# FABRICATION AND CHARACTERISATION OF LASERDOPED REGIONS IN CRYSTALLINE SILICON WAFERS FOR SOLAR CELL APPLICATIONS 

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## Declaration

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

Martin HEINRICH
18 August 2014

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#### Abstract

This thesis investigates the characterisation and application of laser-doped selective emitters on crystalline silicon wafer solar cells. A selective emitter solar cell has two differently doped emitter regions: a lowly-doped emitter under the illuminated area and a highly-doped emitter under the metal contacts. This allows optimization of the illuminated emitter separately from the emitter under the metal contacts regarding the various recombination losses.

In the first part of the thesis, a new characterisation method based on potentialdrop sheet resistance measurements of lines is introduced. Furthermore, the application of four-point probe sheet resistance measurements on laser-doped areas is discussed and methods to extract accurate results on these areas are presented. Both methods, four-point probe and line sheet resistance measurements, are shown to be interchangeable with each other by introducing the concept of laser pulse density (average number of laser pulses which the sample has received).

The second part of the thesis investigates the key parameters for laser doping. The influence of single pulse laser fluence and laser pulse density on doping efficiency is investigated in theory and in experiments. Existing theoretical models for laser doping are extended in cases where it seems necessary. It is observed that a minimum sheet resistance exists depending on the single pulse laser fluence, as well as in the case of an infinite dopant flux. Concerning the laser pulse density, the sheet resistance is shown to decrease until a minimum sheet resistance is reached.


The third part of the thesis analyses solar cells, which are fabricated by using different laser doping processes. A detailed loss analysis is carried out showing that laser doping with laser chemical processing features severe laser-induced damage, which limits the solar cell efficiency. The solar cells with the lowest laser impact, show the best solar cell efficiency overall. However, these solar cells also exhibit negligible laser doping hence this optimisation applies only for currently industrial solar cell concepts where a selective emitter is not essential. Future industrial feasible solar cell concepts may require a selective emitter for contacting of a lowlydoped homogeneous emitter or for other technological reasons. In these cases a heavily-doped emitter, which can be formed by laser chemical processing and optimised by employing sheet resistance measurements can be used.

The last part of the thesis describes a possible technological solution for the background plating problem (i.e. plating of undesired areas), which severely reduced the efficiency of the solar cells in this work. The method removes the background plated metal by a wet-chemical etching process. A model is developed to investigate key factors for the selectivity of etching of the background plated metal vs. the actual metal grid. The results of the model are tested experimentally, giving good overall agreement. Examples for application in the solar cell processing flow are shown, which remove background plating either as final process step or just before the capping layer plating step.

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## List of Abbreviations

| 4PP | Four-point probe |
| :---: | :---: |
| ADE | Alternating direction explicit |
| a-Si | Amorphous silicon |
| BHF | Buffered hydrofluoric acid |
| BIM | Boundary immobilisation method |
| BSF | Back surface field |
| c-Si | Crystalline silicon |
| CW | Continuous-wave |
| Cz | Czochralski |
| DLIT | Dark lock-in thermography |
| EBIC | Electron beam-induced current |
| EBSD | Electron backscattering diffraction |
| ECV | Electrochemical capacitance voltage |
| EQE | External quantum efficiency |
| EROI | Energy return on investment |
| FWHM | Full width at half maximum |
| GILD | Gas immersion laser doping |
| IQE | Internal quantum efficiency |
| LBSF | Local back surface field |
| LCP | Laser chemical processing |
| LFC | Laser fired contacts |
| LIP | Light-induced plating |
| LRM | Line resistance measurement |
| ${ }^{1-S i}$ | Liquid Si |


| PECVD | Plasma enhanced chemical vapour deposition |
| :--- | :--- |
| PERC | Passivated emitter and rear cell |
| PD | Potential drop |
| PSG | Phosphosilicate glass |
| PV | Photovoltaics |
| QSSPC | Quasi-steady-state photo-conductance |
| RCA | Radio Corporation of America |
| R | Reflection |
| ReBEL | Reversed bias electroluminescence |
| SDE | Saw damage etching |
| SEM | Scanning electron microscope |
| SIMS | Secondary ion mass spectrometry |
| SOD | Spin-on doping |
| SP | Screen printing |
| SRH | Shockley-Read-Hall |
| TLM | Transfer length method |
| TOF | Time of flight |
| UV | Ultraviolet |
| WFLD | Wet film laser doping |

