for a first estimation of the material quality and a comparability of different lifetime samples, the square root harmonic mean of lifetime images at a fixed illumination in the range of 0.05-0.1 suns (which is estimated to correspond to injection levels close to MPP-conditions in the solar cell) turned out to be a good figure of merit. Other approaches to obtained valuable lifetime mean values for the different cell parameters are discussed in [105].

#### 3.2.3 Injection-dependent lifetime imaging

Lifetime spectroscopy gives access to defect concentrations and parameters of relevant impurities in crystalline silicon [106]. However, if multiple defects are present in a material, which is usually the case for mc silicon, defect characterization by lifetime spectroscopy is much more challenging. In this thesis, we make use of injection-

dependent lifetime imaging. Beside the determination of charge carrier lifetime or diffusion length at a constant generation rate, PL imaging at different generation rates delivers injection-dependent lifetime images. From a comparison with theoretical injection-dependent lifetime curves for specific defects (Fe<sub>i</sub>, FeSi<sub>2</sub>-precipitates, Cr<sub>i</sub>, ...) or combinations of these, the characteristics of the injection-dependent charge carrier lifetime in different wafer regions provide information about possible material limitations. Furthermore, in combination with PC1D solar cell simulations, the material-related efficiency potential and specific efficiency losses can be assessed, as explained in section 3.3. This makes injection-dependent lifetime imaging an important characterization tool, which is frequently applied in this thesis.

#### Experimental details

Injection-dependent lifetime imaging is identical with PL lifetime imaging as described in the previous section, with the addition of recording several PL images at different generation rates. A typical measurement covers generation rates corresponding to 0.001 - 1.6 suns. The lower limit is given by the desired maximum of integration times, which increase dramatically at low injection levels due to the linear dependence of the PL signal on excess charge carrier density (cf. equation (3.14)). Further, the signal to noise ratio increases at low generation rates. The maximum laser power restricts the generation to an upper limit of approximately 1.6 suns in our setup. Depending on the lifetime, this generation range correlates to injection levels of  $10^{11}$  -  $10^{16}$  cm<sup>-</sup> <sup>3</sup>. For all injection-dependent lifetime imaging measurements, the 1000 nm short-pass filter in front of the camera was applied (cf. section 3.2.1). Lifetime images were derived from PL images by calibrating the 1 sun image of a wafer by harmonically modulated PL as explained in the previous section, and applying the obtained calibration factor to all images measured on this wafer for varying generation. From the injection-dependent lifetime images, plots of  $\tau(\Delta n)$  can be extracted for different wafer regions.

#### 3.2.4 Metastable defect imaging

PL imaging of metastable defects is a powerful tool for the characterization of the concentration and spatial distribution of dissolved defects with a characteristic metastable behavior. In this thesis, metastable defect imaging is applied for the characterization of iron and chromium point defects in mc silicon wafers. The basic idea for measuring iron point defect concentrations by taking advantage of its metastable states was introduced by Zoth and Bergholz [107] and Kittler et al. [108]. In *p*-type silicon, iron point defects can exist in two different chemical states differing in their electrical defect parameters: Due to the Coulomb interaction between positively charged interstitial iron atoms and negatively charged boron atoms in boron-doped silicon, ironboron(FeB)-pairs form in the dark. These pairs can be split by illumination with light [109], leading to the presence of interstitial iron atoms (Fe<sub>i</sub>) instead of FeB-pairs. With the help of lifetime measurements in both states, the concentration of iron point defects can be calculated. Macdonald *et al.* [110] transferred this approach to PL imaging, enabling an imaging of the concentration of iron point defects in silicon wafers. A similar approach was developed by Habenicht *et al.* [111] for imaging the concentration of the metastable defect states and the calculation procedures, the reader is referred to [75, 112].

#### Optimization of measurement procedure

During this thesis, imaging of iron and chromium point defects was optimized. The crucial points are summarized in the following. First, in contrast to earlier procedures, rigorous low injection conditions were applied. Both for iron and chromium imaging, a constant generation rate corresponding to 0.01 suns was chosen. First, this ensures that the measurement is performed away from the "crossover point" for FeB- and Feilimited lifetimes [110], where the two defects cannot be distinguished due to identical defect related lifetimes in both states, and a splitting of FeB-pairs during recording the FeB-image is avoided. As explained in [112], in order to achieve a sufficient PL count rate for the FeB-image, low illumination intensities and long integration times instead of high illumination intensities and short integration times are preferred, since the splitting mechanism is affected by the square of the generation rate whereas only by the first power of time. Second, measurements at low injection conditions enhance the accuracy of both methods significantly, particularly for the case that the imaged defect is not the dominant defect in the sample, due to the following reason. Since charge carrier lifetime differs in the two metastable states, imaging the sample at a constant generation rate leads to different injection levels in the wafer in the two states. This can be expressed by the measured lifetimes  $\tau_{eff,1}(\Delta n_1)$  in state 1 and  $\tau_{eff,2}(\Delta n_2)$  in state 2 as follows:

$$\frac{1}{\tau_{eff,1}(\Delta n_1)} = \frac{1}{\tau_{SRH,1}(\Delta n_1)} + \frac{1}{\tau_{Auger}(\Delta n_1)} + \frac{1}{\tau_{rad}(\Delta n_1)} + \frac{1}{\tau_{surf}(\Delta n_1)} + \frac{1}{\tau_{other}(\Delta n_1)}$$
(3.28)  
$$\frac{1}{\tau_{eff,2}(\Delta n_2)} = \frac{1}{\tau_{SRH,2}(\Delta n_2)} + \frac{1}{\tau_{Auger}(\Delta n_2)} + \frac{1}{\tau_{rad}(\Delta n_2)} + \frac{1}{\tau_{surf}(\Delta n_2)} + \frac{1}{\tau_{other}(\Delta n_2)}$$
(3.29)

Here,  $\tau_{SRH,1}$  and  $\tau_{SRH,2}$  are the SRH-lifetimes of the investigated defect in state 1 and 2, respectively. Except for intrinsic recombination ( $\tau_{Auger}$  and  $\tau_{rad}$ ), which is accounted for as a function of excess charge carrier density, and the known injection dependence of the investigated defect, the evaluation assumes an injection independent

surface recombination  $(\tau_{surf}(\Delta n_1) = \tau_{surf}(\Delta n_2))$  as well as a flat injection dependence of other recombination channels  $(\tau_{other}(\Delta n_1) = \tau_{other}(\Delta n_2))$ . If the investigated defect is the dominant recombination channel, this is a fair assumption. However, usually also other defects contribute to recombination. Especially for the case of other defects being more dominant than the investigated defect and featuring a strong dependence on injection level, this assumption would lead to large errors in the calculated defect concentration, as a difference in  $\tau_{other}(\Delta n_1)$  and  $\tau_{other}(\Delta n_2)$ , which affects the measured lifetimes  $\tau_{eff,1}(\Delta n_1)$  and  $\tau_{eff,2}(\Delta n_2)$ , would be attributed to a difference in  $\tau_{SRH,1}(\Delta n_1)$  and  $\tau_{SRH,2}(\Delta n_2)$ , and, consequently, lead to a miscalculation of the defect concentration. For instance, chromium imaging in wafer areas dominated by interstitial iron would be affected by such artefacts, as interstitial iron limited lifetime features a strong injection dependence. Measuring at rigorous low injection conditions, where charge carrier lifetime features a very weak dependence on injection level, avoids this problem.

The drawback of choosing low generation rates is the requirement of longer integration times. This could lead to other problems correlated to the kinetics of defect formation. Chromium imaging is not affected by this issue, as splitting and pairing of CrB is a purely temperature-driven process [112], such that long integration times for both the CrB- and Cr<sub>i</sub>-image can be chosen. However, as FeB-pairs form in the dark already at room-temperature and can be split by light, long integration times for the PL image in the FeB-state might lead to a significant splitting of FeB-pairs, whereas long integration times for the PL image in the Fe<sub>i</sub>-state at an illumination insufficient for complete splitting might lead to a reformation of FeB-pairs during the measurement. These aspects have been considered and investigated. We monitored the stability of lifetime across a wafer with a spatial variation of Fe<sub>i</sub>-concentrations from approximately  $10^{10}$  -  $10^{12}$  cm<sup>-3</sup> (1  $\Omega$ cm mc *p*-type silicon wafer featuring an edge region of high Fe<sub>i</sub>-concentration) in the Fe<sub>i</sub>- and in the FeB-state during an illumination with the PL laser of 0.01 suns. From the results, we can conclude that long integration times of up to 120 s in the FeB-state and up to 180 s in the Fe<sub>i</sub>-state can be chosen without a significant splitting of FeB-pairs in the FeB-state or a significant re-formation of FeB-pairs in the Fe<sub>i</sub>-state. Additionally, in order to assure a virtually complete and stable splitting of FeB-pairs before recording the PL image in the Fei-state, the sample should be illuminated with maximum laser power corresponding to an illumination of ~1.6 suns for at least 4 min. These findings were taken into account for the measurements performed in this thesis. In addition to the measurement at 0.01 suns in each state, a PL image at one sun in the Fe<sub>i</sub>- or Cr<sub>i</sub>-state was recorded, which served for the calibration procedure explained in section 3.2.2. The setup for iron and chromium imaging is the

same as described in section 3.2.1 with an additional shutter that shades the sample from laser light during laser stabilization in order to avoid splitting of FeB-pairs during the stabilization time of  $\sim$ 4 min.

#### Defect parameters

Knowledge of the electrical defect parameters (capture cross sections for electrons and holes, energy level in the band gap) of Fe<sub>i</sub>, FeB, Cr<sub>i</sub> and CrB is required for the calculation of the concentrations of iron and chromium point defects from the measured effective lifetimes in the two metastable states. These are taken from [113] for Fe<sub>i</sub> and from [114] for FeB. The parameters for Cr<sub>i</sub> and CrB are taken from a recent publication by Sun *et al.* [115] on the reassessment of the recombination parameters of chromium point defects.

#### 3.2.5 Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is a technique for elemental analysis, where samples are atomized and ionized in an inductively coupled plasma before their elemental composition is analyzed by mass spectrometry [116]. In this PhD-thesis we made use of this method for the determination of dopant concentrations in compensated silicon samples, as described in detail in section 4.2. A detailed description of this method can be found in references [116, 117].

### **3.3** Prediction of Solar Cell Efficiency Potential

An "Efficiency limiting bulk recombination analysis" (ELBA), which was developed by Bernhard Michl in the frame of his PhD thesis [20], enables a prediction of the efficiency limits in mc silicon due to injection-dependent bulk recombination in combination with a specific solar cell concept. The local bulk recombination is assessed by injection-dependent lifetime imaging (cf. section 3.2.3) of surface passivated lifetime samples. It is of utmost importance that the bulk recombination in the lifetime samples corresponds to the bulk recombination in the finished solar cells, which is assured by including all high temperature steps of the solar cell concept under investigation in the processing of the lifetime samples. In combination with a local PC1D cell simulation [118] accounting for the characteristics of the chosen cell concept, a spatially resolved material-related upper limit for the solar cell efficiency can be calculated. In mc silicon samples, recombination varies both laterally across the sample as well as with excess charge carrier density. As the injection conditions at open-circuit, short-circuit and maximum power point vary by orders of magnitude, the recombination properties in mc silicon solar cells are typically very different at the different operating points. These variations are all taken into account by an ELBA analysis. As a detailed description of ELBA goes beyond the scope of this work, the reader is referred to chapter 3.1

of Bernhard Michl's PhD thesis [20] and to the corresponding publications [119, 120]. In this thesis, ELBA was applied for the quantification and separation of loss mechanisms in mc silicon. The procedure is described in the following.

#### Application of ELBA for quantification and separation of loss mechanisms

In contrast to the characterization of finished solar cells, ELBA delivers a direct access to bulk-related efficiency losses. In a finished solar cell, effects from the bulk interfere with effects from the solar cell surfaces, such as emitter recombination and recombination at the front and the rear side. Additionally, series resistances or even shunts can influence the measurements on cell level, and local information about recombination can be shadowed by balancing mechanisms through the conducting layers [20, 121, 122]. As it is the aim of this thesis to separate different loss mechanisms in the bulk and to quantify their impact on the efficiency potential of mc silicon solar cells, ELBA was the method of choice.

One of the strengths of the ELBA method is its ability to predict the solar cell efficiency potential with lateral spatial resolution. Specifically for multicrystalline silicon, which features lateral variations in the material quality and, thus, in the efficiency potential, this enables a determination of the physical origins of bulk-related efficiency losses. Figure 3.5, which shows an image of the efficiency potential of an exemplary mc silicon wafer, illustrates how a separation and quantification of efficiency losses in mc silicon is performed: An ELBA analysis within a good grain (green frame in Figure 3.5) predicts the efficiency potential of wafer regions only limited by homogeneously distributed recombination centers, which could be dissolved impurities or background dislocations decorated or not with precipitates. A comparison of this value with the cell limit (i.e. the efficiency without bulk recombination; in the example of Figure 3.5, the cell limit is 21.7%) determines the efficiency loss related to *homogeneously distributed recombination centers*, which is shown as the green part of the bar in the loss diagram in Figure 3.5.

In a next step, the efficiency potential of the central region (without any edge influence) including recombination active structural crystal defects is evaluated by performing a 2D ELBA analysis in this wafer area (gray frame in the image in Figure 3.5). Comparing the average efficiency potential of this area with the cell limit gives access to the efficiency loss related to both homogeneously distributed recombination centers as well as structural crystal defects (probably decorated with impurities), such as dislocation clusters and grain boundaries. The additional loss compared with the loss due to homogeneously distributed recombination centers then quantifies the specific loss due to *recombination active structural crystal defects*, displayed as the gray shaded fraction of the loss bar in Figure 3.5.



Figure 3.5: Quantification of loss mechanisms based on ELBA.

Finally, an ELBA analysis for the whole wafer is performed, which additionally comprises the edge region (red frame in the image in Figure 3.5). This part of the wafer was located close to the crucible during crystallization and is affected by impurities diffused into the crystallized silicon by solid-state diffusion. The additional efficiency loss can thus be attributed to recombination via these impurities in the *edge region* (red part of the loss bar in Figure 3.5).

Thereby, ELBA allows for a separation and quantification of loss mechanisms due to different bulk defects in multicrystalline silicon. Such analyses are performed for mc p-type silicon crystallized in crucibles of different purity in chapter 5.2, for a comparison of the efficiency potential of mc p- and n-type silicon in chapter 5.3, and for a quantification of loss mechanisms in n-type high performance multicrystalline silicon in chapter 5.5.

Furthermore, combining ELBA with iron imaging enables an even deeper physical insight into the efficiency losses. Injection-dependent images of the Fe<sub>i</sub>-limited lifetime, calculated from the measured interstitial iron concentration in mc *p*-type wafers, can be used as input for an ELBA analysis. This enables a quantification of the impact of interstitial iron on solar cell efficiency potential. In combination with the separation of loss mechanisms explained above, also the efficiency losses due to interstitial iron in different wafer regions can be assessed and compared with the total losses, as performed for mc *p*-type silicon crystallized in crucibles of different purity in chapter 5.2.

# 4 Modeling Charge Carrier Mobility in Crystalline Silicon

One of the key parameters for silicon solar cells is charge carrier mobility: As explained in section 2.2, the minority carrier mobility directly influences solar cell efficiency by affecting the diffusion length according to equation (2.4). Also, charge carrier mobilities are directly related to charge carrier conductivities according to equation (2.11), which are of outstanding significance for charge carrier separation in silicon solar cells, as recently highlighted by Würfel *et al.* [56]. Furthermore, device simulations as well as several wide spread PV characterization techniques rely on exact knowledge of charge carrier mobilities, such as lifetime measurements by quasisteady-state photoconductance (QSSPC) [123]. Therefore, the exact determination of charge carrier mobility is essential for state-of-the-art material characterization and device simulation. While generally accepted mobility models exist for uncompensated silicon, strong deviations have been observed in compensated silicon with increasing deviation for higher compensation levels in recent years.

Within this PhD thesis, a unified model for charge carrier mobilities in crystalline silicon was developed, correctly predicting both, mobilities in uncompensated and compensated silicon. To achieve this aim, experimental mobility data in compensated silicon was gathered from literature and was created by the author during his diploma thesis [38] and during this PhD thesis (*cf.* section 4.2). Experiments were performed in close collaboration with Juliane Broisch and results are partially published in her PhD thesis [124]. The model was developed by the author and published in two papers [125, 126]. This chapter is mainly based on these two publications by the author and wording partially coincides with wording in these papers.

Section 4.1 explains the theoretical and historical background, discusses different mobility models, summarizes the latest research results and delivers a literature overview. This section should also serve as a motivation for the development of a new unified mobility model.

Section 4.2 focuses on the experimental methods and results that serve as a basis for the model development, which is presented in section 4.3. To conclude, the chapter is summarized in section 4.4.

## 4.1 Theoretical and Historical Background

This section starts with an historical overview of theoretical mobility calculations before reviewing the most important empirical models based on experimental data. This leads to the introduction of Klaassen's model, which combines an empirical formulation with physical interpretations. Owing to its analytical character, this model is frequently used as the standard mobility model for PV applications and device simulations. The mobility model developed in this PhD thesis is based on Klaassen's model and extends it to correctly describe carrier mobility in compensated silicon and account for deviations observed for the temperature dependence of carrier scattering at phonons. The most relevant publications on mobility in compensated silicon are reviewed in the last part of this section.

### 4.1.1 Theoretical mobility calculations

The movement of charge carriers through the silicon matrix is limited by scattering at ionized impurities, free charge carriers, structural lattice imperfections and phonons. At low concentrations of charge carriers and ionized impurities, *scattering at phonons* of the silicon lattice is the dominating scattering mechanism. Bardeen and Shockley [127] deduced the mobility due to *acoustic phonon scattering* from the band structure, leading to the proportionality

$$\mu_l \propto (m^*)^{-5/2} T^{-3/2} \tag{4.1}$$

where  $m^*$  is the conductivity effective mass and T the temperature.

A complete theoretical description of scattering at phonons was delivered by Szmulowicz [128], who numerically calculated *acoustic and optical-phonon-limited mobilities* in *p*-type silicon within the deformation-potential theory. While originally developed by Bardeen and Shockley [127], Bir and Pikus treated the hole scattering at optical phonons within the deformation-potential theory [129]. Szmulowicz extended the theory of Bir and Pikus for the treatment of non-parabolic bands and combined it with the theory of Tiersten for the calculation of hole scattering at acoustic phonons [130].

When *ionized scattering centers* are present, charge carrier mobility is additionally reduced due to Coulombic interaction. Conwell and Weisskopf [131] described scattering at charged impurities in semiconductors based on Rutherford's scattering formula, which is a Born-approximation for scattering of a charged particle in a Coulomb potential. This formulation leads to a divergent total scattering cross section due to the infinite range of the Coulomb force. Conwell and Weisskopf solved this problem by assuming that scattering at one ion is independent of all other ions. Practically that means that the Coulomb field is arbitrarily cut off at a radius of half the mean distance of two scattering centers.

In order to avoid an infinite total scattering cross section, Brooks and Herring [132, 133] introduced *screening* as a physical explanation. This leads to a scattering potential

decreasing faster than a pure Coulombic potential and thus avoids a divergence of the collision cross section.

Blatt [134] followed the approach by Brooks and Herring using a screened Coulomb potential to calculate the cross section for carrier scattering at ionized impurities. However, he used the partial wave method instead of the Born-approximation, revealing that the Born-approximation loses validity at low temperatures, where it overestimates the scattering cross sections. In his work, the focus was set on the temperature dependence of scattering at ionized impurities, concluding that the usual assumption of  $\mu_{ii} \propto T^{3/2}$ , where  $\mu_{ii}$  is the mobility due to ionized impurity scattering, is not generally valid. Blatt pointed out that the temperature dependence of ionized impurity scattering cannot be expressed by a simple power law. While at high temperature the mobility appears to approach a  $T^{3/2}$  behavior, at temperatures between liquid air and room temperature it increases less rapidly.

Ridley [135, 136] combined the two theories of Conwell and Weisskopf (CW) and Brooks and Herring (BH) in his *statistical screening theory*. On the one hand, the BH formulation was preferred to the one by Conwell and Weisskopf due to its physical interpretation. However, when screening free carriers are lacking, as for example in the case of low temperatures, the BH formula fails and the CW approach is the only possible replacement. Ridley discussed this problem in his paper, leading to a reconciliation of the two approaches by introducing the probability that only one scattering center is active. This delivers a differential collision cross section that does not diverge at small angles even if screening is weak. Thus, a formula for the mobility limited by ionized impurity scattering was derived which merges with the CW formula in the case of weak screening and with the BH approach when screening is strong. The strength of this approach is the delivery of a general expression and the definition of a boundary between the unscreened and screened regions.

Besides scattering at immobile ionized impurities, also *scattering at free carriers* affects mobility in semiconductors, if their concentration is high enough. Fletcher [137] used a classical approach of mutual diffusion of two groups of charged carriers to describe free carrier scattering in germanium, leading to a similar expression as obtained by Conwell and Weisskopf for scattering at fixed ionized impurities, differing by a factor and a mass term accounting for the different effective masses of moving scattering centers.

Davies [138] provided further experimental data on electron-hole scattering in germanium and described free charge carrier scattering in a quantum-mechanical way accounting for screening. However, experimental data by Dannhäuser [139] and Krausse [140] revealed a better agreement with the theoretical curve of Fletcher. Also,

as shown by Dannhäuser, the theoretical mobility expression by Davies diverges for carrier concentrations larger than  $10^{19}$  cm<sup>-3</sup>.

A thorough theoretical calculation accounting for lattice, ionized impurity, and neutral impurity scattering was given by Li and Thurber for electron mobility in n-type silicon for  $10^{13} \le N_D \le 10^{19} \text{ cm}^{-3}$  and  $100 \le T \le 500 \text{ K}$  [141] and by Li for hole mobility in boron doped silicon for  $10^{13} \le N_A \le 3 \cdot 10^{18} \text{ cm}^{-3}$  and  $100 \le T \le 10^{18} \text{ cm}^{-3}$ 400 K [142]. In the first publication, electron-electron scattering was additionally accounted for empirically for dopant densities larger than  $2 \cdot 10^{16}$  cm<sup>-3</sup>. In the second publication, Li approximated the valence band structure of silicon by a three-band model including a spherical, parabolic heavy-hole band, a spherical, non-parabolic light hole band, and a spherical, parabolic spin-orbit band. With the help of the relaxation time approximation, theoretical hole mobility expressions in *p*-type silicon were developed accounting for lattice scattering (acoustical and optical phonons), ionized impurity scattering, neutral impurity scattering, and effects of hole-hole scattering on lattice and ionized impurity scattering mobilities. The theoretical calculations were confirmed by resistivity measurements on boron doped silicon samples with dopant densities in the range of  $10^{14} - 10^{18}$  cm<sup>-3</sup> and by the data of Wagner [143] up to a dopant density of 10<sup>17</sup> cm<sup>-3</sup>. Discrepancies at larger doping concentrations were attributed to incomplete ionization of dopants not accounted for by Wagner.

The work by Li [142] was improved by Linares and Li [144] by additionally accounting for interband transitions in the calculation of scattering relaxation time due to phonons and extended to silicon doped with boron, gallium, and indium.

#### 4.1.2 Analytical mobility expressions

Hitherto, *theoretical mobility calculations* due to lattice, ionized impurity, neutral impurity, and charge-carrier scattering have been discussed. Although ab-initio approaches separately calculating the scattering potential of the different scattering mechanisms are the most physical description of charge carrier mobility, *analytical mobility expressions* are essential for fast device simulations. Since the 1950s, numerous work on experimental data and empirical expressions for charge carrier mobility in silicon has been published, some of which will be discussed in the following.

Morin and Maita [145] studied the temperature dependence of mobility in singlecrystal silicon containing arsenic and boron by conductivity and Hall effect measurements from 10 – 1000 K. They found the temperature dependence of lattice scattering mobility  $\mu_{L,k}$  to be proportional to  $\mu_{L,e} \propto T^{-2.6}$  for electrons and  $\mu_{L,h} \propto T^{-2.3}$  for holes. While acoustical phonon scattering would lead to a theoretical temperature dependence of  $\mu_{L,h} \propto T^{-1.5}$ , accounting for additional scattering at nonpolar optical phonons and the nonparabolicity of valence bands can explain this deviation [142].



Figure 4.1: Electron mobility as a function of donor concentration (left) and hole mobility as a function of acceptor concentration (right) as published by Caughey and Thomas [146]. Both figures are reprinted from [146].

Indeed, the most advanced calculations by Szmulowicz [128] are in good agreement with the experimental findings by Morin and Maita and reveal an average exponent in the region from 100 to 300 K of -2.4. However, the calculations by Szmulowicz also show that the temperature dependence of hole scattering at phonons cannot completely be described by a simple power law.

#### 4.1.2.1 Caughey and Thomas

One of the first approaches for an analytical description of carrier mobilities in silicon as a function of doping concentrations was published in 1967 by Caughey and Thomas [146]. As plots of measured mobilities versus the logarithm of the dopant density resemble a hyperbolic tangent, they fitted the data with the following expression

$$\mu = \frac{\mu_{max} - \mu_{min}}{1 + (N/N_{ref})^{\alpha}} + \mu_{min}$$
(4.2)

*N* denotes the doping concentration, and  $\mu_{max}$ ,  $\mu_{min}$ ,  $N_{ref}$ , and  $\alpha$  are fit parameters, of which only  $\mu_{max}$  can be interpreted as a physical parameter. For zero impurity concentration the mobility is limited by scattering on phonons only, thus  $\mu_{max}$  describes the mobility limited by lattice scattering. Parameters were obtained for electron mobility as a function of donor concentration and hole mobility as a function of acceptor concentration (*cf.* Figure 4.1) by fitting equation (4.2) to experimental mobility data and are summarized in Table 4.1. Additionally, expressions for the electric field dependence of electron and hole mobility are presented in the same publication. The empirical mobility expression (4.2) from Caughey and Thomas (CT) is the starting point for many other empirical or semi-empirical mobility models developed in the following years and can thus be regarded as the prototype of analytical mobility expressions.

Wagner studied the sheet conductivity of bare silicon samples doped with boron from ion implantation [143] and compares his data with the model suggested by Caughey and Thomas. He finds larger mobilities in the doping range  $10^{17} \le N_A \le$  $10^{19}$  cm<sup>-3</sup> than predicted by (4.2) with the parameters from Table 4.1 and therefore suggests a larger value for  $N_{ref} = 1.9 \cdot 10^{17}$  cm<sup>-3</sup>. However, as already mentioned earlier and stated in [142], incomplete ionization of dopants is not taken into account in Wagner's study and might lead to discrepancies at doping concentrations larger than  $10^{17}$  cm<sup>-3</sup>. Nevertheless, later publications confirm a value for  $N_{ref}$  in the range suggested by Wagner [147, 148].

In 1975, Baccarani and Ostoja published new data on electron mobility in phosphorus doped silicon in the range of  $10^{15} \le N_D \le 10^{20}$  cm<sup>-3</sup> [149]. Mobility was deduced from resistivity measurements and dopant concentrations determined by neutron-activation analysis (NAA) assuming  $n_e = N_D$  (i.e. neglecting incomplete ionization). They fitted the CT-expression (4.2) to their experimental data and obtained new values for the four fit parameters.

#### 4.1.2.2 Thurber

Thurber *et al.* published two papers about the resistivity-dopant density relationship in phosphorus- [150] and boron-doped silicon [151]. New electron and hole mobility data was obtained in the range of  $10^{13} \le N_D \le 10^{20}$  cm<sup>-3</sup> and  $10^{14} \le N_A \le 10^{20}$  cm<sup>-3</sup> at temperatures of 296 K and 300 K. They fitted a polynomial expression for electron mobilities to the data and used an expression similar to the one of Caughey and Thomas including an exponential term for the fitting of hole mobilities. In both cases, they accounted for incomplete ionization of dopants according to the calculations by Li [141, 142] to obtain correct values for electron and hole concentrations, respectively. Their fit for hole mobility [151] reveals a good agreement with the theoretical curve from Li [142]. A comparison with the CT-expression shows a better agreement when using the larger  $N_{ref}$  from Wagner [143] instead of the one originally suggested by Caughey and Thomas [146]. In the case of electron mobilities, their fit [150] leads to larger mobilities than the CT-expression and is in reasonable agreement with the theoretical curve from Li and Thurber [141]. The strength of the mobility fits by Thurber *et Table 4.1: Fit parameters for the empirical mobility model (4.2) from Caughey and* 

Thomas	[146].
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	$\mu_{max}$ (cm <sup>2</sup> /Vs)	$\mu_{min}$ (cm <sup>2</sup> /Vs)	α	$N_{ref}$ (cm <sup>-3</sup> )
Holes	495	47.7	0.76	$6.3 \cdot 10^{16}$
Electrons	1330	65	0.72	$8.5\cdot 10^{16}$

*al.* is the good agreement with the theoretical curves. However, the inconsistent expressions for electron mobility (polynomial) and hole mobility (CT-like with an additional exponential summand) significantly reduce the elegancy of their work.

#### 4.1.2.3 Dorkel and Leturcq

One year later, in 1981, Dorkel and Leturcq published a semi-empirical model to predict the dependence of mobility on doping, temperature and injection-level [152]. Their aim was to use simple formulae for a quick calculation procedure that are supported by physical considerations, which distinguishes their approach from purely empirical models. Their model includes lattice scattering and ionized impurity scattering including a correction for charge carrier scattering in the latter term. Scattering at neutral impurities is neglected. Assuming that the concentration of ionized impurities equals the effective doping concentration, they use the relationship of Brooks and Herring [132] for the calculation of the mobility due to ionized impurity scattering and correct that expression for charge carrier scattering. This mobility component is combined with the mobility due to lattice scattering using a formula of Debye and Conwell [153] leading to a global mobility expression. Due to the fact that this global expression includes rather complicated functions, a simplified approximation formula is introduced which is very similar to the empirical CT-expression. They remark that their semi-empirical expression including the approximation formula actually leads to the CT-expression in the case of high doping and low injection level. Thus, a series of simple formulae is obtained which allows for a fast calculation of charge carrier mobility in silicon.

#### 4.1.2.4 Arora

In 1982, Arora *et al.* published an analytical expression for electron and hole mobility in silicon as a function of concentration (up to  $10^{20}$  cm<sup>-3</sup>) and temperature (250-500 K) [154], also choosing a semi-empirical approach. They fitted an analytical expression very similar to the CT-expression to "experimental" mobility data consisting of both purely experimental as well as calculated theoretical mobility values. Theoretical values for ionized impurity scattering were calculated using a modified Brooks-Herring formulation and charge carrier scattering was taken into account following the approach of Li and Thurber [141] for electrons and Li [142] for holes. The four fit parameters of the analytical expression are then obtained for different temperatures. Accounting for the temperature variations of the fit parameters, they arrive at the following analytical expression for charge carrier mobility as a function of doping concentration and temperature



Figure 4.2: Electron mobility in P-doped silicon along the whole carrier concentration range (left) and hole mobility in B-doped silicon for high carrier concentrations (right) as published by Masetti et al. [147]. Both figures are reprinted from [147].

$$\mu_k = \mu_{k,min}(T) + \frac{\mu_{k,0}(T)}{1 + (N/N_{k,ref}(T))\alpha(T)}$$
(4.3)

where the subscript k stands for either electrons (e) or holes (h). Except for  $\mu_{k,0}(T)$ , the temperature dependence of the parameters is identical for electrons and holes. It should be noted that for 300 K the parameters obtained by Arora *et al.* support the values from Baccarani and Ostoja for electron mobility in P-doped silicon.

#### 4.1.2.5 Masetti

Masetti et al. focused on the range of high dopant concentrations and presented empirical mobility expressions for arsenic, phosphorus and boron doped silicon holding in the range  $10^{13} \le N_D \le 5 \cdot 10^{21} \text{ cm}^{-3}$  in *n*-type and  $10^{14} \le N_A \le 1.2 \cdot 10^{21} \text{ cm}^{-3}$  in *p*-type silicon [147]. For the first time, they provide evidence for the quantitative difference between electron mobility in As- and P-doped silicon at doping concentrations larger than 10<sup>19</sup> cm<sup>-3</sup>. While previous analytical mobility expressions featured asymptotical behavior with a maximum mobility  $\mu_{max}$  in the limit of low doping concentration and a minimum mobility  $\mu_{min}$  in the limit of high doping concentration, Masetti et al. observe that mobility is a continuously decreasing function of doping concentration. Up to doping concentrations of  $10^{20}$  cm<sup>-3</sup> mobility values seem to be converging to a constant value  $\mu_{min}$ , whereas at higher doping concentrations an additional kink occurs and mobility starts to decrease more strongly again (cf. Figure 4.2). This observation was made for various kinds of dopants, namely B, P, and As. Masetti et al. account for this by subtracting a suitable increasing function of doping concentration from the CT-expression, leading to the following analytical formulation for electron mobility

$$\mu_e = \mu_{min} + \frac{\mu_{max} - \mu_{min}}{1 + (N/N_{ref,1})^{\alpha_1}} - \frac{\mu_1}{1 + (N_{ref,2}/N)^{\alpha_2}}$$
(4.4)

with the parameters depending on the type of dopant, P or As. For the parameterization of hole mobility in B-doped silicon, they followed the approach suggested by Thurber *et al.* [151] and included an exponential term in  $\mu_{min}$  for better fitting results. Again, the further hole mobility decrease at high doping concentrations was accounted for in the same way as for electron mobility. Thus, the following analytical expression for hole mobility is obtained:

$$\mu_h = \mu_{min} e^{-N_{ref,3}/N} + \frac{\mu_{max}}{1 + (N/N_{ref,1})^{\alpha_1}} - \frac{\mu_1}{1 + (N_{ref,2}/N)^{\alpha_2}}$$
(4.5)

Values for the fitting parameters are summarized in Table 4.2.

#### 4.1.2.6 Klaassen's mobility model

All the mobility expressions discussed hitherto only hold for the presence of one type of dopant with concentration N and do not account for the simultaneous presence of both acceptors and donors as scattering centers. In 1992, Klaassen published a "Unified mobility model for device simulation" [148, 155], which was claimed to be "the first physics-based analytical model (...) that unifies the descriptions of majority and minority carrier mobility and that includes screening of the impurities by charge carriers, electron-hole scattering, clustering of impurities and the full temperature dependence of both majority and minority carrier mobility" [148]. This model is able to separately account for scattering at phonons, ionized impurities and free charge carriers. By distinguishing attractive and repulsive Coulomb potentials of ionized impurities, acceptors and donors are treated separately. In the following, Klaassen's approach for this unified mobility model is roughly sketched. Klaassen starts with the purely empirical Caughey-Thomas expression (4.2), using the fit parameters obtained by Masetti *et al.* [147] listed in Table 4.2. It can thus be classified as a semi-empirical model similar

	Arsenic	Phosphorus	Boron
$\mu_{min}$ (cm <sup>2</sup> /Vs)	52.2	68.5	44.9
$\mu_{max}$ (cm <sup>2</sup> /Vs)	1417	1414	470.5
$\mu_1 (\mathrm{cm}^2/\mathrm{Vs})$	43.4	56.1	29.0
$N_{ref,1}  ({\rm cm}^{-3})$	$9.68 \cdot 10^{16}$	$9.20 \cdot 10^{16}$	$2.23 \cdot 10^{17}$
$N_{ref,2}  ({\rm cm}^{-3})$	$3.43 \cdot 10^{20}$	$3.41 \cdot 10^{20}$	$6.10 \cdot 10^{20}$
$\alpha_1$	0.680	0.711	0.719
α <sub>2</sub>	2.00	1.98	2.00
$N_{ref,3} ({\rm cm}^{-3})$			$9.23 \cdot 10^{16}$

Table 4.2: Fit parameters for the empirical mobility model (4.4) and (4.5) from *Masetti et al.*[147].

to the approaches published by Dorkel and Leturcq [152] or Arora *et al.* [154], as it is based on an empirical expression fitted to experimental data supplied with physical considerations. Although Masetti *et al.* follow the approach by Thurber *et al.* and include an exponential term in  $\mu_{min}$  for holes according to (4.5), Klaassen uses the same expression according to (4.4) for both electron and hole mobility. As the third term in the Masetti expression only becomes important at doping levels larger than  $10^{20}$  cm<sup>-3</sup>, this term is neglected in the beginning, which leads to the familiar Caughey-Thomas expression (4.2). In this formulation,  $\mu_{max}$  is the mobility in the limit of low doping concentrations and can thus be identified with the mobility due to *lattice scattering*:

$$\mu_{k,L} = \mu_{max} \tag{4.6}$$

Here, the subscript k stands for e (electrons) or h (holes).

Subtracting the lattice scattering mobility from equation (4.2) according to Matthiesen's rule, which approximates the reciprocal of the total mobility by adding the reciprocals of the mobility contributions due to different scattering mechanisms, leads to the mobility due to *majority (ionized) impurity scattering* (i.e. electron mobility due to scattering at donors and hole mobility due to scattering at acceptors):

$$\mu_{k,I} = \mu_{k,N} \left(\frac{N_{ref,1}}{N_I}\right)^{\alpha_1} + \mu_{k,c}$$
(4.7)

with

$$\mu_{k,N} = \frac{\mu_{max}^2}{\mu_{max} - \mu_{min}} \tag{4.8}$$

and

$$\mu_{k,c} = \frac{\mu_{min}\mu_{max}}{\mu_{max} - \mu_{min}} \tag{4.9}$$

 $\mu_{k,N}$  and  $\mu_{k,c}$  are abbreviations for the terms depending on  $\mu_{max}$  and  $\mu_{min}$  and without physical meaning. So far, the expressions are just rewritten in a physical meaningful way, but no changes compared to the CT-expression have been made yet. This is done for the first time in the next step: Klaassen includes screening of ionized impurities by charge carriers. As the mobility due to impurity scattering is proportional to the inverse product of the impurity concentration  $N_I$  and the collision cross section  $\sigma$ , the collision cross section can be expressed using (4.7) as:

$$\sigma_{k,I} \propto (N_I \mu_{k,I})^{-1} = \left(\mu_{k,N} \left(\frac{N_{ref,1}}{N_I}\right)^{\alpha_1} N_I + \mu_{k,c} N_I\right)^{-1}$$
(4.10)

As discussed previously, the theoretical collision cross section, assuming a Coulomb potential for each charged scattering center, diverges for small scattering angles. This divergence was avoided by Conwell and Weisskopf by arbitrarily cutting off the Coulomb field at a radius equal to half the mean distance between the scattering centers [131]. As mentioned above, in the approach of Brooks and Herring [132, 133], an arbitrary cutting radius was avoided by introducing screening: At high carrier concentrations, free carriers tend to screen impurities which causes the scattering potential to fall off with distance more rapidly than a pure Coulomb potential would. But as the Brooks-Herring approach fails in the limit of zero screening carriers, here the Conwell-Weisskopf formula becomes the only viable replacement. In the statistical screening theory of Ridley [135, 136], the approaches of Conwell-Weisskopf and Brooks-Herring are combined. Klaassen follows the theory of Ridley and tries to make the collision cross-section a function of the free carrier concentration at high concentrations and a function of  $N_I$  at low concentration. This is done by replacing  $N_I$  in the second term of equation (4.10) with the free carrier concentration c, as this term becomes predominant at high concentrations. By doing so, the divergence of the collision cross section is avoided, as the first term becomes predominant at low concentrations. Recalculating the impurity scattering mobility then leads to the following expression replacing (4.7):

$$\mu_{k,I} = \mu_{k,N} \left( \frac{N_{ref,1}}{N_I} \right)^{\alpha_1} + \mu_{k,c} \left( \frac{c}{N_I} \right)$$
(4.11)

It should be mentioned that this is only one possibility to include screening in this term and the exchange of N with c in the second term is rather arbitrary and not proven with experimental data. The limit of  $c = N_I$  holds for uncompensated silicon. Here, screening is most effective, and we reobtain from eq. (4.11) the Caughey-Thomas expression (4.7). In compensated silicon, however, where the free carrier concentration does not equal the total dopant concentration any more, the modeled mobility is actually affected by this correction. It will be discussed in detail in section 4.3 if this correction appropriately accounts for reduced screening in compensated silicon.

It had already been shown by Blatt [134] that majority impurity scatter more effectively than minority impurities. This is due to a larger collision cross-section for an attractive compared with a repulsive Coulomb potential. Klaassen calculates the ratio G(P) between the collision cross-sections for repulsive  $\sigma_{\tau,rep}$  and attractive  $\sigma_{\tau,attr}$ screened Coulomb potentials with the partial-wave method using the JWKB (Jeffreys-Wentzel-Kramers-Brillouin) approximation for the phase shifts:

$$G(P) = \frac{\sigma_{\tau,rep}}{\sigma_{\tau,attr}} = \frac{\sigma_{min}}{\sigma_{maj}} = \frac{\mu_{maj}}{\mu_{min}} \to \frac{\mu_{e,D}}{\mu_{e,A}} \text{ or } \frac{\mu_{h,A}}{\mu_{h,D}}$$
(4.12)

This means that the ratio of the mobility due to scattering at majority impurities and mobility due to scattering at minority impurities can be expressed as a function of P

$$P = 4k^2 r_0^2 \propto \frac{1}{c}$$
 (4.13)

where k is the wave vector and  $r_0$  the Debye screening length. P can also be expressed as a function of effective mass, temperature and carrier concentration, leading to the proportionality to 1/c. Klaassen describes the ratio G(P) by an analytical fit formula. Thus, the mobility due to *minority (ionized) impurity scattering* can be calculated from the mobility due to majority impurity scattering by

$$\mu_{e,A}(N_A) = \frac{\mu_{e,D}(N_D = N_A, c)}{G(P_e)}$$
(4.14)

for electron scattering at ionized acceptors and

$$\mu_{h,D}(N_D) = \frac{\mu_{h,A}(N_A = N_D, c)}{G(P_h)}$$
(4.15)

for hole scattering at ionized donors. In these expressions, the mobilities  $\mu_{e,D}$  and  $\mu_{h,A}$  are given by eq. (4.11) for majority impurity scattering mobilities. The dependence of P on the effective electron or hole mass is expressed by the subscript e for electrons and h for holes. With  $G(P) \le 1$  it can be seen that scattering at minority (i.e. repulsive) impurities is less effective than scattering at majority (i.e. attractive) impurities.