## List of Symbols

| $A, A_{(.)}$ | Area [ $\mathrm{cm}^{2}$ ], area ratio [\%] |
| :---: | :---: |
| $a, a_{(.)}$ | Square area width [mm] |
| C | Capacitance [ $\mathrm{As} / \mathrm{V}$ ] |
| $C_{A}$ | Dopant concentration [1/cm ${ }^{3}$ ] |
| $C_{p}$ | Specific heat capacity [J/g K] |
| $c_{(.)}$ | Concentration or Molarity [mol/L] |
| $D,\left(D_{l}, D_{s}\right)$ | Diffusion coefficient, (into liquid silicon, into solid silicon) [ $\mathrm{cm}^{2} / \mathrm{s}$ ] |
| $d$ | Pulse-to-pulse distance of laser doped lines [ $\mu \mathrm{m}$ ] |
| $d_{x}$ | Distance between TLM contacting pads [mm] |
| $E_{C}$ | Conduction band energy [ eV ] |
| $E_{F}$ | Fermi level energy [eV] |
| $E_{V}$ | Valence band energy [ eV ] |
| $F_{(.)}$ | Correction factor for single configuration 4PP measurements |
| $f_{(.)}$ | Correction factor ratio for single configuration 4PP measurements |
| FF | Fill factor (of a solar cell $I$ - $V$ curve) [\%] |
| $G$ | Generation rate [ $1 / \mathrm{m}^{3}$ ] |
| H | Enthalpy [J] |
| $h$ | Hatch (line-to-line distance) of laser-doped lines [ $\mu \mathrm{m}$ ] |
| I | Current [A] |
| $J_{01, ~ L D ~}^{\text {d }}$ | Emitter saturation current density of laser-doped patterns [fA/cm²] |
| $J_{0 e}, J_{01}, J_{02}$ | Emitter saturation current density [ $\mathrm{fA} / \mathrm{cm}^{2}$ ], [ $\left.\mathrm{nA} / \mathrm{cm}^{2}\right]$ |
| $J_{\text {in }}$ | Dopant influx on the surface [atoms $/ \mathrm{cm}^{2} \mathrm{~s}$ ] |
| $J_{S C}$ | Short-circuit current density [mA/cm ${ }^{2}$ ] |
| $k_{s}$ | Rate constant of etchant metal reaction $\left[\mathrm{mol} /\left(\mathrm{m}^{2} \mathrm{~s}\right) /\left(\mathrm{mol} / \mathrm{m}^{3}\right)\right]$ |
| $L$ | Avogadro constant [1/mol] |
| $L_{x}$ | Laser-doped lines x |
| $M_{\text {mol }}$ | Molar mass [g/mol] |


| $m$ | Number of active etching molecules |
| :---: | :---: |
| $N$ | Carrier concentration [1/cm ${ }^{3}$ ] |
| $N_{\text {dop }}$ | Bulk dopant concentration [1/cm ${ }^{3}$ ] |
| $N_{L}$ | Number of lines |
| $N_{l}^{\max }, N_{s}^{\max }$ | Solubility limit in liquid silicon, solid silicon [1/cm $\left.{ }^{3}\right]$ |
| $N_{p}$ | Number of laser pulses |
| $n$ | Concentration of negatively charged carriers [1/cm ${ }^{3}$ ] |
| $n_{i}$ | Intrinsic carrier concentration [ $1 / \mathrm{cm}^{3}$ ] |
| $n_{p}, n_{C W}$ | Laser pulse density, density of laser passes using a CW laser |
| $P_{\text {in }}$ | Input Power [ $\mathrm{mW} / \mathrm{cm}^{2}$ ] |
| $p$ | Concentration of positively charged carriers [1/cm $\left.{ }^{3}\right]$ |
| $p F F$ | Pseudo fill factor (of a solar cell $I-V$ curve) [\%] |
| $Q$ | Heat source [J] |
| $q$ | Elementary charge [C] |
| $R_{(.)}, R_{\text {Sh }}, R_{T}$ | Resistance $[\Omega]$, sheet resistance $[\Omega / \mathrm{sq}$.$] , total resistance of$ TLM/LRM structure [ $\Omega$ ] |
| $R_{S}, R_{S,(.)}$ | Area normalized solar cell series resistance [ $\Omega . \mathrm{cm}^{2}$ ] |
| $r$ | Radius plated metal area [ $\mu \mathrm{m}$ ] |
| $r_{p}$ | Radius laser pulse spot [ $\mu \mathrm{m}$ ] |
| $r_{\text {step }}$ | Space steps for simulations |
| $s, s_{(.)}$ | Distance between probes of a (collinear) 4PP setup [mm] |
| T, $T_{m}, T_{b}$ | Temperature, melting temperature, boiling temperature [K] |
| $t, t_{l i}$ | Time, time of substrate in molten phase [s] |
| $t_{\text {step }}$ | time steps for simulations |
| $V, V_{O C}$ | Voltage [mV], open-circuit voltage [mV] |
| $v$ | Valence |
| $v_{s}$ | Velocity of laser beam across a surface [m/s] |
| W | Width of the sample [mm] |
| $w$ | Width of the TLM structure [mm] |


| $w_{F}, w_{L}$ | Metallised finger width [ $\mu \mathrm{m}$ ], line width [ $\mu \mathrm{m}$ ] |
| :---: | :---: |
| $x$ | Location on the surface (1D) |
| $\boldsymbol{x}$ | Space vector (3D) |
| $z_{(.)}$ | Depth in sample [ $\mu \mathrm{m}$ ] |
| $z_{\text {max }}$ | Thickness of doped layer [ $\mu \mathrm{m}$ ] |
| $\alpha$ | Heat diffusivity [ $\mathrm{cm}^{2} / \mathrm{s}$ ] |
| $\alpha_{G}$ | Geometry factor of diffusion equation |
| $\beta_{a b}$ | Absorption coefficient [ $\mathrm{cm}^{-1}$ ] |
| $\beta^{-1}$ | Scaling factor for etching equation |
| $\gamma$ | Implicit factor for solution of Cartesian etching problem |
| $\Delta n$ | Excess minority carrier concentration [1/cm $\left.{ }^{3}\right]$ |
| $\delta, \delta_{0}$ | Metal thickness [ $\mu \mathrm{m}$ ], initial metal thickness [ $\mu \mathrm{m}$ ] |
| $\epsilon, \epsilon_{0}$ | Relative permittivity [ $\mathrm{F} / \mathrm{m}$ ], vacuum permittivity $[\mathrm{F} / \mathrm{m}]$ |
| $\eta$ | Efficiency [\%] |
| $\kappa$ | Thermal conductivity [W/cm K] |
| $\lambda$ | Wavelength [ nm ] |
| $\mu_{n}, \mu_{p}$ | Mobility of free electrons (holes) [ $\left.\mathrm{cm}^{2} /(\mathrm{Vs})\right]$ |
| $\rho_{D}$ | Density [g/cm ${ }^{3}$ ] |
| $\rho_{R}$ | Resistivity [Ohm.m] |
| $\tau_{\text {Auger }}$ | Auger carrier lifetime [ $\mu \mathrm{s}$ ] |
| $\tau_{\text {bulk }}$ | Minority carrier lifetime in the bulk [ $\mu \mathrm{s}$ ] |
| $\tau_{e f f}$ | Effective minority carrier lifetime of a sample [ $\mu \mathrm{s}$ ] |
| $\tau_{r}$ | Radiative carrier lifetime [ $\mu \mathrm{s}$ ] |
| $\tau_{\text {SRH }}$ | Shockley-Read-Hall carrier lifetime [ $\mu \mathrm{s}$ ] |
| $\Phi, \Phi_{p}$ | Intensity, single pulse laser fluence/ single pulse laser energy density [ $\mathrm{J} / \mathrm{cm}^{2}$ ] |
| $\chi$ | Correction factor for dual sheet resistance measurements |