A similar approach is chosen for the calculation of the mobility due to *electron*hole scattering. Holes are regarded as moving donors and electrons as moving acceptors. Using the Brooks-Herring approximation instead of the partial-wave method, the ratio F(P) of mobility due to scattering at stationary secondary scattering centers with infinite mass and the mobility due to scattering at moving secondary scattering centers with finite mass can be calculated. Again, Klaassen provides an analytical fit function for F(P) which depends on the effective masses of electrons and holes, but is independent of temperature. Thus, the electron mobility due to scattering at donors

$$\mu_{e,h}(p,c) = F(P_e)\mu_{e,D}(N_D = p,c)$$
(4.16)

and the hole mobility due to scattering at electrons can be derived from the hole mobility due to scattering at acceptors

$$\mu_{h,e}(n,c) = F(P_h)\mu_{h,A}(N_A = n,c)$$
(4.17)

Again, the mobilities  $\mu_{e,D}$  and  $\mu_{h,A}$  are given by eq. (4.11) for majority impurity scattering. Hence, Klaassen combines an empirical mobility expression for carrier scatter-

ing at majority impurities with physical considerations leading to separate expressions for carrier scattering at minority impurities and free charge carriers. It should be noted at this point that Klaassen does not treat hole-hole or electron-electron scattering separately. In the way Klaassen constructs his model, these scattering mechanisms are included in the contribution of mobility due to lattice scattering and scattering at majority impurities, as these terms directly stem from the empirical mobility expression which was fitted to experimental data. As that data was mainly obtained on samples from uncompensated silicon where hole concentrations equal acceptor concentrations (p-type) or electron concentrations equal donor concentrations (n-type), it intrinsically comprises lattice scattering, scattering at majority impurities and hole-hole (p-type) or electron-electron (n-type) scattering. Since Klaassen only splits the empirical mobility expression (4.2) into a lattice contribution (4.6) and a majority impurity contribution (4.7), these terms still comprise effects of scattering at majority carriers. These effects are nicely discussed for electron-electron scattering in the publication by Li and Thurber [141] and for hole-hole scattering in the publication by Li [142].

In the next step, Klaassen discusses ultra-high concentration effects, which had been neglected so far. At impurity concentrations larger than  $10^{20}$  cm<sup>-3</sup> the third term in the Masetti expressions (4.4) and (4.5) become important. In this PhD-thesis the focus is on compensation effects on mobility at impurity concentrations orders of magnitude below  $10^{20}$  cm<sup>-3</sup>, which is why these effects are not discussed here and neglected in the following.

Finally, Klaassen obtains the electron and hole mobility as a function of acceptor, donor, electron and hole concentration. The total carrier mobility can be obtained from the contributions due to lattice scattering, majority and minority impurity scattering and electron-hole scattering by applying Matthiesen's rule:

$$\mu_k^{-1} = \mu_{k,L}^{-1} + \mu_{k,D}^{-1} + \mu_{k,A}^{-1} + \mu_{k,j}^{-1} = \mu_{k,L}^{-1} + \mu_{k,D+A+j}^{-1}$$
(4.18)

Here, the subscript j = h if k = e and the other way round. In order to obtain a pure two-body scattering, on the right side of the collision cross section (4.10) N has to be replaced by the sum of all scattering centers, which is

$$N_{e,sc} = N_D + N_A + p \tag{4.19}$$

for electrons and

$$N_{h,sc} = N_A + N_D + n \tag{4.20}$$

for holes. This leads to the following expression for the collision cross section replacing eq. (4.10):

$$\sigma_{k,I} \propto (N_I \mu_{k,I})^{-1} = \left(\mu_{k,N} \left(\frac{N_{ref,1}}{N_{k,sc}}\right)^{\alpha_1} N_{k,sc} + \mu_{k,c} c\right)^{-1}$$
(4.21)

and thus to the following expression for majority impurity scattering replacing eq. (4.11):

$$\mu_{k,I} = \mu_{k,N} \left( \frac{N_{ref,1}}{N_{k,sc}} \right)^{\alpha_1} \frac{N_{k,sc}}{N_I} + \mu_{k,c} \left( \frac{c}{N_I} \right)$$
(4.22)

where  $N_I$  is the concentration of the majority impurity,  $N_A$  or  $N_D$ , and  $N_{k,sc}$  the concentration of all scattering centers according to (4.19) or (4.20). In combination with equations (4.14) - (4.17) for minority impurity and free charge carrier scattering, the mobility due to scattering at charged scattering centers  $\mu_{k,D+A+j}$  reads

$$\mu_{k,D+A+j}(N_D, N_A, n, p) = \mu_{k,N} \left(\frac{N_{ref,1}}{N_{k,sc}}\right)^{\alpha_1} \frac{N_{k,sc}}{N_{k,sc,eff}} + \mu_{k,c} \left(\frac{n+p}{N_{k,sc,eff}}\right)$$
(4.23)

with

$$N_{e,sc,eff} = N_D + G(P_e)N_A + \frac{p}{F(P_e)}$$
(4.24)

and

$$N_{h,sc,eff} = N_A + G(P_h)N_D + \frac{n}{F(P_h)}$$
 (4.25)

The total mobility as a function of donor, acceptor, electron and hole concentration is then calculated from the mobility due to lattice scattering and the mobility due to scattering at charged centers via eq. (4.18):

$$\mu_k^{-1}(N_D, N_A, n, p) = \mu_{k,L}^{-1} + \mu_{k,D+A+j}^{-1}(N_D, N_A, n, p)$$
(4.26)

So far, Klaassen's mobility model delivers an analytical expression for electron and hole mobility, distinguishing between scattering at majority and minority dopants and accounting for electron scattering at holes and hole scattering at electrons. It features several physical considerations for the effect of screening, different strength of attractive and repulsive scattering potentials, and difference between stationary and mobile scattering centers. However, it should be mentioned that in the case of uncompensated silicon the calculated majority carrier mobility is negligibly affected by these additional considerations and, thus, Klaassen's expression virtually agrees with the empirical Caughey-Thomas mobility expression. For minority carrier mobility and in the case of compensated silicon, when acceptors and donors are simultaneously present in significant concentrations, Klaassen's calculations become important.

In a second publication, Klaassen also includes the *temperature dependence* in his model [155].

As suggested previously [145], Klaassen uses a simple power law to describe the temperature dependence of *lattice scattering mobility*. Thus, eq. (4.6) is replaced by

$$\mu_{k,L} = \mu_{max} \left(\frac{300}{T}\right)^{\theta_k} \tag{4.27}$$

with  $\theta_e = 2.285$  and  $\theta_h = 2.247$ . These values are in the range of previously reported exponents by Morin and Maita [145] (experimental results,  $\theta_e = 2.6$  and  $\theta_h = 2.3$ ) and by Szmulowicz [128] (average exponent resulting from theoretical calculations  $\theta_{avg} = 2.4$ ). However, Szmulowicz's calculations show that a simple power law cannot describe the exact temperature dependence of lattice scattering mobility. This will be discussed and revised by the mobility model developed in this PhD thesis in section 4.3.

For the description of the temperature dependence of *majority impurity scattering mobility* Klaassen follows the Brooks-Herring and Conwell-Weisskopf approaches. Including the temperature dependence in the terms for  $\mu_{k,N}$  and  $\mu_{k,c}$ , equations (4.8) and (4.9) are replaced by

$$\mu_{k,N} = \frac{\mu_{max}^2}{\mu_{max} - \mu_{min}} \left(\frac{T}{300}\right)^{3\alpha_1 - 1.5}$$
(4.28)

and

$$\mu_{k,c} = \frac{\mu_{min}\mu_{max}}{\mu_{max} - \mu_{min}} \left(\frac{300}{T}\right)^{0.5}$$
(4.29)

Using these expressions in eq. (4.7) then delivers the temperature dependence of mobility due to majority impurity scattering.

The temperature dependence of *minority impurity scattering mobility* is determined by the same temperature dependence stemming from the expression for majority impurity scattering and additionally by the T-dependence of the function G(P) and the parameters  $P_e$  and  $P_h$  themselves. Details can be found in reference [155].

In a similar way, the temperature dependence of *electron-hole scattering* includes the T-dependence from the expression for majority impurity scattering as well as the T-dependence from the parameters  $P_e$  and  $P_h$ . In contrast to the case of minority impurity scattering, the function F(P) itself is temperature independent.
#### 4.1.2.7 Reggiani

To finalize the review of mobility models, the one published by Reggiani *et al.* should be mentioned [156]. They developed a new methodology based on resistivity and Hall measurements to determine the Hall factor and drift mobility as a function of impurity concentration and lattice temperature with the focus on high temperature effects. Bulk mobility was measured in the temperature range 25 - 400 °C. Their approach is a mixture of Masetti's and Klaassen's: while donors and acceptors are treated separately as suggested by Klaassen, their model is still completely empirical starting from Masetti's expression and does not contain any physical considerations:  $\mu(N_D, N_A, T)$ 

$$= \mu_{min}(N_D, N_A, T) + \frac{\mu_{max}(T) - \mu_{min}(N_D, N_A, T)}{1 + (N_D/N_{ref,11}(T))^{\alpha_{11}} + (N_A/N_{ref,12}(T))^{\alpha_{12}}}$$
(4.30)  
$$- \frac{\mu_1(N_D, N_A, T)}{1 + (N_D/N_{ref,21}(T) + N_A/N_{ref,22}(T))^{-2}}$$

The model parameters were adjusted such that (4.30) delivers the same mobility values as Masetti's model at 300 K for uncompensated silicon and the temperature dependence of the parameters was extracted from numerical simulations of the carrier drift velocity as a function of field, impurity concentration and temperature up to 700 K. Fit parameters are given in reference [156]. While mobility predictions by this model are slightly more accurate compared to Klaassen's model for high temperatures, Klaassen's model delivers a better agreement with experimental data between 200 – 300 K. This is due to the fact that Reggiani's model was fitted to numerical data in the temperature range from 300 K to 700 K.

#### 4.1.3 Mobility in compensated silicon

As silicon obtained from low cost purification routes like upgraded metallurgical-grade silicon (umg-Si) typically features high amounts of both types of dopants (called compensated), Klaassen's model was used as the standard model for mobility predictions in silicon used for photovoltaic applications. In the authors diploma thesis [38] it was found that majority carrier mobilities measured in compensated multicrystalline (mc) silicon are significantly lower than predicted by Klaassen's model. One reason could be the possible influences of crystal defects like grain boundaries or dislocations, as they are not taken into account in the model. However, it has been shown in a publication by the author that such crystal defects as occurring in standard mc silicon appear to have only a minor impact on majority carrier mobilities which is insignificant for PV applications [157]. Therefore, lower mobilities can be attributed to compensation, which is also confirmed by the observations in several publications indicating that for an increasing compensation level Klaassen's model overestimates mobilities signifi-

cantly [57, 85, 86, 90, 91, 125, 126, 158-168], both in multicrystalline and in monocrystalline compensated silicon. The essentials of the most important publications will be summaried in the following.

Libal *et al.* [57] measured room temperature Hall mobilities along the block height of a compensated *p*-type Cz ingot which was grown using 10% solar grade silicon. They observed a strong decrease in majority hole mobility towards the bottom of the ingot, where the compensation level is highest. A comparison with simulations reveals a strong overestimation of mobility with increasing compensation level. Crystal defects as a reason for lower mobilities could be excluded by determining the crystal defect density, and to exclude an influence of metal impurities on the mobility, they repeated the measurements after phosphorus gettering with the same results. Thus, the drop in Hall mobility is attributed to compensation. However, this reduction could be either due to an actual decrease in conductivity mobility or to a compensation-correlated decrease in the Hall factor. Later publications by other authors show, that the Hall factor is not affected significantly by compensation and it is indeed the conductivity mobility that strongly decreases with increasing compensation level [38, 91, 125, 162].

Forster et al. [158, 159] and Fourmond et al. [167] investigated boron, phosphorus and gallium co-doped silicon. In B and P doped compensated p-type silicon, the resistivity strongly increases with ingot height due to the difference in segregation coefficients of B and P, typically resulting in a type changeover from p- to n-type. This undesirable effect can be avoided by co-doping with Ga owing to its low segregation coefficient. Regarding mobility, they showed that the impact of Ga on mobility can be compared to B as it is also a singly negative charged scattering center. They also observed a strong reduction in both majority and minority carrier mobility compared to Klaassen's model which is increasing with increasing compensation level. Majority carrier mobilities were obtained from Hall-effect measurements and compared to conductivity mobilities deduced from carrier density measurements by free carrier absorption (FCA) and resistivity measurements. This revealed that compensation leads to an actual mobility reduction rather than to a reduction of the Hall factor  $r_{H}$ . Minority carrier mobility was obtained from minority carrier lifetime measurements by the Sproul technique [92]. Their suggestion of an empirical correction to account for the observed discrepancy between model and experimental data will be discussed in section 4.3. Results published by Forster et al. [158, 159] and Fourmond et al. [167] are also explained in detail in Maxime Forster's PhD thesis [85].

Geilker *et al.* [90] measured majority carrier mobilities in three compensated *p*type Cz silicon ingots made from 100% solar grade feedstock, 50% solar grade feedstock and virgin-grade feedstock intentionally compensated. Conductivity mobility was deduced from resistivity measurements and measurements of the net doping by the FTIR-FCA method introduced in [89] and extended in [90]. They observed that the mobility in the ingots made from 100% and 50% solar grade feedstock agree with mobility models within their error, which is explained by the very low compensation levels between 1.5-2 of these ingots. On samples with larger compensation levels from the intentionally compensated ingot, measured mobilities are lower than predicted by Klaassen's model. Possible reasons are discussed in their work: Uncertainties in the measurement techniques, lateral fluctuations in the doping concentrations in the region of the type changeover leading to deviations in the doping concentration measured at the sideboard and the actual doping concentration of the wafer, and insufficiency in Klaassen's model for high compensation levels.

Rougieux *et al.* [91] determined the conductivity mobility for majority carriers in uncompensated and lowly compensated ( $C_l \leq 5$ ) *p*-type Cz silicon by combining resistivity measurements with electrochemical capacitance-voltage (ECV) measurements of net doping. The minority carrier mobility was measured by the Sproul technique [92]. Comparing their results with Klaassen's mobility model reveals a reasonable agreement for majority carrier mobility, while measured minority carrier mobilities in the compensated samples are significantly lower than predicted by the model. Results for majority carrier mobility were compared to Hall-effect measurements of majority carrier mobility in compensated and uncompensated *p*-type silicon, indicating similar Hall factors in both materials and thus revealing that the Hall factor is not affected significantly by compensation, at least for low compensation levels.

Veirman *et al.* [162] investigated the Hall majority carrier mobility in purely Bdoped Cz silicon compensated by thermal donors. Samples with varying compensation levels were obtained from a step-by-step activation of thermal donors. A strong reduction in majority carrier Hall mobility was observed for both *p*- and *n*-type compensated silicon that could not be predicted by mobility models. By overcompensating a sample from *p*- to *n*-type, the drop in mobility can explicitly be attributed to an effect at high compensation levels, as mobility increases again after the type changeover despite an increase of ionized scattering centers. By comparing Hall mobilities with conductivity mobilities on a selection of samples with different compensation levels, an impact of compensation on the Hall factor is excluded. This again supports the assumptions that charge carrier mobility strongly depends on compensation level and mobility models are not able to predict the mobility drop with increasing compensation. Veirman *et al.* also discuss possible physical reasons: Spatial inhomogeneities in the dopant distribution, particularly due to inhomogeneities in the O<sub>i</sub> concentration and thus the thermal donor distribution, could lead to fluctuations in base resistivity or even to local p-njunctions in the bulk leading to space-charge region scattering [162]. Also the Hall voltage might be affected by spatial inhomogeneities. They further investigate this hypothesis and measured the spatial inhomogeneity of the minority carrier diffusion length in a strongly thermal-donor compensated Cz sample [164]: This reveals a strong large-scale inhomogeneity in the dopant distribution, which could lead to a bias in Hall effect measurements. However, since their observed size by far exceeds the carrier mean free path, they believe the actual effect on mobility to be negligible and conjecture that submicronic inhomogeneities of the electrostatic potential could be responsible for a yet unproven additional scattering mechanism.

At this point it should be mentioned that spatial inhomogeneities in the thermal donor distribution are supposed to be more prominent than inhomogeneities in the standard dopant distribution. Therefore, direct comparisons of B-doped samples compensated by thermal donors or by standard dopants like P should be regarded with care and effects on charge carrier mobility could be different.

A different explanation was given by Lim et al. [168], who suggest that reduced screening of ionized scattering centers by free charge carriers could lead to an additional mobility reduction in compensated silicon. They investigated minority and majority carrier mobilities along a whole multicrystalline silicon block made from upgraded metallurgical-grade (umg) feedstock. Since umg feedstock contains large amounts of both types of dopants, B and P, the material was compensated and featured a changeover from p- to n-type at about 80% block height. Minority carrier mobility was determined by measuring the diffusion-limited lifetime of an unpassivated as-cut wafer cut vertically from the mc ingot. Majority carrier mobility was obtained by measurements of the resistivity and the net doping concentration (ECVmeasurements). For both majority and minority carrier mobility they observe a strong reduction in the region of the type changeover, where the compensation level is highest. Despite the increasing concentration of ionized scattering centers, majority and minority carrier mobility increases in the *n*-type part from the point of the type changeover towards the block top, indicating that the strong mobility reduction in the region of the type changeover is attributed to compensation. They explain this additional mobility reduction by the decrease of free charge carriers with increasing compensation level, leading to a weakened screening of ionized dopants and thus increasing their scattering potential. While previous work focused on compensated monocrystalline silicon, this work shows that also in mc silicon charge carrier mobility is affected by compensation in a similar manner.

In a contribution to the NREL-workshop, Dubois *et al.* [166] supported previous findings on mobility reduction in compensated silicon by comparing Hall and conduc-

tivity mobility data along a whole Cz ingot with Klaassen's model. The ingot was grown from electronic-grade silicon intentionally doped and compensated by B and P, featuring a changeover from p- to n-type at 76% ingot height. These investigations nicely show that an increasing compensation level affects both Hall and conductivity mobilities and leads to a strong reduction that cannot be explained by mobility models. The deviation between experimental data and model becomes striking in the n-type region towards the top of the ingot: While Klaassen's model predicts a decreasing mobility with increasing ingot height due to the increase in ionized dopants acting as scattering centers, a contrary trend is observed for measured mobilities, which are lowest for highest compensation levels close to the type changeover and strongly increase towards the top of the ingot despite the increasing total amount of ionized dopants. Thus, the deviation between model and experimental data is strongly increasing with increasing compensation level, supporting previous observations.

Finally, majority carrier mobility data in compensated multicrystalline p-type silicon obtained by the author during his diploma thesis [38] and published in different papers [125, 161] lead to the same conclusions. Majority carrier mobility was determined by a combination of measurements of resistivity and net doping (FTIR-FCA method [90]) along the block height of two compensated mc p-type silicon blocks featuring different total amount of dopants but similar compensation levels. Additionally, the majority carrier mobility was obtained from Hall effect measurements. These investigations show that majority carrier mobility is lower than predicted by Klaassen's model, and the deviation from the model is increasing with increasing compensation level. Furthermore, a comparison of conductivity mobility and Hall mobility reveals compensation independent Hall factors. This supports the observations by other authors that compensation leads to an actual reduction in mobility [91, 162].

The large amount of mobility data in compensated silicon published by various research groups in recent years clearly reveals the lack of a model that is able to reliably predict charge carrier mobilities in compensated silicon. Even the most elaborate models like Klaassen's, which separately account for scattering at ionized acceptors and donors, strongly overestimate charge carrier mobilities in compensated silicon at high compensation level. It was therefore the aim of this PhD thesis to develop a mobility model, which allows for a consistent prediction of charge carrier mobilities in both uncompensated and compensated silicon. This is done by enhancements of Klaassen's mobility model based on mobility data in compensated silicon obtained from literature and experiments by the author. Section 4.2 describes experimental methods and results of mobility data used for the model development. The model itself is introduced in section 4.3.

# 4.2 Methods and Experimental Results

The model developed in section 4.3 is based on fitting of parameters to mobility data in compensated silicon. The data was obtained at different research institutes by different methods introduced in section 3.1. This part provides details on the methods used by the different research groups, presents experimental data from the author and discusses errors on mobility. The complete list of data used for the model adaption is given in Appendix 8.1.

To understand published data, the investigated materials of each research group (*cf.* Table 4.3) and the applied methods are summarized in the following. Since the focus of this PhD thesis yet is the modeling, this summary only contains the most relevant information. Further details can be found in the corresponding references.

Libal *et al.* published Hall mobility data of compensated *p*-type Cz Si [57], in the following denoted as Cz-Li. The dopant concentrations  $N_A$  and  $N_D$  were obtained from a fit of the charge balance equation to the experimental data of the temperature dependent net doping concentration  $n_h(T)$ . To convert the published Hall mobilities into majority hole conductivity mobilities, a Hall factor of 0.65 was used in this PhD thesis. Here, some comments have to be made on this rather low Hall factor: Libal *et al.* 

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	Crystal name	Dopants	type	Mobility	Publication	
	Cz-Li	B, P	р	$\mu_{maj,h}$	[57]	
	Cz-Ge	В, Р	р	$\mu_{maj,h}$	[90]	
	Cz-Ro	В, Р	р	$\mu_{maj,h}$ , $\mu_{min,e}$	[91]	
	mc-Sc	B, P	p	$\mu_{maj,h}$	[38, 125, 161]	
	Cz-Fo-1	B, Ga, P	p	$\mu_{maj,h}$	[86]	
	Cz-Fo-2/3	B, Ga, P	р	$\mu_{maj,h}$ , $\mu_{min,e}$	[86]	
	Cz-Fo-4	B, P	p	$\mu_{maj,h}$	[126]	
	Cz-Fo-5	B, Ga, P	p	$\mu_{maj,h}$	[126]	
	mc-Fo-1	B, P	p	$\mu_{maj,h}$	[126]	
	mc-Fo-2	B, Ga, P	p	$\mu_{maj,h}$	[126]	
	Cz-Sc-1	B, P	p	$\mu_{maj,h}$	[126]	
	Cz-Fo-6	P, B, Ga	n	$\mu_{maj,e}$ , $\mu_{min,h}$	[86]	
	Cz-Sc-2	P, B	n	$\mu_{maj,e}$	[126]	

*Table 4.3: Publications of mobilities in compensated silicon.* 

propose a Hall factor of 0.74 in the same publication [57]. However, this does not agree with their published data. A comparison of the Hall mobility in the least compensated sample ( $C_l = 1.3$ , virtually uncompensated,  $\mu_H \approx 280 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) and the conductivity mobility predicted by Klaassen's model (which holds for uncompensated silicon) for the same sample ( $\mu_c \approx 429 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , calculated from the dopant concentrations published in [57] for this sample), leads to a Hall factor of  $r_H \approx 0.65$ . As compensation does not seem to have a significant influence on the Hall factor (as discussed in section 4.1.3 and references [38, 91, 125, 162]), this Hall factor is used to deduce conductivity mobilities from the published Hall mobilities also for the compensated samples of reference [57]. Compared to theoretical Hall factors [169, 170] as well as Hall factors measured by the author [125, 157, 161] and published elsewhere [162], a value of 0.65 seems to be rather low. However, it is comparable to the Hall factors measured in reference [91]. As Hall factors directly originate from measured Hall mobilities, a low Hall factor can be explained by an underestimated Hall mobility. A possible explanation for the observed low Hall factor for the data of Libal et al. could be larger contacts on the Hall samples that would lead to lower measured Hall mobilities.

Forster *et al.* published conductivity mobility data obtained from temperaturedependent Hall measurements. For the conversion from Hall to conductivity mobility, the temperature dependent Hall factor from Szmulowicz [170] was used for *p*-type samples and the T-dependent Hall factor from Ohta and Sakata [171] for *n*-type samples. The room temperature mobility data of the *p*-type materials Cz-Fo-1/2/3 and the *n*-type material Cz-Fo-6 was measured and published by Forster *et al.* in reference [86], the room temperature mobility data of the *p*-type materials Cz-Fo-4/5 and mc-Fo-1/2 was measured by Maxime Forster in the frame of his PhD thesis [85] and evaluated and published by the author of this PhD thesis together with Maxime Forster in a joint paper [126]. The temperature dependent mobility data is partially published in references [86] and [126]. The acceptor density  $N_A$  has been inferred from Scheil's law [54] (*cf.* equation (2.3)) from measurements at feedstock level, the donor density  $N_D$  has been calculated using  $N_A$  and the net doping concentration  $n_h$  from Hall measurements according to  $N_D = N_A - n_h$ .

Geilker *et al.* published majority hole conductivity mobilities in compensated *p*-type silicon [90], in the following referred to as Cz-Ge. The majority hole mobility  $\mu_{maj,h}$  was obtained from the measured base resistivity and the net doping obtained via the FTIR-FCA method. The acceptor concentration  $N_A$  was measured by means of iron-acceptor pairing and ICP-MS measurements, the donor concentration was calculated from the acceptor and the net doping concentration via  $N_D = N_A - n_h$ .

Rougieux *et al.* published both Hall and conductivity mobilities in compensated *p*-type Cz silicon [91]. The majority hole mobility was obtained from measurements of resistivity and net doping (ECV), the acceptor concentration from iron-acceptor pairing and the donor concentration calculated according to  $N_D = N_A - n_h$ . Additionally, the minority electron mobility  $\mu_{min,e}$  was determined by the Sproul-method.

Further mobility data in compensated silicon was gathered by the author during his diploma thesis and in close collaboration with Juliane Broisch in the frame of the author's and her PhD theses. Hall and conductivity mobility data in compensated multicrystalline *p*-type silicon obtained by the author during his diploma thesis [38] is published in references [38, 125, 161]. The majority hole mobilities were obtained from 4-point-probe measurements of the resistivity and ECV- or FTIR-FCA-measurements of the net doping. The acceptor concentration was determined by iron-acceptor pairing, and the donor concentration deduced from the acceptor concentration and the net doping via  $N_D = N_A - n_h$ .

In order to obtain additional mobility data in compensated p- and n-type silicon, a joint experiment was performed in the framework of the author's and Juliane Broisch's PhD theses. This experiment is discussed in very detail in the latter PhD thesis [124] and is part of a joint publication [172]. Here, the crucial points of this experiment are depicted. The investigations comprised a compensated *p*-type and a compensated *n*-type Cz crystal, both made from 50% ESS<sup>TM</sup> feedstock and provided by Elkem Solar AS. In the following, this material is denoted by Cz-Sc-1 (p-type) and Cz-Sc-2 (*n*-type). Wafers were selected from different positions homogeneously distributed along the ingot height and cut in half. One half of the wafers was used for the determination of boron and phosphorus concentrations by ICP-MS measurements (cf. section 3.2.5) at an external institute, from the other half  $10 \times 10 \text{ mm}^2$  Hall samples for net doping and majority carrier mobility measurements were prepared (cf. Figure 4.3). For each ingot position, four Hall samples from different radial positions between the wafer center and the edge, as depicted in Figure 4.3, were prepared. As only mean values across the left wafer half for doping concentrations at each ingot position were obtained by ICP-MS measurements, the measurement results of net doping and mobility obtained on the four Hall samples per wafer were also averaged. Due to the radial symmetry of lateral doping distribution [124, 172], the mean values of mobility and net doping can be related to the dopant concentrations obtained on the other wafer half. The Hall data was converted into conductivity data using a Hall factor of  $r_H = 0.77$ from the empirical model developed by the author [157] for *p*-type samples and a doping dependent Hall factor of  $r_H = 1.07 - 1.12$  from reference [173] for *n*-type samples. The Hall factor for *p*-type Si from the empirical model from reference [157]



Figure 4.3: Sample preparation for ICP-MS measurements on wafer level and Hall measurements.

should be best suited for the used Hall setup since the model was developed during the author's diploma thesis based on data obtained from measurements with the identical setup. Boron and phosphorus concentrations were additionally obtained from ICP-MS measurements on feedstock level before crystallization. As described in section 2.1.2, Scheil's equation (2.3) allows for a simple calculation of the doping concentrations in the crystal as a function of relative ingot height. The doping concentrations at each ingot height were now obtained in two different ways:

- i) The measured concentrations on feedstock level were used as input for Scheil's equation.
- ii) The starting concentration in the melt was calculated back from the measured doping concentrations on wafer level for each wafer and the known ingot height using Scheil's equation. Averaging these values de-livers a new starting concentration used as input for Scheil's equation.

Calculations of the net doping concentration according to  $n_k(z) = |N_A(z) - N_D(z)|$ reveal a much better agreement with net doping concentrations obtained from Hall measurements in case ii). This is discussed in more detail in [124] and [172]. Therefore, for the further evaluations boron concentrations calculated according to case ii) are used. The phosphorus concentration is then calculated using the boron concentration and the net doping obtained from Hall measurements. This further increases the accuracy of the determination of dopant concentrations, as Hall measurements are typically more exact than ICP-MS measurements and ICP-MS measurements of the boron concentration are more reliable then ICP-MS measurements of the phosphorus



Figure 4.4: Relative deviation of mobilities measured in silicon compensated by singly ionized dopants (left) and compensated by thermal donors (right) from Klaassen's model. The latter data shows a significantly larger spread.

concentration. Thus, further majority hole and electron mobility data in lowly to moderately compensated *p*- and *n*-type silicon with compensation levels in the range  $C_l = 2 - 13$  was obtained, extending the data base for the model adaption. The dopant concentrations and mobility data obtained from this experiment are summarized in Appendix 8.1.

At this point it should be mentioned that in the author's first publication on modelling mobility in compensated silicon [125] additional mobility data published by Veirman et al. [162] was considered. That data was neglected in the final model adaption as described in reference [126]. In reference [162], compensation of initially purely boron doped samples was achieved by activation of thermal donors, thereby introducing doubly ionized scattering centers. When plotted as a function of the compensation level, these mobility data show a significantly larger spread than mobility data from compensated material solely containing singly charged scattering centers. This is shown in Figure 4.4, where the relative deviation of mobilities in compensated silicon from Klaassen's mobility model is plotted as a function of compensation level, in the left graph for compensated silicon only containing singly charged scattering centers, in the right graph for silicon compensated by activation of thermal donors. The larger spread can be due to several reasons: On the one hand, the scattering power of a doubly ionized scattering center is enhanced by a factor of four compared to a singly charged impurity, thereby changing the ratio of the concentration of donors and their scattering power, which also sensitively influences the definition of the compensation level. Additionally, as discussed in [165], heterogeneities in the doping concentrations are observed across samples compensated by thermal donor activation, even leading to the formation of a n-p-n transistor for high compensation levels arising from the preferential formation of thermal donors in the sample's subsurface. This would have a significant impact on the mobility obtained from Hall measurements and would lead to large uncertainties when plotting the mobility data as a function of compensation level. To keep the uncertainties to a minimum, for the model fit presented in section 4.3 only mobility data from samples compensated by singly ionized dopants is considered.

# 4.3 A Unified Mobility Model

As motivated in the previous sections, none of the hitherto developed models for charge carrier mobility in crystalline silicon is able to correctly describe mobility in compensated silicon, especially at high compensation levels. Even Klaassen's model [148], although accounting for the simultaneous presence of acceptors and donors as scattering centers, fails to correctly describe carrier mobilities in compensated silicon [57, 85, 86, 90, 91, 125, 126, 158-168]. The deviation from Klaassen's model depends on the compensation level, as has been shown in several publications, e.g. [86, 125]. It has been speculated if a new scattering mechanism occurring in compensated silicon might be the reason for lower mobilities [162, 166, 167]. However, all involved scattering partners are taken into account in Klaassen's model and there is no evidence for a further scattering mechanism so far. Thus, a different approach is favored here to resolve the discrepancies between experimental results and Klaassen's model: As Klaassen's model is based on the empirical mobility expression of Caughey and Thomas [146] developed for uncompensated silicon, and parameters are obtained from fitting experimental data in uncompensated silicon, the cause of the deficient prediction of mobilities in compensated silicon is not necessarily an additional scattering mechanism but simply an insufficient parameterization accounting for a compensationdependent reduction of screening of charged impurities. This assumption was first mentioned in [168], put forward by the author in reference [125] and challenged by temperature dependent measurements in other publications [86, 160], suggesting that reduced screening alone cannot explain mobility reductions along the whole temperature range. In the following, it is demonstrated that temperature dependent measurements do not necessarily contradict the hypothesis of reduced screening as a reason for mobility reductions, and the approach for a consistent description of carrier mobilities in uncompensated and compensated silicon is explained in detail. In order to account for deficiencies of Klaassen's model observed for the description of hole mobility due to phonon scattering, in the first step a new phenomenological parameterization for hole scattering at phonons is included in Klaassen's model (cf. section 4.3.1). Then, Klaassen's model including this new parameterization for phonon scattering of holes is extended to correctly describe measured mobilities in compensated silicon. This is done by the introduction of a compensation-dependent term in the empirical Caughey-Thomas mobility-expression used as the starting formula in Klaassen's model. It is

shown that a single set of parameters can be used for the description of both majority hole and electron mobility in compensated silicon at room temperature (*cf.* section 4.3.2.2). Using the same parameter set and introducing an additional dependence on the total dopant concentration also allows for modeling minority electron and hole mobility (*cf.* section 4.3.2.3). In a third step, the model is extended to correctly describe mobility data in compensated silicon along the temperature range from 80 – 350 K (*cf.* section 4.3.2.4). Thus, a unified mobility model is obtained, which merges with Klaassen's mobility model including a new parameterization for hole scattering at phonons in the case of uncompensated silicon.

#### 4.3.1 Phonon scattering

Before discussing the effect of compensation on mobilities, this section sets the focus on phonon scattering. As observed in [165], Klaassen's model seems to overestimate the phonon scattering of holes in the range from 80 - 300 K. This is in agreement with theoretical calculations by Szmulowicz [128] and with experimental data published previously [174]. Szmulowicz numerically calculates acoustic and optical-phononlimited mobilities in *p*-type silicon within the deformation-potential theory [128]. Although such an approach would be the most physical description of phonon scattering, analytical expressions are needed for device simulations. Klaassen's model uses a simple power law for the temperature dependence of phonon scattering of holes:

$$\mu_{phonons,Klaassen} = 470.5 \frac{\text{cm}^2}{\text{Vs}} \cdot \left(\frac{300 \text{ K}}{T}\right)^{2.247}$$
(4.31)

However, this parameterization underestimates Szmulowicz's mobility values in the temperature range from 50 – 300 K. Mobilities recently measured by Veirman *et al.* in ultra-pure lowly doped 5000  $\Omega$ cm *p*-type silicon support this underestimation of  $\mu_{phonons}$  by Klaassen's model [165]. They suggested accounting for this deviation by using an alternative parameterization for the phonon scattering instead

$$\mu_{phonons,Veirman} = exp(aT^6 + bT^5 + cT^4 + dT^3 + eT^2 + fT + g)$$
(4.32)

with the seven parameters *a-g* published in [165]. Veirman's parameterization reproduces the experimental data and Szmulowicz's model for temperatures between 80 K and 300 K. However, due to its polynomial character it is stable only in a certain temperature interval and behaves unphysically at temperatures higher than 350 K (*cf.* Figure 4.5). This will lead to significant errors when using this parameterization at higher temperatures. Therefore, a new parameterization for phonon scattering is needed which behaves physically meaningful in the whole temperature range. We used Klaassen's parameterization for hole scattering at phonons as a starting point and, also



Figure 4.5: Comparison of the three parameterizations for the temperature dependence of phonon scattering of holes suggested by Klaassen [155], Veirman et al. [165] and in this work with experimental data published in [165] and [174].

empirically, added an exponential function to account for the deviation in the temperature range between 80 K and 300 K:

$$\mu_{phonons} = 470.5 \frac{\text{cm}^2}{\text{Vs}} \cdot \left(\frac{300 \text{ K}}{T}\right)^{2.247} + \mu_{corr} \cdot \exp\left(-\left(\frac{T}{T_{corr}}\right)^{\theta_{h,corr}}\right)$$
(4.33)

A fit to the data published in [165], which also includes data from [174], delivers the parameters  $\mu_{corr} = 4800 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ,  $T_{corr} = 120 \text{ K}$  and  $\theta_{h,corr} = 1.9$ . Excellent agreement with the data is achieved (*cf.* Figure 4.5). Compared to the parameterization suggested in [165], our parameterization features the following advantages: It behaves physically meaningful in the whole temperature range and merges with Klaassen's parameterization at high and low temperatures, thus it is able to exclusively account for the deviation in the temperature range covered by experimental data. In particular, it does not diverge for temperature range. Furthermore, this new parameterization suggested in the whole temperature range. Furthermore, this new parameterization suggested in [165].

#### 4.3.2 Modeling mobility in compensated silicon

#### 4.3.2.1 Physical motivation and approach

Let us now focus on the effects of compensation on charge carrier mobility in crystalline silicon. In order to motivate the approach presented in this work, some remarks are required regarding the origin of mobility reductions in compensated silicon. Mobility

reductions in compensated silicon have been frequently observed in the past years [57, 85, 86, 90, 91, 125, 126, 158-168]. The reasons were controversially discussed and different approaches to account for these mobility reductions were suggested. In [167], a mobility correction term  $\mu_{cor} \propto C_l^{-3/4}$  is suggested ( $C_l$  denoting the compensation level), attributed to a specific compensation effect which is not taken into account in the existing mobility models. Adding such a correction term according to Matthiesen's rule  $(1/\mu = 1/\mu_{Klaassen} + 1/\mu_{cor})$  can only be justified with an additional scattering channel in compensated silicon. Such additional scattering mechanisms have been conjectured in references [162, 166, 167], but have not been proven to exist so far. A different explanation is given by Lim et al. [168], who suggested that reduced screening of ionized scattering centers by free charge carriers could lead to an additional mobility reduction in compensated silicon. In [85] it is argued that the discrepancy of experimental and modeled mobility values in compensated silicon highlights the nonphysical character of Klaassen's model rather than a mobility reduction due to compensation, as Klaassen's model is based on a substantial amount of fitting to data in uncompensated silicon. A correct mobility description would therefore require a complete re-assessment of Klaassen's fitting parameters. Alternatively, a very simple empirical correction for compensation is suggested in that work: By multiplying Klaassen's mobility with a prefactor depending on the compensation level and the type of carrier, a good description of mobility in compensated silicon can be achieved. While the simplicity is the strength of this correction, its weakness is its purely empirical nature.

Our approach attempts to stay as close as possible to the largely successful Klaassen-model and explains reduced mobilities in compensated silicon by a reduction of screening that is not accounted for sufficiently in Klaassen's model. In compensated silicon, the free carrier concentration decreases with a simultaneous increase of the ionized dopant concentration with increasing compensation level, which means that screening of ionized scattering centers decreases dramatically. The weakness of the Klassen-model is in our view, that in equation (4.11) reduced screening is only accounted for in the second term, while the first term still stems from the Caughey-Thomas expression for uncompensated silicon. As the first term is predominant for impurity concentrations  $N \leq 10^{18}$  cm<sup>-3</sup>, the decreased screening effect is not taken into account adequately in Klaassen's model in this range of dopant concentrations. This is where our approach sets in to describe mobilities correctly in compensated silicon. By adding a compensation-dependent term accounting for reduced screening in the Caughey-Thomas mobility expression, which is the empirical starting point in Klaassen's model, we tried to keep the physical character of the model. This approach was put forward by the author for modeling majority carrier mobility in compensated silicon at room temperature [125]. However, temperature dependent measurements appeared to contradict this hypothesis, as reducing the temperature increases the compensation level without a further strong mobility reduction [160]. A closer look at the implementation of the T-dependence of impurity scattering in Klaassen's model [155] allows for solving this seeming contradiction:

$$\mu_{k,I} = \frac{\mu_{max}^2}{\mu_{max} - \mu_{min}} \left(\frac{N_{ref,1}}{N_I}\right)^{\alpha_1} \left(\frac{T}{300\text{K}}\right)^{3\alpha_1 - 1.5} + \frac{\mu_{min} \cdot \mu_{max}}{\mu_{max} - \mu_{min}} \left(\frac{c}{N_I}\right) \left(\frac{300\text{K}}{T}\right)^{0.5}$$
(4.34)

The second term in this equation accounts for reduced screening with decreasing carrier concentration c at a constant concentration of ionized scattering centers  $N_I$ . As mentioned before, at room temperature the first term is predominant for dopant concentrations  $N \le 10^{18}$  cm<sup>-3</sup>. With decreasing temperature, however, the second term becomes more important (e.g. at 100 K, the first term is reduced to 50% of its room-T value, while the second term is roughly doubled). This means, the lower the temperature, the more Klaassen's model already accounts for reduced screening in compensated silicon without any correction. Therefore, comparing mobilities with Klaassen's model for the case of an increased compensation level by doping at room temperature and for the case of increased compensation level by a temperature reduction is actually expected to lead to a completely different behavior. Consequently, temperature dependent mobility measurements in compensated silicon are not necessarily in contradiction with the assumption of reduced screening as a reason for reduced mobilities at room temperature. Therefore, we maintained our approach presented in [125] to install a mobility model predicting mobilities in uncompensated and compensated silicon. Our reasoning to put this approach forward is that the introduction of the compensation-dependent correction term in the empirical Caughey-Thomas expression can at least be physically motivated.

Let us now have a closer look at the details of our approach. An increasing compensation level means an increase of ionized scattering centers, while the free carrier concentration decreases simultaneously leading to a much less effective screening of charged impurities. Although Klaassen's model is meant to include a screeningcorrection, this only holds for high impurity concentrations. For PV silicon as investigated here, total base-dopant concentrations are in the range of  $9.4 \cdot 10^{15}$  cm<sup>-3</sup> –  $8.6 \cdot$  $10^{17}$  cm<sup>-3</sup>. In this range of dopant concentrations, the first term in equation (4.11) is predominant. This term stems from the empirical Caughey-Thomas expression for mobility, which is derived from and consequently correctly describes the mobility for the case where the impurity concentration equals the free carrier concentration, i.e. the case of strongly screened impurities. With increasing compensation level the amount of screening carriers decreases, leading to a higher collision cross section of the charged impurities (or, in other words, a higher effective impurity concentration) and therefore to a lower mobility. This is not taken into account in Klaassen's model. As Klaassen's model is currently used as the standard mobility model for device simulation and excellently agrees with experimental mobility data in uncompensated silicon, we basically follow Klaassen's approach for the description of mobilities, but with a modified empirical "Caughey-Thomas mobility expression" as a starting point. We modify the mobility expression of equation (4.2) by inserting a compensationdependent term:

$$\mu = \frac{\mu_{max} - \mu_{min}}{1 + (N/N_{ref,1})^{\alpha_1} + ((C_l - 1)/C_{l,ref})^{\beta_1}} + \mu_{min}$$
(4.35)

For uncompensated silicon, the third term in the denominator vanishes as the compensation level is equal to one and we reobtain the familiar mobility expression from Caughey-Thomas from equation (4.2). With increasing compensation level, this term accounts for a decreased screening leading to lower mobilities. Using this empirical mobility expression as starting point for Klaassen's model, instead of equation (4.11) we obtain the following expression for mobility due to impurity scattering:

$$\mu_{k,l} = \mu_{k,N} \left( \left( \frac{N_l}{N_{ref,1}} \right)^{\alpha_1} + \left( \frac{C_l - 1}{C_{l,ref}} \right)^{\beta_1} \right)^{-1} + \mu_{k,c} \left( \frac{c}{N_l} \right)$$
(4.36)

The further calculations remain the same as in reference [148] and are summarized in section 4.1.2.6. With this modified approach, we obtain two fit parameters in Klaassen's mobility model for the description of reduced screening,  $\beta_1$  and  $C_{l,ref}$ .