## List of Publications

## Journal papers:

[1] M. Heinrich, S. Kluska, Z. Hameiri, B. Hoex and A. G. Aberle, "Extracting physical properties of arbitrarily shaped laser-doped microscale areas in semiconductors," Appl. Phys. Lett., vol. 103, no. 26, p. 262103, 2013.
[2] L. Liu, F. Lin, M. Heinrich, A.G. Aberle and B. Hoex, "Unexpectedly high etching rate of highly doped n-type crystalline silicon in hydrofluoric acid," ECS J. Solid State Sci. Technol., vol. 2, no. 9, pp. P380-P383, 2013.
[3] M. Heinrich, S. Kluska, S. Binder, Z. Hameiri, B. Hoex and A.G. Aberle, "Accurate potential drop sheet resistance measurements of laser-doped areas in semiconductors," J.Appl. Phys., vol. 116, no. 13, p. 134505, 2014

## Conference papers:

[1] M. Heinrich, N. Palina, J. Wong, B. Hoex and A. G. Aberle, "Accurate measurement of laser-doped line sheet resistance for silicon wafer solar cell applications," Technical Digest 21 st International Photovoltaic Science and Engineering Conference (PVSEC-21), Fukuoka, Japan 2011, p. 4D-1P-29.
[2] M. Heinrich, H. Hidayat, Z. Hameiri, B. Hoex and A. G. Aberle, "Dopant profiles of laser-doped multicrystalline silicon wafers from electrochemical capacitance-voltage measurements," Proc. 27th European Photovoltaic Solar Energy Conference and Exhibition, Frankfurt, Germany 2012, vol. 2, pp. 1285-1288.

## Patents:

[1] M. Heinrich, M. Lieder, M. Kamp, M. Glatthaar and A. Kraft, "Verfahren zur selektiven Entfernung von Ghostplating auf Siliziumsolarzellen" (Method for the selective removal of ghostplating on silicon solar cells); German patent application: DE102014211227.3, June 2014

## 1 Introduction

### 1.1 Motivation

The conversion of energy from one energy form (e.g. chemical) to another (e.g. heat) is helping humanity to control and adapt to the environment since the first ancient tribes started to use camp fires. Energy conversion, and especially electric energy generation, has become increasingly important in the last 100 years for another reason: the economic wealth arising from usable energy [1, 2]. The current wealth of societies around the globe can for a large part be attributed to the exploitation of natural energy resources. Currently, the main sources of usable energy are fossil fuels like oil, gas and coal, which have been offering a historically high energy return on investment (EROI, defined as ratio between usable acquired energy and energy expended) since their exploitation. This excessive available amount of energy has no analogy in history of humankind and has fuelled a blossom of wealth in the whole world over decades starting from the industrial revolution. However, these fossil energy resources are finite and they become increasingly more difficult and expensive to harvest, which implies a reduction of the EROI. The British Petroleum statistical review of 2013 [3] names roughly 53 years as limit of global production for oil and gas, considering proven reserves and current production volumes. ${ }^{1}$ The price of oil has increased tremendously over the last decade (as shown in Fig. 1.1), which is also due to a reduction of the EROI (compare to [4]).

[^0]Furthermore, the price of oil has always been strongly affected by political instabilities, as indicated in Fig. 1.1. Some critics even speak of a war about energy resources [5] and some political events may be related to securing natural resources. ${ }^{2}$


Fig. 1.1 Crude oil prices in the period of 1861-2012 in US dollars per barrel with relevant world events indicated at the top of the graph [3].

There is also a high risk for humankind and the environment by continuing the excessive exploitation of natural resources. ${ }^{3}$ It is undeniable that global warming is fuelled by excessive greenhouse gas emissions from burning fossil fuels [6]. Even the usage of natural resources such as nuclear fission, which does not emit large quantities of greenhouse gases, can have catastrophic impacts on the environment. ${ }^{4}$

[^1]For these reasons, governments and companies have started to establish a more sustainable electrical energy production by developing concepts of converting energy from renewable resources such as wind and sun. ${ }^{5}$ An already successful example is Germany, which has accomplished to increase the ratio of renewable energy production to the overall annual electricity production from $6.6 \%$ in 2001 to $24.1 \%$ in $2013 .{ }^{6}$ In fact, the incentive programme became so successful that the German government recently decided to reduce it more strongly and faster than initially planned. ${ }^{7}$

All these government and industry funded concepts and incentive programmes are a step towards a new future. However, societies will always demand a high EROI, to be able to maintain their wealth and growth. Therefore, increasing the EROI of renewable energies is one of the key factors which will facilitate the wealth of future generations.