In the following, this approach will be applied for modeling of majority hole and electron mobilities in compensated *p*- and *n*-type silicon (section 4.3.2.2) and extended to minority hole and electron mobility (section 4.3.2.3). In section 4.3.2.4, the temperature dependence of majority carrier mobilities in compensated silicon from 80 - 350 K will be discussed. Details on the model implementation are summarized in appendix 8.2.

#### 4.3.2.2 Majority hole and electron mobility at room temperature

For a comparison of the published mobility data with Klaassen's mobility model, a well suited and clear representation is a plot of the relative deviation of measured mobilities from the mobility predicted by Klaassen  $(\mu_{exp} - \mu_{Klaassen})/\mu_{Klaassen}$  against the compensation level  $C_l = (N_A + N_D)/c$ , where  $N_A + N_D$  is the sum of ionized acceptors and donors and *c* the free carrier concentration  $n_e + n_h$ . Figure 4.6 shows this representation of the majority mobility data used for the model adaption as



Figure 4.6: Relative deviation of majority hole and electron mobility measured in compensated p- and n-type silicon from Klaassen's model including the new parameterization for phonon scattering. The accepted tolerance due to differences between mobility measurements of uncompensated multi- and monocrystalline silicon is marked in green, the typical uncertainty range of mobility measurements is marked in gray.

described in section 4.2. Note that all data presented in this work was obtained from experiments without injection of carriers for majority carrier measurements and under low injection of carriers for minority carrier measurements. Furthermore, representations of Klaassen's model already include the new parameterization for hole scattering at phonons according to equation (4.33) introduced in section 4.3.1.

In Figure 4.6, a mobility reduction of up to 5% is marked in green, as such a reduction can already occur in uncompensated multicrystalline silicon [157], meaning that deviations in this range are not necessarily attributed to compensation and mobility values can be regarded as correct. Furthermore, a typical relative error of  $\pm 10\%$  on experimental mobility data is assumed. This uncertainty range is marked in gray. With respect to these assumptions we can conclude that for low compensation levels of up to 2-4 Klaassen's model appears to predict mobilities quite well, although a systematic overestimation can already be inferred. With increasing compensation level, the deviation also increases, leading to a dramatic overestimation of mobilities for high compensation levels. For example, at a compensation level of about 30, mobilities are about 30% lower than predicted, and at high compensation levels exceeding 100, the mobility is up to 70% lower than predicted by Klaassen. Figure 4.6 contains both data for majority hole mobility in compensated *p*-type silicon as well as majority electron mobility in compensated *n*-type silicon. Remarkably, relative deviations from Klaas-



Figure 4.7: Relative deviation of majority hole and electron mobility measured in compensated p- and n-type silicon from the corrected model presented here. The accepted tolerance due to differences between mobility measurements of uncompensated multi- and monocrystalline silicon is marked in green, the typical uncertainty range of mobility measurements is marked in gray.

sen's model are the same for majority hole and majority electron mobility. Following the approach presented in section 4.3.2.1 and in reference [125], the parameters  $\beta_1$  and  $C_{l,ref}$  in equation (4.36) are determined by fitting the model to the majority carrier mobility data in compensated silicon as summarized in Figure 4.6. Reducing  $\chi^2$  delivers:

$$C_{l,ref} = 23.2 \pm 2$$
  

$$\beta_1 = 1.01 \pm 0.03$$
(4.37)

As mentioned before and shown in [157], a mobility reduction of about 5% can already occur in uncompensated multicrystalline silicon. As this reduction is not attributed to compensation, data with a maximum reduction of 5% was treated as correct mobility data. Therefore, in the fit  $\chi^2$  was reduced by only accounting for positive deviations or negative deviations larger than 5%. Thus, the systematic overestimation of mobilities in compensated silicon by the model description disappears as well as the trend of an increasing deviation with increasing compensation level (*cf.* Figure 4.7). Excellent agreement between the model and the experimental data is obtained, both for majority hole mobilities in compensated *p*-type silicon and majority electron mobilities in compensated *n*-type silicon, with maximum relative deviations of +10% and -15%, which are in the range of estimated uncertainties of mobility measurements. Note that this error comprises both errors of the measured mobility itself as well as errors of the modelled mobility due to uncertainties of dopant and carrier concentrations, which are the input parameters for the modelled mobility.

To summarize, by introducing a compensation-dependent correction term in the empirical mobility expression by Caughey-Thomas, we are able to predict majority carrier mobilities with Klaassen's model in good agreement with published data in compensated *p*- and *n*-type silicon. It should be mentioned that predictions of mobilities in uncompensated silicon remain unaffected, as the correction term disappears for  $C_l = 1$ . This means that this correction can simply be implemented in standard programs without changing predictions for uncompensated silicon but with significant improvement for the prediction of majority carrier mobilities in compensated silicon.

#### 4.3.2.3 Minority hole and electron mobility at room temperature

A significant reduction compared to Klaassen's model is also observed for minority carrier mobilities in compensated *p*- and *n*-type silicon [86, 91]. By applying the model developed for majority carrier mobilities from section 4.3.2.2, the deviation is decreased, but a pronounced dependence on compensation level remains. Even a new fit of the parameters  $C_{l,ref}$  and  $\beta_1$  based on the data for minority carrier mobilities does not lead to a good description of the experimental data. This indicates that the deviation is not only a function of the compensation level. We observe that this deviation is additionally a function of the total ionized dopant concentration  $(N_A + N_D)$ , which is illustrated in Figure 4.8 where the relative deviation of minority electron and hole mobilities published in references [86] and [91] from Klaassen's model is plotted as a function of  $(N_A + N_D) \cdot C_l$ . Thus, this observation may be accounted for by weighting the correction term in equation (4.35) obtained for majority carriers accordingly, leading to the expression

$$\left(\left[\frac{N_A + N_D}{N_{ref,3}}\right] \cdot \left[\frac{C_l - 1}{C_{l,ref}}\right]\right)^{\beta_1} \tag{4.38}$$

By inserting one new parameter,  $N_{ref,3} = (1.2 \pm 0.1) \cdot 10^{17} \text{ cm}^{-3}$ , while leaving  $C_{l,ref}$  and  $\beta_1$  unchanged, the same correction can be applied for minority carrier mobilities. Results are shown in Figure 4.9. Some remarks regarding the interpretation of this data are to be given at this point: Compared to majority carrier mobilities from Hall measurements, experimental data of minority carrier mobilities are affected with a significantly larger error due to the complexity of the measurements. Details on the measurement technique for minority carrier mobilities can be found in section 3.1. We assume an error of  $\pm 15\%$  indicated by the gray band in Figure 4.8 and Figure 4.9.



*Figure 4.8: Deviation of minority electron and hole mobility measured in compensated silicon from Klaassen's model.* 

While Klaassen's model significantly overestimates the majority of the data (cf. Figure 4.8), good agreement between most experimental data and the model presented here is obtained (cf. Figure 4.9). The deviation between model and data published by Rougieux et al. [91] ("Cz-Ro") is only slightly decreased by applying the new model instead of Klaassen's, which is due to the rather low compensation level of these samples in the range of 3 - 4.3 leading to a small correction only. These larger deviations might be partly attributed to the measurement technique as indicated by the data for uncompensated silicon published in the same paper ("Cz-Ro reference" in Figure 4.8 and Figure 4.9), which feature mobility reductions of up to -15% compared with the model. The outlier from material "Cz-Fo-3" at highest compensation level, featuring a relative deviation from the corrected model of -26%, can be relativized by looking at the very low absolute mobility value of this sample: While the measured minority electron mobility is 27 cm<sup>2</sup>/Vs, Klaassen's model predicts a value of 309 cm<sup>2</sup>/Vs. Agreement with the new model predicting a value of 36 cm<sup>2</sup>/Vs is much better and the absolute deviation is relatively small (9  $\text{cm}^2/\text{Vs}$ ). However, due to the low absolute mobility level of this sample, this leads to the rather high relative deviation.



Figure 4.9: Deviation of minority electron and hole mobility measured in compensated silicon from the corrected model presented in this work.

The additional term introduced for minority carrier mobilities in equation (4.38) weights the compensation level with the total ionized dopant concentration. As the definition of the compensation level is a priori arbitrary, one could also regard this term as a redefinition of the compensation level emphasizing the ionized dopant concentration in a more pronounced way than the free carrier concentration. This means that with increasing compensation the minority carrier mobility reacts more sensitively to an increase in the total dopant concentration than the majority carrier mobility. In other words, for a constant total dopant concentration and an increasing compensation level, the minority carrier mobility reacts less sensitively to a decrease in the free carrier concentration  $n_e + n_h$  than the majority carrier mobility. This shall be tentatively explained in the following. Klaassen's model accounts for the attractive interaction potential for free carrier scattering. Due to the higher concentration of majority carriers acting as scattering centers for minority carriers, this term is much more important for minority carriers. Furthermore, for the minority carrier mobility in uncompensated silicon scattering at carriers is even more important than scattering at majority impurities. This is due to the larger scattering potential of attractive free carriers compared to repulsive stationary scattering centers as explained in [148]. Therefore, tuning the compensation level has a different impact on minority and majority carriers: When compensation is increased by solely decreasing the free carrier concentration while leaving the total dopant concentration constant, the majority carrier mobility is reduced due to reduced screening of the impurity scattering potential. The minority carrier mobility is also affected by the reduced screening of the impurity scattering potential, but at the same time, scattering at free majority carriers is reduced. Consequently, increasing the compensation level by increasing the total dopant concentration reduces the minority carrier mobility more strongly than increasing the compensation level by reducing the free majority carrier concentration. This can be accounted for in the model by weighting the compensation correction term with the total dopant concentration according to equation (4.38). More experimental data for minority carrier mobilities in compensated silicon would be useful to strengthen this hypothesis.

The model implementation is explained in more detail in appendix 8.2.

#### 4.3.2.4 Temperature dependence of mobility in compensated silicon

At low temperatures, mobilities in compensated and uncompensated silicon behave significantly different. Due to incomplete ionization at low temperatures [160], phonon scattering is important in the entire temperature range in uncompensated silicon. In compensated silicon incomplete ionization is less pronounced, as the total density of ionized dopants cannot decrease below  $2 \cdot N_{dop,min}$ , where  $N_{dop,min}$  denotes the minority dopant concentration [160]. As a consequence, in compensated silicon ionized impurity scattering becomes more important with decreasing temperature than in uncompensated silicon. However, a good description of the temperature dependence of mobilities in compensated silicon is still lacking [85, 165].

In this section we will discuss the temperature dependence of majority carrier mobility in compensated silicon. Figure 4.10 shows mobility data obtained from Hall measurements and recalculated with the temperature dependent Hall factor from reference [170] in a compensated *p*-type sample featuring a compensation level of 31, an acceptor concentration of  $2.80 \cdot 10^{17}$  cm<sup>-3</sup> and a donor concentration of  $2.62 \cdot 10^{17}$  cm<sup>-3</sup> at room temperature. Measurements were conducted in the frame of Maxime Forster's PhD thesis [85]. We compare the experimental data to Klaassen's model and to three variations of the model which are summarized below. We use the new parameterization for phonon scattering of equation (4.33) presented in section 4.3.1 for all models.



Figure 4.10: Hole mobility in a compensated p-type sample (Cz-Fo-3-298) obtained from Hall measurements compared to Klaassen's model including the new parameterization for phonon scattering and three variations of the model presented in this work.

In order to leave the compensation-dependent correction term introduced for room temperature in section 4.3.2.1 unaffected by the temperature dependence of Klaassen's model, we account for the temperature dependence in the impurity scattering term before introducing the compensation-dependent term, leading to the following expression for impurity scattering:

$$\mu_{k,I} = \frac{\mu_{k,N}}{\left(\frac{N_I}{N_{ref,1}}\right)^{\alpha_1} / \left(\frac{T}{300\text{K}}\right)^{3\alpha_1 - 1.5} + \left(\frac{C_l(T) - 1}{C_{l,ref}}\right)^{\beta_1} + \mu_{k,c} \left(\frac{c}{N_I}\right) \left(\frac{300\text{K}}{T}\right)^{0.5}$$
(4.39)

 $C_l(T)$  is the compensation level at the corresponding temperature *T*. As the free carrier concentration strongly decreases with decreasing temperature, the compensation level strongly increases. Using this temperature dependent compensation level in the correction term leads to a large underestimation of mobilities by the model. This is depicted by case (i) in Figure 4.10. To illustrate the correction using a temperature independent compensation level as input, we also plotted the modelled mobility using the following expression for impurity scattering:

$$\mu_{k,I} = \frac{\mu_{k,N}}{\left(\frac{N_I}{N_{ref,1}}\right)^{\alpha_1} / \left(\frac{T}{300\text{K}}\right)^{3\alpha_1 - 1.5} + \left(\frac{C_{l,RT} - 1}{C_{l,ref}}\right)^{\beta_1} + \mu_{k,c} \left(\frac{c}{N_I}\right) \left(\frac{300\text{K}}{T}\right)^{0.5}$$
(4.40)

 $C_{l,RT}$  denotes the compensation level at room temperature which in case (ii) is used for modelling mobilities along the whole temperature range. As shown in Figure 4.10, this leads to an overestimation of mobilities at low temperatures. This is not surprising, as

the compensation level increases with decreasing temperature, which is not accounted for in case (ii). However, as shown in case (i), taking into account the actual compensation level at each temperature leads to a strong underestimation of mobilities at low temperatures. This seeming contradiction can be explained as outlined in section 4.3.2.1: Adjusting the compensation level by changing the temperature leads to a different behavior than adjusting the compensation level just by doping. Hence, the compensation term introduced for the room temperature correction of mobilities is not necessarily directly transferable to the whole temperature range.

As compensation indeed depends on the temperature, but using the actual compensation level at each temperature overemphasizes the correction term at low temperatures, we start with the room temperature compensation level and implement an empirical temperature dependence accounting for the increasing compensation level with decreasing temperature. As the compensation correction at 300 K is also an empirical correction, it is justified to introduce a further empirical correction in this term to account for the temperature dependence. This can be done with the following expression for impurity scattering:

$$\mu_{k,I} = \frac{\mu_{k,N}}{\left(\frac{N_{I}}{N_{ref,1}}\right)^{\alpha_{1}} / \left(\frac{T}{300\text{K}}\right)^{3\alpha_{1}-1.5} + \left(\frac{C_{l,RT}\beta_{2}(T)}{C_{l,ref}} - 1\right)^{\beta_{1}}} + \mu_{k,c} \left(\frac{c}{N_{I}}\right) \left(\frac{300\text{K}}{T}\right)^{0.5}}$$

$$(4.41)$$

 $C_{l,RT}$  is the room temperature compensation level and  $\beta_2(T)$  is a temperature dependent term accounting for an increasing compensation level with decreasing temperature

$$\beta_2(T) = 1 + \frac{60}{\sqrt{C_{l,RT}}} exp\left(-\left(\frac{T}{T_{ref}} + 1.18\right)^2\right)$$
(4.42)

where  $T_{ref}$  denotes a reference temperature depending on the room temperature compensation level and the total dopant concentration

$$T_{ref} = 37.9K \cdot ln\left(\frac{C_{l,RT}^2 \cdot (N_A + N_D)}{10^{19} \,\mathrm{cm}^{-3}} + 3.6\right)$$
(4.43)

The derivation of  $\beta_2(T)$  is explained in detail in appendix 8.2. Using  $C_{l,RT}^{\beta_2(T)}$  in the correction term leads to case (iii) in Figure 4.10.



Figure 4.11: Experimental T-dependent majority carrier mobility of (a) seven compensated p-type and (b) two compensated n-type samples with a wide range of compensation levels compared to Klaassen's model (dashed lines) and the model of this work (solid lines).

As explained in more detail in appendix 8.2,  $\beta_2(T)$  was adjusted to correctly describe the temperature dependence of the majority carrier mobility of a large set of about 30 samples stemming from three different compensated *p*-type ingots and one compensated *n*-type ingot covering a wide range of compensation levels ( $C_{l,RT} = 5 -$ 145) as well as dopant concentrations, net doping concentrations and resistivities ( $N_A + N_D = (1 - 9) \cdot 10^{17} \text{ cm}^{-3}$ ;  $n_h(300 \text{ K}) = (0.6 - 7) \cdot 10^{16} \text{ cm}^{-3}$ ;  $\rho(300 \text{ K}) =$ (0.5 - 19)  $\Omega$ cm). Therefore, the description of the temperature dependence of mobility in compensated silicon over the temperature range 80-350 K is experimentally validated in this range of compensation levels and doping concentrations, which gives confidence that it is valid for compensated silicon in general. For the sake of clarity, not all temperature dependent data can be shown here. Figure 4.11 exemplarily shows the experimental data of seven compensated *p*-type samples and two compensated *n*-type samples with room temperature compensation levels covering a range from 15-146. Room temperature values of ionized dopant concentrations and compensation levels are listed in Table 4.4. Excellent agreement between data and the model presented here (equation (4.41)) is obtained for all temperatures and compensation levels with the same set of fitting parameters. The data plotted in Figure 4.11 is a representative selection of nine of about 30 samples investigated in this work. Agreement between measured mobility and model for all other samples not shown in the graph is of similar quality. Measurements were conducted in the frame of Maxime Forster's PhD thesis [85] and partly published in [85, 86, 160]. Details on the measurement techniques and the calculation of the ionized dopant concentrations including incomplete ionization can also be found in these publications.

Details on implementing the corrections in Klaassen's model and a discussion about a preliminary description of the temperature dependence of the minority carrier mobility in compensated silicon can be found in appendix 8.2.

Sample	Туре	$N_A ({\rm cm}^{-3})$	$N_D  ({\rm cm}^{-3})$	$C_{l,RT}$
Cz-Fo-6-012	n	$9.20 \cdot 10^{16}$	$1.00 \cdot 10^{17}$	24
Cz-Fo-6-326	n	$2.02 \cdot 10^{17}$	$2.14 \cdot 10^{17}$	34
Cz-Fo-2-200	р	$9.83 \cdot 10^{16}$	$8.60 \cdot 10^{16}$	15
Cz-Fo-3-130	р	$2.32 \cdot 10^{17}$	$2.09 \cdot 10^{17}$	19
Cz-Fo-3-298	р	$2.80 \cdot 10^{17}$	$2.62 \cdot 10^{17}$	31
Cz-Fo-3-353	р	$3.07 \cdot 10^{17}$	$2.95 \cdot 10^{17}$	47
Cz-Fo-3-396	р	$3.37 \cdot 10^{17}$	$3.27 \cdot 10^{17}$	67
Cz-Fo-3-449	р	$3.90 \cdot 10^{17}$	$3.84 \cdot 10^{17}$	119
Cz-Fo-3-478	р	$4.34 \cdot 10^{17}$	$4.28 \cdot 10^{17}$	146

Table 4.4: Ionized dopant concentrations and compensation level at 300K for the samples shown in Figure 4.11.

# 4.4 Conclusion and Discussion

Mobility measurements in compensated silicon revealed a systematic overestimation of majority and minority carrier mobilities in compensated p- and n-type silicon by standard models, which increases with increasing compensation level. Additionally, the hole scattering at phonons seems to be overestimated by Klaassen's model in the temperature range from 80 - 300 K.

In this chapter a modified mobility model based on the approach of Klaassen for the description of mobilities in compensated silicon was developed. We argue that Klaassen's model does not account for decreased screening with increasing compensation level in the range of dopant concentrations typically occurring in compensated PV silicon, as the model is based on an empirical mobility expression for uncompensated silicon. In our approach, we introduce an additional compensation-dependent term into the empirical mobility expression of Caughey-Thomas. Based on this modified expression, Klaassen's model predicts majority and minority hole and electron mobilities in compensated silicon in good agreement with experimental data. Predictions of mobilities in uncompensated silicon remain unaffected as the compensation-dependent term disappears for  $C_l = 1$ .

Furthermore, the inconsistencies observed in the temperature range from 80 - 350 K were accounted for. This comprises a new parameterization for hole scattering at phonons and an expression for the temperature dependence of the compensation correction term for majority carrier mobility.

Thus, a model for carrier mobilities in silicon which merges with Klaassen's model including a new parameterization for hole scattering at phonons in the case of uncompensated silicon has been developed. To the best knowledge of the author no published temperature dependent data of minority carrier mobilities in compensated silicon exists so far. As long as this data is not available, we suggest using the room temperature compensation correction also for modelling the temperature dependence of minority carrier mobilities in compensated silicon. This is also explained in more detail in appendix 8.2, where an in-depth description of the model implementation is given.

In the following, the strength of the new mobility model is demonstrated by some examples, and remarks on the further development of mobility models and the validity of the physical interpretation are given.

The new parameterization for hole scattering at phonons is of particular importance for very lowly doped *p*-type samples in the temperature range 100 - 300 K (*cf.* Figure 4.5). However, its benefit is also observable for the case of compensated silicon. Figure 4.12 shows exemplarily the temperature dependence of the hole mobility in the compensated *p*-type sample Cz-Fo-2-200 listed in Table 4.4. The experi-



Figure 4.12: Experimental hole mobility in a compensated p-type sample compared to Klaassen's model and the model presented in this work including or not the new parameterization for phonon scattering.

mental data is compared to Klaassen's model, which overestimates the mobility in the whole temperature range. The comparison of the data with the model suggested in this work shows, that including the parameterization of phonon scattering from equation (4.33) significantly better describes the data in the temperature range from 100 - 300 K (green line) than the same model including Klaassen's parameterization of phonon scattering (red dashed line). Note that for this sample, the temperature correction  $\beta_2(T)$  significantly influences the modelled mobility only below 120 K. This demonstrates again the accurate description of phonon scattering by the parameterization.

Furthermore, the mobility results of the *n*-type samples shown in Figure 4.11b suggest that a modification of the electron scattering at phonons would be beneficial as well, as the curvature of the data is larger than the curvature of the modelled values. This could be considered in a similar way as presented here for hole scattering at phonons. Therefore, temperature dependent data on high purity and high resistivity *n*-type silicon would be needed to transfer the approach presented in this work to electron phonon scattering.

In the following, a crucial advantage of the new mobility model on the example of compensated *n*-type silicon shall be highlighted: Figure 4.13 shows the majority electron mobility obtained from Hall measurements in a compensated *n*-type Cz ingot ("Cz-Sc-2") as a function of block height (black symbols).



Figure 4.13: Majority electron mobility in a compensated n-type Cz ingot as a function of ingot position. Experimental mobility values obtained from Hall measurements are compared with Klaassen's mobility model and the mobility model developed in this PhD thesis. Note that the green shaded uncertainty range comprises errors on the compensation level only; further errors especially affecting mobilities close to the tail end of the crystal are discussed in the text.

Due to the larger segregation coefficient of boron, in a compensated *n*-type ingot compensation is highest close to the seed end of the crystal. With increasing ingot height, compensation decreases, while the total amount of dopants increases. This leads to a peculiar behavior of mobility: despite the increase in the total amount of dopants acting as ionized scattering centers, majority carrier mobility increases in the first part of the ingot due to a decrease of the compensation level. In the second half of the ingot, where compensation effects are of less importance, majority carrier mobility decreases due to the increasing amount of ionized dopants. Let us now compare this behavior with the predictions from mobility models. As input for the modeling, we use dopant concentrations obtained from Scheil's equation as explained in case ii) in section 4.2 and in more detail in [124, 172]. Klaassen's model (black dashed line) not only overestimates mobilities along the whole ingot, but also fails to describe these characteristics and predicts a monotonically decreasing mobility due to the increasing doping concentration. In contrast, the mobility model developed in this work (green line) is able to predict this particular behavior, an increasing mobility in the first part and a decreasing mobility in the second part of the crystal. Very good agreement with experimental data is obtained for high compensation levels close to the seed end of the ingot, deviations occur towards the tail end. Still, deviations between experimental data and model are larger for Klaassen's model along the whole ingot. Deviations

towards the tail end of the crystal might be attributed to uncertainties in the Hall factor used for the recalculation of mobilities from Hall mobilities, uncertainties in the dopant concentrations used as input for modeled mobilities due to an insufficient prediction by Scheil's equation, as well as uncertainties in the exact distance from the seed. These uncertainties increase with increasing distance from the seed and, thus, could explain the deviations between model and experimental data for the ingot positions close to the crystal tail. Further details can be found in [124, 172]. Figure 4.13 also shows an error estimation on modeled mobilities in compensated silicon (green shaded area): Assuming a relative error of  $\pm 3\%$  on dopant concentrations in the melt leads to a negligible error on mobility for low compensation levels close to the tail end of the crystal, whereas the error becomes significant with increasing compensation level towards the seed end of the crystal. This can be explained as follows. With increasing compensation, the acceptor concentration approaches the donor concentration. Thus, even a small error on the dopant concentration leads to a large error on the compensation level and consequently to a large error on the compensation-dependent correction term in the mobility model. This highlights the importance of exact knowledge of dopant concentrations and compensation levels for a reliable prediction of mobilities. Note that this error estimation does not account for errors due to an insufficient prediction of dopant concentrations by Scheil's equation or uncertainties in the ingot position, as previously mentioned. Considering these errors would additionally increase the error on modeled mobility values in the upper part of the crystal. However, these uncertainties are difficult to assess and therefore not included in this error estimation.

To conclude, the mobility model developed in this PhD thesis is an analytical model based on Klaassen's approach, leading to identical results as the latter (apart from the adapted phonon scattering) for uncompensated silicon and significantly better results for compensated silicon. The compensation correction accounts for majority and minority hole and electron mobility at room temperature and includes an empirical expression for the temperature dependence of the compensation correction term for majority carrier mobilities. Due to the lack of temperature dependent data for minority carrier mobilities. As long as no data is available we suggest to use the room temperature compensation correction along the whole temperatures in highly compensated silicon as suggested in Figure 4.10 for majority carrier mobility by the cyan dashed-dotted line. Still, compared to Klaassen's model, the overestimation will be smaller along the whole temperature range.

Our justification for a compensation correction term was the hypothesis of reduced screening not accounted for sufficiently in Klaassen's model. So far, no experimental results contradict this hypothesis. A seeming contradiction by temperature dependent measurements could be ruled out, as argued in section 4.3.2.1. Still, there is no experimental evidence that proves our hypothesis. In order to get more insight on the physical reason for reduced mobilities in compensated silicon and to test the hypothesis of reduced screening, a mobility round robin with mobility experts from different research groups is running at the moment. The aim of this round robin is to tune the compensation level and to adjust screening in compensated silicon samples by injection of carriers. This should give hints if reduced mobilities in compensated silicon can indeed be attributed to reduced screening or if other yet unknown mechanisms are responsible. Additionally, temperature dependent mobility data on high resistivity n-type silicon are to be obtained within this round robin, which could serve as a data base for a new parameterization of electron scattering at phonons similar to the approach presented in this work.

The mobility model developed here is starting to win recognition in the PV community. It is available at the website of PV-Lighthouse (http://www.pvlighthouse.com.au), and it is also implemented in the latest version of command line PC1D (PC1Dmod 6.1) [175].

# 5 Towards High Efficiency Multicrystalline Silicon Solar Cells

Beside mobility, the second key parameter directly influencing minority charge carrier diffusion length and thus solar cell efficiency is minority carrier lifetime (*cf.* section 2.2). As outlined in section 2.2.2, minority carrier lifetime is limited by different recombination channels. In multicrystalline (mc) silicon, the main contributions are SRH recombination at dissolved metallic impurities, recombination at precipitates as well as recombination at structural crystal defects such as decorated dislocations and grain boundaries.

This PhD thesis assesses the question of the material related efficiency limit of multicrystalline silicon solar cells by identifying and quantifying the loss mechanisms in mc silicon. After putting this work into the context of the historical background (section 5.1), section 5.2 focuses on the influence of impurities from the crucible system on the material quality of *p*-type mc silicon, examining the differences between crucibles of industrial material quality and very pure electrically fused silica. A quantification of loss mechanisms separates the influence of impurities incorporated in the material by diffusion into the liquid melt from impurities stemming from solid-state indiffusion into the crystallized block and evaluates the impact of homogeneously distributed impurities and recombination active crystal defects. These investigations are extended to a detailed analysis of the impact of interstitial iron on the different solar cell parameters. Predictions of the solar cell efficiency potential after a high efficiency cell process reveal a considerable benefit from high-purity crucibles.

In sections 5.3-5.5 the role of doping is investigated in detail. By changing the type of doping from p- to n-type, a significant gain in efficiency potential is predicted for mc silicon crystallized in industrial quality crucibles (*cf.* section 5.3). This analysis also includes a thorough investigation of the influence of the variation in base resistivity. In section 5.4, the main metal impurities responsible for recombination in mc n-type silicon are identified. Attributing the main losses in mc n-type silicon to recombination active crystal defects, a route towards high efficiency mc silicon solar cells is demonstrated in section 5.5: In order to reduce material related efficiency losses to a minimum, n-type high performance multicrystalline silicon (HPM Si) with an optimized crystal structure featuring a very low density of dislocations is combined with a high efficiency cell concept featuring a full area passivated rear contact (TOPCon) [176]. We demonstrate the general applicability of this cell concept to multicrystalline silicon. In addition, a detailed loss analysis shows that material-related losses after this

high efficiency cell process are very low (<  $1\%_{abs}$ ). Thus, *n*-type HPM silicon seems to be a promising material for the production of low cost high efficiency solar cells.

Note that for the crystallization of each mc silicon ingot investigated in this chapter, high purity feedstock from the Siemens process with a purity level of ~9N (bulk metal concentration  $\leq 2$  ppbw) was used. We greatfully acknowledge the feedstock supply by Wacker Polysilicon.

Results presented in section 5.2 were published by the author in [177, 178], and results from sections 5.3-5.5 in [179-183]. As these chapters are mainly based on these publications, wording partially coincides with wording in the papers published by the author.

### 5.1 Historical Background

#### 5.1.1 Impact of crucible and coating on impurities in multicrystalline silicon

While costs and energy consumption for the crystallization of multicrystalline silicon are lower than for monocrystalline silicon, the fabrication of high efficiency crystalline silicon solar cells is still limited to monocrystalline wafers due to its lower impurity content and the absence of crystal defects. Although feedstock quality and crystallization processes of mc silicon have improved significantly in recent years, its electrical material quality is still limited by metal impurities and crystal defects. As the feedstock purity is typically high enough (as shown in reference [40], the iron concentration in the crystallized silicon stemming from the feedstock is around one order of magnitude lower than the total iron concentration in the crystal additionally accounting for diffusion of iron into the melt), the quartz crucible and the crucible coating remain the main sources for impurities. Several groups have been investigating the crucial role of crucible and coating on impurities in crystallized silicon [40, 45-47, 184-186]. Impurities can diffuse into the liquid silicon melt and during the crystallization be incorporated into the crystal lattice leading to a background impurity concentration which increases towards the top of the crystal due to the very low segregation coefficients of metals. Additionally, solid-state diffusion from the crucible and its coating into the solidified part of the ingot takes place, leading to an edge region of very high impurity concentration and low bulk lifetimes. Both, the background impurity concentration and the high concentration in the edge region limit the bulk lifetime and thereby material quality of multicrystalline silicon. Improving the purity of the crucible and its coating is one approach to reach better electrical material quality and thereby higher efficiencies on multicrystalline silicon solar cells.

In the following, a short review of previous work regarding the role of the crucible system on impurities in multicrystalline silicon ingots is given.

One of the first investigations regarding the interaction between crucible system and multicrystalline silicon ingots was performed by Binetti *et al.* [184]. Structural, spectroscopic and electrical techniques revealed a high density of silicon nitride and iron silicide particles in the areas of low lifetime close to the crucible walls. They conclude that a reaction occurs between the silicon nitride coating and the silicon during the growth process, and suppose that nitrogen is incorporated into the silicon by erosion and dissolution of nitride particles from the coating, whereas iron as a fast diffuser is incorporated by solid state diffusion from the crucible and its coating into the silicon ingot.

In 2005, Geyer *et al.* [45] investigated the influence of the purity of fused silica crucibles and silicon nitride coating on minority carrier lifetime of multicrystalline silicon blocks. They observed an increased yield of good quality wafers by using a highly pure silicon nitride coating, which was also reflected by higher solar cell efficiencies for certain block positions. Applying high purity crucibles also leads to increased ingot lifetimes, its effect on solar cell efficiencies was not reported in the paper.

Buonassisi *et al.* [185] analyzed impurity-rich particles of silicon nitride crucible coating powder as well as as-grown mc silicon material by synchrotron-based microprobe techniques and found correlations between the element species, chemical states, particle sizes, relative concentrations and locations of several impurities, such as Fe, Ti, Ca, Zn, Ni, Cu, N, and C. Thus, they conclude that the silicon nitride coating could be a significant source of impurities during crystallization of multicrystalline silicon blocks.

Liu *et al.* [187] developed a model for analyzing the casting process and studied the temperature and iron distributions in a silicon block during crystallization by simulations. They conclude that iron diffused into the silicon block even after solidification, which leads to a U-shaped iron profile in z-direction with regions of increased iron concentrations at the bottom and the top of the ingot.

Olsen *et al.* [46] report on the development of a method based on acid leaching for removing metal impurities, namely Al, Fe, and Ti, from commercial silicon nitride powders used for crucible coatings. Clean synthetic fused silica crucibles as well as normal sintered natural quartz crucibles were coated with commercial or purified silicon nitride powder. Lifetime measurements on mc silicon ingots crystallized in these different crucible systems revealed a significant benefit from both cleaner crucibles and cleaner coatings.

In 2008, Kvande *et al.* [47] investigated the material quality of several multicrystalline silicon ingots crystallized in a pilot-scale furnace with crucibles and coatings of different purity by lifetime measurements. A significant increase in lifetime was observed if a higher purity crucible and coating was used. Their investigations also included a crystallization in a standard grade silica crucible with a high purity silica layer between the crucible and the silicon nitride coating, which could have a positive effect on material quality as long as it is sufficiently thick. Furthermore, they tested different silicon nitride layers with varying concentrations of nitride and oxide for improved loading and transfer conditions.

In the same year, Naerland *et al.* [186] performed thorough analyses regarding the origin of the low lifetime edge region close to the crucible system in a *p*-type mc silicon block, applying several electrical, spectroscopic, and microscopic techniques for the identification of impurity concentrations and lifetime. Their investigations revealed that light elements such as O, N, and C, as well as the dislocation density did not increase in the edge zone, whereas an increase in both total and interstitial iron concentration towards the crucible was observed. They attributed the major part of recombination in the edge region to iron point defects, which were suggested to stem from solid state diffusion from crucible and coating.

While previous work was basically restricted to lifetime measurements in the asgrown state of mc silicon blocks and details on the incorporation of specific impurities into the silicon are scarce, knowledge about the interaction between crucible, coating, and silicon during crystallization of mc silicon ingots increased significantly during the time of this PhD thesis owing to the results obtained within the research project SolarWinS [188]. An overview of the impact of impurities from crucible and coating on the material quality of mc silicon is given by Schubert et al. [40]. The investigations of that work included crucibles of standard and very high purity. It was found that the main source for iron impurities in mc silicon blocks crystallized in standard industrial quality crucibles is the crucible itself, whereas cobalt is mainly incorporated from the crucible coating. Thus, the role of crucible and coating could be analyzed separately by measuring the concentrations of iron and cobalt in the crystalized silicon as well as in the crucible and its coating by means of ICP-MS measurements. Additionally, iron point defects were detected by iron imaging. Measurements were compared with simulations for iron and cobalt in-diffusion by Sentaurus Process, and conclusions about the role of impurities from crucible and coating were drawn for large-scale crystallization furnaces.

Contributions to the SolarWinS project by the author of this thesis were published in several papers [40, 48, 69, 101, 177, 178] and are also partly included in the PhD thesis by Bernhard Michl [20]. Section 5.2 is based on references [177, 178] and focuses on the most relevant results obtained by the author.



Figure 5.1: Ratio of minority electron mobility in p-type silicon and minority hole mobility in n-type silicon as a function of resistivity.

# 5.1.2 Impact of *p*- or *n*-type doping on the electrical quality of multicrystalline silicon

For the fabrication of high efficiency solar cells, high quality bulk material with low recombination activity is essential. Regarding the type of doping, *n*-type silicon features advantages like a smaller impact of many metal impurities such as interstitial iron on the electrical material quality due to their lower capture cross sections for minority carriers [73], and the absence of the boron-oxygen-related degradation [28, 29]. On the other hand, minority electron mobility in *p*-type silicon exceeds minority hole mobility in *n*-type silicon by a factor of  $\sim 2-3$  (depending on the doping concentrations). Figure 5.1 shows this ratio as a function of resistivity. Thus, in order to reach a similar minority carrier diffusion length in both materials, excess carrier lifetime in *n*-type silicon has to exceed excess carrier lifetime in *p*-type silicon by this factor to compensate the lower minority carrier mobility. A nice overview of the advantages and disadvantages of using p- or n-type silicon for the production of solar cells is given by Macdonald [189]. From a historical point of view, p-type silicon was preferred over *n*-type due to its larger tolerance against radiation damage for space applications [5]. Another advantage of *p*-type silicon is the lower temperature required for phosphorus diffusions for the emitter formation compared with the temperature of boron diffusions typically required for the formation of the p-n junction on *n*-type substrate [189]. Also, the more uniform resistivity profile of *p*-type ingots due to the lower segregation coefficient of boron compared to phosphorus was assumed to be beneficial [189].

A look at state of the art high efficiency solar cell concepts reveals a significant share of *n*-type solar cells achieving record efficiencies [13]. This also includes the current efficiency world record solar cell by Panasonic, which features a conversion efficiency of 25.6% on *n*-type Cz-substrate [13, 14, 190]. These results reflect the high material quality of *n*-type silicon. In contrast, commercially available multicrystalline
silicon solar cells, including the world record mc-Si solar cell recently presented by Trina Solar [13, 15, 16], are exclusively based on *p*-type substrate, and research on mc *n*-type silicon is scarce. One reason for this might be that the advantage of smaller capture cross sections of several metal impurities is estimated to be less pronounced, as a significant fraction of carriers in mc silicon recombines via decorated extended defects, such as dislocation clusters and grain boundaries. Recombination at such crystal defects plays an important role in mc *n*-type silicon, as for example shown in [77, 191], which is also confirmed by experiments by the author presented in chapter 5.3. In addition, if impurities are present in the form of precipitates, their recombination activity is comparable in mc silicon of both doping types. Metal precipitates will be charged by majority charge carriers, thus attracting minority charge carriers and thereby being an effective recombination center in both mc p- and n-type silicon [69, 192]. Still, the smaller impact of certain transition metals on minority carrier diffusion length in *n*-type silicon could be of notable advantage concerning recombination via dissolved impurities within the grains, and thus lead to a superior efficiency potential of mc *n*-type silicon compared with mc *p*-type silicon, which will be discussed in detail in chapter 5.3. In the following, a short overview of research on mc *n*-type silicon is presented, with the focus on material-related issues. An overview of results for mc *n*-type silicon solar cells can be found in Table 5.1.

First research results on multicrystalline *n*-type silicon were reported by Karg *et al.* [193] in 2000. They focused on the low lifetime area close to the crucible bottom in lowly doped mc *n*- and *p*-type ingots by optical and electrical characterization techniques like FTIR, DLTS, and Hall effect measurements. Microwave photoconductance decay measurements reveal a decreased effective lifetime in as-grown wafers from this region, which is attributed to thermal donors, O1-/O2-defects as well as interstitial vanadium (V<sub>i</sub>) and chromium (Cr<sub>i</sub>) detected by DLTS measurements. After a thermal annealing step (820°C, 1h), the oxygen-related peaks disappear in the DLTS-spectrum, and previously hidden peaks of interstitial titanium (Ti<sub>i</sub>) become visible.

In 2002, Cuevas *et al.* [194] observed exceptionally high minority carrier lifetimes above 1 ms in mc *n*-type silicon after phosphorus gettering. The highest lifetimes reported in their paper are 1.6 ms averaged over several grains and 2.8 ms within the best grains. Furthermore, they observe a dependence of lifetime on doping, decreasing from above 1 ms for 2.3  $\Omega$ cm to 500 µs for 0.9  $\Omega$ cm and 100 µs for 0.36  $\Omega$ cm (all values after P-diffusion gettering). In addition, a slight light induced degradation was observed for gettered mc *n*-type silicon wafers. After 18-20 h of exposure to light from a halogen lamp with an intensity of 100 mW/cm<sup>2</sup> at a temperature of 25°C, a decrease from 1.3 ms 800 µs for 2.3  $\Omega$ cm and a decrease from 530 µs to 440 µs for the 0.9  $\Omega$ cm material was observed. A full lifetime recovery was achieved by a forming gas anneal at 400°C. They suggest that the relatively mild degradation could be due to residual boron in the *n*-type wafers in combination with oxygen. In a further publication by Cuevas *et al.* [195], these results were discussed in more detail with the help of spatially resolved lifetime mappings obtained from infrared carrier density imaging. Additionally, hydrogenation experiments were performed, which turned out to be incapable of improving the material quality. They conclude that "these results open the way for a class of silicon solar cells based on *n*-type mc-Si. High efficiency devices, including rear junction and bifacial designs, are certainly feasible using material of such quality. Based on the experiments presented here, these devices should be stable under illumination." [194]. However, it should last more than ten years that mc *n*-type silicon solar cells deserving the title "high efficiency devices" were actually fabricated (cf. section 5.5).

High minority carrier lifetimes in mc *n*-type silicon were also reported by Schmiga *et al.* [196] in 2004. Stable area-averaged lifetimes of 200  $\mu$ s were measured in the asgrown state. Phosphorus gettering with a subsequent bulk hydrogenation step increased the average minority carrier lifetime to 700  $\mu$ s, with local values exceeding 1 ms. Remarkably, especially the hydrogenation step leaded to a substantial increase. They also fabricated rear-junction Al-emitter solar cells with an efficiency up to 16.0% on monocrystalline *n*-type silicon and up to 11.8% on planar mc *n*-type silicon substante.

From 2004 to 2007, Libal et al. published several papers about mc n-type silicon [197-201] and treated this topic in his PhD thesis [202]. In [197], they report on minority charge carrier lifetimes above 100 µs in as-grown mc *n*-type silicon wafers and above 200 µs (whole wafer average) after P- or Al-gettering, detected by microwave photocurrent decay measurements. Furthermore, the applicability of a BBr<sub>3</sub>-diffusion (935°C, 1 h) without degrading the material quality compared with the initial state was demonstrated. First cell results were reported in [198, 199]. 14.7% were achieved on front junction mc *n*-type silicon solar cell [198]. The cell process featured a BBr<sub>3</sub> emitter diffusion, a POCl<sub>3</sub> back-surface-field diffusion, an oxide emitter passivation and a double antireflection coating (DARC). Bulk lifetime was monitored during the solar cell process by µW-PCD measurements, revealing stable lifetimes between 130  $\mu$ s and 170  $\mu$ s averaged over 5  $\times$  5 cm<sup>2</sup> throughout the whole cell process. The cell process was slightly modified in [199], leading to an efficiency of 15.2% on an mc *n*-type silicon solar cell with an area of 4 cm<sup>2</sup>. Applying an adapted cell process, led to an efficiency of 14.1% on large area  $(12.5 \times 12.5 \text{ cm}^2)$  screen-printed mc *n*-type silicon solar cells. Further optimization of the process introduced in [198] led to a  $2 \times 2$  cm<sup>2</sup> mc *n*-type silicon solar cell with a record efficiency of 16.1% [201]. In [200], Libal *et al.* determined the electrical characteristics and the recombination activity of extended defects in compensated mc *n*-type silicon. A comparison of minority carrier lifetime measurements and temperature-dependent EBIC measurements reveals a strong lifetime increase in defect-free areas after a phosphorus diffusion, whereas only a moderate lifetime increase is observed in areas containing recombination active grain boundaries. Further details on the results for mc *n*-type silicon published by Libal *et al.* [197-200] can be found in his PhD thesis [202].