Converting light (from the sun) into electrical energy by the use of solar cells ('photovoltaics' or PV) is one of the increasingly established sustainable electrical energy generation techniques [7]. Further improvements of the energy conversion efficiency may help to increase the EROI of this technology and therefore further increase the usage of solar cells as a sustainable electrical energy source throughout the world [8]. The International Technology Roadmap for PV in 2014 [9]

[^2]identifies several trends along the whole value chain of solar cell production, which may help to increase the EROI. One example for the standard $p$-type silicon (Si) solar cell is an improvement of the electron collector layer (also called 'emitter') on the front surface. The goal is to reduce charge carrier recombination in the emitter by reducing the doping level. However, this reduction in doping level causes an increased charge carrier recombination at the metal contacts of the front surface. Therefore, a so-called selective emitter with a high doping level under the front contacts is introduced, which reduces the charge carrier recombination losses at the front contacts [10]. Additionally, the contact resistance between the doped Si and the metal contacts is reduced by the selective emitter.

Laser doping is one key technology for fabrication of selective emitter solar cells with the potential to enable industrial-scale processing. Laser doping applies a very high photon flux locally, which induces or enhances physical or chemical reactions. In particular, the photon flux may heat and melt a substrate, which increases the diffusion rate of dopant atoms into the substrate locally. The possibility to focus a laser beam down to a few micrometres in diameter and to use a fast scanning across the sample surface makes lasers in principle an ideal choice for local doping in high volume manufacturing. Laser doping has the advantage to be essentially wear-free, since no direct contact with the substrate is necessary. Furthermore, very small laser-doped areas can be realised.

The method of laser doping (as applied in this thesis) also allows the usage of plating as metallisation scheme instead of the industry standard screen printing (SP) technique. Plating is a self-aligned metallisation which allows the usage of
cheaper conductive materials for metallisation (e.g. Cu ). Plating also has the potential to reduce the shading of the metal contacts due to smaller widths of the front contacts, therefore enabling higher efficiencies of solar cells [11].

### 1.2 Objective

In this thesis, the fabrication and characterisation of laser-doped regions in crystalline silicon wafers for solar cell applications is investigated.

The foundation for optimising the laser doping process is the ability to accurately characterise laser-doped areas. Hence the first part of the thesis aims to establish accurate characterisation methods that can be used to analyse laser-doped samples.

The laser doping efficiency depends on several different processing conditions, such as laser pulse energy density or dopant flux. Therefore, it is important to understand the influence of the key parameters on doping efficiency in order to develop a robust and industrially feasible laser doping process. The final solar cell efficiency is not only influenced by the doping efficiency but also by the induced defects due to laser doping. It was also aimed to understand the influence of processing conditions on the final solar cell efficiency.

Another goal of this thesis was the implementation of the laser doping process in combination with a subsequent plating process. One of the main challenges of plating is the so-called "background plating", which refers to the metallisation of areas which are not intended to be plated. Background plating may prevent an in-
dustrially feasible process integration of laser doping in combination with plating, since it increases the fraction of sub-standard solar cells in a production line (i.e. reduced manufacturing yield). Thus, the aim was to develop a method which allows the etching of background plated metal.

### 1.3 Outline

The thesis is structured in 7 Chapters. Chapter 2 introduces the main solar cell concepts and processes which are used in this thesis. The theoretical background of laser doping, the relevant laser doping methods as well as the most important characterisation methods are discussed.

Chapter 3 deals with characterisation methods to measure the doping efficiency in laser-doped areas. A new characterisation method based on potential-drop sheet resistance measurements of lines is introduced. Furthermore, the application of four-point probe sheet resistance measurements on laser-doped areas is discussed and methods to extract accurate results on these areas are presented. Both methods, four-point probe and line sheet resistance measurements, are shown to be interchangeable by introducing the concept of 'laser pulse density' (i.e., average number of laser pulses on the sample).

The key parameters for laser doping are identified and motivated in Chapter 4. The influence of single pulse laser fluence and laser pulse density on doping efficiency is investigated in theory and in experiments. Existing theoretical models for laser doping are extended in cases where it deems necessary.

Chapter 5 analyses solar cells which were fabricated using different laser doping processes. A detailed loss analysis is carried out for each fabricated solar cell batch. The different losses in open-circuit voltage, short-circuit current density and fill factor are analysed. The key factors resulting in differences between the various groups within the batches are identified and investigated.

Chapter 6 describes a possible solution for background plating. The method removes background plating by etching of the plated metal. A model is developed to investigate key influences on the selectivity of etching of background plating to etching of the metal grid. The results of the model are compared with experimental results. Examples for application of selective etching in the solar cell processing flow are shown.

Chapter 7 summarises the results of the Chapters 3 to 6 and gives an outlook for further developments based on the results of this work.

## 2 Fundamentals

This chapter discusses the fundamentals of laser doping with respect to the formation of a selective emitter in silicon wafer solar cells. Relevant solar cell concepts and fabrication processes which are important for this thesis are introduced in Sec. 2.1. The macroscopic theories describing laser doping are discussed in Sec. 2.2. Section 2.3 discusses various laser doping techniques for silicon solar cells. Finally, state-of-the-art characterisation methods which are applicable for laserdoped areas are reviewed in Sec. 2.4.