During the time of Libal's PhD thesis, further publications on the topic of mc *n*-type silicon co-authored by Libal were published by Kopecek *et al.* [203], Acciarri *et al.* [191, 204, 205], and Buck *et al.* [206], which will now be discussed in more detail.

Kopecek *et al.* [203] characterized three mc *n*-type ingots differing in their doping elements (Sb, P, As). They found excellent transport properties with Hall mobilities close to the theoretical limit, and lifetimes exceeding 120  $\mu$ s averaged over large areas detected by  $\mu$ W-PCD, which did not degrade during a BBr<sub>3</sub>-diffusion at moderate temperatures.

Acciarri *et al.* [204] focused on the impact of recombination active defects related to microstructure disorder and impurity contamination on the material quality of mc n-type silicon by spectrally resolved photoluminescence and EBIC measurements. In addition, interstitial oxygen and substitutional carbon concentrations were determined by FTIR measurements. They observe a correlation between an increasing EBIC contrast in the lower and the upper part of the ingot and a decreasing minority carrier diffusion length for the same ingot positions. Grain boundaries, precipitates, and iron impurities were assumed to be the major detrimental defects, whereas the relatively high material quality confirmed the lower sensitivity of n-type silicon to certain metal impurities.

Phosphorus-gettering on mc *n*- and *p*-type silicon was investigated in another publication by Acciarri *et al.* [205], concluding that the beneficial effect of P-gettering does not affect both materials in a significantly different way. A strong increase of lifetime was observed in good grains, whereas gettering of impurities is suppressed by the presence of certain grain boundaries, which even feature an increased recombination activity after P-gettering due to the segregation of impurities. However, the recombination activity of twins was reduced.

These studies on the recombination behavior of grain boundaries and dislocations in mc *n*-type silicon by microwave-detected photoconductance decay ( $\mu$ W-PCD), electron beam induced current (EBIC), and PL spectroscopy before and after phosphorus diffusion were discussed in more detail by Acciarri *et al.* in [191]. They observed a high material quality of mc *n*-type silicon and an increase in average lifetime after Pdiffusion. However, EBIC measurements revealed that the high-temperature Pdiffusion also leads to an increase in recombination activity of certain grain boundaries, which they explain by a redistribution of impurities at the processing temperature and a capture at the deepest sinks. Thus, this work highlights the importance of recombination at extended defects in mc *n*-type silicon.

Buck *et al.* [206] report on advancements of the low cost process for mc *n*-type silicon solar cells introduced by Libal *et al.* [198, 199], which featured a BBr<sub>3</sub>-diffused emitter at the front side and a POCl<sub>3</sub>-diffused rear side. In addition, a bifacial cell geometry was applied in this work. This resulted in a cell efficiency of 14.7% on large area mc *n*-type Si substrate (front illumination), exceeding 17% on Cz substrate. In addition, they report on lifetime measurements before and after boron diffusion with in-situ oxidation at 900°C, which revealed an improvement of material quality, suggesting a gettering effect of the applied B-diffusion. These effects are discussed in more detail in an earlier publication by Libal *et al.* [199].

Martinuzzi *et al.* [207] compared different scanning techniques for the characterization of mc *p*- and *n*-type silicon, such as reflected microwave intensity, spectroscopic photoluminescence, and light beam-induced current. They observed large minority charge carrier lifetimes and diffusion lengths in as-grown *n*-type wafers, which strongly increased after a phosphorus diffusion at 900°C for 1 h.

In 2007, Geerligs *et al.* [77] investigated the effect of phosphorus gettering and hydrogenation on the recombination activity of crystal defects in mc p- and n-type silicon, with the focus on activation and passivation of extended crystal defects. In agreement with results from Acciarri *et al.* [205], they observe an increased recombination activity of extended crystal defects after gettering or annealing, which could be reversed by a subsequent hydrogenation step. Results were similar for both types of doping, with a slight indication of better response to P-gettering of extended crystal defects in mc p-type silicon. Additionally, they investigated the effect of a boron diffusion. Grain boundary recombination was significantly higher after the B-diffusion compared with the P-diffusion, and passivation of extended crystal defects by hydrogenation was less effective. An important conclusion of their work is that hydrogenation seems to be able to passivate the recombination activity of precipitates.

In 2008, Coletti *et al.* [208] focused on the effect of iron contamination in intentionally contaminated mc *p*- and *n*-type silicon ingots. In the as-grown state, minority carrier lifetimes (measured by QSSPC at an excess carrier density of  $10^{15}$  cm<sup>-3</sup>) in the *n*-type wafers exceeded those in the *p*-type wafers by approximately a factor of 6, which was explained with SRH-recombination via interstitial iron. A phosphorus diffusion and an additional hydrogenation step led to a significant increase in minority carrier lifetimes in both ingots, reaching a maximum value of about 50 µs in the *p*-type ingot and above 100 µs in the *n*-type ingot. This correlates with a decrease in interstitial iron concentration from about  $10^{13}$  cm<sup>-3</sup> to  $10^{11}$  cm<sup>-3</sup>. After B/P co-diffusion and hydrogenation, maximum lifetimes in the *p*-type ingot are below 20 µs, whereas the *n*-type ingot still featured minority carrier lifetimes up to 90 µs. The lower lifetime values compared to the phosphorus diffusion were attributed to the lower gettering effectiveness of boron/phosphorus co-diffusion, which was also reflected by higher interstitial iron concentrations in the range of  $10^{12}$  cm<sup>-3</sup>. In addition, this work reports on the characterization of solar cells fabricated from both materials as well as reference mc *p*- and *n*-type silicon ingots.

Very recently, Vähänissi *et al.* [209] studied the impact of boron and phosphorus diffusion gettering on the low lifetime edge region in mc *n*-type silicon. They found that a specific boron diffusion gettering at higher temperatures (930°C) can be more effective than phosphorus diffusion gettering (here 870°C), leading to an improvement of average minority carrier lifetimes from 5  $\mu$ s to 270  $\mu$ s, with local values up to 670  $\mu$ s, in the edge region.

Michl et al. [210] focused on the impact of the high-temperature steps in cell processing, especially the boron diffusion, on the material quality of industrial mc p- and *n*-type silicon wafers. In order to evaluate the impact of material quality on solar cell performance, they suggest focusing on the harmonically averaged diffusion length measured at a generation rate of 0.05 suns with calibrated PL imaging. This accounts for the difference in minority carrier mobility in *p*- and *n*-type silicon and represents the material quality close to maximum power point conditions of a solar cell. After identical processing, the investigated mc *n*-type silicon features superior material quality compared with the mc *p*-type material, and average diffusion length values of 770 µm are reported for mc *n*-type wafers after phosphorus diffusion with a subsequent firing step. For comparison, mc p-type wafers featured an average diffusion length of 540 µm after the same process sequence. However, as typical *n*-type solar cell processing includes a boron diffusion, the solar cell efficiency potential of mc ptype silicon after P-diffusion and firing is compared with that of mc *n*-type silicon after the processing steps of a high-efficiency *n*-type boron front emitter and phosphorus back surface field cell structure (P-diffusion + B-diffusion + firing). A thorough material analysis with the ELBA method (cf. section 3.3) revealed a comparable material related efficiency potential of mc p- and n-type silicon after these processes. Further details on these investigations can be found in Bernhard Michl's PhD thesis in chapter 5.3 [20].

Further publications treating mc *n*-type silicon focused on solar cell fabrication. Results are summarized in Table 5.1, detailed information can be found in the corresponding publications [196, 198, 199, 201, 206, 211-219]. The highest efficiency for a multicrystalline *n*-type silicon solar cell to date was reported by Mihailetchi *et al.* [215] and Komatsu *et al.* [218], who presented a large area (156 cm<sup>2</sup>) screen-printed mc *n*-type silicon solar cell with a boron-diffused emitter and a phosphorus-diffused back surface field, featuring a conversion efficiency of 16.4%.

Publication and year	Comment	
Cuevas et al., 2003 [211]	4 cm <sup>2</sup> back junction (Al-emitter) solar cell	
Schmiga et al., 2004 [196]	4 cm <sup>2</sup> rear-junction solar cell with screen-printed Al-emitter (planar)	
Tool et al., 2004 [212]	156 cm <sup>2</sup> front-junction solar cell (B-diffused emitter and P-diffused BSF)	
Libal <i>et al.</i> , 2005 [198]	4 cm <sup>2</sup> front-junction solar cell (B-diffused emitter and P-diffused BSF)	
Libal et al., 2005 [199]	4 cm <sup>2</sup> solar cell with optimized process from [198] 12.5 $\times$ 12.5 cm <sup>2</sup> solar cell with adapted process	15.2 14.1
Buck <i>et al.</i> , 2005 [213]	<ul> <li>151 cm<sup>2</sup> screen-printed back-junction (Al-emitter)</li> <li>solar cell with P-diffused front surface field</li> <li>25 cm<sup>2</sup> solar cell, same process</li> </ul>	14.4 14.8
Buck et al., 2006 [206]	144 cm <sup>2</sup> bifacial solar cell with optimized process from [198]. Efficiency for front illumination	14.7
Geerligs et al., 2006 [214]	144 cm <sup>2</sup> front-junction solar cell (B-diffused emitter and P-diffused BSF)	
	150 cm <sup>2</sup> rear-junction (Al-emitter) solar cell (untextured)	14.4
Libal et al., 2007 [201]	4 cm <sup>2</sup> B-diffused front emitter and P-diffused BSF	16.1
Mihailetchi <i>et al</i> , 2007 [215], and Komatsu <i>et al.</i> , 2009 [218]	156 cm <sup>2</sup> screen-printed front-junction solar cell (B-diffused emitter, P-diffused BSF, bifacial concept). Efficiency for front illumination	16.4

Table 5.1: Reported efficiencies of mc n-type silicon solar cells.

Dross et al., 2008 [216]	$5 \times 5$ cm <sup>2</sup> rear-junction solar cell (Al-alloy emitter and phosphorus-diffused front surface field)	15.0
Saynova et al. 2008 [217]	156 cm <sup>2</sup> rear-junction solar cell (screen-printed Al-alloy emitter and P-diffused front surface field)	13.6
Singh <i>et al.</i> 2011 [219]	120 cm <sup>2</sup> rear-junction solar cell (screen-printed Al-alloy emitter and P-diffused front surface field)	15.8

5 Towards High Efficiency Multicrystalline Silicon Solar Cells

Despite these partly promising results, especially regarding the superior material quality, mc *n*-type silicon disappeared from the sight of PV research in the last years. This might be due to the more complex processing and the higher costs of high efficiency solar cell concepts, which makes them economically cost-effective only for very high material quality. In addition, fast progress was made in the development of industrially relevant high efficiency *p*-type cell concepts, such as PERC (passivated emitter and rear cell) solar cells featuring point contacts at the rear side. This has led to efficiencies exceeding 19% on large-area multicrystalline *p*-type silicon [220] and a very recently presented new world record mc-Si solar cell featuring an efficiency of 21.25% [13, 15, 16].

Nevertheless, mc *n*-type silicon remains a promising research topic with several unexplored fields:

- A direct comparison of mc n- and p-type silicon crystallized in the same crystallization furnace under identical crystallization conditions has not been performed so far. The availability of such blocks enables to assess the impact of impurities and solar cell processing steps on mc silicon only differing in the doping type. Predictions of the efficiency potential of state of the art mc n-type silicon compared to mc p-type silicon for a complete block are not available, despite their commercial significance. Such investigations in consideration of the material quality after different solar cell processes and the base resistivity variation along the block height are performed in this work and presented in chapter 5.3.
- Due to the identical crystallization of the two blocks, their impurity content can be assumed to be very similar. Thus, measurements of the concentrations of interstitial iron and chromium in the *p*-type block give access to their concentrations in the sister *n*-type block. Together with simulations, this allows for an insight in the recombination mechanisms in mc *n*-type silicon, which will be presented in chapter 5.4.

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• In spite of the very promising electrical material quality, no mc *n*-type silicon solar cells with exceptionally high efficiencies have been fabricated so far. In chapter 5.5, a possible road towards high efficiency multicrystalline silicon solar cells is suggested. This includes the characterization of *n*-type high performance multicrystalline silicon ("HPM-Si") with an optimized crystal structure featuring a very low density of dislocation clusters. In combination with a high efficiency cell concept, which is able to exploit the high electrical quality of this material, mc *n*-type solar cells with very high efficiencies can be fabricated. This is demonstrated by ELBA predictions and solar cell results.

## 5.2 Origin of Impurities in Multicrystalline Silicon

For the fabrication of high efficiency silicon solar cells, bulk material with low recombination losses is required. Crystal defects and impurities from feedstock and crucible system (quartz crucible and coating) harm the electrical material quality of multicrystalline silicon wafers. In this section, the influence of impurities from the crucible system on solar cell efficiency losses in mc silicon solar cells is investigated, focusing on the limitation due to iron. Therefore, the material quality and the efficiency potential of wafers from two different *p*-type multicrystalline silicon blocks are compared: One block was crystallized in a G1 sized crucible of industrial material quality and the other in a crucible of very pure electrically fused silica. To separate the influence of the different crucible materials from other aspects affecting the material quality, the crystallizations were conducted under comparable conditions (temperature profiles, crystallization time, gas flows) in the same crystallization furnace, and a comparable crucible coating as well as the same silicon feedstock was used. This allows for directly assessing the impact of impurities from the crucible on solar cell efficiency. While in this section the influence of the crucible system is discussed, the impact of the coating on contamination is separated from the influence of the crucible in reference [40], where we show that for the high purity crucible the finite impurity source provided by the coating is the main source of iron diffusing into the silicon melt, while for the standard crucible the flux of iron from the crucible dominates after the consumption of iron from the coating. Impurity concentrations in the crucibles and the coating can also be found in references [40, 221]. The material quality is analyzed by imaging the bulk lifetime and the interstitial iron concentration during the solar cell process. Spatially resolved efficiency losses in multicrystalline silicon are estimated from injectiondependent bulk lifetime measurements by an ELBA analysis (cf. section 3.3), and the impact of decorated crystal defects, dissolved impurities diffused into the silicon melt, and impurities diffused into the crystallized silicon by solid-state diffusion is separated and quantified by evaluating the efficiency losses in different regions. The impact of

interstitial iron is determined by the same approach based on spatially resolved measurements of the interstitial iron concentration. Two different cell processes are compared, a standard PERC process with a phosphorous diffusion and a high efficiency PERC approach including an additional oxidation for front surface passivation. Additionally, an atomistic insight into the recombination losses in mc silicon solar cells is obtained by analyzing the role of interstitial iron in detail. Therefore, measurements of the interstitial iron concentration by PL imaging are compared with interstitial iron concentrations extracted from 2-dimensional simulations of iron precipitation at crystal defects during the crystallization process and redistribution during further processing. Finally, a comparison of the injection-dependent lifetime in regions with different interstitial iron allows for a thorough examination of its impact on the crucial solar cell parameters.

Results of this section are published in [177, 178] by the author. They were obtained in collaboration with Bernhard Michl and are also partially published in chapter 5.2 of his PhD thesis [20]. Wafer processing was planned and supervised together with Bernhard Michl. The lifetime and iron evaluations were performed by the author. Efficiency predictions based on spatially resolved and injection-dependent bulk lifetime measurements and interstitial iron concentrations with ELBA were done by Bernhard Michl in collaboration with the author. Detailed analyses of the efficiency data and the injection-dependent impact of interstitial iron on solar cell parameters were performed by the author. Simulations of iron precipitation at crystal defects during crystallization and redistribution during processing with *Sentaurus Process* were done by Jonas Schön.

#### 5.2.1 Materials and methods

For our investigations, boron-doped *p*-type multicrystalline material from two G1 crystallizations ( $\sim 220 \times 220 \times 128 \text{ mm}^3$ ) was used. The crystallizations differed only in the material quality of the crucibles, while the furnace and process recipe remained unchanged. One crystallization was realized in a crucible of standard industrial quality ("*SQ*"), the other one in a crucible of very high purity ("*HP*"). For both crystallizations, high purity feedstock from the Siemens process with a purity level of  $\sim 9N$  was used.

The ingots were cut asymmetrically from the block (*cf.* Figure 5.2, view from above). In this study, we focus on 125 mm  $\times$  62.5 mm-sized wafers, such that impurities diffused into the crystallized block by solid-state diffusion affect only one edge of the wafers (in the following referred to as "edge region"; the rest of the wafer, where no edge-influence on bulk lifetime is visible, is denoted as "central region").



*Figure 5.2: Position of the investigated wafers from G1 crystallization (top view). Figure reprinted from [178].* 



*Figure 5.3: Sample Processing. Diffusion, oxidation and etching are double-side processes. Figure reprinted from [178].* 

Figure 5.3 shows the high temperature processing steps of the different wafers: Three 125 mm  $\times$  62.5 mm sister wafers were chosen from each ingot as sketched in Figure 5.2 and from a central block height. One served as ungettered reference ("Initial"), the other two were subjected to all high temperature steps including phosphorous diffusion of two different cell processes ("PD" and "PD+Ox") and served as

lifetime samples for cell simulations. The only difference between "PD" and "PD+Ox" is the oxidation at 840 °C, which is applied to achieve better front surface passivation in the solar cell. For the lifetime samples, the oxide films and emitter layers were etched away prior to passivating the samples with Al<sub>2</sub>O<sub>3</sub> in order to obtain lifetime samples with identically passivated surfaces. The passivation of the wafers from "PD" and "PD+Ox" was furthermore fired at a temperature of 860 °C. This ensures that all high temperature steps of the corresponding solar cell process were applied to these wafers and the material quality corresponds to that of the final cells.

The high-temperature steps of "PD" correspond to those of a standard PERC process, while the additional oxidation in "PD+Ox" is part of a high efficiency PERC process with a lower front surface recombination based on the additional oxidepassivation.

The material quality of each wafer was investigated by photoluminescence imaging (PLI) calibrated by harmonically modulated luminescence (cf. section 3.2) to obtain images of the minority charge carrier bulk lifetime and images of the interstitial iron concentration (cf. section 3.2). This also allows for imaging the relative carrier bulk lifetime limitation due to interstitial iron. For comparison, local concentrations of iron-boron pairs in as-grown wafers were measured with a conventional Deep Level Transient Spectroscopy (DLTS) [222] setup using the lock-in detection at Dresden University of Technology. As DLTS-measurements are conducted in the dark, iron point defects should exist as FeB-pairs and therefore measured FeB concentrations should be quantitatively comparable with Fe<sub>i</sub> concentrations obtained from lifetime measurements. Injection-dependent PLI calibrated by harmonically modulated luminescence allows for an estimation of the bulk limited cell efficiency potential by the "Efficiency limiting bulk recombination analysis" (ELBA) (cf. section 3.3): Based on the injection-dependent bulk lifetime images, pseudoefficiencies are calculated via PC1D models. The cell structure is a passivated emitter and rear LFC cell with a honeycomb texture. The front, emitter and back side recombination parameters and optics for the PC1D model "PD+Ox" are taken from Reference [223]. In [223] the model was adjusted to measurements of external and internal quantum efficiency and reflection of a honeycomb textured LFC cell that featured also the "PD+Ox" front side. The emitter saturation current density  $J_{0e}$  calculated from  $J_{sc}$  and  $V_{oc}$  is 180 fA/cm<sup>2</sup> for the "PD+Ox" model. The "PD" model differs only from the "PD+Ox" model in the front and emitter recombination. These were adjusted to a  $J_{0e}$  of 630 fA/cm<sup>2</sup> measured on honeycomb textured samples with SiN<sub>x</sub> passivated emitter without oxidation. The higher value reflects the missing oxide passivation and the missing improvements of the emitter profile during the oxidation, which is especially important for a honeycomb

texture due to the large surface area. The base doping of the cell models is taken from the mc samples,  $1.4 \times 10^{16}$  cm<sup>-3</sup> for the *SQ*-material and  $1.7 \times 10^{16}$  cm<sup>-3</sup> for the *HP*material. This allows for a calculation of the pseudo-efficiency limit of the cells (limit due to the cell concept neglecting series resistance losses and bulk recombination, in the following described as "cell limit"): The pseudo-efficiency limit of "PD" is 20.0% for both materials; the limit of "PD+Ox" is slightly higher for the *HP*-wafers (21.3%) than for the SQ-wafers (21.2%). This is due to the higher doping of the *HP*-wafers, and thus, higher  $V_{oc}$  values and will be taken into account when discussing the material related losses in section 5.2.2.2.

The 2-D simulations of the iron precipitation at crystal defects during the crystallization process and redistribution during further processing are performed with Sentaurus Process [224]. The comparison of simulation and measurement allows detailed analyses, and thus, a better understanding of the gettering processes. The Fe distributions before solar cell processing are taken from our experimentally verified simulations of the Fe contamination during the crystallization process [40]. For these simulations only the measured iron concentrations in the crucible, coating, and feedstock are needed as input. In our model for heterogeneous precipitation, iron silicide could nucleate at crystal structures that are inhomogeneously distributed in the 2-D model structure. We assume a mean grain width of 2 mm and a dislocation density of  $8 \times 10^3$  $cm^{-2}$  as in previous simulations [225]. The Fokker-Planck equation, which is used for iron precipitates of different size [226], enables us to predict the precipitate size distributions, the growth rates, and thus, the decrease of the interstitial iron concentration [227]. For the simulation of the phosphorus diffusion, the predictive model from Ref. [228] is used. The phosphorus diffusion gettering model, based on segregation, is taken from [229].

All model parameters, like the segregation coefficient of iron for PDG [229] and the parameters that describe the precipitation at crystal defects [225, 226, 230] are taken from former model calibrations. Thus, the simulations are performed independently of the measurements, using the known temperature profiles as input parameters. For the comparison with the measurements, we averaged the simulated interstitial iron concentration in the 2–D structure excluding the emitter.

#### 5.2.2 Results

5.2.2.1 Defect redistribution during the solar cell process

In order to understand the role of impurities for efficiency losses in mc silicon solar cells, in a first step, the impact of high temperature steps on the impurity distribution in the wafers has to be analyzed. This is done in detail in this section.

Images of bulk lifetime, concentration of interstitial iron, and fraction of recombination due to interstitial iron compared with the total recombination ("FoR<sub>Fei</sub>",  $\tau_{eff}/\tau_{SRH,Fei}$ ) are evaluated in the as-grown state, after a phosphorous diffusion and after a phosphorous diffusion followed by an additional oxidation (*cf.* Figure 5.4 and Figure 5.5). Images of carrier bulk lifetime and fraction of recombination due to Fe<sub>i</sub> are taken at a constant generation rate of 0.1 suns, which is estimated to correspond to an injection level close to MPP-conditions in the solar cell.

1) Before high temperature processing ("Initial"): A significant difference in the material quality of SQ- (cf. Figure 5.4) and HP-wafers (cf. Figure 5.5) is visible prior to any gettering or high temperature step ("initial"): The HP-wafers feature significantly higher bulk lifetimes, lower concentrations of interstitial iron, and a much smaller edge region (cf. left column in Figure 5.4 and Figure 5.5).

2) After gettering ("PD"): During the phosphorous diffusion, impurities are gettered efficiently in both materials, which leads to higher bulk lifetimes and lower Fe<sub>i</sub> concentrations across the whole wafers as well as to a significant reduction of the width of the edge region (*cf.* central column in Figure 5.4 and Figure 5.5). Because of the efficient gettering, the difference in material quality of SQ- and HP-wafers is smaller than in the as-cut state, but the influence of the edge region is still significant for the SQ-material.

3) After gettering and oxidation ("PD+Ox"): Applying an oxidation at 840 °C leads to "poisoning" [231, 232] of the bulk material in both the *HP*- as well as the *SQ*-wafers (*cf.* right column in Figure 5.4 and Figure 5.5). This high temperature step can dissolve iron-precipitates and iron-agglomerations at crystal defects, formed during the crystallization, and leads to a back-diffusion of previously gettered iron from the phosphorous layer into the silicon bulk leading to a higher concentration of interstitial iron across the whole wafers. In addition, the edge zone becomes wider in both materials compared with "PD". Still, after the oxidation the *HP*-wafers feature better material quality than the *SQ*-wafers, both in good grains as well as in the edge region of the wafers, and the edge region is much smaller.



Figure 5.4: SQ-Crucible: Images of bulk lifetime at 0.1 suns generation, interstitial iron concentration, and fraction of recombination due to interstitial iron (FoR<sub>Fei</sub>) at 0.1 suns generation after different processing steps. The edge region of the wafer close to the crucible wall is visible in the top part of the images. Left column: Initial. Central column: After "PD". Right column: After "PD+Ox". Figure based on [178].



Figure 5.5: HP-Crucible: Images of bulk lifetime at 0.1 suns generation, interstitial iron concentration, and fraction of recombination due to interstitial iron (FoR<sub>Fei</sub>) at 0.1 suns generation after different processing steps. The edge region of the wafer close to the crucible wall is visible in the top part of the images. Left column: Initial. Central column: After "PD". Right column: After "PD+Ox". Gray shaded areas indicate the detection limit of Fe-imaging (here: injection level close to cross over point). Figure based on [178].



Figure 5.6: Averaged concentrations of interstitial iron in the two materials after different processing steps. The left half of the graph shows the results of the wafers from the standard quality crucible, the right half the results of the wafers from the high purity crucible. Experimental results determined from carrier lifetime measurements are shown with closed symbols, simulations with Sentaurus Process of the interstitial iron concentrations are shown with open symbols. Measured values below  $1 \times 10^{10}$  cm<sup>-3</sup> are in the range of the detection limit and should be interpreted as upper limit for Fe<sub>i</sub> concentrations. Excellent agreement is found for values determined from DLTS on as grown SQ-wafers. Figure reprinted from [178].

4) Comparison with simulations: We compare the experimentally observed effects with simulations with Sentaurus Process [224] as described in section 5.2.1: Figure 5.6 shows the measured concentrations of interstitial iron in both materials, averaged in the central region (circles) and in the edge of the wafers (triangular symbols), as well as the corresponding simulated concentrations before and after the different high-temperature steps (open symbols). The simulations are in very good agreement with our measurements for values of interstitial iron concentrations above 10<sup>11</sup> cm<sup>-3</sup> for the SQ-material, deviations occur for the HP-material and for low concentrations of interstitial iron below 10<sup>10</sup> cm<sup>-3</sup>. This is due to different reasons: experimental values below  $10^{10}$  cm<sup>-3</sup>, as measured in the central region of the *HP*-wafers after diffusion, are in the range of the detection limit and should be interpreted as upper limit for Fe<sub>i</sub> concentrations. As the visible edge region in the *HP*-wafers is very small and does not reach the plateau of constant interstitial iron concentration as in the case of the SQ-wafers, here experimental values were extracted from the very edge of the wafer. However, the distance from the crucible wall is not known exactly. A deviation in the distance from the crucible between measurements and simulations might explain the differing values in the edge region, as a small deviation in the distance leads to a significant deviation in the concentration of interstitial iron. Still, both measurements and simulations show the same trend, an increasing concentration of interstitial iron in the edge region after the oxidation. As a further verification for the interstitial iron concentrations determined from carrier lifetime measurements, we include in Figure 5.6 values for [FeB] determined from DLTS in as grown *SQ*-wafers. Excellent agreement is found for measurements in the edge region. In the central region, the high detection limit of DLTS ( $4 \times 10^{11}$  cm<sup>-3</sup> for this sample) does not allow a quantitative comparison with iron imaging. The value determined by iron imaging is significantly lower than the DLTS detection limit ( $1.1 \times 10^{11}$  cm<sup>-3</sup>).

5) The role of interstitial iron: The role of interstitial iron as recombination channel can be evaluated by measuring the fraction of recombination due to interstitial iron compared with the total carrier recombination in the wafers ( $\tau_{eff}/\tau_{SRH,Fei}$ ). This is shown in the third row in Figure 5.4 and Figure 5.5. After gettering and oxidation, in the edge region, about 60%-70% of the total recombination is due to Fe<sub>i</sub> in the *HP*-material and even 80%-90% in the *SQ*-material. In the central region, recombination via Fe<sub>i</sub> is less important (15%-20% for *SQ* and less than 10% for *HP*). These results highlight the prominent role of iron as a recombination channel in multicrystalline silicon wafers, especially in crystal regions close to the crucible. As in the central region of the *HP*-wafers limitations are mainly due to crystal defects decorated with metal impurities, the impurity transport from the crystallization environment into the silicon bulk has to be reduced even further. This indicates that besides a high purity crucible also a crucible coating of highest purity has to be used [40].

#### 5.2.2.2 Bulk limited cell efficiency potential

As discussed in the previous section, the additional oxidation harms the material quality of mc wafers. On the other hand, the oxidation leads to a significantly better frontsurface passivation in the solar cell. Hence, for a prediction of cell performances, material limitations as well as limitations due to the cell concept have to be taken into account. This is done in the following by an "Efficiency limiting bulk recombination analysis" (ELBA) (*cf.* section 3.3), which combines measurements of spatially resolved and injection-dependent bulk lifetime with a cell-simulation based on PC1D as explained in section 5.2.1. Modelling the open-circuit voltage  $V_{oc}$ , the short-circuit current  $J_{sc}$ , the pseudo fill factor PFF<sub>bulk</sub> (neglecting series resistance losses, only lower than ideal fill factor due to injection-dependent bulk recombination) and the pseudo efficiency P $\eta_{bulk}$  (neglecting series resistance losses) from the injection-dependent bulk lifetimes and averaging across the wafer delivers the results listed in Table 5.2 for the mc wafers.



Figure 5.7: Spatially resolved simulated cell efficiency potential ( $P\eta_{bulk}$ ). The left half of the images refers to the cell process without oxidation ("PD"), the right half with the additional oxidation ("PD+Ox"). (a) Standard Quality crucible. (b) High Purity crucible. Figure reprinted from [178].

In combination with the spatially resolved simulated pseudoefficiency  $P\eta_{bulk}$ , these values can be discussed in detail. Figure 5.7(a) shows  $P\eta_{bulk}$  for the *SQ*-wafer, Figure 5.7(b) for the *HP*-wafer. The left half of the images refers to the cell process without oxidation, the right half to the high-efficiency cell process. Both materials benefit from the additional front-surface passivation, which leads to a strong increase in  $V_{oc}$  (*cf.* first row in Table 5.2) which is visible in a homogeneous increase in efficiencies in the good grains. On the other hand, the increase in  $J_{sc}$  is smaller and PFF<sub>bulk</sub> even

	SQ PD	SQ PD+Ox	HP PD	HP PD+Ox
$V_{\rm oc}~({\rm mV})$	625	639	628	646
$J_{\rm sc}~({\rm mA/cm^2})$	36.7	37.0	37.1	37.5
PFF <sub>bulk</sub> (%)	82.7	82.4	83.0	82.8
$P\eta_{\text{bulk}}$ (%)	19.0	19.5	19.3	20.1
cell limit (%)	20.0	21.2	20.0	21.3
$\eta \ loss (\%_{abs})$	-1.0	-1.7	-0.7	-1.2

*Table 5.2: Globally averaged cell parameters simulated from injection dependent bulk lifetime measurements.* 



Figure 5.8: Spatially resolved simulated  $J_{sc}$  after the cell process with oxidation ("PD+Ox"). (left) Standard Quality crucible. (right) High Purity crucible. Figure reprinted from [177].

decreases after the additional oxidation due to the material degradation during the high-temperature step. As we will discuss in more detail in section 5.2.2.3, the bulk lifetime in regions of low material quality like the edge region or dislocation clusters features strong injection dependence. As the injection conditions at  $J_{sc}$  and MPP are significantly lower than at  $V_{oc}$ , the global values of  $J_{sc}$  and PFF<sub>bulk</sub> especially suffer from the material degradation after oxidation in these regions. Figure 5.8 highlights this effect:  $J_{sc}$ -losses after oxidation are particularly high in regions of low material quality, which leads to a decrease in efficiency potential at dislocation clusters and in the edge region after "PD+Ox" (cf. Figure 5.7). These results show the double-edged impact of the high efficiency solar cell process "PD+Ox": While  $V_{oc}$  benefits strongly from the additional oxide passivation on the front side, the benefit in  $J_{sc}$  is smaller and PFF<sub>bulk</sub> even decreases due to the lower material quality after the high temperature step. In combination, the high efficiency cell process leads to a raise in pseudo efficiency from 19.0% to 19.5% for the SO-material and from 19.3% to 20.1% for the HPmaterial (cf. Table 5.2). Due to the better material quality of the HP-wafers, the efficiency boost obtained by "PD+Ox" on these wafers (+0.8%<sub>abs</sub>) is larger than on the SQ-wafers ( $+0.5\%_{abs}$ ). This elucidates the benefit of crucibles of higher purity: While for the standard cell process the difference in material quality is less critical for solar cell efficiencies, it becomes more important for high-efficiency cell processes.

In a last step, we discuss the origin of the efficiency losses after the high-temperature oxidation in detail. Therefore, we evaluated the efficiency potential in the best 1 cm  $\times$  1 cm area, which is virtually void of crystal defects in both materials. The



Figure 5.9: Efficiency losses in multicrystalline silicon from (left) standard crucible and from (right) high purity crucible after the "PD+Ox" process. Figure based on [178].

loss compared with the cell limit can be attributed to homogeneously distributed impurities that diffused into the liquid silicon melt before crystallization and remained after processing (*cf.* first (orange) part of the columns in Figure 5.9). To assess the influence of decorated crystal defects such as dislocations and grain boundaries, in a second step the efficiency potential in the central region (without any edge influence) is evaluated. The additional loss can then be attributed to recombination via impurities at dislocations and grain boundaries ("decorated crystal defects", *cf.* second (cyan) part of the columns in Figure 5.9). In a last step, by evaluating the efficiency potential of the whole wafer, also the edge region and therefore the efficiency loss due to impurities diffused into the crystal by solid-state diffusion is taken into account ("edge region", *cf.* third (gray) part of the columns in Figure 5.9).

The main losses in the SQ-material can be attributed to the remaining homogeneously distributed impurities that had diffused into the melt before crystallization (- $0.6\%_{abs}$ ) and impurities diffused into the solidified crystal by solid-state diffusion visible in the large edge region (width on the wafer ~25 mm; - $0.6\%_{abs}$ ). In contrast, in the HP-material, the main losses can be attributed to recombination active crystal defects like dislocation clusters and grain boundaries (- $0.7\%_{abs}$ ). In total, the losses sum up to - $1.7\%_{abs}$  in the SQ-material and - $1.2\%_{abs}$  in the HP-material, leading to a significantly higher efficiency potential in the HP-material of 20.1% compared with 19.5% in the SQ-material (additional + $0.1\%_{abs}$  due to higher doping in HP). As the losses in the HP-material related to decorated crystal defects are even higher than in the SQ-material (HP: - $0.7\%_{abs}$ ; SQ: - $0.5\%_{abs}$ ), the benefit from purer crucible materials could be even stronger if the crystal quality of both materials was comparable. In this specific case, the same temperature profiles for crystallization were used for SQ and HP without optimizing the profile for the thinner HP crucible. This might be a reason for the lower crystal quality of the HP-material. In general, using a high purity crucible should not impact the crystal quality if the temperature profiles were adapted to the thinner crucible.

With the help of measured images of interstitial iron concentrations, we can now evaluate the impact of interstitial iron on cell level. To do so, we performed the same simulations as previously mentioned with the measured concentration of interstitial iron as the only bulk lifetime limiting recombination channel (input for cell simulation: injection dependent images of  $\tau_{SRH,Fei}$ ). The result is plotted in Figure 5.9 as the columns labelled "Fe<sub>i</sub>", which express the corresponding efficiency losses due to interstitial iron. A major part of the losses due to segregated impurities that had diffused into the melt can be attributed to interstitial iron (~40% for both materials), losses due to the edge region are even dominated by interstitial iron (~90%). In contrast, interstitial iron plays a negligible role for losses due to decorated defects. However, these losses might also be attributed to iron or iron precipitates bound to crystal defects.

#### 5.2.2.3 Injection-dependent impact of interstitial iron on cell parameters

As already shown in the previous section, interstitial iron plays a major role concerning efficiency losses in mc silicon. In the following, we want to shed more light on the injection dependence of recombination via Fe<sub>i</sub> and its meaning for the different solar cell parameters. Therefore, we analyzed injection dependent bulk lifetimes on two different spots of the HP-wafer after phosphorous diffusion and oxidation (cf. Figure 5.10). Trends for the SQ-wafer are the same and will therefore not be discussed here. Spot 1 with some good grains as well as some dislocations and grain boundaries features a medium bulk lifetime at 0.1 suns and a low to medium concentration of interstitial iron, whereas spot 2 features a high concentration of interstitial iron due to its closer position to the crucible wall. In Figure 5.10, injection dependent bulk lifetimes in the two spots (square root harmonic mean) are shown and compared with the SRH-limit (including Auger-recombination) due to the measured concentration of interstitial iron on the same spots. The spatially resolved Fe<sub>i</sub> concentrations were recalculated according to the SRH-theory with the parameters published by Istratov et al. [113] including Auger-recombination to spatially resolved and injection-dependent bulk lifetimes, which were then averaged according to a square root harmonic mean. This ensures that calculated bulk lifetimes from Fe<sub>i</sub> are averaged like the measured bulk lifetimes.



Figure 5.10: Injection dependent bulk lifetimes on different spots of a wafer compared with the SRH-limit due to the concentration of interstitial iron [24] on the same spot. Spot 1 features a rather flat dependence on the injection level and a low limitation due to interstitial iron, whereas Spot 2 shows a strong injection dependence of bulk lifetime due to the higher concentration of interstitial iron. The fraction of recombination due to interstitial iron increases strongly for lower injection levels. (a) Bulk lifetime map at 0.1 suns. (b) Injection-dependent bulk lifetime. (c)  $Fe_i$  map. (d) Limitation due to  $Fe_i$ . Figure based on [178].

Because of the higher concentration of interstitial iron, spot 2 features a much stronger injection dependence than spot 1. The injection dependence of the Fe<sub>i</sub>-limited bulk lifetime shows a very similar trend compared with the measured bulk lifetime supporting the accuracy of measurements of the interstitial iron concentration by means of FeB-pairing, as this curve does not depend on the splitting and pairing of

FeB-pairs. A very important point has to be emphasized here: measured bulk lifetimes on spot 2 are higher than on spot 1 for generation rates above one sun (injection levels higher than  $10^{15}$  cm<sup>-3</sup> in the graph), while this is not the case for lower injection due to the stronger impact of interstitial iron. This is of utmost importance for material characterization, as the injection level under MPP-conditions in a solar cell made from this wafer is around  $3 \times 10^{13}$  cm<sup>-3</sup>. This means that bulk lifetimes measured at an injection level above  $10^{15}$  cm<sup>-3</sup> would lead to misleading interpretations of the material quality. Bulk lifetimes in the low injection regimes that represent MPP- or  $J_{sc}$ -conditions are easily accessible experimentally by using the self-consistent calibration by harmonically modulated luminescence, whereas a QSSPC-measurement [123] could be affected by trapping at these injection levels.

Figure 5.10(d) shows the fraction of recombination due to interstitial iron (FoR<sub>Fei</sub>, SRH- and Auger-recombination considered) as a function of excess carrier density. While the dependence on injection level is rather low for spot 1, the limitation due to interstitial iron is increasing strongly for lower injection levels on spot 2. This behavior is crucial for the solar cell parameters, as has also been discussed by Macdonald *et al.* in [233]. While the influence of interstitial iron on  $V_{oc}$  is rather small (high injection level above  $10^{14}$  cm<sup>-3</sup>, FoR<sub>Fei</sub> around 30%), it affects  $J_{sc}$ , MPP and the fill factor more strongly (*cf.* Table 5.2) as the excess carrier density is much lower under these conditions (FoR<sub>Fei</sub> around 60%). For even lower injection levels, Fe<sub>i</sub> becomes the most dominant recombination channel (FoR<sub>Fei</sub> around 80% for an excess carrier density of  $10^{12}$  cm<sup>-3</sup>).

It has to be kept in mind that these evaluations only treat the concentration of interstitial iron. The total impact of iron will be even stronger, especially for higher injection levels, as here the role of iron precipitates becomes more important compared with interstitial iron [69]. This highlights the dominant role of iron as a recombination active impurity in multicrystalline silicon.

## 5.2.3 Conclusion

In this study, we showed for G1 sized crucibles that efficiency losses in multicrystalline silicon can be reduced by crystallizing high purity feedstock from the Siemens process with a purity level of ~9N in crucibles of pure material quality (here electrically fused silica). While the difference in material quality of wafers from a standard quality crucible and wafers from a high purity crucible is less critical for a standard solar cell process, the benefit of the high purity crucible is especially notable in solar cell efficiencies after a high efficiency solar cell process comprising a high temperature oxidation. In the high purity wafers, the loss in good grains due to remaining dissolved impurities that had diffused into the silicon melt is reduced by around 40% compared with the standard quality material. Additionally, the wider edge region in material from standard quality crucibles plays a crucial role, in our case losses due to the edge region are reduced by 85% in the material from the high purity crucible, mainly because the size of the edge region on the wafers decreases from about 25 mm to 6 mm. However, as the crystal structure of the material from the standard crucible is better, losses due to decorated crystal defects are larger in the material from the high purity crucible. This should be avoidable by applying a crystallization process adapted to the thermal properties of the high purity crucible, which differ from those of the standard crucible mainly due the different crucible thickness. Limitations like crystal defects decorated with metal impurities indicate that besides a high purity crucible also a crucible coating of highest purity has to be used to reduce the impurity transport from the crystallization environment into the silicon bulk as far as possible.

In industry, larger crucibles of up to 1000 kg of silicon (G6) are used. On the basis of the experimentally validated simulations, our results on G1 blocks (14 kg) can be transferred directly to these ingot sizes [40]. Our general conclusions remain valid as the major part of the wafers will still be influenced by the edge region (20 from 36 wafers in G6 are "edge wafers") and the edge region itself even becomes wider. However, the width of the edge region in the wafers depends strongly on the fraction cut off from the entire block. Further details on the transfer to larger crucible sizes can be found in [40]. The cost difference between the standard quality and the high purity crucible is difficult to assess, as the high purity crucible used for this work was a custom product for laboratory experiments.