### 2.1 Relevant solar cell concept and processes

This section introduces the relevant Si wafer solar cell concepts and the main fabrication processes besides laser doping, which are used in this work. First, the fundamentals of a solar cell are briefly discussed in Sec. 2.1.1. Section 2.1.2 introduces the solar cell concepts, which are used in this work. The last part of this section deals with plating as an alternative metallisation technique for Si wafer solar cells. Plating is a self-aligned metallisation method, which is increasingly researched for solar cell applications.

### 2.1.1 Solar cell fundamentals

A Si wafer solar cell converts light into electricity via the photovoltaic effect [8, 12]. Incoming light with photon energies larger than the band gap of Si can generate electron-hole pairs, meaning free electrons in the conduction band and free holes in the valence band. The electrons and holes are diffusing randomly within
the semiconductor until they are separated through e.g. a $p-n$ junction. Following the separation they can be collected at the contacts and the electrons are then available for powering an external load.

The efficiency of a solar cell $(\eta)$ is given by:

$$
\begin{equation*}
\eta=\frac{V_{O C} I_{S C} F F}{P_{i n}} \tag{2.1}
\end{equation*}
$$

with $V_{O C}$ is the open-circuit voltage, $J_{S C}$ is the short-circuit current density, $F F$ is the fill factor and $P_{\text {in }}$ is the input power. The solar cell efficiency can be increased by increasing the absorption of light in the Si material, which influences $J_{S C}$. The absorption of light in the Si material is increased by decreasing reflection losses at the front side (e.g. by reducing shading caused by the front contacts) and increasing the internal reflection at the rear and front side leading to increased light trapping in the solar cell.

The solar cell efficiency can also be increased by decreasing the recombination of the electron-hole pairs in the solar cell, which affects both, $V_{O C}$ and $J_{S C}$. The recombination of electron-hole pairs in the solar cell bulk material is described by the minority charge carrier lifetime $\left(\tau_{\text {bulk }}\right)[13]$ :

$$
\begin{equation*}
\frac{1}{\tau_{\text {bulk }}}=\frac{1}{\tau_{r}}+\frac{1}{\tau_{S R H}}+\frac{1}{\tau_{\text {Auger }}}, \tag{2.2}
\end{equation*}
$$

where $\tau_{r}$ is the radiative recombination lifetime, $\tau_{S R H}$ is the Shockley-Read-Hall (SRH) recombination lifetime and $\tau_{\text {Auger }}$ is the Auger recombination lifetime. Additionally, recombination at the front and rear surface or the emitter of the solar cell is also important. Radiative recombination is the reverse process of photon absorption where an electron energetically drops down to the valance band and
emits a photon. As crystalline Si is an indirect-bandgap semiconductor radiative recombination is not the dominant recombination process. Auger recombination is the recombination of an electron with a hole where the excess energy is transferred to another electron or hole. As Auger recombination is a three-particle process it is most relevant at very high carrier densities (such as in an emitter of a solar cell). Bulk SRH recombination is recombination of electron-hole pairs via defects in the bulk, such as metallic impurities or crystallographic defects.

A special form of SRH recombination is surface recombination, which occurs at surface defects such as dangling bonds. The surface recombination has a significant influence on the solar cell efficiency but can be reduced by carefully optimising the solar cell fabrication process. One example to reduce the surface recombination is the use of a highly doped region. The highly doped region reduces the mobility of minority carries and has a larger gradient of the Fermi energy level of minority carriers. Therefore, diffusion of minority carriers to the surface is less likely. However, the Auger recombination rate increases with active dopant atoms concentration. Therefore, surface passivation is applied additionally, to reduce surface recombination. Surface passivation reduces the number of dangling bonds at the surface. Both methods are commonly used together for the front surface of solar cells since many carriers are generated in its vicinity. The doped layer is commonly referred to as "emitter", if it also forms the $p-n$ junction by doping a layer with dopant atoms of the opposing doping type as the bulk material into the Si wafer. The terminology "emitter" is a semiconductor term originally indicating the region of a bipolar transistor that produces current, which is in contrast to the
"emitter" in solar cells [14]. Here the main function of the "emitter" is to collect electrons.

The solar cell efficiency is also increased by decreasing resistance or thermal losses, which both affect $F F$ and $V_{O C}$. Thermal losses occur due to the excess energy of the incoming light, which is not used to generate electron-hole pairs. Resistance losses of the solar cell are quantified by a low parallel resistance and/or a high series resistance. A low parallel resistance results from shunting of the $p-n$ junction, meaning that the observed electric field is locally reduced or absent (e.g. where metal contacts are spiking through the $p-n$ junction). A high series resistance results from either a low conductivity of the majority carriers in the semiconductor, or a high contact resistance between the metal contacts and the semiconductor, or a low conductivity within the metal contacts.

### 2.1.2 Selective Emitter AI-BSF and AI-LBSF Solar Cell Concepts

The solar cell concept which will be used here in this thesis is the selective emitter Si wafer solar cell. Selective emitter solar cells have two differently doped emitter regions on the front side of the solar cell: A homogeneously, lowly doped emitter under the illuminated areas and a highly doped emitter under the metal contacts of the solar cell $[10,15]$.

The selective emitter concept was developed since the absence of front surface passivation underneath the metal contacts can cause significant recombination losses [15]. Therefore, two opposing optimisation routes of front side emitters occur: First, the optimisation of the non-metallised emitter with surface passivation
(homogeneous emitter) concerning low Auger recombination losses and secondly, the optimisation of the emitter underneath the metal contacts to decrease the contact resistance and recombination losses at the metal-Si interface. Another more recently occurring optimisation of the emitter underneath the metal contacts is the prevention of annealing-induced shunts at the contacts when using plating as metallisation scheme [16-18]. These shunts arise due to annealing of the plated Ni , which was shown to be beneficial for contact formation and adhesion [18]. The annealing causes formation of Ni silicides, which may occur as spikes reaching through the $p-n$ junction or even into the bulk material depending on the annealing temperature and time applied [16].