Additionally, we elaborated on the role of interstitial iron and showed that it plays a major role for losses due to segregated impurities and dominates the losses in the edge region. At crystal defects, other impurities than interstitial iron are dominating the losses, which may well be iron precipitates or iron bound to dislocations or grain boundaries. The strong injection dependence of recombination at interstitial iron is crucial for the solar cell parameters: while  $V_{oc}$  is weakly influenced, Fe<sub>i</sub> affects  $J_{sc}$ , MPP and the fill factor more strongly.

# 5.3 *n*-type Doping: Increasing the Efficiency Potential of Multicrystalline Silicon

The work presented in this chapter aims for a quantitative investigation of the material limitations and the efficiency potential of an entire multicrystalline *n*-type silicon block in comparison to a multicrystalline *p*-type block of the same purity level in order to predict the potential of mc *n*-type silicon for the industrial production of solar cells. Therefore, two standard multicrystalline silicon blocks were crystallized under identical conditions (same high purity feedstock, crucible system, and temperature profiles),

only differing in their type of doping. The material quality of wafers along the whole block height is analyzed after different solar cell process steps by photoluminescence imaging of the diffusion length. The bulk recombination related efficiency losses are assessed by the ELBA method (*cf.* section 3.3) combining injection dependent lifetime images with PC1D cell simulations. The influence of the base resistivity variation along the block is considered in the PC1D cell simulations and backed up by Sentaurus Device simulations. This analysis predicts a significantly higher material-related efficiency potential after typical solar cell processes along the whole block height for mc n-type silicon compared to mc p-type silicon. In addition the efficiency potential for mc n-type silicon depends less on block position.

In the first part, the investigated material, the sample processing, and the characterization techniques as well as the performed simulations are introduced. In the second part, evaluations of the material quality, the influence of the base resistivity variation, and the efficiency potential combined with a detailed quantification of the efficiency losses are presented. Thus, the origins of the efficiency gain of mc n-type silicon compared to mc p-type silicon can be understood in detail. Finally, we suggest a resistivity optimization for a further efficiency gain in mc n-type silicon.

Results of this section are published in [179, 180] by the author. They were obtained in collaboration with Andreas Kleiber and are also partially included in his bachelor thesis [234], which was supervised by the author. The mc silicon ingots were crystallized by the crystallization group of Fraunhofer ISE under supervision of Stephan Riepe and Patricia Krenckel. Wafer processing was planned by the author and supervised by the author together with Andreas Kleiber. Characterization of the material was performed by the author together with Andreas Kleiber, efficiency predictions based on spatially resolved and injection-dependent bulk lifetime measurements were done by the author in collaboration with Bernhard Michl. PC1D-simulations, detailed analyses of the efficiency data and the estimation of the benefit from a lower base resistivity were performed by the author. 3-D simulations with Sentaurus Device were done by Heiko Steinkemper in collaboration with the author.

#### 5.3.1 Materials and methods

#### A. Crystallization and sample processing

For our investigations, an mc *n*-type silicon block and an mc *p*-type silicon block, differing only in their type of doping, were crystallized at Fraunhofer ISE. The same high purity feedstock (purity level of ~9N), standard quartz crucible, and crucible coating are used for the crystallization of both blocks in the same laboratory crystallization furnace adapted for the crystallization of G1 and G2 size silicon blocks. This ensures a comparable impurity distribution in both blocks. Each G2 size block was cut



Figure 5.11: Photography of one of the investigated blocks.  $125 \times 125 \text{ mm}^2$  wafers were cut from the lower central brick (" $A_{middle}$ ") as depicted by the white frame. Figure reprinted from [180].

into three bricks, one of which was positioned symmetrically in one half. In this work we focused on  $125 \times 125 \text{ mm}^2$  wafers from a brick "A<sub>middle</sub>" as depicted in Figure 5.11 featuring an edge region with limited material quality only at one side. In Figure 5.16 and Figure 5.18, this region of limited material quality is visible at the right edge of the images.

To investigate the material quality along the whole block height, wafers were selected from three block positions, in the following denoted as "bottom", "middle" and "top". Identical block heights were chosen for the *n*- and the *p*-type wafers to ensure comparable impurity content in each group of wafers.

Lifetime samples were produced from these wafers: the wafers were subjected to the high temperature steps of three different solar cell processes depicted in Figure 5.12, representing a range of current high-efficiency processing development for both doping types. Wafers without any high temperature step from the initial group served as references. The *n*-type wafers were surface-passivated with a SiN-layer deposited at 250°C, the *p*-type wafers with a  $Al_2O_3$ -layer deposited at 200°C prior to an anneal at 400°C (*n*- and *p*-type wafers). The processes included all steps of the corresponding solar cell process except the metallization. This ensures that the material quality of the lifetime samples is identical to the material quality of the final cell and allows for an analysis of the material related efficiency losses. By investigating samples from bottom to top of the blocks we account for all effects like variations in doping and defect distribution. The process steps of the group "P-Diff+Firing" (phosphorus diffusion and firing) are representative for a PERC cell concept [220] on *p*-type substrate, those of the group "B-Diff" (boron diffusion) are typical for a PassDop cell



Figure 5.12: Sample Processing. The process steps of the group "P-Diff+Firing" (phosphorus diffusion and firing) are representative for a PERC cell concept [220] on p-type substrate, those of the group "B-Diff" (boron diffusion) are typical for a PassDop cell concept with low-temperature metallization [235] on n-type substrate. Figure adapted from [180].

concept with low-temperature metallization [235] on *n*-type substrate. In the group "P-Diff" (phosphorus diffusion), the high temperature firing step was left out. By comparing wafers from this group with the material after P-Diff+Firing, we could assess the influence of the firing step on the material quality of mc p- and *n*-type Si.

## B. Characterization Methods

The material quality of each wafer was investigated by photoluminescence imaging (PLI) calibrated by harmonically modulated photoluminescence [100] to obtain images of the minority carrier diffusion length. Although in terms of recombination properties a comparison of excess carrier lifetimes of mc n- and p-type silicon would be the method of choice, we prefer a comparison of the diffusion length, which is the better figure of merit for solar cell efficiencies. By comparing diffusion lengths, the large difference in minority carrier mobility in n- and p-type silicon is accounted for, which allows for a better comparability of the material quality. Calibrated PLI was also applied to image the concentration of interstitial iron in the p-type wafers [110]. As discussed before, this also gives access to the interstitial iron concentration in the n-type wafers, as the impurity content should be comparable due to the identical crystallization conditions.

Finally, injection-dependent calibrated PLI allows for an estimation of the solar cell efficiency potential by the ELBA method (*cf.* section 3.3): Efficiency maps are calculated based on the injection dependent images of bulk recombination combined with PC1D cell simulations. The efficiency potential is predicted for *p*-type wafers of the process group "P-Diff+Firing" (a typical PERC cell concept on *p*-type), and *n*-type wafers of the group "B-Diff" (a typical PassDop cell concept with low-temperature

metallization) and "P-Diff". The choice of these groups will be motivated in detail in section 5.3.2-C. In this work, the cell concepts used for the simulations were chosen such that the efficiency limit without any bulk recombination ("cell limit") is the same for all concepts and both *n*- and *p*-type material. This allows for a direct comparison of the material related efficiency losses. For the *n*-type samples of the process group "B-Diff", the PassDop concept described in [235] in combination with a Honeycomb texture [223] is used. This leads to an efficiency limit without bulk recombination of 21.8%. The same model was used for the *n*-type material investigated here. For the *p*-type samples of the process group "P-Diff+Firing", also a model with a dielectric rear surface passivation [220] with the same optics and the same dark saturation current densities for the front and rear side as in the *n*-type model ( $J_{0,rear} = 45$  fA/cm<sup>2</sup>,  $J_{0,front} = 25$  fA/cm<sup>2</sup>) is used. This leads to nearly the same efficiency limit without bulk recombination current densition of 21.7%.

The varying base resistivity is accounted for in the PC1D simulations. To support the quality of the predictions from PC1D, independent 3D simulations with Sentaurus Device were performed. *N*- and *p*-type PERC structures featuring point contacts and local back surface fields on the rear side were investigated for different rear contact pitches. In contrast to the PC1D simulations lateral effects, for example transport of majority carriers to the point contacts at the backside, are accounted for as well. The cell efficiency is predicted for a variation of the bulk lifetime from 1  $\mu$ s to 10 ms. To determine the influence of the base resistivity, simulations were performed for 1  $\Omega$ cm and 3  $\Omega$ cm material, which correspond to the base resistivity extremes in the *n*-type wafers investigated in this work. Results are presented in section 5.3.2-A.

#### 5.3.2 Results

#### A. Crystallization and sample processing

Before discussing the recombination properties of the material, we will first focus on the doping variation along the block height. Figure 5.13 shows the base resistivity as a function of the block height for the *p*- and the *n*-type brick. While the *p*-type brick features a very homogeneous resistivity along the whole block height due to the segregation coefficient of boron of 0.8, the lower segregation coefficient of phosphorus (0.35) leads to a large variation in the resistivity from higher than 3  $\Omega$ cm at the block bottom to lower than 1  $\Omega$ cm at the block top of the *n*-type crystal. As depicted in the graph, wafers were selected from three block positions corresponding to a base resistivity of 1.1  $\Omega$ cm (bottom), 1.1  $\Omega$ cm (middle), and 0.9  $\Omega$ cm (top) in the *p*-type brick and 2.8  $\Omega$ cm (bottom), 2.1  $\Omega$ cm (middle), and 1.3  $\Omega$ cm (top) in the *n*-type brick. These values were obtained from inductive measurements on wafer level. Slight devia-



Figure 5.13: Resistivity profiles of the n- and p-type bricks along the block height obtained from Eddy Current measurements at the block sides and inductive measurements at wafer level. Figure reprinted from [180].

tions compared to Eddy Current measurements on block level plotted in Figure 5.13 are attributed to a non-planar crystallization front and changing convection patterns in the silicon melt during crystallization leading to lateral inhomogeneities as well as to uncertainties in the measurement techniques.

As shown in [236, 237], the base resistivity can have a significant influence on solar cell efficiency. In section 5.3.2-C, a prediction of the efficiency potential is done in based on a PC1D model. In order to validate the procedure of accounting for the base resistivity variation in the one-dimensional PC1D simulations, the influence of a base resistivity variation on the cell efficiency is compared with 3D simulations using Sentaurus Device as explained in the last section. Figure 5.14a) shows the cell efficiency as a function of bulk lifetime simulated with the PC1D cell models used in this work for *n*- and *p*-type silicon with a base resistivity of 1  $\Omega$ cm and 3  $\Omega$ cm. In both cases, a lower base resistivity leads to higher efficiencies for low to medium bulk lifetimes. For very low bulk recombination, the base resistivity does not significantly influence the cell efficiency any more. As efficiencies are compared as a function of lifetime, the *p*-type curves are shifted to higher values compared to the *n*-type curves due to the higher minority carrier mobility.



Figure 5.14: Impact of base resistivity on the simulated cell efficiency. Graph a) shows the efficiency simulated with the PC1D cell models used in this work as a function of bulk lifetime for n- and p-type silicon with a base resistivity of 1  $\Omega$ cm and 3  $\Omega$ cm. Graph b) compares the efficiency gain obtained with a 1  $\Omega$ cm base compared to a 3  $\Omega$ cm base as a function of bulk lifetime simulated with PC1D and Sentaurus Device. Excellent agreement is obtained for n-type silicon up to 1 ms. Figure reprinted from [180].

The Sentaurus Device simulations revealed that the optimum pitch did not depend significantly on the resistivity variation or the lifetime variation. This allows the choice of one pitch regardless of the resistivity or the lifetime leading to maximum differences in the efficiency of less than  $0.05\%_{abs}$  compared to the optimum pitch at the specific resistivity and lifetime. Figure 5.14b) highlights the efficiency gain obtained with a 1  $\Omega$ cm base compared to a 3  $\Omega$ cm base as a function of bulk lifetime simulated with Sentaurus Device (3D) (at the optimum pitch of 160 µm for *n*-type and 320 µm for *p*-type) and with PC1D. This efficiency gain features a maximum at low to medium bulk lifetime values between 10 µs and 100 µs. For high lifetimes, the base resistivity does not impact the efficiency significantly. Especially for *n*-type silicon, the PC1D



Figure 5.15: Harmonically averaged diffusion length across wafers from three different positions of the n-type block (filled columns) and the p-type block (dashed columns) at a generation rate of 0.05 suns, which is estimated to correspond to an injection level close to MPP-conditions in the solar cell. The n-type samples feature significantly higher diffusion lengths along the whole brick after all process steps. Figure reprinted from [180].

and Sentaurus Device simulations of efficiency gains are in very good agreement. This supports the approach of considering the base resistivity variation in the PC1D cell models for the prediction of the efficiency potential with ELBA applied in this work. The slight deviation at high lifetimes is due to lateral effects (transport of majority carriers to the point contacts at the backside) which are not accounted for in the 1D simulations with PC1D.

## B. Material Quality

In a second step, the material quality after different solar cell process steps is evaluated. Figure 5.15 shows the harmonically averaged diffusion length across wafers from three different positions of the *n*-type block (filled columns) and the *p*-type block (dashed columns) at a generation rate of 0.05 suns, which is estimated to correspond to an injection level close to MPP-conditions in the solar cell. As mentioned before, comparing the diffusion length in *n*- and *p*-type silicon already accounts for the lower minority carrier mobility in n-type, such that this allows for a direct comparison of the material quality of mc *n*- and *p*-type silicon.

The *n*-type samples feature significantly higher diffusion lengths along the whole brick after all process steps. Applying a phosphorus diffusion improves the diffusion

length in both blocks due to gettering of impurities. Especially in the *n*-type wafers, the diffusion length is increased significantly (excess carrier lifetimes averaged across the best  $1 \times 1$  cm<sup>2</sup> exceed 2 ms). A subsequent firing step further enhances the diffusion length in *p*-type silicon, which can be attributed to a hydrogen passivation from the silicon nitride stack [238], while it significantly reduces the diffusion length in the mc *n*-type wafers. Cooling to room temperature is typically much faster in a firing step compared with doping process in a tube furnace. Thus a possible explanation of the decrease in diffusion length could be initially large precipitates that dissolve and redistribute to a higher density of smaller precipitates or dissolved impurities limiting in *n*-type silicon. These dissolved impurities could be  $Co_s$ ,  $Cr_i$  or other defects that have comparable or even higher impact on the charge carrier lifetime in *n*-type. An alternative explanation is the diffusion of formerly gettered impurities from the emitter into the bulk [232, 239]. The boron diffusion degrades the material quality of both, the *n*- and *p*-type wafers, compared to the initial state. However, the diffusion length in *n*-type is still on a high level ( $\geq 300 \mu m$ ; excess carrier lifetimes averaged across the best  $1 \times 1$  cm<sup>2</sup> exceed 1 ms) and much larger than in *p*-type after any process step. This is of importance, as a standard *n*-type solar cell process includes a boron diffusion. The material degradation after the boron diffusion is attributed to the higher temperature (890°C) compared with the phosphorus diffusion (800°C) and to the lower gettering efficacy of the boron diffusion. The effectiveness of boron diffusion gettering strongly depends on the process parameters, as discussed in detail in [79]: While an optimized boron diffusion gettering can effectively getter metal impurities such as Fe and, thus, increase the electrical quality of the bulk material, a standard boron diffusion can be virtually ineffective in terms of gettering at temperatures above 850°C and even harm the material quality due to a potential cross-contamination from the furnace tube at high temperatures, as suggested in [79]. The higher temperatures of a boron diffusion also lead to a stronger dissolution of precipitates compared with a phosphorus diffusion at lower temperatures, which could additionally harm the material quality. Since it is the aim of this study to investigate the influence of high performance cell processes on the material quality of mc silicon, the boron diffusion chosen here was optimized for emitter and solar cell performance and features a rather weak gettering efficacy.

Focusing on the material quality along the block height, we observe a different trend in the n- and p-type block: While the material quality increases towards the top in the p-type brick, it decreases in the n-type brick after most process steps. This can be explained by the different limitations in mc n- and p-type silicon, which can be observed in the diffusion length images. Figure 5.16 shows the central stripe of each wafer after each process step from the block bottom to the block top for n-type (left



Figure 5.16: Diffusion length images. Blurring was reduced by the use of a 1000-nm short-pass filter. Each image shows the diffusion length of a central stripe  $(125 \times 31.25 \text{ mm}^2)$  of the wafers at a generation rate of 0.05 suns after each process step for a certain block position. The impact of the edge region close to the crucible is visible on the right side of the wafers. The left column shows the results on the n-type wafers, the right column on the p-type wafers. Note the factor of four in the scale of the n-type wafers compared with the p-type wafers. Figure reprinted from [180].

column) and *p*-type (right column). Blurring in the PL images was reduced by applying a 1000-nm short-pass filter in addition to the standard set of long-pass filters in front of the charge-coupled device camera.

The increasing material quality in the *p*-type wafers towards the block top can be explained as follows: The lowest position is still affected by dissolved impurities diffused into the crystallized block from the crucible bottom by solid-state diffusion, especially iron. This lowers the diffusion length across the whole wafer. Iron imaging revealed a concentration of interstitial iron of  $3 \times 10^{11}$  cm<sup>-3</sup> in the center of the initial wafer from the block bottom, limiting the lifetime in 1.1  $\Omega$ cm *p*-type silicon to 8µs at low level injection. At the medium block height, the measured concentration of interstitial iron in the center of the initial wafer is one order of magnitude lower  $(2.5 \times 10^{10} \text{ cm}^{-3})$  than at the block bottom. Here, only the edge region is limited by a large concentration of interstitial iron of  $1 \times 10^{12}$  cm<sup>-3</sup>. The additional increase in the averaged diffusion length from medium block height to the block top can be attributed to the smaller edge region, which has nearly completely disappeared in the wafers from the block top. The edge region is limited by impurities diffused into the crystallized block by solid-state diffusion during the cooling of the block, mainly iron. As the upper part crystallized later, here the time for in-diffusion and, thus, the width of the edge region is reduced. As it is mainly dissolved impurities that limit the diffusion

length in mc *p*-type silicon, these effects lead to the observed trends in the material

quality along the block height.

In mc *n*-type silicon, the recombination properties of impurities are significantly different. We will discuss the effect on the example of interstitial iron. Iron imaging performed on the *p*-type wafers revealed a maximum concentration of interstitial iron of  $3 \times 10^{12}$  cm<sup>-3</sup> in the edge region of initial wafers from the block bottom. Due to the asymmetrical capture cross sections for electrons and holes, lifetime in 1.1 Ωcm *p*-type silicon is limited by this concentration of interstitial iron below 1 µs at low level injection, while the limitation in *n*-type silicon is well above 400 µs. Measured lifetimes in the edge region of an initial *n*-type wafer from the block bottom are lower than 100 µs, which is why we can exclude a strong limitation by interstitial iron. However, iron precipitates could contribute significantly to the recombination in the edge region [69, 192], which will be discussed in more detail in section 5.4. As discussed before, the maximum concentration of interstitial iron in the central parts of the wafers was measured to be  $3 \times 10^{11}$  cm<sup>-3</sup> before processing for wafers from the block bottom, which limits the lifetime in *n*-type silicon above 4 ms. Therefore, we can also exclude a limitation by interstitial iron in the central parts of the *n*-type wafers. As visible in the diffusion length images in Figure 5.16, it is mainly extended crystal defects, probably decorated with impurities, that limit the material quality in mc *n*-type silicon. As the density of crystal defects, such as grain boundaries and dislocation clusters, increases towards the block top [240], the averaged diffusion length decreases with increasing block height in the *n*-type brick in the initial state and after the P- and B-diffusion. An exception is observed after firing, which increases the impact of homogeneously distributed impurities and inverts the trend. The diffusion length image of the *n*-type wafer from the block bottom reveals a significantly larger edge region of low diffusion length after P-diffusion and firing. The reason for this is still unclear and currently under investigation. As mentioned above, it could be attributed to either a redistribution of precipitates or the dissolution of impurities with a comparable or even higher impact on the charge carrier lifetime in *n*-type.

#### C. Solar cell efficiency potential

Combining injection-dependent bulk lifetime images with PC1D cell simulations as explained in section 5.3.1-B, the efficiency potential is predicted for *p*-type wafers of the process group "P-Diff+Firing", and *n*-type wafers of the group "B-Diff" and "P-Diff". These processing groups have been chosen for the following reasons: As explained in section 5.3.1-A, the processing conditions from group "P-Diff+Firing" on *p*-type and "B-Diff" on *n*-type are representative for typical cell concepts. A comparison of *n*-type wafers from the group "B-Diff" with *p*-type wafers from the group "P-Diff+Firing" therefore allows for a fair-minded comparison of the material quality and the efficiency potential of both materials after cell process steps suitable for the production of solar cells on each material. On p-type, the standard processing "P-Diff+Firing" also leads to the best material quality (see section 5.3.2-B). On the *n*-type material, the highest diffusion lengths are achieved after P-diffusion, which could be due to a limitation by a metal like chromium, which is also harmful in *n*-type [241] but can be effectively gettered [242]. The limitation by chromium will be discussed in detail in section 5.4. Therefore, we also include these samples in the evaluation in order to assess the upper limit of the efficiency potential in this material. However, an advanced cell concept would have to be applied to these samples to realize a solar cell on *n*-type base material after a P-diffusion without a further B-diffusion and high temperature step. A possibility would be a cell structure with a low temperature emitter (e.g., a hetero structure).

Figure 5.17 illustrates the global efficiencies for these three processing groups as a function of block height. In combination with the spatially resolved efficiency maps (*c.f.* Figure 5.18), the pre-characterization of the material quality, and the influence of the base resistivity in sections 5.3.2-A and B, these results will now be discussed in detail.

The mc *p*-type wafers feature an efficiency potential between 18% at the block bottom and 19% at the block top. The increase in efficiency towards the block top correlates with the increase in material quality as demonstrated in section 5.3.2-B. The



Figure 5.17: Efficiency potential as a function of block height for mc p-type after Pdiffusion and firing, mc n-type after B-diffusion, and mc n-type after P-diffusion. The efficiency limit (without SRH recombination) of the cell concept is 21.7% for p-type and 21.8% for n-type. Figure reprinted from [180].

variation of the base resistivity is negligible along the *p*-type brick and does not affect the efficiency potential.

A significant increase in efficiency is observed for the mc *n*-type wafers after the boron diffusion compared with the *p*-type wafers: The efficiency potential of these wafers is at a stable level of about 19.2% along the whole block height, which corresponds to an increase averaged along the block height of  $+0.7\%_{abs}$  compared with the *p*-type wafers after P-diffusion and firing. The *n*-type wafers after a P-diffusion feature the best efficiency potential: A stable level of about 20.0% is reached along the whole block height. Compared to the *p*-type wafers, this means a considerable gain in efficiency of  $+1.5\%_{abs}$  averaged along the brick.

To understand the stable efficiency level of the *n*-type wafers, we have to go back to the results of sections 5.3.2-A and 5.3.2-B. On the one hand, the material quality of the *n*-type wafers decreases towards the block top, as explained in section 5.3.2-B. On the other hand, the base resistivity decreases from 2.8  $\Omega$ cm for wafers from the bottom to 1.3  $\Omega$ cm for wafers from the top, which leads to an efficiency gain of approximately (0.5-1)%<sub>abs</sub> for lifetimes between 1 µs and 1 ms, as illustrated in Figure 5.14. Thus, with increasing block height the decrease in material quality is compensated by a resistivity-related efficiency gain, leading to a very stable efficiency level along the whole height of the *n*-type block.


Figure 5.18: Spatially resolved efficiency potential of mc p-type after P-Diff+Firing (bottom), mc n-type after B-Diff (middle), and mc n-type after P-Diff (top). The images show the central quarter stripe of wafers from the block bottom, middle and top. Figure reprinted from [180].

A spatially resolved analysis (*c.f.* Figure 5.18) shows that while in the *p*-type sample the efficiency is below 20% also in the best grains, the best  $1 \times 1$  cm<sup>2</sup> area in the *n*-type sample "B-Diff" from the medium block height features an efficiency of 21%.



Figure 5.19: Efficiency losses in mc p-type after P-Diff+Firing (left), mc n-type after B-Diff (center), and mc n-type after P-Diff (right) for three different block positions (left to right within each group: bottom – middle – top). Figure reprinted from [180].

In the *n*-type sample "P-Diff" from the medium block height, the efficiency potential in the best  $1 \times 1$  cm<sup>2</sup> areas (21.5%) is already close to the cell limit.

## D. Efficiency losses

In a last step, we quantify the efficiency losses and specify their origin in each material. This is done by evaluating the efficiency potential in the best  $1 \times 1$  cm<sup>2</sup> area virtually free of extended crystal defects. The loss occurring in this region compared to the cell limit can be attributed to homogeneously distributed recombination centers (orange part of the columns in Figure 5.19). This comprises dissolved impurities stemming from

- i) the feedstock;
- the in-diffusion from the crucible system into the liquid silicon before crystallization and;
- iii) the solid-state in-diffusion from the crucible bottom (for the lowest block position);

that remained after processing, as well as dissolved impurities additionally incorporated during processing.

The additional recombination loss via extended crystal defects such as dislocation clusters and grain boundaries (probably) decorated with impurities (cyan dashed part of the columns in Figure 5.19) can be assessed by evaluating the efficiency loss in the whole wafer excluding the edge region. Finally, an evaluation of the whole wafer

additionally takes into account the losses in the edge region due to impurities diffused into the solid crystal from the crucible walls (grey part of the columns in Figure 5.19).

The following conclusions can be drawn from this analysis: While in mc *p*-type silicon dissolved impurities lead to an efficiency loss of  $1.9\%_{abs}$  (middle, top) up to  $2.7\%_{abs}$  (bottom, see discussion in section 5.3.2-B) and limit the global efficiency potential, efficiency losses in the *n*-type samples are mainly due to decorated extended crystal defects (-(1.1-1.6)%<sub>abs</sub> after B-diffusion and -(0.8-1.3)%<sub>abs</sub> after P-diffusion). Especially after the P-diffusion, efficiency losses in the good grains of the *n*-type wafer from medium block height are very low (-0.3%<sub>abs</sub>), which leads to an efficiency potential close to the cell limit in these areas. As measured effective lifetimes in these grains exceed 2 ms, remaining limitations could even partially be attributed to recombination at the surfaces of the SiN-passivated samples.

As mentioned in section 5.3.2-C, efficiency losses in the bottom part of the *n*-type brick are as large as in the top part, despite the larger diffusion length in the bottom part. This is attributed to the higher base resistivity. In a last estimation, we want to discuss the benefit from a lower base resistivity. Besides raising the cell efficiency potential, a lower base resistivity and thus a higher doping concentration also comes along with two disadvantages. First, it leads to a lower minority carrier mobility. This impact, however, is negligible: A base resistivity decrease from 2.8  $\Omega$ cm to 1  $\Omega$ cm is correlated with a decrease of the minority hole mobility of about 4%, leading to a reduction in the diffusion length of about 2%. Second, a higher doping concentration leads to an increased Auger- and SRH-recombination and thus lower charge carrier lifetimes. The efficiency gain obtained by a lower base resistivity is estimated as follows. We fit the measured injection dependent lifetime averaged across the whole wafer (square root harmonic mean) with two fictive defect levels according to the SRH-statistics. This delivers an analytical expression for the injection-dependent lifetime at the actual doping concentration. By changing the doping concentration in this expression, we obtain an estimation for the injection-dependent lifetime of the same sample at another base resistivity. Now, we read out the generation rate at MPP conditions from the original curve. The new expression for the injection-dependent lifetime delivers the corresponding lifetime value at the same generation rate for the new doping concentration. Thus we take an enhanced recombination at an increased doping concentration into account. It should be mentioned that, as the injectiondependent lifetime is simulated with two fictive defect levels, the actual lifetime value at a higher doping concentration could deviate from the simulated value. Still, in our opinion the lifetime obtained from this approach is a better estimate for the real conditions than not taking into account changes in lifetime due to increased recombination



Figure 5.20: Efficiency losses as a function of block height for mc n-type after Bdiffusion and mc n-type after P-diffusion. The white shaded parts of the columns illustrate the additional efficiency loss due to the actual base resistivity compared to a virtual base resistivity fixed at 1  $\Omega$ cm along the whole brick. Figure reprinted from [180].

at all. Using this lifetime and the new resistivity as input for a PC1D simulation with the models introduced before delivers an estimation for the efficiency potential. As the input is the lifetime value, even the change in minority carrier mobility is taken into account directly by the cell model. We apply this approach to the *n*-type samples after both B- and P-diffusion, assuming a constant base resistivity of 1  $\Omega$ cm along the whole brick (in reality, this could be achieved by continuous feeding of undoped silicon feedstock during the crystallization process). This allows for a quantification of the efficiency gain due to an optimized base resistivity. Similar to the illustration of losses in Figure 5.19, Figure 5.20 shows the bulk related efficiency losses for the mc *n*-type wafers at a virtual base resistivity of 1  $\Omega$ cm and quantifies the additional losses due to the higher actual resistivity.

The resistivity-related loss analysis shows, that a shift to lower base resistivity would be beneficial for mc *n*-type solar cell efficiencies. Thus, the advantage of mc *n*-type compared with mc *p*-type silicon is even more obvious comparing both materials at a similar base resistivity.

A general discussion on the impact of SRH-recombination on the choice of the optimal base resistivity can be found in [237]. There it is shown, that *p*-type silicon dominated by recombination via impurities with asymmetrical capture cross sections would benefit from higher resistivities, due to the strong injection-dependence of minority carrier lifetime. In our investigated mc *n*-type silicon, however, the injectiondependence of minority carrier lifetime is rather weak, such that decreasing the resistivity leads to a relatively small decrease in carrier lifetime and a net gain in efficiency.

## 5.3.3 Conclusion

A comprehensive analysis of the efficiency potential of multicrystalline *n*-type silicon after typical solar cell processing steps in comparison to mc *p*-type silicon of comparable impurity level along the whole brick highlights the high potential of mc *n*-type silicon. Compared with a standard solar cell process (P-diffusion + firing) on mc *p*-type silicon produced with identical feedstock and under identical crystallization conditions, an average efficiency potential gain of  $0.7\%_{abs}$  along the whole block height is found by changing the type of doping and applying a standard solar cell process on *n*-type (B-diffusion). If an advanced cell process including solely a P-diffusion is applied to the mc *n*-type material, a huge gain of  $1.5\%_{abs}$  on average along the whole block is observed compared with the with the maximum efficiency potential of the mc *p*-type silicon.

We showed that the large efficiency gain can be attributed to the significantly lower impact of homogeneously distributed recombination centers on the material quality. The main source of efficiency losses in mc n-type silicon was found to be structural crystal defects probably decorated with impurities. Thus, a further gain can be expected by optimizing the crystallization, which suggests a high potential of n-type high performance multicrystalline silicon with a low density of dislocation clusters (see also chapter 5.5).

The efficiency potential of the *p*-type material shows a significant dependence on the block position correlated to the material quality. In contrast, despite the decreasing material quality towards the block top, the efficiency potential of the mc *n*-type silicon brick is stable along the whole block height. This is attributed to the decreasing base resistivity, which leads to a higher efficiency potential and thus compensates the lower material quality. Finally, we showed that a higher doping concentration along the entire brick could be beneficial for the efficiency potential of mc *n*-type silicon.

A detailed analysis of the limitations in mc n-type silicon will be presented in section 5.4, and results on n-type high performance multicrystalline silicon will be discussed in section 5.5.

# 5.4 Understanding the Limitations in Multicrystalline *n*-type Silicon

The work presented in this chapter aims for a quantitative assessment of the impact of specific metal impurities on recombination in mc *n*-type silicon. On the one hand, mc

*n*-type silicon is less sensitive to many metal point defects compared with mc *p*-type silicon [73]. However, improvement of minority carrier lifetime in mc *n*-type silicon during phosphorus diffusion (*cf.* chapter 5.3 and for instance references [180, 194, 209]) indicates a limitation by metallic impurities before gettering. This is also confirmed by lower minority carrier lifetimes observed in the regions of higher concentrations of metal impurities [180, 209], such as the bottom, edge, and top regions, which are affected by solid-state in-diffusion of impurities from the crucible (bottom and edge) or a back-diffusion from segregated metallic impurities (top).

Although the impact of interstitial iron is assumed to be of minor importance for recombination in *n*-type silicon, a study on intentionally Fe-contaminated mc *n*-type silicon revealed significantly lower minority carrier lifetimes in this material compared with a reference block [208]. Additionally, Vähänissi *et al.* [209] report on the impact of a low temperature anneal after a P-diffusion on minority carrier lifetime in edge wafers of an mc *n*-type silicon block. They observe that the gain in lifetime decreases towards the wafer edge close to the crucible, which is attributed to the increasing concentration of precipitated impurities. Both results indicate that iron might play a bigger role for recombination in mc *n*-type silicon than expected, which could be due to the presence of FeSi<sub>2</sub>-precipitates.

In contrast to interstitial iron, which features a significantly lower capture cross section for holes compared with electrons, other metal point defects, such as Co, Cr, and Ni, exhibit large capture cross sections for holes and might therefore be detrimental for minority carrier lifetime in *n*-type silicon [241]. However, so far no experimental evidence for carrier lifetime limitation by these impurities in pure mc *n*-type silicon has been reported.

In the following, the limitation of charge carrier lifetime in mc *n*-type silicon before and after phosphorus diffusion is evaluated. After introducing the investigated material in the first part, the second part introduces the simulations of impurity distribution after crystallization and after P-diffusion, which give access both to the concentration of dissolved impurities as well as to the precipitate size distribution. Additionally, a short introduction to a model for charge carrier recombination at precipitates will be presented. In combination with measurements of the interstitial iron and chromium concentration in a *p*-type sister block (see also chapter 5.3) and injection-dependent minority carrier lifetime measurements in the *n*-type wafers, the limitation by Fe<sub>i</sub>, Cr<sub>i</sub>, and FeSi<sub>2</sub>-precipitates can be assessed and discussed in detail in the third part.

A major part of the results of this section is published in [181]. Some results were obtained in collaboration with Andreas Kleiber and Michael Knörlein, and are also partially included in their bachelor theses [234, 243], which were supervised by the

author. The mc silicon ingots were crystallized by the crystallization group of Fraunhofer ISE under supervision of Stephan Riepe and Patricia Krenckel. Wafer processing was planned by the author and supervised by the author together with Andreas Kleiber (standard mc *p*- and *n*-type silicon) and Michael Knörlein (compensated block). Characterization of the material was performed by the author together with Andreas Kleiber or Michael Knörlein, advanced evaluations of the measurements were done by the author. Simulations of impurity distribution after crystallization and redistribution during processing with *Sentaurus Process* were done by Jonas Schön. The model for charge carrier recombination at precipitates was developed by Wolfram Kwapil [69], experiments included in that paper were performed by the author and are partly presented in section 5.4.3.4.

## 5.4.1 Experimental

The mc *p*- and *n*-type silicon "sister" blocks of size G2 investigated here are the same as introduced in section 5.3.1 of the last chapter, where a detailed description of the samples can be found. Differing only in their type of doping, direct conclusions from impurity measurements on *p*-type wafers can be drawn for their concentrations in the *n*-type wafers from corresponding block positions. A third overcompensated brick (size G1) was included in the studies, which was purely P-doped in the bottom part, and then intentionally overcompensated by adding boron during the crystallization. This delivers mc *n*- and *p*-type "sister" wafers with virtually identical crystal structure and very similar impurity concentration taken from a block height just before and after the type-changeover. Investigations at this block are unaffected by uncertainties arising from different crystallizations, such as slight variations in the temperature profiles or the exact thickness of the edge cut-off before wafering.

The investigations of this chapter focus on *n*- and *p*-type "sister" wafers from the G2 blocks of the process groups "Initial" and "P-Diff" as introduced in section 5.3.1 and illustrated in Figure 5.12, and initial passivated *n*- and *p*-type "sister" wafers from the overcompensated G1 block. Additionally, minority carrier bulk lifetime is measured at a vertical unpassivated slice of the latter block, applying the method presented in [101].

Photoluminescence imaging (PLI) calibrated by harmonically modulated photoluminescence [100] was applied on wafer level to obtain injection-dependent images of minority carrier lifetime. Additionally, by measuring the minority carrier lifetime in the interstitial and the boron-paired state at a generation level of 0.01 suns, metastable defect imaging of the concentrations of interstitial iron (Fe<sub>i</sub>) and chromium (Cr<sub>i</sub>) [75, 110, 111] in the *p*-type wafers gives access to their concentrations in the *n*-type wafers as well, as explained previously. This assumes similar precipitation kinetics for iron and chromium in n- and p-type silicon, which is justified for high temperatures at which the Fermi-level effect is negligible [181].

## 5.4.2 Simulations

5.4.2.1 Diffusion and precipitation during solidification and high-temperature steps

A. Iron

The simulations solve the differential equations for the diffusion of dissolved iron and phosphorus (which is important for the P-diffusion), as well as the dissolution and growth of iron precipitates, including their interaction terms. The calculation of dissolution and growth rates of FeSi<sub>2</sub> precipitates is based on the Fokker-Planck equation [226, 244], which also gives access to the size distribution of precipitates. Further details about the model and the parameters can be found in [225]. The precipitation of iron was simulated with a modified structure of the models described in [225], featuring a smaller area of  $20 \times 20$  nm<sup>2</sup> around one dislocation line with enhanced nucleation site density. Further details on the modifications are explained in detail in [181].

For the in-diffusion of iron from the crucible system into the silicon melt and the solidified crystal, the diffusion of Fe in the silicon crystal, coating and crucible is described by Fick's law. The segregation coefficient of Fe between coating and silicon as well as the diffusivity of iron in the crucible and its silicon nitride coating determined in [40] are used. A complete mixing of Fe in the liquid silicon is assumed. Combined with a modified Scheil equation and the precipitation model, this allows for predicting the iron distribution in the crucible and the silicon crystal [40, 245].

Modeling P-diffusion gettering assumes an increased solubility of Fe in highly Pdoped silicon [229, 246], which leads to a segregation of dissolved iron into the emitter. We applied the segregation coefficient depending on the active phosphorus concentration from [232] and the phosphorus diffusion model from [228].

## B. Chromium

The in-diffusion of Cr from the crucible system was simulated with the same model as for Fe [40], with an adapted diffusivity inside the crucible and the coating as well as an adapted segregation coefficient between crucible system and solidified silicon. Details can be found in [181]. Applying the diffusivity [247] and solubility [248] of chromium in silicon, the model for Fe precipitation can be transferred to Cr.

## 5.4.2.2 Injection-dependent charge carrier recombination at precipitates

Recombination at precipitates is modeled by means of finite-element simulations as explained in detail in [69]. In the two-dimensional model structure, the  $FeSi_2$  precipitates are aligned along the axis of rotational symmetry, which represents the dislocation line, with their size distribution taken from the simulations described in the previ-



Figure 5.21: Measured and calculated charge carrier lifetime after phosphorus diffusion in an edge grain of an mc p-type wafer. The  $Fe_i$ -limited lifetime was calculated from the measured  $Fe_i$  concentration ( $Fe_i \sim 3x10^{11} \text{ at/cm}^3$ ), the precipitate-limited lifetime was simulated assuming the precipitate distribution 2 from [69]. The resulting effective lifetime is in good agreement with the measured lifetime. Figure adapted from [69].

ous section 5.4.2.1. The radius of the simulation domain is determined by the dislocation density, assuming lateral periodicity. The interface between  $FeSi_2$  precipitates and silicon is assumed to represent an internal Schottky contact, which can be described by its Schottky barrier. This leads to the formation of a space charge region around the precipitates. While in thermal equilibrium, the net fluxes of electrons and holes to the precipitates are zero, the electric fields around the precipitates decrease under injection of carriers, leading to a flux of electrons and holes towards the precipitates, where they recombine [69].

As shown in [69], recombination at FeSi<sub>2</sub> precipitates plays an important role in the edge region of mc *p*-type silicon, also after P-diffusion. Figure 5.21 shows the measured effective minority carrier lifetime in an edge grain of a mc *p*-type wafer after phosphorus diffusion (*SQ*-wafer after "*PD*" from section 5.2, *cf.* central column of Figure 5.4), together with the Fe<sub>i</sub>- and FeSi<sub>2</sub>-precipitate-limited lifetimes [69]. While in the low-injection regime, recombination via interstitial iron dominates the lifetime (orange dotted curve in Figure 5.21), for injection levels above  $\sim 2 \times 10^{13}$  cm<sup>-3</sup>, iron precipitates start to limit the charge carrier lifetime (cyan dashed curve in Figure 5.21). Taking both interstitial iron and FeSi<sub>2</sub>-precipitates into account, the injectiondependence of the measured lifetime can be explained very well (gray solid curve in Figure 5.21).



Figure 5.22: Charge carrier lifetime of an n-type wafer before (a) and after (b) phosphorus diffusion at 19% block height at a generation rate of 0.05 suns. The injection dependent lifetime in the color marked rectangles are shown in Figure 5.27 and Figure 5.28. Figure adapted from [181].

As the recombination activity of  $\text{FeSi}_2$ -precipitates in *n*-type silicon is only slightly lower than in *p*-type silicon [192], they should also be considered as potential recombination centers in the edge region of mc *n*-type silicon wafers. Their impact on charge carrier lifetime will be discussed in detail in section 5.4.3.4.

## 5.4.3 Limitations of minority carrier lifetime in mc *n*-type silicon

In this section, the role of important metal impurities, namely chromium and iron, for recombination in mc *n*-type silicon is examined. Figure 5.22 shows the minority carrier lifetime of passivated mc *n*-type sister wafers of 19% block height before (left) and after P-diffusion (right), measured at an illumination of 0.05 suns. Although not included in standard *n*-type solar cell processes, the effect of a P-diffusion on minority carrier lifetime delivers a first insight into the material limitation. The strong increase of lifetime within the grains after phosphorus diffusion indicates a limitation in asgrown grains by a defect, which is getterable and mobile at 800°C. Furthermore, the increase in minority carrier lifetime in the edge region and in areas of dislocation clusters is much smaller, which hints at the presence of additional less mobile or not getterable defects in these regions. These will be discussed in the following.

5.4.3.1 Cr<sub>i</sub>

A metal impurity, which is assumed to be detrimental for charge carrier lifetime in both *p*- and *n*-type silicon, is chromium [241]. This is attributed to its similar capture cross sections for electrons and holes (capture cross sections for Cr<sub>i</sub> from [115]:  $\sigma_n = 2.4 \times 10^{-14} \text{ cm}^2$ ;  $\sigma_p = 0.8 \times 10^{-14} \text{ cm}^2$ ).

Charge carrier lifetime  $(\mu s)$ 

Assuming similar diffusion and precipitation in mc *p*- and *n*-type silicon, we assess the fraction of recombination due to interstitial chromium (FoR<sub>Cri</sub>) in an ungettered mc *n*-type wafer from 45% block height as follows. We measure the concentration of interstitial chromium in a *p*-type wafer from the same position of the *p*-type "sister" block by Cr-imaging. This delivers an image of the interstitial chromium concentration. We observe a rather homogeneous distribution of Cr<sub>i</sub> in the area of the wafer not affected by the edge region. In the edge region, the lower lifetime leads to a significantly higher detection limit, which is why we have no experimental access to the concentration of Cr<sub>i</sub> in this region. Therefore, we extract the concentration of Cr<sub>i</sub> in this region from the simulations and, thus, extrapolate the measured concentration of Cr<sub>i</sub> from the center towards the edge region. The result is shown in Figure 5.23(b), which displays the horizontal Cr<sub>i</sub> profile across a wafer from 45% block height. In vertical direction, the Cr<sub>i</sub> profile does not change. A lifetime image of the *n*-type wafer at an illumination of 0.05 suns is shown in Figure 5.23(a). The edge region close to the crucible is on the right side of the image.

Now, we are able to calculate the fraction of charge carrier recombination via Cr<sub>i</sub> in the mc *n*-type silicon wafer. With the measured spatially resolved excess carrier density at an illumination of 0.05 suns and the spatially resolved concentration of Cr<sub>i</sub>, the corresponding Cr<sub>i</sub>-limited lifetime  $\tau_{SRH,Cri}$  is calculated for each pixel, applying the defect parameters from [115]. Together with the actual measured effective minority carrier lifetime  $\tau_{eff}$  at 0.05 suns from Figure 5.23(a), this delivers an image of the fraction of recombination due to Cr<sub>i</sub> (FoR<sub>Cri</sub> =  $\tau_{eff}/\tau_{SRH,Cri}$ ), which is displayed in Figure 5.23(c). Note that after crystallization the concentration of Cr<sub>i</sub> at structural crystal defects is lower compared with surrounding grains. This leads to a slight overestimation of the fraction of recombination due to Cr<sub>i</sub> at these defects, as the applied analysis assumes the smooth Cr<sub>i</sub>-profile from Figure 5.23(b) without local variations due to structural crystal defects.

From this analysis, we can conclude that interstitial chromium contributes significantly to recombination in as-grown grains. In the major part of as-grown grains, 20-60% of charge carrier recombination is due to  $Cr_i$ , while in the grains with the highest lifetime, up to 70% of charge carrier recombination can be attributed to  $Cr_i$ . In contrast, recombination via  $Cr_i$  is of minor importance in areas with a high density of recombination active structural defects, such as dislocation clusters. Additionally, we do not observe an increase in  $FoR_{Cri}$  in the edge region, meaning that other defects dominate the recombination in these areas.



(c) Fraction of recombination due to  $Cr_i$  (%)



## (b) Cr<sub>i</sub> and Fe<sub>i</sub> profiles



(c) Fraction of recombination due to  $Fe_i$  (%)



Figure 5.23: (a) Charge carrier lifetime measurement of an n-type wafer  $(12.5 \times 12.5 \text{ cm}^2)$  from 45% block height illuminated by 0.05 suns (edge region close to the crucible on the right side of the image). The fraction of charge carrier recombination due to  $Cr_i$  and  $Fe_i$  is shown in (c) and (d). Note the different scale of (c) and (d). The  $Cr_i$  and  $Fe_i$  profiles used for the calculation of (c) and (d) are extracted from a p-type wafer of the same block height and shown in (b). The solid part of the blue line depicts the measured average concentration of  $Cr_i$ , the dashed part is extrapolated from simulations. Figure reprinted from [181].



Figure 5.24: (a) Measured injection dependent lifetime in a grain from center region (green triangles: green rectangle in Figure 5.23(a)). The simulated effective lifetime (green solid curve) due to Auger-recombination (gray dashed curve) and recombination at  $Cr_i$  (green dotted curve;  $Cr_i$  concentration measured at the p-type wafer from the sister block) can explain a significant part of the injection-dependence of the measured lifetime. Figure adapted from [181]. (b) Fraction of recombination (FoR) due to  $Cr_i$  and  $Cr_i + Auger$  in the same grain as a function of injection level. This explains up to 80% of recombination at high injection levels.

So far, we discussed the recombination due to interstitial chromium at a constant illumination of 0.05 suns. Further insight can be gained by investigating the injection-dependent charge carrier lifetime. Figure 5.24(a) shows the measured minority carrier

lifetime in the good grain marked by a green square in Figure 5.23(a) as a function of excess carrier density (green triangles). In addition, we include the calculated Crilimited lifetime  $\tau_{SRH,Cri}$  for the measured concentration of Cr<sub>i</sub> of 1.4 × 10<sup>10</sup> cm<sup>-3</sup> (green dotted line) and the Auger-limit (gray dashed line). The resulting effective lifetime (green solid line) explains the measured lifetime for excess carrier densities larger than 10<sup>15</sup> cm<sup>-3</sup> reasonably well, whereas in low-level injection, an additional defect is needed to explain the measured lifetime. This is also highlighted in Figure 5.24(b), which depicts the fraction of recombination due to Cr<sub>i</sub> and Auger as a function of injection level. For injection levels larger than 10<sup>15</sup> cm<sup>-3</sup>, more than 70% of the total recombination is attributed to SRH-recombination at Cr<sub>i</sub> and Auger-recombination. Due to the decrease of  $\tau_{SRH,Cri}$  with increasing excess carrier density, charge carrier recombination is dominated by  $Cr_i$  for injection levels in the range of  $10^{15}$  cm<sup>-3</sup>, before additionally the increasing Auger-recombination contributes significantly to charge carrier recombination at higher injection levels. This is reflected by the second curve in Figure 5.24(b), which shows a maximum in the fraction of recombination due to  $Cr_i$  at an excess charge carrier density of approximately  $2 \times 10^{15}$  cm<sup>-3</sup>.

These results for charge carrier recombination due to interstitial chromium were obtained for the as-grown state. It should be mentioned that the concentration of interstitial chromium is expected to be strongly reduced after high temperature steps. Particularly, a phosphorus diffusion can effectively getter Cr<sub>i</sub> [242]. Thus, also the impact of interstitial chromium on charge carrier lifetime will decrease.

## 5.4.3.2 Fe<sub>i</sub>

A similar evaluation can be performed for interstitial iron. As Fe<sub>i</sub> features a much smaller capture cross section for holes ( $\sigma_p = 6.8 \times 10^{-17}$  cm<sup>2</sup> for T = 300 K [113]), its impact on minority carrier lifetime is assumed to be negligible in mc *n*-type silicon. However, previous studies on intentionally Fe-contaminated mc *n*-type silicon blocks reported on significantly lower lifetimes in that material compared with uncontaminated reference material [208].

Our wafers feature an edge region of increased iron concentration. Thus, by extracting the Fe<sub>i</sub>-profile from Fe-imaging measurements at the *p*-type wafer from the same position of the "sister" block (*cf.* red line in Figure 5.23(b)), we can study the impact of Fe<sub>i</sub> concentrations in the range of  $2-3 \times 10^{10}$  cm<sup>-3</sup> to  $1 \times 10^{12}$  cm<sup>-3</sup> on recombination in the as-grown mc *n*-type silicon wafer. The procedure is the same as for Cr<sub>i</sub>. The Fe<sub>i</sub>-limited lifetime  $\tau_{SRH,Fei}$  is calculated for each pixel from the spatially resolved concentration of Fe<sub>i</sub>, accounting for the measured spatially resolved injection level at an illumination of 0.05 suns, with the defect parameters from [113]. In combination with the measured effective minority carrier lifetime  $\tau_{eff}$  at 0.05 suns from



Figure 5.25: Fraction of charge carrier recombination due to Cri and Fei in an n-type wafer  $(12.5 \times 12.5 \text{ cm}^2)$  from 45% block height at an illumination of 0.05 suns (block edge on the right side).

Figure 5.23(a), we obtain an image of the fraction of recombination due to Fe<sub>i</sub> (FoR-Fei =  $\tau_{eff}/\tau_{SRH,Fei}$ ; *cf.* Figure 5.23(d)). While for the major part of the wafer, which is not affected by solid-state in-diffusion of impurities from the crucible, recombination due to interstitial iron is negligible ([Fe<sub>i</sub>] in the range of 2-3 × 10<sup>10</sup> cm<sup>-3</sup>), in grains in the edge region with a low density of structural crystal defects, ~20% of charge carrier recombination can be attributed to Fe<sub>i</sub> ([Fe<sub>i</sub>] up to 1 × 10<sup>12</sup> cm<sup>-3</sup>). This means that also in mc *n*-type silicon, recombination via interstitial iron should be considered in areas of high iron concentrations, such as the edge, bottom or top regions of a block.

Also  $Fe_i$  can be effectively gettered by a phosphorus diffusion, which would reduce its impact on charge carrier lifetime [225].

## 5.4.3.3 Combined impact of Cr<sub>i</sub> and Fe<sub>i</sub>

From the analyses of the previous sections, the combined impact of  $Cr_i$  and  $Fe_i$  on charge carrier lifetime in mc *n*-type silicon can be assessed. Figure 5.25 shows the fraction of charge carrier recombination due to both  $Cr_i$  and  $Fe_i$  in the as-grown mc *n*-type wafer from 45% block height at an illumination of 0.05 suns. A significant part of recombination in the good grains across the whole wafer can be attributed to these two impurities.

## 5.4.3.4 FeSi<sub>2</sub>-precipitates

As mentioned before, the recombination activity of  $\text{FeSi}_2$ -precipitates is only slightly lower in *n*-type compared with *p*-type silicon [192]. Thus, it is worth taking a closer look at the edge regions of mc *p*- and *n*-type silicon, which feature a high total concentration of iron from solid-state in-diffusion from the crucible system and, thus, also a significant concentration of  $\text{FeSi}_2$ -precipitates [40]. As the distribution of  $\text{FeSi}_2$ -precipitates is not experimentally detectable on a macroscopic scale, we compare in the upper graph of Figure 5.26(a) the measured concentration of Fe<sub>i</sub> with the simulated concentrations of Fe<sub>i</sub> and FeSi<sub>2</sub>-precipitates as a function of the distance from the crucible wall at 19% block height. The lower graph shows the normalized measured lifetime profiles on *p*- and *n*-type wafers from the same block position as a function of the distance from the crucible edge.

While in the *p*-type wafer, the decrease in lifetime towards the crucible correlates with the increase in the Fe<sub>i</sub> concentration, the decrease in lifetime in the *n*-type wafer correlates with the increase in the concentration of FeSi<sub>2</sub>-precipitates. Thus, recombination at FeSi<sub>2</sub>-precipitates could be the reason for the low lifetime in the edge region of mc *n*-type silicon (*cf.* Figure 5.22). It also explains the slightly smaller width of the edge region compared with mc *p*-type silicon and is in agreement with the low gettering response of this area, which was a hint of the presence of less mobile or not getterable defects, as mentioned before.

The smaller width of the edge region in mc n-type silicon is confirmed by Figure 5.26(b), which shows a bulk lifetime image of a vertical cross section from the changeover region from n- to p-type doping in the overcompensated G1 block. It illustrates both the higher lifetime level in mc n-type silicon in the lower part as well as the slightly wider edge region in mc p-type silicon in the upper part of the image. If the block was not overcompensated by boron, the edge region in the upper part would be even smaller than in the lower part, as the edge region decreases with increasing block height due to the shorter time of solid-state in-diffusion of impurities from the crucible system. This would pronounce the effect of the smaller edge region in mc n-type silicon yet more strongly.



Figure 5.26: (a) Upper graphs:  $Fe_i$  profile measured at the p-type block at 19% block height compared with the simulated profiles of precipitated Fe and Fe<sub>i</sub>. Lower graphs: Measured normalized lifetime in n- and p-type wafers from the same block height (n-type wafer from Figure 5.22(a)). (b) Bulk lifetime image of a vertical cross section from the transition region of the overcompensated block, obtained from PL based lifetime measurement [101], accounting for the variation in doping concentration and charge carrier mobility. The edge region of lower lifetime close to the crucible (left side of the image) is visible in n- and p-type Si. The area of artificially low lifetime in the PL lifetime image (dark horizontal line) corresponds to the changeover from n- to p-type doping, featuring a very low net doping concentration. Figure reprinted from [181].



Figure 5.27: Measured injection dependent lifetime in an edge grain of the as-grown *n*-type wafer from 19% block height (blue circles: blue rectangle in Figure 5.22(a)). The sum of the inverse background lifetime measured in a center grain of the same wafer (black diamonds: black rectangle in Figure 5.22(a)), and the simulated inverse lifetime due to FeSi<sub>2</sub> precipitates and enhanced concentrations of Fe<sub>i</sub> and Cr<sub>i</sub> in the edge region (blue line), explain the major part of the measured recombination in the edge grain. Figure adapted from [181].

#### *A.* Injection-dependent lifetime in the as-grown state

In order to confirm the impact of FeSi<sub>2</sub>-precipitates on recombination in the edge region of mc *n*-type silicon blocks, we investigated the injection dependence of charge carrier lifetime in the edge region of the *n*-type G2 block. Figure 5.27 shows the measured minority carrier lifetime (blue circles) in an edge grain of the as-grown *n*-type wafer from 19% block height (indicated by the blue rectangle in Figure 5.22(a)) as a function of excess carrier density. The simulations predict a total iron concentration in this grain of approximately  $4 \times 10^{13}$  cm<sup>-3</sup>, which results in the simulated lifetime due to recombination at FeSi<sub>2</sub>-precipitates (for the simulated precipitate size distribution) depicted by the blue dotted line in Figure 5.27. In order to compare the measured lifetime with simulations, we additionally account for the recombination due to Fe<sub>i</sub> (simulation:  $[Fe_i] = 1.1 \times 10^{12} \text{ cm}^{-3}$ ), due to the increased concentration of Cr<sub>i</sub> (cf. Figure 5.23(b):  $[Cr_i] = 2.8 \times 10^{10} \text{ cm}^{-3}$  simulated for the edge grain, compared with  $[Cr_i] = 1.4 \times 10^{10} \text{ cm}^{-3}$  measured in the center), and account for a background recombination due to other impurities by adding the measured recombination in a center grain (black diamonds in Figure 5.27, grain indicated by the black rectangle in Figure 5.22). This can be justified, since in the edge region at least as many other defects are present



Injection level (cm<sup>-3</sup>)

Figure 5.28: Measured injection dependent lifetime in a grain from the edge after Pdiffusion (blue squares: blue rectangle in Figure 5.22(b)). The inverse of the sum of the inverse background lifetime (black stars: black rectangle in Figure 5.22(b)) and the simulated inverse lifetime due to FeSi<sub>2</sub> precipitates and Fe<sub>i</sub> is slightly above the measurement in the edge grain. Additionally, the limitation by FeSi<sub>2</sub> precipitates after phosphorus diffusion gettering for an initial Fe concentration of  $1.5 \times 10^{14}$  cm<sup>-3</sup> is shown. Figure reprinted from [181].

as in a center grain without a significant limitation by Fe. The resulting injectiondependent lifetime, depicted by the blue solid line in Figure 5.27, can explain a significant part of the measured injection-dependent lifetime in the edge grain. As the concentrations of all other metals not explicitly accounted for increase towards the edge, we indeed expect a slightly lower measured lifetime compared to the modeled curve due to additional recombination at these defects, such as SRH-defects, precipitates or decorated dislocations. The slighter slope of the measured injection-dependent lifetime indicates that the lifetime correlated to the additional defects does not feature a strong injection-dependence.

## B. Injection-dependent lifetime after phosphorus diffusion

As mentioned previously, also after phosphorus gettering, recombination at  $FeSi_2$ precipitates can have a significant influence, as precipitates are less effectively gettered than most dissolved impurities due to their incomplete dissolution during P-diffusion. Figure 5.28 shows the measured minority carrier lifetime in the same edge grain of the mc *n*-type sister wafer from 19% block height after P-diffusion (blue squares, grain indicated by the blue rectangle in Figure 5.22(b)) as a function of excess carrier density. The simulation of the precipitate-related lifetime accounts for phosphorus diffusion, gettering, and precipitate dissolution, resulting in the dashed blue curve for an initial total iron concentration of  $4 \times 10^{13}$  cm<sup>-3</sup>, which we expect for the edge grain. For this initial total iron concentration, we compare the measured lifetime with the simulated effective lifetime curve (blue line in Figure 5.28), accounting for recombination at FeSi<sub>2</sub>-precipitates, recombination due to Fe<sub>i</sub>, and an additional background recombination due to other impurities, taken from injection-dependent lifetime measurements in a center grain (black stars in Figure 5.28). While the measured injection-dependent lifetime and the simulated FeSi<sub>2</sub>-related lifetime only slightly increase after P-gettering (*cf.* Figure 5.27 for comparison), the simulated effective lifetime shows a stronger increase due to the large increase in the background lifetime in the center grain (compare solution).

Thus, we can explain approximately 50% of the recombination in the edge grain. The edge grain might feature a higher density of structural crystal defects compared to the center grain, resulting in a weaker gettering response. This could explain further recombination in the edge. Also, an uncertainty in the distance of the analyzed grain from the crucible wall ( $\pm 5$  mm) results in a large uncertainty in the total iron concentration (*cf.* Figure 5.26(a)) and thus in the precipitate size distribution. Due to this uncertainty, total iron concentrations even in the range of  $1.5 \times 10^{14}$  cm<sup>-3</sup> cannot be fully excluded in the investigated edge grain, which would result in the FeSi<sub>2</sub>-related lifetime indicated by the dashed olive curve in Figure 5.28, which is close to the measured lifetime. The smaller injection dependency for higher initial iron concentrations is attributed to larger precipitates [69].

## C. Conclusions from overcompensated G1 block

Besides the previously discussed smaller edge region in the *n*-type part of the overcompensated G1 block (*cf.* Figure 5.26(b)), further results obtained from iron imaging at *p*-type wafers and injection-dependent lifetime measurements at *n*-type sister wafers from this block also point at a limitation of mc *n*-type silicon by FeSi<sub>2</sub>-precipitates in regions of high total iron concentrations. These results are discussed in detail in [243].

## 5.4.4 Conclusion and outlook

From our results we can draw the following conclusions for recombination in mc n-type silicon, crystallized with high purity feedstock (purity level of ~9N) and standard industrial quality crucible and coating, which are the main sources for impurities:

• Cr<sub>i</sub> plays an important role for recombination in as-grown grains. Our results for a block height of 45% indicate a limitation by Cr<sub>i</sub> of up to 70% in certain grains at an illumination of 0.05 suns. After P-diffusion gettering, the limitation by Cr<sub>i</sub> is expected to be of minor importance.

- Fe<sub>i</sub>, although featuring a small capture cross section for holes, can have an impact on recombination in as-grown grains with high initial iron concentrations. Our results indicate a limitation by Fe<sub>i</sub> of up to 25% in as-grown grains in the edge region at an illumination of 0.05 suns. Fe<sub>i</sub> can be neglected in center parts of the block.
- Minority carrier lifetime in mc *n*-type silicon features only a moderate injection-dependence, compared to the steeper injection-dependence of minority carrier lifetime in mc *p*-type silicon.
- Recombination at FeSi<sub>2</sub>-precipitates plays a dominant role in the edge region, both before and after P-gettering. In combination with other background defects, the measured injection-dependent lifetime in edge grains for a block height of 19% can be explained fairly well. Furthermore, the smaller width of the edge region in mc *n*-type silicon is attributed to FeSi<sub>2</sub>-precipitates being the dominant defects, whereas the broader width of the edge region in mc *p*-type silicon can be explained by Fe<sub>i</sub> being the most important recombination center there. A similar impact of FeSi<sub>2</sub>-precipitates is expected for the top region of a block.
- FeSi<sub>2</sub>-precipitates also explain the poor gettering response of the edge region compared to center grains in mc *n*-type silicon.

The results presented so far were obtained by the author or in close collaboration with the author, as described in the introduction of this chapter. In the paper [181], further experimental results for other metal impurities obtained from Neutron Activation Analysis (NAA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) performed at other institutes are included. Based on these measurements and simulations in combination with the presented results, further conclusions for the limitations of mc n-type silicon by other metal impurities can be drawn. In order to present a general view and put the presented results into the context of the current state of knowledge, the most important findings are summarized here:

- Cu<sub>3</sub>Si- and NiSi<sub>2</sub>-precipitates may significantly contribute to recombination in the block center and can be associated with the getterable recombination centers other than Cr<sub>i</sub> in these regions.
- Significant fractions of dissolved Cu and Ni can only be achieved after fast cooling, due to their high diffusivity.
- Co can have a severe impact after process steps including fast cooling.
- Ti, measured in significant concentrations in the crucible and its coating, can be excluded as dominant recombination center due to the high values of



Figure 5.29: Fraction of inverse lifetime due to the different defects in three block regions. Note that the lifetime is taken from the whole center/edge regions of the wafers including dislocation clusters and not only from the grains analyzed in section 5.4.3. The hatched bars indicate the uncertainties of the precipitate simulations and can either be attributed to the corresponding precipitates or assigned to "crystal defects + other impurities" depending on the actual precipitate concentration. Figure reprinted from [181].

measured lifetimes in the good grains after gettering. This is in contrast to the weak gettering response of Ti due to its low diffusivity.

- Also, a significant influence of W and Mo on charge carrier lifetime can be excluded, as their measured concentrations are small or below the detection limit.
- Besides dissolved and precipitated impurities, dislocations decorated with single impurity atoms contribute to charge carrier recombination. However, a quantification of the fraction of recombination and gettering response of single impurity atoms at dislocations is challenging.
- The recombination activity of structural crystal defects, such as dislocation clusters, can partly be explained by metal precipitates preferentially nucleating in areas with imperfect crystal structure. In addition, a significant fraction of recombination in these areas could be attributed to dislocations decorated with single impurity atoms.

Figure 5.29 visualizes the fraction of recombination in three different block regions (center at 45% block height and center and edge at 19% block height) by plotting the inverse lifetime due to the different analyzed defects.

## 5.5 High Efficiency Multicrystalline *n*-type Silicon Solar Cells

As already stated by Cuevas et al. in a publication from 2003, the main challenge for mc *n*-type silicon "is to improve its homogeneity and minimize the occurrence of low lifetime regions [...]. This should be possible by optimizing the crystallization process." [195]. The results presented in the last two chapters support this statement, revealing that the main losses in mc *n*-type silicon occur due to recombination active structural crystal defects. In recent years, the development of so-called "highperformance multicrystalline silicon" (HPM-Si) was put forward [43]. The basic idea behind this crystallization technique is to control the development of the crystal structure during crystal growth, usually by making use of a seed layer in the crucible bottom or a structured crucible bottom. Thereby, the development of harmful structural crystal defects like dislocation clusters can be reduced significantly, and a material with a homogeneous distribution of small grains of high electrical quality is obtained (see also section 2.1.2). Thus, the main challenge for mc *n*-type silicon raised by Cuevas et al. [195] could be addressed by taking advantage of this new crystallization technique, which has evolved to be the standard for industrial crystallization of mc *p*-type silicon. While already significantly increasing the efficiency potential of mc *p*-type silicon [43], the benefit of a lower dislocation density is estimated to be even larger for mc *n*-type silicon, which features larger relative efficiency losses due to recombination active structural crystal defects (cf. chapter 5.3). Hence, the use of HPM-Si in combination with *n*-type doping seems to be a promising option for the fabrication of high efficiency solar cells on low-cost multicrystalline silicon substrate.

This topic is addressed in the following, where we demonstrate the potential of n-type HPM-Si for the fabrication of highly efficient mc-Si solar cells. We investigate systematically the recombination properties and efficiency potential of n-type HPM-Si and demonstrate the applicability of a high efficiency n-type solar cell concept with a full-area Tunnel Oxide Passivated rear Contact (TOPCon) [176] to multicrystalline substrate, which is able to exploit the high electrical material quality of n-type HPM-Si. After introducing the investigated material and the applied characterization methods in section 5.5.1, we focus on the material-related limitations in n-type HPM-Si and review the impact of the doping type on the material quality of mc silicon in section 5.5.2. Finally, the efficiency potential of the material under investigation is assessed by an ELBA analysis [119], and TOPCon solar cell results on n-type HPM-Si are presented and discussed in detail in section 5.5.3.

This chapter is based on the results published in [182, 183] by the author. The HPM-Si ingots were crystallized by the crystallization group of Fraunhofer ISE under supervision of Stephan Riepe and Patricia Krenckel. Lifetime sample processing was

planned by the author and supervised by the author together with Jan Benick. Characterization of material quality and limitations was performed by the author, supporting 2-D simulations of chromium in-diffusion and precipitation were done by Jonas Schön. Efficiency predictions based on spatially resolved and injection-dependent bulk lifetime measurements were done by the author in collaboration with Bernhard Michl. Detailed evaluations of the efficiency data were performed by the author. The precharacterization of the TOPCon-layer on mc silicon was performed by the author (test of passivation quality) and Frank Feldmann (measurements of contact resistance on TLM-structures). Planning of the TOPCon cell batch on *n*-type HPM-Si was done by Jan Benick in close collaboration with the author, the fabrication of *n*-type HPM-Si TOPCon solar cells was performed by the group for high efficiency silicon solar cells at Fraunhofer ISE. Solar cell characterization was performed by Elisabeth Schäffer (IV-measurements) and the author together with Bernhard Michl (imaging).

#### 5.5.1 Material and methods

## A. Crystallization, lifetime sample and solar cell processing

For our investigations, a G1 size *n*-type HPM-Si ingot (width 22 cm; height 12.8 cm; weight ~14 kg) with a homogeneous distribution of small grains and a low density of dislocations was produced from high-purity feedstock (purity level of ~9N) by seed assisted growth in a laboratory crystallization furnace adapted for the crystallization of G1 and G2 size silicon ingots at Fraunhofer ISE. In order to obtain material with a very low impurity concentration, a high-purity crucible and coating, high-purity granular silicon as seed layer in the crucible bottom, and high-purity polysilicon feedstock for the main volume were chosen. A *p*-type HPM-Si ingot, crystallized under identical conditions (same seed and feedstock, crucible system, and temperature profiles; differing only in the type of doping) served as reference. The resistivity of the *p*-type block is in the range of 1.1-1.4  $\Omega$ cm, whereas the *n*-type block features a stronger variation along the block height from 0.5 to 1.3  $\Omega$ cm due to the smaller segregation coefficient of phosphorus. As we expect a similar impurity concentration in the *p*-type "sister" block due to the identical crystallization conditions, metastable defect imaging of interstitial iron and chromium at wafers from the *p*-type block should give access to their concentrations also in the *n*-type block.  $15.6 \times 15.6$  cm<sup>2</sup> bricks were cut symmetrically from the center of the blocks (cf. Figure 5.30) to avoid an impact of the edge region of low lifetime affected by solid-state in-diffusion of impurities from the crucible on the investigated wafers (gray shaded area in Figure 5.30). Due to sizerestrictions of certain processing steps,  $12.5 \times 12.5$  cm<sup>2</sup> wafers were cut from the original  $15.6 \times 15.6$  cm<sup>2</sup> wafers, and for cell processing, seven  $2 \times 2$  cm<sup>2</sup> cells were fabricated on round 4-inch wafers cut symmetrically from the  $12.5 \times 12.5$  cm<sup>2</sup> wafers



Figure 5.30: Sketch of a crystallized block (top view). The investigated wafers are depicted by the red square,  $2 \times 2$  cm<sup>2</sup> solar cells were fabricated on round wafers from the central part. Figure reprinted from [183].

at Fraunhofer ISE's cleanroom. The investigated samples and fabricated solar cells are sketched in Figure 5.30.

Lifetime samples were fabricated from wafers from the upper third of the blocks corresponding to a net doping concentration of approximately  $1.3 \times 10^{16}$  cm<sup>-3</sup> (*p*-type) and  $(7-8) \times 10^{15}$  cm<sup>-3</sup> (*n*-type). These wafers were subjected to a variety of solar cell process steps suited for the production of high-efficiency solar cells as indicated in Figure 5.31a. Wafers without high-temperature treatment from the initial group served as references.

The choice of process steps includes a sequence suited for the fabrication of highefficiency TOPCon solar cells ("B+P+Anneal"). Note that the standard process sequence for TOPCon solar cells does not necessarily include a phosphorus diffusion, which was included in our investigations to apply an additional gettering step. However, as will be discussed later, for the fabrication of high-efficiency TOPCon solar cells on mc *n*-type substrate, this step is not urgently required. The treatment with all hightemperature steps also included in the cell processing ensures that the material quality of lifetime samples corresponds to that of the final cell and thus allows for a thorough analysis of the material-related efficiency losses. Furthermore, process sequences including solely a boron diffusion at 890°C or a phosphorus diffusion at 800°C were applied to study their impact on the material quality separately. In order to obtain an injection-independent surface passivation of the lifetime samples, *p*-type wafers were passivated with Al<sub>2</sub>O<sub>3</sub>-films and *n*-type wafers with SiN<sub>x</sub>-films.



Figure 5.31: a) Processing of lifetime samples. Cleaning steps are not listed, hightemperature steps are highlighted in red. The surface passivation is  $Al_2O_3$  for the p-type wafers and  $SiN_x$  for the n-type wafers. b) Processing of mc n-type TOPCon solar cells. Figure reprinted from [183].

Seven  $2 \times 2$  cm<sup>2</sup> TOPCon solar cells were fabricated on several parallel *n*-type wafers of medium block height as sketched in Figure 5.30, according to the cell process sequence shown in Figure 5.31b. The key feature of the TOPCon cell is the ultra-thin wet chemical oxide layer (~14 Å) grown at the rear side in combination with a 15 nm thick phosphorus-doped Si layer deposited on top of the tunnel oxide. This TOPCon layer provides a highly efficient passivated rear contact featuring an excellent interface passivation, an efficiently doped layer for maintaining the quasi-Fermi level separation (for high  $V_{oc}$ ), as well as an efficient majority carrier transport (for high fill factors) by tunneling through the ultra-thin oxide layer [249]. Lifetime samples were also fabricated with the same process sequence except for the metallization from parallel wafers. For this TOPCon cell batch on multicrystalline silicon, we applied the standard process sequence without phosphorus gettering diffusion in order to reduce process complexity to a minimum, although an additional P-gettering would result in a better material quality, as will be shown in section 5.5.2. The main difference compared with the TOPCon process on monocrystalline silicon is the surface texturing. For our mc samples, we applied a double-sided acidic texture prior to a planarization of the rear side by chemical polishing, where the tunnel oxide passivated contact will be located. The boron diffusion for the front emitter formation at 890°C differs from the advanced Bdiffusion featuring a drive-in oxidation, which can be applied for monocrystalline silicon. In our work, the high-temperature drive-in oxidation was excluded, as the mc material quality would suffer from this step. After the boron diffusion, the TOPCon

layer is deposited at the rear side followed by an annealing step at 800°C. Finally, after deposition of an  $Al_2O_3$ -SiN<sub>x</sub>-stack serving as passivation and anti-reflection layer on the front side, front and rear side metal contacts were formed.

#### B. Characterization Methods

The material quality of the lifetime samples was investigated by photoluminescence imaging (PLI) calibrated by harmonically modulated photoluminescence [100] in order to obtain images of the minority charge carrier lifetime and diffusion length. While the minority charge carrier lifetime delivers a more direct access to the recombination properties in the samples, the minority charge carrier diffusion length is preferred for a comparison of *n*- and *p*-type material quality, as it accounts for the large difference in minority electron and hole mobility. On *p*-type samples, metastable defect imaging by calibrated PLI allows for spatially resolved measurements of the concentrations of interstitial iron (Fe<sub>i</sub>) [110] and chromium (Cr<sub>i</sub>) [75]. The SRH-parameters for Fe<sub>i</sub> are taken from [113], for FeB from [114], and for Cr<sub>i</sub> and CrB from [115]. Due to the identical block crystallizations, this also gives access to their concentrations in the *n*-type block.

Further insight into the recombination properties of HPM-Si is gained by injectiondependent calibrated PLI. This also enables a prediction of the solar cell efficiency potential by an "Efficiency limiting bulk recombination analysis" (ELBA) [119] (with the modifications described in [120]): Efficiency maps can be calculated by combining injection-dependent images of bulk recombination with PC1D cell simulations. Based on the spatially resolved efficiency potential, specific bulk-related defects limiting the solar cell efficiency can be assessed. We performed ELBA analyses for *n*-type HPM-Si lifetime samples from the TOPCon process sequence with or without the P-diffusion. The parameters for the PC1D model were taken from recombination current prefactor  $(J_0)$  measurements of the TOPCon rear side  $(J_{0,rear} = 7 \text{ fA/cm}^2)$  and the isotextured boron diffused front side ( $J_{0e} = 110 \text{ fA/cm}^2$ ), reflection measurements of an isotextured front side with identical anti-reflection coating and base resistivity measurements of the mc-Si material  $(n_0 = (7-8) \times 10^{15} \text{ cm}^{-3})$ . Further, a cell thickness of 160 µm and a series resistance of 0.55  $\Omega$ cm<sup>2</sup> were assumed in the PC1D simulations. Thus, the cell limit without bulk recombination losses would be 20.9%. The difference to the much higher efficiency potential of TOPCon reported in [176] results from the higher emitter recombination as no drive-in oxidation can be applied to mc-Si samples and the higher optical reflectance of the acidic isotexture compared with an alkaline pyramidal texture. For an estimation of the efficiency gain by improvements of the front surface reflectance, in a second simulation we applied the front surface reflection of a random pyramid surface, while keeping all other parameters unchanged. In this case, the cell

limit without bulk recombination losses is significantly increased to 22.4%. Although on mc silicon a random pyramid structure cannot be achieved, surfaces with similarly low reflectance such as a honeycomb structure could be applied.

## 5.5.2 Material quality of HPM-Si

#### A. Lifetime and diffusion length

In a first step, we compare minority carrier lifetime and diffusion length in *p*- and *n*-type HPM-Si after the different high-temperature steps from Figure 5.31a. Figure 5.32 illustrates square root harmonic mean (lifetime) and harmonic mean (diffusion length) values averaged across a representative central quarter stripe  $(3.125 \times 12.5 \text{ cm}^2)$  of the lifetime samples, obtained at constant illumination of 0.05 suns, which is estimated to correspond to an injection level close to MPP conditions in the solar cell. Minority carrier diffusion length images after the corresponding process steps are shown in Figure 5.32c.

The *n*-type HPM-Si samples feature significantly higher minority carrier lifetimes after all processing steps (Figure 5.32a). The remarkably high lifetime in the initial state (lifetime within the grains up to 800 µs, square root harmonic mean across the wafer > 350  $\mu$ s, exceeding the initial lifetime in *p*-type by more than a factor of five) reflects the larger tolerance of mc *n*-type silicon towards typical metal impurities present in the material after crystallization compared with mc *p*-type silicon. These large differences in lifetime are partly compensated by the larger minority carrier mobility in *p*-type, thus leading to smaller differences in terms of diffusion lengths. Still, in the initial state and after a boron diffusion, also the average diffusion lengths are significantly larger in the *n*-type samples than in the corresponding *p*-type samples. The drop in material quality after boron diffusion compared with the initial state is attributed to the high temperature (890°C) of the applied B-diffusion and its lower gettering efficiency compared to a P-diffusion, which strongly depends on the process parameters [79]. We also observed this effect on standard *p*- and *n*-type mc silicon and discussed it in detail in chapter 5.3. A look at the spatially resolved diffusion length (cf. Figure 5.32c) reveals that the drop in the average diffusion length is caused by a strong increase in recombination activity of structural crystal defects (grain boundaries, dislocation clusters), whereas the diffusion length within good *n*-type grains even improves. This effect will be discussed in more detail in section 5.5.2 B. It should be noted that despite the decrease in material quality, average diffusion lengths across the whole wafer are still above 500 µm in *n*-type HPM-Si, which is of importance for the applicability of the standard TOPCon solar cell process to this material, as we will discuss in section 5.5.3.



Figure 5.32: Minority carrier lifetime (a) (square root harmonic mean) and diffusion length (b) (harmonic mean) at an illumination of 0.05 suns, averaged across a representative central quarter stripe  $(3.125 \times 12.5 \text{ cm}^2)$  of p- and n-type HPM-Si lifetime samples after the processing steps of Figure 5.31a. The corresponding minority carrier diffusion length images of the central stripe of the wafers are shown below the graph (c). Figure reprinted from [183].

After processes including a phosphorus diffusion, minority carrier diffusion lengths strongly increase in the *p*-type samples, which is an indication to a limitation by a getterable metal impurity such as interstitial iron or chromium. The fact that the phosphorus gettering barely improves the material quality of the *n*-type samples compared with the initial state additionally points at a limitation by a metal impurity with a larger capture cross section for electrons than for holes, which supports our assumption that interstitial iron could be a candidate for a lifetime limiting defect in *p*-type HPM-Si before gettering. The limitation of *p*- and *n*-type HPM-Si by iron and chromium will be discussed in the next subsection 5.5.2 B. After processes including a P-diffusion, both *p*- and *n*-type samples feature average diffusion lengths above 600  $\mu$ m, exceeding 1000  $\mu$ m in good grains (*cf.* Figure 5.32b and Figure 5.32c), which highlights the excellent electrical quality of the investigated material.

#### B. Limitations of minority carrier diffusion length

As mentioned in the previous subsection, the limitation of minority carrier lifetime in *p*-type HPM-Si is due to a getterable metal impurity with a large capture cross section for electrons, which makes interstitial iron a probable candidate [113]. Additionally, interstitial chromium is a getterable impurity [242, 250] which is harmful in both *p*- and *n*-type silicon [241] and contributes significantly to recombination in as-grown grains of standard mc *n*-type silicon, as shown in chapter 5.4. Therefore, it should also be considered as possible candidate for a dominant defect in p- and n-type HPM-Si in the initial state. To investigate the limitations by Fe<sub>i</sub> and Cr<sub>i</sub> in detail, their concentrations were measured by means of metastable defect imaging on the *p*-type samples in the initial state, after boron diffusion and after phosphorus diffusion. As explained in section 5.5.1, we assume the same concentrations as measured in the *p*-type samples also in the *n*-type wafers. This allows for assessing the fraction of recombination due to interstitial iron ("FoR<sub>Fei</sub>") compared to the total recombination in the samples of both doping types by comparing the SRH-lifetime calculated from the average concentration of Fe<sub>i</sub> with the measured effective lifetime (FoR<sub>Fei</sub> =  $\tau_{eff}$ /  $\tau_{SRH,Fei}$ ). In the same way, the fraction of recombination due to interstitial chromium ("FoR<sub>Cri</sub>") in the *n*-type samples and chromium-boron-pairs ("FoR<sub>CrB</sub>") in the *p*-type samples can be assessed. Note that in thermal equilibrium at room temperature, the majority of dissolved chromium atoms are present as chromium-boron-pairs in the *p*-type samples, which is why we focus on the limitation due to CrB-pairs rather than Cr<sub>i</sub> here. In the following, the limitations due to Fe<sub>i</sub> and CrB or Cr<sub>i</sub> in *p*- and *n*-type HPM-Si are discussed before and after processing.

1) Before high-temperature processing: In the initial state, we measure an average Fe<sub>i</sub> concentration of  $3.5 \times 10^{10}$  cm<sup>-3</sup>. Chromium imaging reveals a CrB/Cr<sub>i</sub> concentration below the detection limit, which is in the range of  $5 \times 10^9$  cm<sup>-3</sup> for the investigated samples. This is in agreement with the concentration of interstitial chromium of  $3 \times 10^9$  cm<sup>-3</sup> obtained from 2-D simulations for the in-diffusion of chromium from the high-purity crucible system and precipitation during crystallization. The simulation model is explained in detail in [181]. With the measured Fe<sub>i</sub>-concentration, the simu-



Figure 5.33: Fraction of recombination due to interstitial iron (a) and chromiumboron pairs (b) in the initial state of p-type HPM-Si, and fraction of recombination due to interstitial iron (c) and chromium (d) in the initial state of n-type HPM-Si at a generation rate corresponding to 0.05 suns. Note the different scale of (a). Figure reprinted from [183].

lated  $Cr_i$ -concentration, and the measured lifetime images, we can calculate images of the fraction of recombination due to Fe<sub>i</sub> and CrB/Cr<sub>i</sub> at an illumination intensity of 0.05 suns, which are shown in Figure 5.33 for the *p*-type wafer (a, b) and for the *n*-type wafer (c, d).

In the *p*-type sample, a large part of recombination within grains can be attributed to Fe<sub>i</sub> (FoR<sub>Fei</sub>  $\approx$  40%), whereas the impact of chromium is smaller (FoR<sub>CrB</sub>  $\approx$  10%). In contrast, due to its significantly smaller capture cross section for holes, an interstitial iron concentration of  $3.5 \times 10^{10}$  cm<sup>-3</sup> does not contribute to recombination in the *n*-type sample ( $\tau_{SRH,Fei} \approx$  40 ms). However, the relative impact of Cr<sub>i</sub> in good grains of the *n*-type sample (FoR<sub>Cri</sub>  $\approx$  10%) is comparable with the relative impact of CrB in grains of the *p*-type sample. Despite the slightly lower capture cross section for holes of Cr<sub>i</sub> compared with the capture cross section for electrons of CrB, the higher lifetime level in the *n*-type sample leads to a similar relative limitation by chromium, which highlights the important role of chromium for both doping types. Thus, we can conclude that prior to high-temperature processing, about 50% of recombination in grains of *p*-type HPM-Si is attributed to Fe<sub>i</sub> (40%) and CrB (10%). A similar contribution to recombination in grains of *n*-type HPM-Si is found for Cr<sub>i</sub> (10%), whereas recombination at interstitial iron is negligible.

After high-temperature treatment: Cr<sub>i</sub> is gettered effectively both by the bo-2) ron or the phosphorus diffusion, such that its concentration is lower than  $10^9 \text{ cm}^{-3}$  (and thus significantly below the detection limit) and does not contribute to recombination neither in the *p*-type nor in the *n*-type HPM-Si samples after these processes. The average Fe<sub>i</sub> concentration slightly increases after *B*-diffusion to  $4 \times 10^{10}$  cm<sup>-3</sup>, which could be attributed to a potential cross-contamination from the furnace tube at elevated temperatures, as suggested in [79]. Also, the higher temperatures of the boron diffusion could lead to a dissolution of precipitates in the vicinity of structural crystal defects, which would lead to a lifetime degradation in these areas. As we observe a homogeneous increase of the Fe<sub>i</sub> concentration across the whole wafer, the first explanation could hold for Fe<sub>i</sub>, whereas the dissolution of other metal precipitates could be responsible for an increased recombination in areas of structural crystal defects. While the Fe<sub>i</sub> concentration of  $4 \times 10^{10}$  cm<sup>-3</sup> is responsible for about 50% of recombination within the grains of the *p*-type sample, it still does not contribute significantly to recombination in *n*-type HPM-Si. After B-diffusion, the *n*-type sample even features an increased lifetime within the grains compared to the initial state (cf. Figure 5.32c), which could be partly attributed to an effective gettering of Cr<sub>i</sub> by the applied Bdiffusion. In contrast, in the *p*-type sample the reduced concentration of CrB is compensated by the slight increase in the Fe<sub>i</sub>-concentration, thus leading to very similar lifetimes within the grains before and after B-diffusion (cf. Figure 5.32c). In both samples, the decrease in average lifetime after B-diffusion can be explained by a strongly increased recombination at structural crystal defects, such as grain boundaries and dislocation (cf. Figure 5.32c). As mentioned before, a dissolution and redistribution of previously large metal precipitates to a higher density of smaller metal precipitates could be a possible explanation and highlights the limitation of mc *n*-type silicon by precipitates and structural crystal defects rather than by dissolved impurities. At this point we can conclude that the asymmetric capture cross sections of Fe<sub>i</sub> for electrons and holes are a major reason for the superior material quality of *n*-type compared to *p*-type HPM-Si after processes without P-diffusion (*cf.* Figure 5.32).