The rear surface of the solar cell typically has a large-area Al 'back surface field' (Al-BSF), or more recently, an Al 'local back surface field' (Al-LBSF). Figure 2.1 shows a schematic of an Al-BSF p-type selective emitter solar cell. The substrate of the solar cell is a p-type Si wafer, which is either multicrystalline Si or Czochralski (Cz) grown monocrystalline Si . The wafer thickness is typically in the range of 150-200 $\mu \mathrm{m}$.


Fig. 2.1 Schematic illustration of a selective emitter multicrystalline Si wafer solar cell with plated contacts. The light grey colour indicates the p-type bulk, the dark grey colour indicates the Al back contact and the gradient between these colours indicates the BSF. The blue colour indicates the surface passivation and the red colour indicates the emitter region. The beige colour indicates the plated contacts (e.g. plated Ag ) and the green colour indicates the seed layer (e.g. plated Ni ).

The front side of the solar cell is textured with a random pyramid texture in case of Cz -Si or a random valley texture ('iso-texture') in case of multicrystalline Si , as shown in Fig. 2.1. The surface texture reduces the light reflection on the front side of the solar cell. The front surface is passivated with a passivation layer, which also acts as antireflection layer. The layer commonly consists of a plasmaenhanced chemical vapour deposited (PECVD) silicon nitride $\left(\mathrm{SiN}_{\mathrm{x}}\right)$ layer (blue layer in Fig. 2.1). Underneath the surface passivation layer is the homogeneously phosphorus doped shallow emitter with a low surface dopant concentration and a small depth. The deep emitter underneath the metallisation has ideally a high surface dopant concentration and a large depth. Together, both emitters form the selective emitter. The metallisation of the front contacts can, e.g., be performed by means of plating, which is discussed in Section 2.1.3.

The rear surface of the solar cell in Fig. 2.1 has a full-area BSF layer, which is obtained by alloying Al from the back contact into the bulk Si in a rapid hightemperature firing step. This Al-BSF is a highly doped region, therefore reducing recombination at the rear surface. The disadvantage of this full-area BSF is that light is absorbed in the Al and the BSF does not very efficiently reduce recombination at the rear surface [19]. Therefore, a 'local back surface field' (LBSF) [19, 20] or the 'passivated emitter and rear cell' (PERC) [10] concepts were developed, which contain a locally opened passivation on the rear surface. In case of a Al-LBSF solar cell, the BSF is only localised around these contact openings and is realised e.g. by laser firing of the Al layer on the rear surface [21].

Figure 2.2 shows a schematic of the processing steps which are generally used within this work to prepare laser-doped selective emitter solar cells. The starting point is an as-cut $p$-type Si wafer, which will be mainly $p$-type multicrystalline Si wafers in this thesis. The wafers receive a cleaning, and in case of $\mathrm{Cz}-\mathrm{Si}$, a saw damage etching (SDE). The subsequent texturisation process is an etching either with an alkaline solution resulting in a random pyramid texture for $\mathrm{Cz}-\mathrm{Si}$ wafers or an etching with an acidic solution resulting in an iso-texture for multicrystalline Si wafers.


Fig. 2.2 Typical process flow chart for an Al-BSF selective emitter solar cell based on p-type multicrystalline or Cz -Si wafers and with a self-aligned front surface metallisation.

After texturisation the wafers receive an HF-dip to remove the native oxide layer from the Si wafers. Subsequently, the emitter is formed by diffusion of dopant atoms into the heated Si wafer surface. The emitter diffusion forms the $p$ - $n$ junction of the solar cell by doping the surface of the wafer with dopants of the opposite doping type, such as phosphorus in the case of $p$-type wafers.

The next step after emitter diffusion in the processing scheme in Fig. 2.2 is the chemical edge isolation. Edge isolation improves the solar cell efficiency and is necessary for plating as metallisation scheme. Chemical edge isolation was shown to be the most effective edge isolation method for laser-doped selective emitter solar cells [22]. During chemical edge isolation, any diffused emitter on the rear surface and on the edge of the wafer is etched away.

After the chemical edge isolation the phosphosilicate glass (PSG) layer, which forms during emitter diffusion is etched and a dielectric layer such as $\operatorname{SiN}_{\mathrm{x}}$ (or silicon dioxide $\mathrm{SiO}_{2}$ ) is deposited onto the front side by means of PECVD. The dielectric coating simultaneously acts as surface passivation and as antireflection coating. In case of an Al-LBSF solar cell, a dielectric layer is also deposited onto the rear surface. Afterwards, the rear surface of the solar cell is screen-printed with Al paste, which is subsequently fired to form a rear surface BSF in case of the Al-BSF solar cells. In case of Al-LBSF solar cells, one approach to achieve the LBSF is by alloying the aluminium locally using the laser fired contacts (LFC) method [21].

The first step for the metallisation of the front surface is the laser doping process. The front surface dielectric is also removed during this step. After laser doping, the solar cells undergo plating, which consist of 4 sub-steps including pretreatment of the laser-doped areas, followed by plating of the seed, conducting and capping layer and an optional annealing. Plating is discussed in more detail in the following section.

### 2.1.3 Plating of solar cells

Plating is currently intensively investigated as a potential alternative industrial metallisation method to screen printing [9]. Extremely small finger widths (25-40 $\mu \mathrm{m})$ with high aspect ratios (1:2-1:4) as well as silver free metallisation of solar cells is possible using plating [11, 23-26]. A common form of plating is lightinduced plating (LIP). Figure 2.3 shows a schematic of the LIP process.


Fig. 2.3 Schematic illustration of the experimental setup used for light-induced plating (LIP). Here the fabrication of front side metal contacts for p-type silicon solar cells in a galvanic element under the influence of a light source is shown [11].

During LIP, the light source generates electron-hole pairs in the $p$-type solar cell precursor, such that electrons move to the front surface and holes to the rear surface. Positively charged metal ions in the solution are attracted and adhere to the front at locations which are not electrically isolated. Dissolution of the rear surface is prevented by applying an optimised bias voltage between the rear surface and an auxiliary anode, such that the net dissolution rate at the rear surface is zero.

Plating can be used to metallise a conducting surface with nearly any metal. Before the plating a pre-treatment of the Si surface removes any oxide on the surface
(such as the native oxide), which would otherwise increase the contact resistance or even electrically isolate the surface such that plating would not occur. For silicon wafer solar cells, $\mathrm{Ni}, \mathrm{Cu}, \mathrm{Ag}$ and Sn are most commonly used materials for plating. Ni is typically used as a seed layer as it forms a good electrical contact with $\mathrm{Si} . \mathrm{Cu}$ or Ag are used as main conductor due to their excellent electrical properties and Sn (or Ag ) is used to protect the Cu layer from corrosion.

The application of Ni and Cu on solar cells is non-trivial, since Ni and Cu can induce deep-level defects in Si [27]. These defects act as recombination centres or the occurring silicide precipitates may even shorten the $p$ - $n$ junction [28]. It was shown that the influence of Ni on the electrical performance of solar cells is significantly less severely than the influence of Cu [11]. It is known that the diffusion of Cu at room temperature (or at solar cell operating temperature) is significantly faster than the diffusion of Ni. Thus to avoid the diffusion of Cu into Si at low temperatures, Ni is used as diffusion barrier for Cu atoms.

The deposition of the metal ions occurs only on surfaces which are not electrically isolated, e.g. a seed layer or bare Si. A dielectric layer prevents the deposition of metals on undesired areas. However, a deposition on defects in the dielectric layer may also occur, which is commonly referred to as "background plating", "ghostplating", "parasitic plating" or "overplating". Background plating is a severe challenge for metallisation by plating due to the unpleasant aesthetically impression and increased reflection of the solar cell [29-33]. Braun et al. [32] identified three reasons for background plating: (a) Inhomogeneities in the dielectric layer, (b)
particles on the surface before deposition of the dielectric layer and (c) cracks or pinholes of the dielectric layer.

Avoiding background plating in the first place is the preferred method. Possible ways to avoid background plating are the use of double-layer antireflection coatings [34], the application of a 'rounding etch' before antireflection coating deposition, which rounds the sharp edges of e.g. acid textured Si [29], or simply more careful handling of the samples prior to the plating process. However, all these methods need altering of existing processing flows and may not be able to completely eliminate background plating. Avoiding background plating on multicrystalline Si wafers is particularly challenging, due to their complex surface structure [35].

### 2.2 Theory of laser doping

Laser doping is the process where laser energy is used to diffuse dopant atoms into a semiconductor. The heat imposed from the high flux of photons impinging onto the semiconductor surface is used to increase the diffusion rate of dopant atoms into the semiconductor. In general the term laser doping refers to laser processes whereby the substrate is molten. Melting the substrate increases the diffusion rate of dopant atoms by several orders of magnitudes compared to diffusion rates into solid substrates as shown in Table 2.1 in the case of Si . Another advantage offered by laser doping is that the solubility limits of dopant atoms are generally higher in the liquid state compared to the solid state (see e.g. for phosphorous and boron in Table 2.1). Therefore, a higher concentration of dopant atoms can be achieved in laser-doped areas than in areas, which are diffused without
melting the substrate. This effect is also called hyper-doping [36]. These higher doped areas may be beneficial for low contact resistances to metal contacts if the dopant atoms are electrically active incorporated. However the used metallization method (i.e. plating as discussed in Sec. 2.1.3) is able to maintain a good ohmic contact even at dopant concentrations in the range of $10^{19}$ atoms $/ \mathrm{cm}^{3}$ [37].

Table 2.1 Diffusion rates $D_{1}$ and $D_{s}$ at the melting point and maximum solubility limits $N_{l}{ }^{\text {max }}$ and $\mathrm{N}_{\mathrm{s}}{ }^{\text {max }}$ of phosphorous and boron dopants into liquid and solid Si, respectively.

|  | $\boldsymbol{D}_{l}\left[\mathbf{c m}^{2} / \mathbf{s}\right]$ | Ref. | $\boldsymbol{N}_{l}^{\max }$ <br> $[\mathbf{a t o m s} /$ | Ref. | $\boldsymbol{D}_{s}\left[\mathrm{~cm}^{2} / \mathbf{s}\right]$ | Ref. | $\boldsymbol{N}_{s}^{\max }$ <br> $[\mathbf{a t o m s} /$ | Ref. |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\left.\mathbf{c m}^{3}\right]$ |  |  |  |  |  |  |  |  |

The following two subsections will discuss a general macroscopic model of laser doping. Section 2.2.1 reviews the theory for heat influence of a laser source and Sec. 2.2.2 reviews the theory of dopant diffusion. Finally, Sec. 2.2.3 discusses key results of current models for the used laser systems in this thesis.