After processes including a *P-diffusion*, the concentration of interstitial iron is considerably below  $10^{10}$  cm<sup>-3</sup> and thus of minor importance for recombination even in *p*-type HPM-Si, which explains the strong increase in minority carrier diffusion length in the *p*-type wafers after P-gettering. However, even a very low concentration of Fe<sub>i</sub> in this range could still have a slight impact on the stronger injection-dependence of minority carrier lifetime, which we observe in the *p*-type samples, compared with the rather flat injection-dependence measured on *n*-type samples. This is illustrated in Figure 5.34, which shows the minority carrier diffusion length in the *p*-type sample



Figure 5.34: Injection-dependent minority charge carrier diffusion length (good grains and harmonic mean across whole wafers) in n-type HPM-Si after "B+P+Anneal" and p-type HPM-Si after P-diffusion. Note the lower Auger-limit for diffusion lengths in n-type attributed to the lower minority carrier mobility. The stronger injectiondependence in p-type can be explained by a remaining impact of Fe<sub>i</sub>. Figure adapted from [182].

after P-diffusion and in the *n*-type sample after "B+P+Anneal" as a function of excess carrier density. A comparison of the diffusion lengths in both materials after these processes is fair minded, as it focuses on the material quality after processes relevant for solar cell fabrication on HPM-Si of both doping types, respectively.

While minority charge carrier diffusion lengths in the *n*-type sample are larger at low illumination, the stronger injection-dependence in the *p*-type sample leads to a cross over point of very similar diffusion lengths for illuminations of 0.03-0.1 suns, which also covers the injection level at MPP conditions in the solar cell. At high illumination, minority carrier diffusion lengths in the *p*-type sample exceed minority carrier diffusion lengths in the *n*-type sample, which is attributed to the higher Augerlimit in *p*-type [63] due to the larger minority carrier mobility. Accounting for the different Auger-limits, we can conclude that extrinsic recombination losses in the *n*-type sample are smaller than in the *p*-type grains with the simulated diffusion length for an Fe<sub>i</sub> concentration of  $5 \times 10^9$  cm<sup>-3</sup> shows that even a very low concentration of interstitial iron can explain the stronger injection-dependence of minority charge carrier diffusion length compared with the *n*-type sample.

#### C. Comparison with standard mc silicon

In chapter 5.3 we have shown that standard mc *n*-type silicon features significantly higher material quality and efficiency potential compared with standard mc p-type silicon of comparable impurity content crystallized under identical conditions. On the first glance, the results discussed in the previous sections seem to contradict those findings. However, it has to be considered that beside the granular seed layer assisting the growth of the HPM-Si blocks investigated in this work, also different crucibles were used for crystallization. The standard mc silicon blocks investigated in chapter 5.3 were crystallized in G2 size crucibles of standard industrial quality, whereas the HPM-Si blocks were grown in G1 size crucibles of high purity. Thus, metal impurity concentrations in the HPM-Si blocks are lower than in the standard mc-Si blocks of chapter 5.3. The wafers investigated in chapter 5.3 additionally featured an edge region of low material quality affected by solid-state in-diffusion of impurities from the crucible, where  $Fe_i$  is the dominant defect in the *p*-type wafers and  $FeSi_2$ -precipitates in the *n*-type wafers (*cf.* chapter 5.4). In contrast, due to the crystallization in high-purity crucibles, the HPM-Si blocks feature a significantly smaller edge region, which has been cut off entirely and, consequently, does not affect the material quality of the wafers investigated here (cf. Figure 5.30). Considering these differences, we can conclude that for mc silicon with a higher concentration of dissolved metal impurities, such as edge wafers or wafers from blocks crystallized in crucibles of standard quality in industrial production, a gain in material quality and efficiency potential could be achieved by *n*-type doping. Of course, size scaling effects for larger industrial crystallizations have to be taken into account [40]. For the investigated HPM-Si blocks of this chapter, the higher material quality is notable only for processes without P-diffusion, as dissolved impurities become less important after P-gettering, thus leading to comparable diffusion lengths in the investigated p- and n-type HPM-Si after processes including a phosphorus diffusion.

## 5.5.3 High efficiency mc silicon solar cells

## A. Applicability of TOPCon to mc silicon substrate

For the fabrication of high-efficiency mc silicon solar cells, a high-efficiency cell concept is needed, which is able to exploit the high electrical material quality of HPM-Si. A promising cell concept with a full-area Tunnel Oxide Passivated rear Contact (TOPCon) [176] has been developed at Fraunhofer ISE in the past years, featuring high efficiencies of up to 25.1% on monocrystalline *n*-type silicon [251]. However, the applicability of this cell concept to multicrystalline silicon has not been proven so far, and depends crucially on the following issues:



Figure 5.35: Diffusion length image (at 1 sun illumination) of an n-type HPM-Si sample symmetrically passivated with a TOPCon-layer, revealing a good passivation quality of the layer on the chemically polished mc silicon surface. Figure reprinted from [182, 183].

- Does the TOPCon-layer passivate the mc silicon surface? The passivation quality might depend on the different crystal orientation of the grains due to an inhomogeneous thickness of the tunnel oxide.
- Is the contact resistance of the TOPCon-layer on the mc silicon surface low enough? The tunnel transport might be affected by different thicknesses of the tunnel oxide in different grains.
- Is the material quality of the mc silicon bulk after the high-temperature steps of the TOPCon process high enough for the fabrication of high-efficiency so-lar cells?

In order to answer the first two questions, symmetric lifetime samples were fabricated, passivated with a TOPCon-layer on both chemically polished sides of the wafer. After deposition of the layer (ultra-thin wet chemical oxide layer (~14 Å) in combination with a 15 nm thick phosphorus-doped Si layer deposited on top of the oxide), the samples were subjected to an annealing step at 800°C for one hour. Calibrated PL imaging at an illumination of one sun reveals homogeneous minority charge carrier diffusion lengths within the grains on a high level of up to 800  $\mu$ m (*cf.* Figure 5.35), which proves the good passivation quality of the TOPCon-layer on the chemically polished mc-Si surface, irrespective of the crystal orientation. Note that the thickness was adapted to monocrystalline <100> silicon and that a possible thickness variation of the layer depending on grain orientation was not investigated. Measured contact resistivities on TLM-structures (transmission line model measurements, [252]) on the same samples (2-3 m $\Omega$ cm<sup>2</sup>) are even lower than results obtained on FZ reference samples (~10 m $\Omega$ cm<sup>2</sup>), which indicates that no problems related to high contact resistances should occur on mc silicon surfaces.

The third question regarding the material quality can partly be answered by the results of section 5.5.2. Figure 5.32 shows that average minority carrier diffusion lengths in *n*-type HPM-Si are on a very high level after a TOPCon sequence including a Pgettering step (> 600  $\mu$ m). Even after a boron diffusion without a further P-diffusion gettering step, average diffusion lengths exceed 500  $\mu$ m. The additional annealing step at 800°C, which is included in the standard TOPCon process sequence (*cf.* Figure 5.31b), does not change the material quality compared to the single boron diffusion (results not shown in Figure 5.32). Thus, the material quality of the investigated *n*-type HPM-Si should be high enough for the fabrication of high-efficiency solar cells.

The results on passivation quality, contact resistance, and material quality show that there are no principal restrictions for the transfer of the TOPCon concept to *n*-type HPM-Si.

In order to assess the material-related efficiency losses quantitatively, an ELBA analysis is performed in the next section, before the first cell results are presented in section 5.5.3 C.

## B. Efficiency potential

As explained in section 5.5.1 B, predictions of the efficiency potential are performed by an ELBA analysis for three cases:

- Standard TOPCon process (B-Diff+Anneal) on isotextured surface (cell limit: 20.9%)
- ii) TOPCon process including additional P-gettering (B+P+Anneal) on isotextured surface (cell limit: 20.9%)
- iii) TOPCon process including additional P-gettering (B+P+Anneal) with optimized surface texture (cell limit: 22.4%)

The first analysis delivers a realistic estimation of the efficiency potential after the standard TOPCon process, whereas the second analysis gives access to the efficiency gain due to the better material quality after P-gettering. Finally, the third analysis is included to obtain an estimation of the efficiency gain by improvements of the front surface reflectance, e.g. by applying a honeycomb texture. The better reflectance of the front surface alone increases the cell limit from 20.9% (case i and ii) to 22.4%. All analyses are performed on large-area wafers (round 4-inch wafers for case i,  $12.5 \times 12.5$  cm<sup>2</sup> wafers in ii and iii). The results of the ELBA analyses are summarized in Table 5.3. Efficiency images of large-area wafers for cases ii and iii are shown in


Figure 5.36: ELBA prediction of the spatially resolved efficiency potential after the TOPCon-process (including an additional phosphorus gettering diffusion) with a) an isotextured surface or with b) a honeycomb texture for a full-area  $12.5 \times 12.5 \text{ cm}^2$  n-type HPM-Si wafer. Figure adapted from [182].

Figure 5.36, and for case i, the spatially resolved efficiency for the central  $2 \times 2$  cm<sup>2</sup> area is shown in Figure 5.37a.

Applying the standard TOPCon process to the investigated *n*-type HPM-Si results in an efficiency potential 19.9%, which corresponds to a material-related loss of  $-1.0\%_{abs}$  compared with the cell limit. The spatially resolved analysis allows for separately assessing losses due to homogeneously distributed recombination centers by

	i) TOPCon isotextured	ii) TOPCon + P-Diff isotextured	iii) TOPCon + P-Diff honeycomb textured
$V_{\rm oc}({\rm mV})$	662	668	670
$J_{\rm sc}~({\rm mA/cm^2})$	37.3	37.5	40.2
FF <sub>bulk</sub> (%)	80.6	80.7	80.5
η <sub>bulk</sub> (%)	19.9	20.2	21.7
cell limit (%)	20.9	20.9	22.4
$\eta \ loss \ (\%_{abs})$	-1.0	-0.7	-0.7

Table 5.3: Globally averaged cell parameters simulated from injection dependent bulk lifetime measurements.

evaluating the efficiency potential in grains, and losses due to decorated structural crystal defects by comparing the total losses with the efficiency losses in grains. Thus, after the standard TOPCon process, the major part of material-related efficiency losses can be attributed to decorated structural crystal defects ( $-0.7\%_{abs}$ ), whereas losses due to homogeneously distributed recombination centers are low ( $-0.3\%_{abs}$ ), leading to an efficiency potential close to the cell limit in the best grains. This is also highlighted in Figure 5.37a. It should be noted that also the losses due to structural crystal defects are significantly lower than in standard mc *n*-type silicon (*cf.* chapter 5.3), reflecting the good crystal quality of the investigated HPM-Si.

Including an additional P-diffusion in the TOPCon process significantly reduces the losses due to decorated structural crystal defects to  $-0.5\%_{abs}$  and losses due to homogeneously distributed recombination centers to a very low level ( $-0.2\%_{abs}$ ), which results in a larger efficiency potential of 20.2%. Finally, an improvement of the front surface reflectance leads to a strong increase in  $J_{sc}$ , while the material-related losses are unchanged. Thus, the increase in the cell limit ( $+1.5\%_{abs}$ ) would lead to an efficiency potential of 21.7% for *n*-type HPM-Si TOPCon solar cells featuring a honeycomb texture on the front side. Both results support the high efficiency potential of *n*-type HPM-Si with material-related losses of only 0.7%<sub>abs</sub>.

#### C. Solar cell characterization

The promising results of the pre-characterization of section 5.5.3 A and the predicted efficiency potential of section 5.5.3 B encouraged us to fabricate TOPCon solar cells according to the standard processing of Figure 5.31b on *n*-type HPM-Si substrate. From the ELBA simulations, we would expect an efficiency potential of 19.9% for this process on large area 4-inch wafers. Seven  $2 \times 2$  cm<sup>2</sup> solar cells were fabricated per wafer as described in section 5.5.1 A (*cf.* Figure 5.30). Thus, the efficiency potential on the cell areas could slightly differ from the average efficiency potential of the whole wafer. However, due to the very homogeneous material quality (*cf.* Figure 5.35), these deviations are expected to be small, such that the efficiency of  $2 \times 2$  cm<sup>2</sup> solar cells is representative for the efficiency of solar cells on large area. This is also confirmed by an ELBA analysis of a  $2 \times 2$  cm<sup>2</sup> area (corresponding to the region of the best solar cell), which predicts an efficiency potential of 20.0% after the standard TOPCon process. The predicted solar cell parameters, which only slightly differ from the predictions on large area (*cf.* Table 5.3), are included in Table 5.4, and the spatially resolved efficiency prediction is shown in Figure 5.37a.



Figure 5.37: a) ELBA prediction of the spatially resolved efficiency potential after the standard TOPCon process for the  $2 \times 2$  cm<sup>2</sup> region corresponding to the cell area. b) Spatially resolved  $J_{sc}$  of the best solar cell with DARC, obtained from  $J_{sc}$ -density mapping [253]. Slight differences in crystal structure visible in the two images are due to a small difference in block position. Figure reprinted from [183].

The best multicrystalline *n*-type TOPCon solar cell after the standard TOPCon process features an efficiency of 19.3%, which was independently confirmed by Fraunhofer ISE Callab (cf. Table 5.4, ARC). The measured  $V_{oc}$  of 663.0 mV is in excellent agreement with the value predicted by ELBA, and in the range of world record mc-Si solar cells. For comparison, the world record mc-Si solar cells presented by TRINA solar ( $\eta = 20.8\%$  [254] and, very recently,  $\eta = 21.25\%$  [15]) feature a  $V_{oc}$ of 662.6 mV [30] and 667.8 mV [13], respectively, and the previous world record mc-Si solar cell from Schultz et al. [255] ( $\eta = 20.4\%$ ) a  $V_{oc}$  of 664 mV [256]. Also, the measured  $J_{sc}$  of 38.04 mA/cm<sup>2</sup> is on a high level and in reasonable agreement with the ELBA prediction. However, our solar cell suffers from a rather low fill factor of only 76.4%, which is significantly lower than the predicted value of 80.7%. This results in the measured efficiency of 19.3% instead of the predicted efficiency of 20.0%. We can attribute the low fill factor to high series resistance losses in the front metal grid due to processing issues during plating, which we also observed on FZ reference cells. Additionally, measured pseudo-fill factors on mc *n*-type TOPCon solar cells were up to 81.8%. From these results, a material-related issue can be excluded, and we expect even higher solar cell efficiencies in the range of 20% for the same process and material without problems during plating. Additionally, as discussed before, including a Pgettering diffusion in the TOPCon solar cell process would decrease the materialrelated losses by ~0.3%<sub>abs</sub> (*cf.* Table 5.3). Furthermore, a large increase in  $J_{sc}$  could be achieved by an advanced front surface texture instead of the applied acidic texture, which would significantly increase the solar cell efficiency by approximately 1.5%<sub>abs</sub>. Thus, accounting for these two aspects, efficiencies of 21-22% should be attainable on *n*-type HPM-Si TOPCon solar cells (*cf.* Table 5.3), which is a very promising prospect for multicrystalline *n*-type silicon solar cells.

A slight improvement of the front surface reflectance can already be achieved by a double anti-reflection coating, which we applied to the front side of the record mc *n*-type TOPCon solar cell in a second step. This leads to an increase in  $J_{sc}$  to a value of 38.87 mA/cm<sup>2</sup> and, thus, to an efficiency of 19.6% for the same cell (*cf.* Table 5.4, DARC). To our knowledge, this is the highest efficiency reported for a solar cell on multicrystalline *n*-type silicon substrate, exceeding previously published values by more than  $3\%_{abs}$  [215, 218].

In order to understand the losses occurring in this solar cell compared with the Auger lifetime limit, we performed a complete cell analysis as described in detail in [257]. Good agreement between global cell results (*cf.* Table 5.4, DARC) and average values for  $J_{sc}$  (38.7 mA/cm<sup>2</sup>),  $V_{oc}$  (663.9 mV), and fill factor (75.3%) obtained from the different imaging methods included in this loss analysis is observed. This confirms the applicability of such analysis for a spatially resolved insight into the specific loss mechanisms. Exemplarily, Figure 5.37b shows the  $J_{sc}$  map of the solar cell measured by short-circuit current density mapping [253], which nicely reveals the  $J_{sc}$ -nap of the solar cell and the predicted efficiency image from Figure 5.37a are due to slightly different block heights of the lifetime sample and the solar cell. In total, compared with the Auger-limit, 15% of the efficiency losses can be attributed to series resistance

Table 5.4: Result of an ELBA analysis on a representative  $2 \times 2$  cm<sup>2</sup> area, and solar cell results of the best multicrystalline n-type TOPCon solar cell featuring a standard anti-reflection coating (ARC, independently confirmed) and a double anti-reflection coating (DARC).

	ELBA prediction	Best solar cell (ARC)	Best solar cell (DARC)
$V_{\rm oc}~({\rm mV})$	664	663.0	663.7
$J_{\rm sc}~({\rm mA/cm^2})$	37.4	38.04	38.87
FF (%)	80.7	76.4	75.9
η (%)	20.0	19.3	19.6

losses and 20% to optical losses, whereas the major part is due to recombination losses in the emitter and the bulk. As outlined before, the series resistance losses should already be significantly reduced without processing issues during plating, and the application of an improved front surface texture, e.g. a honeycomb texture, would strongly reduce the optical losses. These will be the next steps towards highly efficient multicrystalline *n*-type silicon solar cells beyond 21%.

#### 5.5.4 Conclusion

This chapter focused on the limitations and the material quality of identically crystallized *p*- and *n*-type high performance multicrystalline silicon, as well as on the efficiency potential of *n*-type HPM-Si and its suitability as base material for high efficiency solar cells.

Measuring the concentrations of interstitial iron and chromium at the *p*-type block reveals that Fe<sub>i</sub> is a dominant defect in *p*-type HPM-Si before processing and after B-diffusion, whereas after processes including a P-diffusion it is only of minor impact for recombination. This explains the large increase in diffusion lengths in the *p*-type material after P-diffusion. In contrast, the *n*-type HPM-Si starts at a very high diffusion length level before processing and is not affected by recombination at Fe<sub>i</sub>. Its smaller sensitivity to interstitial iron is also the reason for the significantly larger minority charge carrier diffusion length in *n*- compared with *p*-type HPM-Si after the investigated boron diffusion.

The relative impact of chromium point defects on recombination is comparable in both p- and n-type HPM-Si in the initial state. The B- and the P-diffusion effectively getter Cr<sub>i</sub>, which therefore becomes of minor importance for recombination after processing. Especially after the boron diffusion, it is mainly recombination active structural crystal defects that limit the material quality of n-type HPM-Si. After processes including a phosphorus diffusion, p- and n-type HPM-Si end up at a very similar level of high diffusion lengths. The low impact of dissolved impurities after gettering is partly attributed to the use of high-purity crucibles for crystallization.

The applicability of the high-efficiency TOPCon cell concept to multicrystalline silicon was demonstrated, and a high efficiency potential of *n*-type HPM-Si after the TOPCon cell process was confirmed by an ELBA analysis, predicting efficiencies exceeding 20% on isotextured samples and close to 22% on samples with an improved texture. Finally, a multicrystalline *n*-type TOPCon solar cell featuring an efficiency of 19.6% was fabricated, which is a record efficiency reported for a solar cell on multicrystalline *n*-type silicon substrate. By improving the optics and avoiding large series resistance losses, efficiencies exceeding 21% should be attainable on mc *n*-type TOP-Con solar cells based on the material investigated here.

### 6 Extended Summary & Outlook

#### Modeling Charge Carrier Mobility in Crystalline Silicon (chapter 4)

A main topic of this thesis was the development of a charge carrier mobility model, which is able to predict mobilities both in compensated and uncompensated crystalline silicon. Generally accepted models exist for mobility predictions in uncompensated silicon. However, each of them fails to correctly describe mobilities in compensated silicon, especially for high compensation levels. Klaassen's approach is used as the basis for the model developed here. The deficient mobility prediction in compensated silicon by Klaassen's model is attributed to its semi-empirical character: its starting expression is the purely empirical mobility expression of Caughey and Thomas, which was developed for uncompensated silicon with parameters stemming from fitting experimental data in uncompensated silicon. The mobility model developed in this work keeps the semi-empirical character of Klaassen's model and compensates the insufficient parameterization of the latter by incorporating a new compensationdependent correction term in the empirical Caughey-Thomas expression. This enables to stay as close as possible to the largely successful Klaassen-model and delivers a physical explanation for reduced mobilities in compensated silicon on the hypothesis of reduced screening that is not accounted for sufficiently in Klaassen's model. Further, a new phenomenological parameterization for hole scattering at phonons is included in Klaassen's model, and the model is extended to correctly describe mobility data in compensated silicon along the temperature range from 80 - 350 K. This leads to a unified charge carrier mobility model, which merges with Klaassen's model in the case of uncompensated silicon.

#### Towards High Efficiency Multicrystalline Silicon Solar Cells (chapter 5)

"What is the material related efficiency limit that can be reached with multicrystalline silicon solar cells?" The second main part of this thesis addresses this question by identifying and quantifying the loss mechanisms in mc silicon, including studies on the impact of different crucible purities, different doping types, as well as advanced crystallization techniques.

In the first part, the influence of impurities from the crucible system on the material quality and the solar cell efficiency potential of mc *p*-type silicon is evaluated and the benefit of crystallizing mc silicon blocks in crucibles of high purity is demonstrated successfully. In addition, a specification of loss mechanisms separates the influence of impurities incorporated in the material by diffusion into the liquid melt, by solid-state in-diffusion into the crystallized block and evaluates the impact of homogeneously distributed recombination centers and recombination active structural crystal defects. Finally, an evaluation of the impact of interstitial iron reveals its strong contribution to losses related to homogeneously distributed recombination centers and its dominant role with regard to losses in the edge region. Due to the strong injection dependence of recombination at interstitial iron, the solar cell parameters are affected differently: while  $V_{oc}$  is weakly influenced, Fe<sub>i</sub> affects  $J_{sc}$ , MPP and the fill factor more strongly.

The second part addresses the impact of doping. A comparison of mc *n*- to *p*-type silicon of comparable impurity level along the whole block suggests a significant reduction of efficiency losses by changing the type of doping. The gain in efficiency potential can be attributed to the significantly lower impact of homogeneously distributed recombination centers. The main source of efficiency losses in mc *n*-type silicon is found to be recombination active structural crystal defects, which suggests a high efficiency potential of *n*-type high performance multicrystalline silicon with an improved crystal structure. An issue frequently mentioned with regard to *n*-type doping is the larger resistivity variation along the ingot due to the smaller segregation coefficient of phosphorus compared with boron. Despite the decreasing material quality towards the block top, the efficiency potential of the mc *n*-type silicon brick is stable along the whole block height. This is attributed to the decreasing base resistivity, which compensates the lower material quality. Thus, for the investigated mc *n*-type silicon block, the large resistivity variation ensures a stable efficiency by compensating the variation in material quality. Finally, it is shown that a higher doping concentration along the entire brick could be beneficial for the efficiency potential of mc *n*-type silicon.

The third part presents a detailed analysis of the limitations in mc *n*-type silicon, crystallized with high purity feedstock and standard industrial quality crucible and coating. While  $Cr_i$  plays an important role for recombination in as-grown grains and Fe<sub>i</sub> can have an impact on recombination in as-grown grains with high initial iron concentrations, e.g. in grains in the edge region, their impact is expected to be of minor importance after P-diffusion gettering. In the edge region, recombination at FeSi<sub>2</sub>-precipitates plays a dominant role, both before and after gettering. This explains the smaller width of the edge region in mc *n*-type silicon compared to the edge region in mc *p*-type silicon, where charge carrier lifetime is mainly limited by recombination at interstitial iron. The poor gettering response of the edge region in mc *n*-type silicon is also attributed to the limitation by FeSi<sub>2</sub>-precipitates. Finally, a general observation is the moderate injection dependence of minority charge carrier lifetime in mc *n*-type silicon, compared to the steeper injection-dependence of minority charge carrier lifetime in mc *n*-type silicon.

The major part of recombination losses in mc *n*-type silicon is attributed to recombination active structural crystal defects, either due to a recombination activity of the structural crystal defect itself, or due to a decoration with impurities, e.g. FeSi<sub>2</sub>-precipitates in the edge region. This suggests a strong reduction of recombination losses in mc *n*-type silicon with an improved crystal structure, such as high performance multicrystalline silicon, which is investigated in the last part of this thesis.

The fourth and final part proposes an approach for the fabrication of high efficiency multicrystalline silicon solar cells. Efficiency losses can be reduced by making use of

- a high purity crucible in order to reduce impurity incorporation during crystallization,
- *n*-type doping in order to take advantage of its observed increased efficiency potential,
- a material with an optimized crystal structure featuring a very low density of dislocations in order to reduce recombination at structural crystal defects and precipitates.

Therefore, high performance multicrystalline *n*-type silicon crystallized in a high purity crucible seems to be a very promising material for the production of low cost high efficiency solar cells, which is exploited by combination with a high-efficiency solar cell concept in the final part of this thesis. From measurements of the Fe<sub>i</sub> and Cr<sub>i</sub> concentrations at a *p*-type sister block, the higher minority carrier diffusion length in *n*-type HPM-Si in the as-grown state as well as after a boron diffusion can be attributed to its smaller sensitivity to interstitial iron. The low impact of dissolved impurities after P-diffusion gettering in both p- and n-type HPM-Si is attributed to the use of high-purity crucibles for crystallization. Subsequently, the applicability of the TOP-Con-concept to mc silicon is demonstrated, and a high efficiency potential of *n*-type HPM-Si after the TOPCon cell process with material-related losses below 1% abs is predicted by an ELBA analysis. Finally, the high efficiency potential is confirmed on device level by fabricating multicrystalline *n*-type TOPCon solar cells: the best cell features an efficiency of 19.6%, which is a record efficiency reported for a solar cell on multicrystalline *n*-type silicon substrate and a very high efficiency for an mc silicon solar cell with an isotextured front surface. By improving the optics and avoiding large series resistance losses, efficiencies in the range of 22% should be attainable on mc *n*-type TOPCon solar cells based on the material investigated here.

To conclude, a tentative answer to the question posed at the beginning shall be given: The material-related efficiency losses of state-of-the-art high performance multicrystalline silicon after the investigated high-efficiency solar cell process are in the range of  $1\%_{abs}$  and below. Thus, if a given high-efficiency solar cell process can be adapted to mc silicon, the attainable efficiency limit should be less than  $1\%_{abs}$  lower than the cell limit without bulk recombination losses.

### Outlook

#### Unified mobility model

At the time of this PhD thesis, temperature dependent data for minority carrier mobilities in compensated silicon were lacking. If such data is achieved in the future, an empirical expression for the temperature dependence of the compensation correction term for minority carrier mobilities could be developed. As long as no data is available, it is suggested to use the room temperature compensation correction along the whole temperature range for minority carrier mobilities, as motivated in detail in section 4.4.

The development of the compensation correction term in the model developed in this thesis is physically motivated by the hypothesis of reduced screening not accounted for sufficiently in Klaassen's model. Up to now, no experimental results contradict this hypothesis. On the other hand, there is no physical evidence that proves this hypothesis, neither. At the moment, a joint experiment on mobilities in compensated silicon together with experts from different research groups aims for testing the hypothesis of reduced screening. In this experiment, the compensation level is tuned and screening is adjusted by injection of charge carriers. Mobility measurements at different injection levels should therefore deliver deeper insights into the physics behind the mobility reduction in compensated silicon. Further, the collection of temperature dependent mobility data in high resistivity *n*-type FZ silicon could serve as a data base for a new parameterization of electron scattering at phonons similar to the approach presented in this thesis.

#### Multicrystalline silicon

By taking advantage of high purity crucibles and seed-assisted growth for the crystallization of high performance multicrystalline silicon from high purity feedstock, efficiency losses in mc silicon solar cells can be reduced significantly. The results presented in this thesis are obtained for a feedstock purity level of ~9N and for G1 or G2 sized laboratory crucibles. In industry, however, larger crucibles of up to 1200 kg of silicon (G7) are used. On the basis of experimentally validated simulations, the results obtained in chapter 5.2 for G1 blocks (14 kg) can be transferred directly to larger ingot sizes [40], and the general conclusions drawn for G1 sized crucibles remain valid: Both, the impurity concentration in the center of an ingot as well as the depth of solidstate in-diffusion can be reduced significantly by a crystallization in a high purity crucible [40]. This is illustrated in Figure 6.1, which shows the depths of iron profiles



Figure 6.1: Calculated depths of iron profiles from solid-state in-diffusion (left) and estimated iron concentration in the center of an ingot at 50% block height (right) as a function of crucible size for a feedstock purity of ~9N. Comparisons should be made between G1 and G2 or G4-G6, as the research crystallization recipes used as input for the calculations for G1 and G2 differ significantly from high-throughput recipes used in the calculations for G4-G6. Figures based on the calculations from [40]. The right graph additionally highlights the total iron concentration in the center of an ingot at 50% block height stemming from the feedstock for different feedstock purity levels. For a feedstock purity level  $\leq$  7N, the feedstock becomes the main source for metal impurities.

from solid-state in-diffusion (defined as the area with more than five times higher iron concentration compared to the center) together with the estimated iron concentration in the center of an ingot for different crucible sizes based on the calculations from [40].

While a crystallization in a larger standard quality crucible already reduces the impurity concentration in the center due to the decreased ratio of Si volume to crucible contact area, a crystallization in a high purity crucible further reduces this impurity concentration significantly and comes along with a smaller edge region. This is of importance even for industrial size crucibles, as a large part of the wafers will still be influenced by the edge region (e.g., 24 from 49 wafers in G7 are "edge wafers"). The level of impurity concentrations in the center that is tolerable for solar cell fabrication strongly depends on the applied cell concept and the desired efficiency. E.g., for the fabrication of a standard Al-BSF silicon solar cell an iron concentration in the range of  $3 \times 10^{10} \, \text{cm}^{-3}$  as present in the center of a G6 ingot crystallized in a standard quality crucible would be low enough, whereas a high efficiency solar cell that relies on large minority carrier diffusion lengths could benefit from a material crystallized in a high purity crucible. Of course, in this context also the applied gettering process steps are of importance. Furthermore, due to the smaller edge region, the use of high purity crucibles could increase the yield of industrial mc silicon ingots. If the application of high purity crucibles in industry is economical depends critically on the cost difference

between the standard quality and the high purity crucible and the achievable efficiency of solar cells based on the corresponding material.

Another aspect that has to be taken into account is the feedstock purity. The mc silicon ingots investigated in this thesis were crystallized from high purity feedstock with a bulk metal concentration below 2 ppbw, which corresponds to a purity level of  $\sim 9$ N. To address the impact of the feedstock purity on the total metal concentration in the crystallized ingot, the right graph in Figure 6.1 also shows the total iron concentration in the center of an ingot stemming from the feedstock for different feedstock purity levels, calculated with Scheil's equation for a block height of 50%. In this calculation, a segregation coefficient of iron of  $k_{Fe,seg} = 2 \cdot 10^{-5}$  was used, and the purity level refers to the iron concentration by weight, i.e., 9N corresponds to an iron concentration in the feedstock of 1 ppbw or an atom density of  $2.5 \times 10^{13}$  cm<sup>-3</sup>. A comparison of the iron concentration incorporated from the crucible system with the iron concentration stemming from the feedstock leads to the following conclusions: While for a feedstock purity  $\geq$  9N, the crucible system is the main source for metal impurities in mc silicon ingots, concentrations of metal impurities stemming from the feedstock are in the range of those stemming from high purity crucibles for a feedstock purity level of 8N and from standard quality crucibles for a feedstock purity level of 7N. For a purity level below 7N, the feedstock becomes the main source for metal impurities in mc silicon ingots. This can deliver guidelines for the purification of metallurgical silicon by alternative routes as well as for the crystallization of umg-Si feedstock: While a gain in mc umg-Si solar cell efficiency can be expected for an increasing feedstock purity of up to 8N, a further purification does not seem to be necessary, as then the crucible system becomes the main impurity source. Crystallizing the silicon feedstock in high purity crucibles becomes worthwile for feedstock purity levels  $\geq 8$ N. Regarding umg-Si, also compensation effects due to the simultaneous presence of acceptors and donors have to be kept in mind, especially their impact on charge carrier mobility. For typical compensation levels  $\leq 10$ , relative average mobility reductions in compensated silicon compared with uncompensated silicon of equal total dopant concentrations are below 20%. A minority charge carrier mobility reduction of -20% would reduce the minority charge carrier diffusion length by approximately -10%. Thus, the impact of reduced charge carrier mobilities on charge carrier diffusion lengths in compensated umg-Si is estimated to be relatively small for moderate compensation levels  $\leq$  10. Therefore, compensated umg-Si can be a promising material even for the fabrication of highly efficient mc silicon solar cells, if the purification route enables moderate compensation level  $\leq 10$  and a feedstock purity level  $\geq 7$ N.

While the application of high purity crucibles in industry is a complex topic, the crystallization technique for the production of HPM-Si by seed-assisted growth has already become industrial standard. As shown in this thesis, a combination of high purity crucibles with a HPM-Si crystallization leads to high quality mc silicon with very low efficiency losses, both in p- and n-type HPM-Si. Thus, mc silicon as substrate for solar cells remains a very promising material. If mc *n*-type silicon becomes relevant for industrial solar cell fabrication strongly depends on the future cell concept development. In November 2014, Trina Solar presented their efficiency world record (20.8%) based on a p-type HPM-Si PERC solar cell [254] and, in June 2015, reported on their aim to achieve 21.3% conversion efficiency with the same cell concept [258], which was achieved very recently with the announcement of a new efficiency world record of 21.25% for a multicrystalline silicon solar cell [13, 15, 16]. This solar cell already features an advanced front surface texture. The predictions presented in this thesis show that efficiencies in the range of 22% should be attainable on *n*-type HPM-Si TOPCon solar cells with an advanced front surface texture. These results are based on *n*-type HPM-Si crystallized in a G1 sized high purity crucible. As mentioned before, a crystallization of *n*-type HPM-Si in larger crucibles could further increase its material quality and, consequently, its efficiency potential. A glance in the crystal ball regarding the future of mc silicon solar cells reveals an industry that is mainly focused on *p*-type HPM-Si PERC cells, whereas some startups might emerge focusing on the fabrication of high-efficiency *n*-type HPM-Si solar cells.

## 7 Detaillierte Zusammenfassung

Modellierung von Ladungsträgerbeweglichkeiten in kristallinem Silizium (Kapitel 4) Ein Hauptaspekt dieser Dissertation war die Entwicklung eines Modells für Ladungsträgerbeweglichkeiten in kristallinem Silizium, das verlässliche Vorhersagen von Mobilitäten sowohl in kompensiertem als auch in unkompensiertem Silizium ermöglicht. Momentan existieren anerkannte Modelle zur Vorhersage von Beweglichkeiten in unkompensiertem Silizium, mit denen jedoch eine zuverlässige Beschreibung von Beweglichkeiten in kompensiertem Silizium nicht möglich ist. Besonders für hohe Kompensationsgrade wurden starke Abweichungen zwischen modellierten und gemessenen Mobilitäten beobachtet. Das Mobilitätsmodell von Klaassen wird als Grundlage für das hier entwickelte Modell verwendet. Die fehlerhafte Vorhersage von Mobilitäten in kompensiertem Material durch Klaassens Modell wird auf dessen semiempirische Beschaffenheit zurückgeführt: Als Ausgangsformel wird der rein empirische Mobilitätsausdruck von Caughey und Thomas verwendet, der zur Beschreibung von Mobilitäten in unkompensiertem Silizium auf Basis eines Fits an Messdaten in unkompensiertem Silizium entwickelt wurde. Bei der Entwicklung des Mobilitätsmodells in dieser Dissertation wurde der semi-empirische Charakter des Klaassenmodells beibehalten und dessen ungenügende Parametrisierung durch die Einführung eines kompensationsabhängigen Korrekturterms in der empirischen Caughey-Thomas Ausgangsformel behoben. Dieser Korrekturterm beruht auf der Hypothese, dass das Klaassenmodell für kompensiertes Silizium die reduzierte Abschirmung ionisierter Dotierstoffe durch freie Ladungsträger nicht ausreichend berücksichtigt. Dadurch liefert dieser Ansatz eine physikalische Erklärung für reduzierte Mobilitäten in kompensiertem Silizium und ermöglicht zugleich, das für unkompensiertes Silizium weitgehend erfolgreiche Klaassenmodell beizubehalten. Zusätzlich wurde Klaassens Parametrisierung zur Beschreibung von Löcherstreuung an Phononen durch eine neue phänomenologische Parametrisierung ersetzt, die besser mit experimentellen Daten und numerischen Mobiltätsberechnungen übereinstimmt. Schließlich wurde das Mobilitätsmodell zusätzlich erweitert, um Mobilitäten in kompensiertem Silizium im Temperaturbereich von 80 – 350 K richtig zu beschreiben. Dadurch wird ein einheitliches Ladungsträgermobilitätsmodell erhalten, das für unkompensiertes Silizium mit dem Klaassenmodell übereinstimmt.

#### Hocheffiziente multikristalline Siliziumsolarzellen (Kapitel 5)

Der zweite Hauptaspekt dieser Dissertation beschäftigte sich mit der Frage nach der materialbedingten Wirkungsgradobergrenze, die mit multikristallinen Siliziumsolarzellen erreicht werden kann. Zur Beantwortung dieser Frage wurden Verlustmechanismen in multikristallinem Silizium aufgrund von Verunreinigungen aus dem Tiegelsystem identifiziert und quantifiziert, der Einfluss unterschiedlicher Dotierungen untersucht, sowie das Potential von multikristallinem Silizium, das durch neuartige Kristallisationsmethoden hergestellt wurde, analysiert.

Im ersten Teil wird der Einfluss von Verunreinigungen aus dem Tiegelsystem auf die Materialqualität und den Solarzellenwirkungsgrad von multikristallinem p-Typ Silizium untersucht und der Gewinn durch die Verwendung hochreiner Kristallisationstiegel aufgezeigt. Die Analyse umfasst auch eine Spezifizierung und Quantifizierung der Verlustmechanismen, wobei der Einfluss von Verunreinigungen, die während der Kristallisation in die Siliziumschmelze diffundierten, von solchen, die durch Festkörperdiffusion in den bereits erstarrten Kristall diffundierten, unterschieden wird und Verluste aufgrund von homogen verteilten Rekombinationszentren und rekombinationsaktiven strukturellen Kristalldefekten quantifiziert werden. Schließlich zeigt eine Detailanalyse zum Einfluss von interstitiellem Eisen, dass ein großer Teil der Verluste aufgrund von homogen verteilten Rekombinationszentren auf Fe<sub>i</sub> zurückzuführen ist und Verluste im Randbereich durch Fe<sub>i</sub> dominiert werden. Aufgrund der starken Injektionsabhängigkeit von interstitiellem Eisen werden die Solarzellenparameter unterschiedlich beeinflusst: Während  $V_{oc}$  nur gering von Fe<sub>i</sub> beeinträchtigt wird, wirkt es sich stärker auf MPP, den Füllfaktor und besonders auf  $J_{sc}$  aus.

Der zweite Teil behandelt den Einfluss der Dotierung. Ein Vergleich von mc *n*- und *p*-Typ Blöcken ähnlichen Verunreinigungsniveaus zeigt, dass Wirkungsgradverluste durch einen Wechsel des Dotiertyps deutlich verringert werden können. Der Wirkungsgradgewinn kann auf den geringeren Einfluss homogen verteilter Rekombinationszentren zurückgeführt werden. Als Hauptverlustmechanismus in multikristallinem n-Typ Silizium können rekombinationsaktive strukturelle Kristalldefekte ausgemacht werden, was auf ein hohes Wirkungsgradpotential von n-Typ HPM-Si mit verbesserter Kristallstruktur schließen lässt. Als möglicher Nachteil in Zusammenhang mit n-Dotierung wird oft die größere Schwankung des Basiswiderstands als Funktion der Blockhöhe aufgrund des kleineren Segregationskoeffizienten von Phosphor angeführt. Trotz abnehmender Materialqualität Richtung Blockkappe ist das Wirkungsgradpotential des n-Typ Blocks entlang der ganzen Blockhöhe nahezu konstant. Dies ist auf den abnehmenden Basiswiderstand zurückzuführen, der die abnehmende Materialqualität kompensiert. Somit führt im hier untersuchten multikristallinen n-Typ Block die starke Änderung des Basiswiderstands sogar zu einer Stabilisierung des Wirkungsgradpotentials. Abschließend wird der Gewinn im Wirkungsgradpotential entlang der gesamten Blockhöhe, der durch eine höhere Dotierstoffkonzentration im multikristallinen n-Typ Block erreicht werden könnte, abgeschätzt.

Der dritte Teil behandelt die Limitierungen in multikristallinem *n*-Typ Silizium, das unter Verwendung von hochreinem Siliziumfeedstock in Standardindustrietiegeln kristallisiert wurde, im Detail. Während ein signifikanter Rekombinationsanteil in guten Körnern unprozessierter ("as-grown", nur oberflächenpassiviert) Wafer auf Cr<sub>i</sub> zurückzuführen ist und Fei in as-grown Körnern mit hoher initialer Eisenkonzentration, wie z.B. in Randkörnern, die Gesamtrekombination beeinflussen kann, ist deren Einfluss nach Phosphordiffusionsgettern von geringer Bedeutung. Im Randbereich dominieren FeSi<sub>2</sub>-Präzipitate sowohl vor als auch nach Gettern die Rekombination. Dadurch kann die schmalere Randzone in multikristallinem *n*-Typ Silizium im Vergleich zu multikristallinem p-Typ Silizium, in dem die Ladungsträgerlebensdauer in der Randzone vor allem durch interstitielles Eisen limitiert ist, erklärt werden. Zusätzlich liefert die Limitierung durch Eisenpräzipitate eine Erklärung dafür, dass sich die Lebensdauer in Randkörnern in multikristallinem n-Typ Silizium durch Getterprozesse weniger stark verbessert als Körner im Zentrum. Schließlich wurde allgemein in multikristallinem n-Typ Silizium eine geringere Injektionsabhängigkeit der Ladungsträgerlebensdauer als in multikristallinem p-Typ Silizium beobachtet.

Rekombinationsverluste in multikristallinem *n*-Typ Silizium sind größtenteils auf rekombinationsaktive strukturelle Kristalldefekte zurückzuführen. Dabei kann die Rekombinationsaktivität entweder auf den strukturellen Kristalldefekt selbst oder auf eine Dekoration mit Verunreinigungen, wie z.B. FeSi<sub>2</sub>-Präzipitate, zurückgeführt werden. Daher wird vermutet, dass Rekombinationsverluste in multikristallinem *n*-Typ Silizium durch eine bessere Kristallstruktur, die durch die Kristallisation von HPM-Si erhalten werden kann, stark reduziert werden.

Der letzte Teil dieser Dissertation widmet sich daher der Untersuchung von Wirkungsgradverlusten in HPM-Si und schlägt eine Vorgehensweise zur Herstellung hocheffizienter multikristalliner Siliziumsolarzellen vor. Wirkungsgradverluste können verringert werden, indem

- hochreine Kristallisationstiegel zur Verringerung des Verunreinigungseintrags aus dem Tiegelsystem verwendet werden,
- die Vorteile einer *n*-Typ Dotierung ausgenutzt werden,
- ein Material mit optimierter Kristallstruktur zur Reduzierung rekombinationsaktiver struktureller Kristalldefekte und Präzipitate eingesetzt wird.

Daher scheint in einem hochreinen Tiegel kristallisiertes *n*-Typ HPM-Si ein sehr vielversprechendes Material zur Herstellung günstiger und hocheffizienter Siliziumsolarzellen zu sein, wenn es zusätzlich mit einem Hocheffizienzzellkonzept kombiniert werden kann. Der letzte Teil dieser Arbeit widmet sich dieser Aufgabe. Durch Messungen der Fe<sub>i</sub> und Cr<sub>i</sub> Konzentrationen an einem *p*-Typ "Schwesterblock" lassen sich die höheren Diffusionslängen der Minoritätsladungsträger im n-Typ Material vor Prozessierung und nach Bordiffusion auf den geringeren Einfluss interstitiellen Eisens zurückführen. Durch die Anwendung eines hochreinen Kristallisationstiegels sind die Rekombinationsverluste aufgrund von gelösten Verunreinigungen nach einer Phosphordiffusion sowohl in p- als auch in n-Typ HPM-Si sehr gering. Im zweiten Teil dieses Kapitels wird die Anwendbarkeit des Hocheffizienzzellkonzepts TOPCon auf multikristallinem Silizium nachgewiesen sowie ein hohes Wirkungsgradpotential von *n*-Typ HPM-Si in Kombination mit diesem Zellkonzept durch ELBA Analysen und auf Zellniveau bestätigt. Materialbedingte Wirkungsgradverluste liegen hierbei unter  $1\%_{abs}$ . Die beste multikristalline *n*-Typ TOPCon Solarzelle, die in dieser Charge hergestellt wurde, weist einen Wirkungsgrad von 19.6% auf. Dies entspricht einem Rekordwert für multikristalline n-Typ Siliziumsolarzellen und ist allgemein ein hoher Wirkungsgrad für isotexturierte multikristalline Si-Solarzellen. Durch eine Verbesserung der Vorderseitenoptik und die Vermeidung hoher Serienwiderstände im Vorderseitenkontakt ließe sich mit einer multikristallinen n-Typ TOPCon Solarzelle unter Verwendung des hier untersuchten Materials ein Wirkungsgrad von knapp 22% erreichen.

Zusammenfassend soll eine vorsichtige Antwort auf die Frage der materialbedingten Wirkungsgradobergrenze multikristalliner Siliziumsolarzellen gegeben werden: Materialbedingte Wirkungsgradverluste von modernstem HPM-Si liegen für das hier untersuchte Hocheffizienzzellkonzept im Bereich von  $1\%_{abs}$  und darunter. Abhängig davon, ob ein bestimmter Hocheffizienzzellprozess auf multikristallines Silizium anwendbar ist, sollte die materialbedingte Wirkungsgradobergrenze weniger als  $1\%_{abs}$ unter dem zellkonzeptbedingten Effizienzlimit ohne Volumenrekombinationsverluste liegen.

# 8 Appendix

### 8.1 Mobility Data in Compensated Silicon

Data used for fitting of model parameters

i)	Majority hole mobility in compensated <i>p-type</i> Silicon			
Sample	<i>T</i> (K)	$N_A(\mathrm{cm}^{-3})$	$N_D(\mathrm{cm}^{-3})$	$\mu_{maj,h}(\mathrm{cm}^2/\mathrm{Vs})$
Cz-Li_01	300	$1.02 \cdot 10^{16}$	$2.60 \cdot 10^{15}$	411
Cz-Li_02	300	$9.53 \cdot 10^{15}$	3.39·10 <sup>15</sup>	383
Cz-Li_03	300	$1.06 \cdot 10^{16}$	$5.43 \cdot 10^{15}$	363
Cz-Li_04	300	$9.97 \cdot 10^{15}$	$6.44 \cdot 10^{15}$	367
Cz-Li_05	300	$1.47 \cdot 10^{16}$	$1.32 \cdot 10^{16}$	290
Cz-Ge_01	300	$2.66 \cdot 10^{16}$	$1.51 \cdot 10^{16}$	334
Cz-Ge_02	300	$3.09 \cdot 10^{16}$	$1.95 \cdot 10^{16}$	352
Cz-Ge_03	300	$3.75 \cdot 10^{16}$	$2.94 \cdot 10^{16}$	336
Cz-Ge_04	300	$3.79 \cdot 10^{16}$	$3.06 \cdot 10^{16}$	332
Cz-Ge_05	300	$3.84 \cdot 10^{16}$	$3.15 \cdot 10^{16}$	308
Cz-Ge_06	300	$3.75 \cdot 10^{16}$	$3.33 \cdot 10^{16}$	282
Cz-Ge_07	300	$3.16 \cdot 10^{16}$	$7.40 \cdot 10^{15}$	369
Cz-Ge_08	300	$3.38 \cdot 10^{16}$	$8.60 \cdot 10^{15}$	374
Cz-Ge_09	300	$2.99 \cdot 10^{16}$	$8.48 \cdot 10^{15}$	373
Cz-Ge <sup>10</sup>	300	$4.81 \cdot 10^{16}$	$1.46 \cdot 10^{16}$	351
Cz-Ge <sup>11</sup>	300	$5.07 \cdot 10^{16}$	$1.60 \cdot 10^{16}$	342
Cz-Ge_12	300	$4.42 \cdot 10^{16}$	$9.18 \cdot 10^{15}$	345
Cz-Ro_01	300	$8.10 \cdot 10^{16}$	$4.05 \cdot 10^{16}$	291
Cz-Ro_02	300	$4.00 \cdot 10^{16}$	$2.50 \cdot 10^{16}$	365
mc-Sc_01	300	$3.33 \cdot 10^{16}$	$7.00 \cdot 10^{15}$	342
mc-Sc_02	300	$3.40 \cdot 10^{16}$	$7.74 \cdot 10^{15}$	338
mc-Sc_03	300	$3.50 \cdot 10^{16}$	$9.40 \cdot 10^{15}$	325
mc-Sc_04	300	$3.61 \cdot 10^{16}$	$1.23 \cdot 10^{16}$	314
mc-Sc_05	300	$4.69 \cdot 10^{16}$	$2.54 \cdot 10^{16}$	305
mc-Sc_06	300	$4.37 \cdot 10^{16}$	$1.20 \cdot 10^{16}$	341
mc-Sc_07	300	$4.49 \cdot 10^{16}$	$1.33 \cdot 10^{16}$	338
mc-Sc_08	300	$4.61 \cdot 10^{16}$	$1.56 \cdot 10^{16}$	327
mc-Sc_09	300	$4.76 \cdot 10^{16}$	$2.03 \cdot 10^{16}$	313
mc-Sc_10	300	$5.59 \cdot 10^{16}$	$3.01 \cdot 10^{16}$	307
mc-Sc_11	300	$4.53 \cdot 10^{16}$	$1.88 \cdot 10^{16}$	310
mc-Sc_12	300	$6.08 \cdot 10^{16}$	$3.74 \cdot 10^{16}$	261
Cz-Fo-1 01	300	$1.63 \cdot 10^{17}$	$1.09 \cdot 10^{17}$	226
Cz-Fo-1_02	300	$1.76 \cdot 10^{17}$	$1.24 \cdot 10^{17}$	208
Cz-Fo-2_01	300	$7.22 \cdot 10^{16}$	$6.65 \cdot 10^{16}$	216
Cz-Fo-2 02	300	$7.32 \cdot 10^{16}$	$6.76 \cdot 10^{16}$	231
Cz-Fo-2_03	300	$8.28 \cdot 10^{16}$	$7.40 \cdot 10^{16}$	222
Cz-Fo-2_04	300	$9.83 \cdot 10^{16}$	$8.60 \cdot 10^{16}$	222
Cz-Fo-2_05	300	$1.10 \cdot 10^{17}$	9.51·10 <sup>16</sup>	223
Cz-Fo-2_06	300	$1.24 \cdot 10^{17}$	$1.07 \cdot 10^{17}$	221
Cz-Fo-2_07	300	$1.44 \cdot 10^{17}$	$1.22 \cdot 10^{17}$	216
Cz-Fo-2_08	300	$1.73 \cdot 10^{17}$	$1.37 \cdot 10^{17}$	209
Cz-Fo-2_09	300	$2.21 \cdot 10^{17}$	$1.80 \cdot 10^{17}$	203
Cz-Fo-2_10	300	$2.89 \cdot 10^{17}$	$2.29 \cdot 10^{17}$	173
Cz-Fo-2_11	300	$3.12 \cdot 10^{17}$	$2.48 \cdot 10^{17}$	199

Sample	<i>Т</i> (К)	$N_A(\mathrm{cm}^{-3})$	$N_D(\mathrm{cm}^{-3})$	$\mu_{maj,h}$ (cm <sup>2</sup> /Vs)
Cz-Fo-2_12	300	3.18·10 <sup>17</sup>	$2.52 \cdot 10^{17}$	203
Cz-Fo-3 01	300	$2.32 \cdot 10^{17}$	$2.09 \cdot 10^{17}$	177
Cz-Fo-3 02	300	$2.35 \cdot 10^{17}$	$2.13 \cdot 10^{17}$	176
Cz-Fo-3 03	300	$2.46 \cdot 10^{17}$	$2.25 \cdot 10^{17}$	169
Cz-Fo-3_04	300	$2.62 \cdot 10^{17}$	$2.43 \cdot 10^{17}$	160
Cz-Fo-3_05	300	$2.80 \cdot 10^{17}$	$2.62 \cdot 10^{17}$	148
Cz-Fo-3_06	300	$3.07 \cdot 10^{17}$	$2.95 \cdot 10^{17}$	125
Cz-Fo-3_07	300	$3.37 \cdot 10^{17}$	$3.27 \cdot 10^{17}$	104
Cz-Fo-3_08	300	$3.90 \cdot 10^{17}$	$3.84 \cdot 10^{17}$	73
Cz-Fo-3_09	300	$4.34 \cdot 10^{17}$	$4.28 \cdot 10^{17}$	58
Cz-Fo-4_01	300	$2.64 \cdot 10^{16}$	$1.05 \cdot 10^{16}$	356
Cz-Fo-4_02	300	$2.71 \cdot 10^{16}$	$1.07 \cdot 10^{16}$	349
Cz-Fo-4_03	300	$2.79 \cdot 10^{16}$	$1.17 \cdot 10^{16}$	348
Cz-Fo-4_04	300	$2.89 \cdot 10^{16}$	$1.35 \cdot 10^{16}$	350
Cz-Fo-4_05	300	$3.05 \cdot 10^{16}$	$1.55 \cdot 10^{16}$	338
Cz-Fo-4_06	300	$3.31 \cdot 10^{16}$	$2.18 \cdot 10^{16}$	318
Cz-Fo-5_01	300	$4.14 \cdot 10^{16}$	$3.39 \cdot 10^{16}$	281
Cz-Fo-5_02	300	$4.51 \cdot 10^{16}$	$3.66 \cdot 10^{16}$	285
Cz-Fo-5_03	300	$5.01 \cdot 10^{16}$	$4.16 \cdot 10^{16}$	275
Cz-Fo-5_04	300	$5.64 \cdot 10^{16}$	$4.76 \cdot 10^{16}$	254
Cz-Fo-5_05	300	$6.61 \cdot 10^{16}$	$5.69 \cdot 10^{16}$	246
Cz-Fo-5_06	300	$8.62 \cdot 10^{16}$	$7.51 \cdot 10^{16}$	222
Cz-Fo-5_07	300	$1.32 \cdot 10^{17}$	$1.11 \cdot 10^{17}$	197
mc-Fo-1_01	300	$9.37 \cdot 10^{16}$	$7.66 \cdot 10^{16}$	239
mc-Fo-1_02	300	$8.54 \cdot 10^{16}$	$6.01 \cdot 10^{16}$	268
mc-Fo-1_03	300	$8.03 \cdot 10^{16}$	$5.23 \cdot 10^{16}$	289
mc-Fo-1_04	300	$7.74 \cdot 10^{16}$	$4.58 \cdot 10^{16}$	291
mc-Fo-1_05	300	$7.45 \cdot 10^{16}$	$4.38 \cdot 10^{16}$	294
mc-Fo-1_06	300	$7.30 \cdot 10^{16}$	$4.14 \cdot 10^{16}$	296
mc-Fo-2_01	300	$9.51 \cdot 10^{16}$	$6.35 \cdot 10^{16}$	275
mc-Fo-2_02	300	$9.59 \cdot 10^{16}$	$6.70 \cdot 10^{16}$	251
mc-Fo-2_03	300	$9.67 \cdot 10^{16}$	$6.67 \cdot 10^{16}$	247
mc-Fo-2_04	300	$1.21 \cdot 10^{17}$	$9.58 \cdot 10^{16}$	240
mc-Fo-2_05	300	$1.30 \cdot 10^{17}$	$1.06 \cdot 10^{17}$	227
mc-Fo-2_06	300	$1.43 \cdot 10^{17}$	$1.18 \cdot 10^{17}$	222
mc-Fo-2_07	300	$1.89 \cdot 10^{17}$	$1.64 \cdot 10^{17}$	205
Cz-Sc-1_01	295	$1.16 \cdot 10^{16}$	$5.17 \cdot 10^{15}$	382
Cz-Sc-1_02	295	$1.20 \cdot 10^{16}$	$6.01 \cdot 10^{15}$	368
Cz-Sc-1_03	295	$1.25 \cdot 10^{16}$	$6.57 \cdot 10^{15}$	368
Cz-Sc-1_04	295	$1.30 \cdot 10^{16}$	8.48·10 <sup>15</sup>	359
Cz-Sc-1_05	295	$1.39 \cdot 10^{16}$	9.85·10 <sup>15</sup>	349
Cz-Sc-1_06	295	$1.56 \cdot 10^{16}$	$1.34 \cdot 10^{16}$	308

ii) Majority electron mobility in compensated *n*-type Silicon

	in the second se				
Sample	<b>T</b> (K)	$N_A(\mathrm{cm}^{-3})$	$N_D(\mathrm{cm}^{-3})$	$\mu_{maj,e}(\mathrm{cm}^2/\mathrm{Vs})$	
Cz-Fo-6_01	300	$9.20 \cdot 10^{16}$	$1.00 \cdot 10^{17}$	472	
Cz-Fo-6_02	300	$1.01 \cdot 10^{17}$	$1.10 \cdot 10^{17}$	439	
Cz-Fo-6_03	300	$1.17 \cdot 10^{17}$	$1.28 \cdot 10^{17}$	419	
Cz-Fo-6_04	300	$1.46 \cdot 10^{17}$	$1.60 \cdot 10^{17}$	381	
Cz-Fo-6_05	300	$2.02 \cdot 10^{17}$	$2.14 \cdot 10^{17}$	308	
Cz-Sc-2_01	295	$1.17 \cdot 10^{16}$	$1.38 \cdot 10^{16}$	832	

iv)

Sample	<i>T</i> (K)	$N_A(\mathrm{cm}^{-3})$	$N_D(\mathrm{cm}^{-3})$	$\mu_{maj,e}(\mathrm{cm}^2/\mathrm{Vs})$
Cz-Sc-2_02	295	$1.19 \cdot 10^{16}$	$1.44 \cdot 10^{16}$	833
Cz-Sc-2_03	295	$1.22 \cdot 10^{16}$	$1.62 \cdot 10^{16}$	859
Cz-Sc-2_04	295	$1.37 \cdot 10^{16}$	$2.29 \cdot 10^{16}$	863
Cz-Sc-2_05	295	$1.51 \cdot 10^{16}$	$3.17 \cdot 10^{16}$	837
Cz-Sc-2_06	295	$1.58 \cdot 10^{16}$	$3.72 \cdot 10^{16}$	816

iii) Minority electron mobility in compensated *p-type* Silicon

Sample	<i>T</i> (K)	$N_A(\mathrm{cm}^{-3})$	$N_D(\mathrm{cm}^{-3})$	$\mu_{min,e}(\mathrm{cm}^2/\mathrm{Vs})$
Cz-Ro_01	300	$8.10 \cdot 10^{16}$	$4.05 \cdot 10^{16}$	476
Cz-Ro_02	300	$4.00 \cdot 10^{16}$	$2.50 \cdot 10^{16}$	660
Cz-Fo-2_13	300	$7.39 \cdot 10^{16}$	$6.82 \cdot 10^{16}$	452
Cz-Fo-2_14	300	$1.00 \cdot 10^{17}$	$8.79 \cdot 10^{16}$	499
Cz-Fo-2_15	300	$1.28 \cdot 10^{17}$	$1.11 \cdot 10^{17}$	441
Cz-Fo-2_16	300	$1.83 \cdot 10^{17}$	$1.47 \cdot 10^{17}$	475
Cz-Fo-3_10	300	$2.39 \cdot 10^{17}$	$2.16 \cdot 10^{17}$	270
Cz-Fo-3 11	300	$2.44 \cdot 10^{17}$	$2.21 \cdot 10^{17}$	257
Cz-Fo-3_12	300	$2.70 \cdot 10^{17}$	$2.51 \cdot 10^{17}$	198
Cz-Fo-3_13	300	$3.06 \cdot 10^{17}$	$2.88 \cdot 10^{17}$	146
Cz-Fo-3_14	300	$3.13 \cdot 10^{17}$	$3.00 \cdot 10^{17}$	135
Cz-Fo-3_15	300	$3.46 \cdot 10^{17}$	$3.36 \cdot 10^{17}$	95
Cz-Fo-3_16	300	$4.48 \cdot 10^{17}$	$4.42 \cdot 10^{17}$	27

Minority hole mobility in compensated *n*-type Silicon

		· ·		
Sample	<b>T</b> ( <b>K</b> )	$N_A(\mathrm{cm}^{-3})$	$N_D(\mathrm{cm}^{-3})$	$\mu_{min,h}(\mathrm{cm}^2/\mathrm{Vs})$
Cz-Fo-6_06	300	$9.17 \cdot 10^{16}$	9.98·10 <sup>16</sup>	193
Cz-Fo-6_07	300	$1.02 \cdot 10^{17}$	$1.11 \cdot 10^{17}$	187
Cz-Fo-6_08	300	$1.18 \cdot 10^{17}$	$1.29 \cdot 10^{17}$	153
Cz-Fo-6_09	300	$1.45 \cdot 10^{17}$	$1.59 \cdot 10^{17}$	136
Cz-Fo-6_10	300	$2.08 \cdot 10^{17}$	$2.20 \cdot 10^{17}$	95

### 8.2 Derivation of $\beta_2(T)$ and Model Implementation

In this section, the origin of the expression for  $\beta_2(T)$  from equation (4.42) is explained. We observe that for lowly compensated silicon, applying the room temperature correction for compensation with the room temperature compensation level along the whole temperature range delivers very good agreement with experimental data. However, experimental mobility decreases faster than predicted by the room temperature correction. Down to a certain reference temperature  $T_{ref}$  the room temperature correction works well before the experimental mobility starts to decrease more strongly with decreasing temperature than predicted (*cf.* Figure 4.10). We observe that this reference temperature is a function of the total dopant concentration and the compensation level. Fitting the reference temperature plotted as a function of  $C_{l,RT}^2 \cdot (N_A + N_D)$  delivers the expression from equation (4.43). To account for the stronger decrease starting at

the reference temperature  $T_{ref}$ , the room temperature compensation level is modified with a function starting to increase for temperatures lower than  $T_{ref}$  and corresponding to one for temperatures higher than  $T_{ref}$ . This leads to the expression of equation (4.42) in the exponent of the room temperature compensation level. Thus, the compensation level used in the correction term equals the room temperature compensation level for temperatures larger than  $T_{ref}$  and increases for temperatures lower than  $T_{ref}$ which leads to excellent agreement between model and experimental data.

To facilitate the implementation of the model adaptions to Klaassen's mobility model presented in this work, the crucial points are summarized in the following. For modelling carrier mobilities at room temperature, equation (4.11) from section 4.1.2.6 (equation (5) in reference [148]) has to be replaced by

$$\mu_{k,I} = \frac{\mu_{k,N}}{\left(\frac{N_{I}}{N_{ref,1}}\right)^{\alpha_{1}} + \left(\frac{C_{l,RT} - 1}{C_{l,ref}}\right)^{\beta_{1}}} + \mu_{k,c}\left(\frac{c}{N_{I}}\right)$$
(8.1)

for majority carrier mobilities and by

$$\mu_{k,I} = \frac{\mu_{k,N}}{\left(\frac{N_I}{N_{ref,1}}\right)^{\alpha_1} + \left(\left[\frac{N_A + N_D}{N_{ref,3}}\right] \cdot \left[\frac{C_{l,RT} - 1}{C_{l,ref}}\right]\right)^{\beta_1} + \mu_{k,c}\left(\frac{c}{N_I}\right)$$
(8.2)

for minority carrier mobilities with the parameters  $C_{l,ref}$ ,  $\beta_1$ , and  $N_{ref,3}$  from section 4.3.2. This leads to a modification of equation (4.23) from section 4.1.2.6 (equation (20) in reference [148]) to

 $\mu_{k,D+A+j}$ 

$$=\mu_{k,N}\frac{N_{k,sc}}{N_{k,sc,eff}}\left(\left(\frac{N_{k,sc}}{N_{ref,1}}\right)^{\alpha_1} + \left(\frac{C_{l,RT}-1}{C_{l,ref}}\right)^{\beta_1}\right)^{-1} + \mu_{k,c}\left(\frac{n+p}{N_{k,sc,eff}}\right)$$
(8.3)

for majority carriers and to

 $\mu_{k,D+A+j}$ 

$$= \mu_{k,N} \frac{N_{k,sc}}{N_{k,sc,eff}} \left( \left( \frac{N_{k,sc}}{N_{ref,1}} \right)^{\alpha_1} + \left( \left[ \frac{N_A + N_D}{N_{ref,3}} \right] \cdot \left[ \frac{C_{l,RT} - 1}{C_{l,ref}} \right] \right)^{\beta_1} \right)^{-1}$$

$$+ \mu_{k,c} \left( \frac{n+p}{N_{k,sc,eff}} \right)$$

$$(8.4)$$

for minority carriers.

To correctly account for the temperature dependence, the expression for the lattice scattering mobility in equation (4.27) from section 4.1.2.6 (equation (1) in reference [155]) should be replaced by equation (4.33) of this work for holes. To additionally include the temperature dependence of the majority carrier mobility due to scattering at ionized impurities accounting for compensation, equation (8.3) converts to

 $\mu_{k,D+A+j}$ 

$$= \mu_{k,N} \frac{N_{k,sc}}{N_{k,sc,eff}} \left( \left( \frac{N_{k,sc}}{N_{ref,1}} \right)^{\alpha_1} / \left( \frac{T}{300 \text{K}} \right)^{3\alpha_1 - 1.5} + \left( \frac{C_{l,RT}}{C_{l,ref}}^{\beta_2(T)} - 1 \right)^{\beta_1} \right)^{-1} + \mu_{k,c} \left( \frac{n+p}{N_{k,sc,eff}} \right) \left( \frac{300 \text{K}}{T} \right)^{0.5}$$
(8.5)

Note that in this formulation,  $\mu_{k,N}$  and  $\mu_{k,c}$  are the temperature independent expressions from equations (4.8) and (4.9) from section 4.1.2.6 (equations (3b) and (3c) in reference [148]) and  $\beta_2(T)$  is the temperature dependent term from equation (4.42) of this work. As there is no data for temperature dependent minority carrier mobilities in compensated silicon,  $\beta_2(T)$  could not be adjusted for minority carriers. As long as there is no data available, we suggest to use the following expression for modelling temperature dependent minority carrier mobilities

$$\mu_{k,D+A+j}$$

$$= \mu_{k,N} \frac{N_{k,SC}}{N_{k,SC,eff}} \left( \left( \frac{N_{k,SC}}{N_{ref,1}} \right)^{\alpha_1} / \left( \frac{T}{300 \text{ K}} \right)^{3\alpha_1 - 1.5} + \left( \left[ \frac{N_A + N_D}{N_{ref,3}} \right] \cdot \left[ \frac{C_{l,RT} - 1}{C_{l,ref}} \right] \right)^{\beta_1} \right)^{-1} + \mu_{k,c} \left( \frac{n + p}{N_{k,SC,eff}} \right) \left( \frac{300 \text{ K}}{T} \right)^{0.5}$$
(8.6)

which includes the room temperature compensation correction term over the whole temperature range. As shown in Figure 4.10 for majority carrier mobilities, this would probably overestimate the mobility for highly compensated silicon at low temperatures. Still, this error will be smaller over the whole temperature range than modelling without any compensation correction.

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# Nomenclature

Acronym	Description
AM1.5(G)	air mass 1.5 (global)
ARC	anti-reflection coating
BSF	back surface field
СР	chemical polishing
СТ	Caughey and Thomas
Cz	Czochralski
DARC	double anti-reflection coating
DS	directional solidification
DLTS	Deep Level Transient Spectroscopy
EBIC	electron beam induced current
ECV	electrochemical capacitance-voltage
ELBA	Efficiency limiting bulk recombination analysis
FCA	free carrier absorption
FTIR	Fourier Transform Infrared Spectroscopy
FZ	float(ing) zone
G17	generation 17
HP	high purity
HMPL	harmonically modulated photoluminescence
HPM-Si	high performance multicrystalline silicon
ICP-MS	inductively coupled plasma mass spectrometry
mc	multicrystalline
MPP	maximum power point
NAA	neutron-activation analysis
PassDop	layer acting as surface passivation and doping source
PDG	phosphorus diffusion gettering
PERC	passivated emitter and rear cell
PL	photoluminescence
PLI	photoluminescence imaging
ppbw	parts per billion by weight
PV	photovoltaics
QSSPC	quasi-steady-state photoconductance
SQ	standard quality
SRH	Shockley-Read-Hall
TCS	trichlorosilane
TLM	transmission line model
TOPCon	Tunnel Oxide passivated rear Contact
umg	upgraded metallurgical grade
VGF	vertical gradient freeze
μW-PCD	microwave-detected photoconductance decay

Constant	Description	Value
$k_B$	Boltzmann constant	8.617 3324·10 <sup>-5</sup> eV/K
е	elementary charge	1.602 176 565·10 <sup>-19</sup> C

Symbol	Description	Unit
a	PL calibration factor	cm <sup>o</sup>
$\stackrel{B}{\rightarrow}$	coefficient of radiative recombination	$cm^3 \cdot s^{-1}$
$\vec{B}$	magnetic field	N/m/A
С	free carrier concentration	cm <sup>-3</sup>
$C_n, C_p$	Auger coefficients	cm <sup>6</sup> ·s <sup>-1</sup>
$C_l$	compensation level	
$C_{l,RT}$	room temperature compensation level	
$D_k$	charge carrier diffusion coefficient	cm <sup>2</sup> /s
$\vec{E}$	electric field strength	V/m
FoR	fraction of recombination	%
EQE	external quantum efficiency	
FF	fill factor	%
$G_k$	generation rate	cm <sup>-3</sup> ·s <sup>-1</sup>
$\tilde{G_0}$	steady-state generation rate	cm <sup>-3</sup> ·s <sup>-1</sup>
$J_k$	charge current density	A/cm <sup>2</sup>
$J_{\rm sc}$	short-circuit current density	A/cm <sup>2</sup>
$J_0$ front/rear	dark saturation current densities for the front/rear side	A/cm <sup>2</sup>
i <sub>v</sub>	photon flux density	$\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$
ki sea	segregation coefficient of impurity I	
Ldiff harm	harmonic mean of minority charge carrier diffusion length	cm
L(min/mai) k	(minority/majority) charge carrier diffusion length	cm
$m^{(mn/maj),\kappa}$	effective mass	kg
N	doning concentration	cm <sup>-3</sup>
N <sub>A</sub>	acceptor concentration	cm <sup>-3</sup>
N <sub>A</sub> -	concentrations of ionized acceptors	cm <sup>-3</sup>
NG	effective density of states in the conduction band	cm <sup>-3</sup>
Np	donor concentration	cm <sup>-3</sup>
$N_{\rm D}^+$	density of ionized donors	cm <sup>-3</sup>
N <sub>don</sub> win/wai	minority/majority doning concentration	cm <sup>-3</sup>
1 чаор,тіп/тај <b>И</b> 11	Hall net doning concentration	cm <sup>-3</sup>
n;	intrinsic charge carrier density	cm <sup>-3</sup>
NLawstal	impurity or doping concentration in the crystal	cm <sup>-3</sup>
n <sub>k</sub>	charge carrier concentration	cm <sup>-3</sup>
$n_{k0}$	charge carrier concentration in thermal equilibrium w/o carrier injection	cm <sup>-3</sup>
$n_{k1}$	SRH-densities	cm <sup>-3</sup>
nmin/mai	minority/majority charge carrier concentration	cm <sup>-3</sup>
n <sub>mat</sub>	net doning concentration	cm <sup>-3</sup>
N <sub>t</sub>	trap or defect density	cm <sup>-3</sup>
$N_V$	effective density of states in the valence band	cm <sup>-3</sup>
PFF	pseudo fill factor	%
Pn	pseudo efficiency	%
R	reflection	
Raah. Rakh	rates of Auger recombination (eeh and ehh process)	$cm^{-3} \cdot s^{-1}$
reen - enn r	Hall (scattering) factor	0
$R_H$	Hall coefficient	cm <sup>3</sup> /A/s
$R_k$	Recombination rate	$cm^{-3} \cdot s^{-1}$
Rrad	rate of radiative recombination	$cm^{-3} \cdot s^{-1}$
RSRH	rate of Shocklev-Read-Hall recombination	$cm^{-3} \cdot s^{-1}$
T	temperature	K
$U_H$	Hall voltage	v
$V_d$	drift velocity	cm/s
Voc	open-circuit voltage	V
Vth	thermal velocity of electrons and holes	cm/s
$Z_k$	pre-factor for electrons ( $z_e = -1$ ) and holes ( $z_h = 1$ )	
$\Delta n$	excess charge carrier density	cm <sup>-3</sup>
$\Delta n_i$	local excess charge carrier density for camera pixel <i>i</i>	cm <sup>-3</sup>
$\Lambda n_{k}$	excess charge carrier density	cm <sup>-3</sup>
Ec	energy of the lower edge of the conduction band	eV
J.		

Symbol	Description	Unit
$\mathcal{E}_F$	Fermi energy	eV
$\mathcal{E}_{FC}$	(quasi-) Fermi energy of electrons in the conduction band	eV
$\mathcal{E}_{FV}$	(quasi-) Fermi energy of holes in the valence band	eV
$\mathcal{E}_t$	energy level of a trap	eV
$\mathcal{E}_V$	energy of the upper edge of the valence band	eV
η	energy conversion efficiency	%
$\eta_k$	electrochemical potential	eV
μ	charge carrier mobility	cm <sup>2</sup> /V/s
$\mu_{C}$	conductivity mobility	cm <sup>2</sup> /V/s
$\mu_H$	Hall mobility	cm <sup>2</sup> /V/s
$\mu_{(min/mai),k}$	(minority/majority) charge carrier mobility	cm <sup>2</sup> /V/s
ρ	specific resistance of silicon (resistivity)	Ω·cm
σ	total conductivity	A/V/cm
$\sigma_k$	charge carrier conductivity	A/V/cm
$\sigma_{n/p}$	capture cross section for electrons/holes	cm <sup>2</sup>
τ	charge carrier lifetime	S
$\tau_{Auger}$	Auger lifetime	S
$ au_{bulk}$	bulk lifetime	S
$ au_{eff}$	effective charge carrier lifetime	S
$\tau_i$	local charge carrier lifetime for camera pixel <i>i</i>	S
$ au_k$	charge carrier lifetime	S
$\tau_{n/p0}$	Shockley-Read-Hall electron/hole capture time constant	S
$\tau_{rad}$	lifetime due to radiative recombination	S
$ au_s$	mean scattering time	S
$\tau_{ m sqrt,harm}$	square root harmonic mean of lifetime	S
$ au_{SRH}$	SRH-lifetime	S
$\tau_{surf}$	lifetime due to surface recombination	S
$ au_{1/L}$	square root harmonic mean of lifetime	S
φ	electric potential	V
$\varphi_i$	local PL intensity for camera pixel <i>i</i>	
$\phi$	PL intensity	
$\Phi_{\operatorname{chem} k}$	chemical potential	eV

### **Publications and Awards**

In the following, the papers published in peer-reviewed journals, the contributions to international conferences, and the awards obtained within the framework of this thesis are listed.

#### **Peer-reviewed Journal Publications**

- F. Schindler, J. Schön, B. Michl, S. Riepe, P. Krenckel, J. Benick, F. Feldmann, M. Hermle, S. W. Glunz, W. Warta, and M. C. Schubert, "High Efficiency Multicrystalline Silicon Solar Cells: Potential of n-type Doping," *IEEE Journal of Photovoltaics*, vol. 5, pp. 1571-1579, 2015.
- F. Schindler, B. Michl, A. Kleiber, H. Steinkemper, J. Schön, W. Kwapil, P. Krenckel, S. Riepe, W. Warta, and M. C. Schubert, "Potential Gain in Multicrystalline Silicon Solar Cell Efficiency by n-Type Doping," *IEEE Journal of Photovoltaics*, vol. 5, pp. 499-506, 2015.
- F. Schindler, M. Forster, J. Broisch, J. Schön, J. Giesecke, S. Rein, W. Warta, and M. C. Schubert, "Towards a unified low-field model for carrier mobilities in crystalline silicon," *Solar Energy Materials and Solar Cells*, vol. 131, pp. 92-99, 2014.
- 4) F. Schindler, B. Michl, J. Schön, W. Kwapil, W. Warta, and M. C. Schubert, "Solar cell efficiency losses due to impurities from the crucible in multicrystalline silicon," *IEEE Journal of Photovoltaics*, vol. 4, pp. 122-129, 2014.
- 5) **F. Schindler**, M. C. Schubert, A. Kimmerle, J. Broisch, S. Rein, W. Kwapil, and W. Warta, "Modeling majority carrier mobility in compensated crystalline silicon for solar cells," *Solar Energy Materials and Solar Cells*, vol. 106, pp. 31-36, 2012.
- 6) J. Schön, F. Schindler, W. Kwapil, M. Knörlein, P. Krenckel, S. Riepe, W. Warta, and M. C. Schubert, "Identification of the most relevant metal impurities in mc n-type silicon for solar cells," *Solar Energy Materials and Solar Cells*, vol. 142, pp. 107-115, 2015.
- 7) J. Broisch, F. Schindler, M. C. Schubert, F. Fertig, A.-K. Soiland, and S. Rein, "Resistivity, Doping Concentrations, and Carrier Mobilities in Compensated nand p-Type Czochralski Silicon: Comparison of Measurements and Simulations and Consistent Description of Material Parameters," *IEEE Journal* of Photovoltaics, vol. 5, pp. 1276-1284, 2015.

- L. E. Mundt, M. C. Schubert, J. Schön, B. Michl, T. Niewelt, F. Schindler, and W. Warta, "Spatially Resolved Impurity Identification via Temperatureand Injection-Dependent Photoluminescence Imaging," *IEEE Journal of Photovoltaics*, vol. 5, pp. 1503-1509, 2015.
- 9) J. A. Giesecke, M. C. Schubert, F. Schindler, and W. Warta, "Harmonically Modulated Luminescence: Bridging Gaps in Carrier Lifetime Metrology Across the PV Processing Chain," *IEEE Journal of Photovoltaics*, vol. 5, pp. 313-319, 2015.
- B. Michl, M. Padilla, I. Geisemeyer, S. T. Haag, F. Schindler, M. C. Schubert, and W. Warta, "Imaging Techniques for Quantitative Silicon Material and Solar Cell Analysis," *IEEE Journal of Photovoltaics*, vol. 4, pp. 1502-1510, 2014.
- W. Kwapil, J. Schön, F. Schindler, W. Warta, and M. C. Schubert, "Impact of Iron Precipitates on Carrier Lifetime in As-Grown and Phosphorus-Gettered Multicrystalline Silicon Wafers in Model and Experiment," *IEEE Journal of Photovoltaics*, vol. 4, pp. 791-798, 2014.
- 12) M. C. Schubert, J. Schön, F. Schindler, W. Kwapil, A. Abdollahinia, B. Michl, S. Riepe, C. Schmid, M. Schumann, S. Meyer, and W. Warta, "Impact of Impurities From Crucible and Coating on mc-Silicon Quality the Example of Iron and Cobalt," *IEEE Journal of Photovoltaics*, vol. 3, pp. 1250-1258, 2013.
- P. Löper, M. Canino, J. López-Vidrier, M. Schnabel, F. Schindler, F. Heinz, A. Witzky, M. Bellettato, M. Allegrezza, D. Hiller, A. Hartel, S. Gutsch, S. Hernández, R. Guerra, S. Ossicini, B. Garrido, S. Janz, and M. Zacharias, "Silicon nanocrystals from high-temperature annealing: Characterization on device level," *physica status solidi (a)*, vol. 210, pp. 669-675, 2013.
- J. A. Giesecke, F. Schindler, M. Bühler, M. C. Schubert, and W. Warta, "Accurate determination of minority carrier mobility in silicon from quasisteady-state photoluminescence," *Journal of Applied Physics*, vol. 113, p. 213705, 2013.

#### **Contributions to Conferences and Workshops and Associated Papers**

1) IEEE PVSC 2015:

**F. Schindler**, J. Schön, B. Michl, S. Riepe, P. Krenckel, J. Benick, F. Feldmann, M. Hermle, S. W. Glunz, W. Warta, and M. C. Schubert, "High Efficiency Multicrystalline Silicon Solar Cells: Potential of n-type Doping," *IEEE Journal of Photovoltaics*, vol. 5, pp. 1571-1579, 2015.

- Oral presentation
- Paper invited for publication in IEEE Journal of Photovoltaics
- o Rewarded with Best Student Paper Award
- 2) SiliconPV 2015:

**F. Schindler**, B. Michl, P. Krenckel, S. Riepe, F. Feldmann, J. Benick, W. Warta, and M. C. Schubert, "Efficiency potential of p- and n-type high performance multicrystalline silicon," *Energy Procedia*, vol. 77, pp. 633-638, 2015. (peer-reviewed)

- Oral presentation
- 3) 50. Punktdefekttreffen 2014:

**F. Schindler**, M. Forster, J. Broisch, J. Schön, J. Giesecke, S. Rein, W. Warta, and M. C. Schubert, "A low-field charge carrier mobility model for crystalline silicon"

- Oral presentation (invited talk)
- 4) EU PVSEC 2014:

**F. Schindler**, B. Michl, A. Kleiber, H. Steinkemper, J. Schön, W. Kwapil, P. Krenckel, S. Riepe, W. Warta, and M. C. Schubert, "The Potential of Multicrystalline n-type Silicon for High Efficiency Solar Cells," in *Proceedings of the 29th European Photovoltaic Solar Energy Conference and Exhibition*, Amsterdam, The Netherlands, 2014, pp. 441-445.

- Oral presentation
- 5) SiliconPV 2014:

**F. Schindler**, M. Forster, J. Broisch, J. Schön, J. Giesecke, S. Rein, W. Warta, and M. C. Schubert, "Towards a unified low-field model for carrier mobilities in crystalline silicon," *Solar Energy Materials and Solar Cells*, vol. 131, pp. 92-99, 2014.

- o Oral presentation
- Paper invited for publication in Solar Energy Materials and Solar Cells
- Rewarded with SiliconPV Award

6) EU PVSEC 2013:

**F. Schindler**, B. Michl, J. Schön, W. Kwapil, W. Warta, and M. C. Schubert, "Material limitations due to crucible impurities in multicrystalline silicon for high efficiency solar cells," in *Proceedings of the 28th European Photovoltaic Solar Energy Conference and Exhibition*, Paris, France, 2013, pp. 1710-1714.

- o Visual presentation
- Rewarded with Poster Award
- 7) SiliconFOREST 2013:

**F. Schindler**, M. C. Schubert, A. Kimmerle, J. Broisch, S. Rein, W. Kwapil, and W. Warta, "Ladungsträgermobilität in kompensiertem Silicium"

- o Oral presentation (invited talk)
- 8) SiliconPV 2012:

**F. Schindler**, M. C. Schubert, A. Kimmerle, J. Broisch, S. Rein, W. Kwapil, and W. Warta, "Modeling majority carrier mobility in compensated crystalline silicon for solar cells," *Solar Energy Materials and Solar Cells*, vol. 106, pp. 31-36, 2012.

- o Oral presentation
- o Paper invited for publication in Solar Energy Materials and Solar Cells
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   F. Schindler, "Multikristallines Silicium zur Herstellung von Solarzellen Elektrische Transporteigenschaften"
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- 15) B. Michl, J. Schön, F. Schindler, W. Warta, and M. C. Schubert, "Reducing the impact of iron on carrier lifetimes in multicrystalline silicon wafers by optimized diffusion temperature profiles," in *Proceedings of the 27th European Photovoltaic Solar Energy Conference and Exhibition*, Frankfurt, Germany, 2012, pp. 709-713.

#### Awards

- Best Student Paper Award (IEEE PVSC 2015) for "High Efficiency Multicrystalline Silicon Solar Cells: Potential of n-type Doping"
- SiliconPV Award (SiliconPV 2014) for "Towards a unified low-field model for carrier mobilities in crystalline silicon"
- Poster Award (EU PVSEC 2013) for "Material limitations due to crucible impurities in multicrystalline silicon for high efficiency solar cells"

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Increasing the efficiency and reducing the production costs are the two main goals of the optimization of crystalline silicon solar cells. This thesis addresses the impact of efficiency-limiting defects in crystalline silicon from cheaper production routes, namely upgraded metallurgical grade silicon and multicrystalline silicon, and presents an approach for the fabrication of high efficiency solar cells on low-cost multicrystalline silicon substrate.

Upgraded metallurgical grade silicon typically features significant amounts of both types of dopants, acceptors and donors, which leads to a so-called charge carrier compensation. The impact of compensation on charge carrier mobility is investigated and a unified model for charge carrier mobilities in uncompensated and compensated silicon is developed.

Multicrystalline silicon features structural crystal defects, such as grain boundaries and dislocations, as well as a large amount of metal impurities incorporated from the crucible system into the silicon during crystallization. In this thesis, efficiency losses due to impurities from the crucible system are quantified, the role of the doping type is evaluated, and the efficiency limit for solar cells based on high performance multicrystalline silicon substrate is assessed.