### 2.2.1 Heat influence model

The interaction of laser light with a substrate surface is typically described as the propagation of electromagnetic waves at an interface [42, 43]. At the substrate surface the electromagnetic waves are either reflected, or transmitted into the material. The Fresnel laws describe the relationship between transmitted and reflected electromagnetic waves as a function of the incident angle and the wavelength dependent complex refractive indices of both media. Only the transmitted portion of the electromagnetic wave is interacting with the material, which is described as absorbance according to the Beer-Lambert law: $\Phi=\Phi_{0} e^{-\beta_{a b}{ }^{z}}$, where $\Phi$ is the intensity of the transmitted light at depth $z$ in the sample, $\Phi_{0}$ is the intensity of the
incident light and $\beta_{a b}$ is the absorption coefficient of the material. The absorption coefficient $\beta_{a b}$ depends on the wavelength and on the medium.

The absorption of light in a solid occurs in two steps:

1. The electrons interact with the photons of the incoming light. The photons pass their energy to the electrons, which are moving to a higher energy level (excitation).
2. The electrons lose their excitation energy by interaction with phonons, which are vibrational states of the atomic lattice. The excitation of the phonons is in principal an increase of atom oscillations, which is measurable as heat. Direct interaction of photons in the visible range with phonons is only very small since the momentum of the photons is too small for interaction with atom oscillations.

Both energy transfer processes may occur on different time scales, which also depend on the type of material. This has been investigated for laser melting of metals by e.g. Chichkov et al. [44]. In metals, light is almost solely absorbed by conduction band electrons via intraband transitions which have a short relaxation time in the order of 10 fs to 1 ps . The relaxation time is typically longer in non-metals where it is typically an interband process with time scales between 1 ps to $1 \mu \mathrm{~s}$. It may even be longer at defects, impurities or surfaces. The interaction between electrons and phonons on the other hand occurs at a time scale of 1 ps to 100 ps [42]. These considerations show that in case of semiconductors, where the relaxation times from electron-electron interactions and electron-phonon interactions are roughly at the same time scale, a separate treatment of electron system and lattice
system is not necessary. The heat distribution in semiconductors can be described by a single heat equation.

The heat distribution in any material is described in general by the heat equation:

$$
\begin{equation*}
\frac{\partial T(x, t)}{\partial t}-\alpha \Delta T(x, t)=0 \tag{2.3}
\end{equation*}
$$

where $T$ is the temperature, $\boldsymbol{x}$ is the space vector of a location in the sample, $t$ is the time and $\alpha$ is the heat diffusivity given by:

$$
\begin{equation*}
\alpha=\frac{\kappa}{\rho_{D} C_{p}}, \tag{2.4}
\end{equation*}
$$

where $\kappa$ is the thermal conductivity, $\rho_{D}$ the mass density and $C_{p}$ the specific heat capacity. Here it is assumed that these constants are independent of temperature and that the material is uniform and isotropic. For convenience, Table 2.2 shows an overview of the main thermal characteristics of amorphous $\mathrm{Si}(\mathrm{a}-\mathrm{Si})$, crystalline $\mathrm{Si}(\mathrm{c}-\mathrm{Si})$ and liquid $\mathrm{Si}(\mathrm{l}-\mathrm{Si})$.

Table 2.2 Overview of important thermal characteristics of amorphous Si ( $\mathrm{a}-\mathrm{Si}$ ), crystalline Si (cSi ) and liquid $\mathrm{Si}(1-\mathrm{Si})$ under standard conditions ( 300 K ).

| Material | Density <br> $\boldsymbol{\rho}_{\boldsymbol{D}}$ <br> $\left[\boldsymbol{g} / \mathbf{c m}^{3}\right]$ | Melting <br> temp. <br> $\boldsymbol{T}_{\boldsymbol{m}}[\mathbf{K}]$ | Boiling <br> temp. <br> $\boldsymbol{T}_{\boldsymbol{b}}[\mathbf{K}]$ | Specific <br> heat <br> $\boldsymbol{C}_{\boldsymbol{p}}[\mathbf{J} / \mathbf{g ~ K}]$ | Thermal con- <br> ductivity <br> $\boldsymbol{\kappa}[\mathbf{W} / \mathbf{c m ~ K}]$ | Heat dif- <br> fusivity <br> $\boldsymbol{\alpha}\left[\mathbf{c m}^{2} / \mathbf{s}\right]$ |
| :--- | :--- | :--- | :--- | :--- | :---: | :---: |
| $\mathbf{a - S i}$ | 2.28 | 1420 |  | 0.8 | 0.018 | 0.0097 |
| $\mathbf{c - S i}$ | 2.32 | 1690 | 2654 | 0.71 | 1.5 | 0.85 |
| $\mathbf{l - S i}(\mathbf{1 8 0 0} \mathbf{K})$ | 2.52 |  |  | 0.91 | 0.53 | 0.29 |

Generally, it cannot be assumed that the heat diffusivity is constant. The laser heat may even cause a phase change such that the diffusivity changes rapidly (e.g. as shown in Table 2.2. for the case of Si ). Equation (2.3) then becomes:

$$
\begin{equation*}
\rho_{D}(T) c_{p}(T) \frac{\partial T(\boldsymbol{x}, t)}{\partial t}-\nabla[\kappa(T) \nabla T(\boldsymbol{x}, t)]=0, \tag{2.5}
\end{equation*}
$$

The impinging laser beam also needs to be considered as a heat source term $Q(x, t)$, which is moving across the surface with a velocity $\boldsymbol{v}_{s}$. The heat equation then becomes:

$$
\begin{align*}
& \rho_{D}(T) c_{p}(T) \frac{\partial T(\boldsymbol{x}, t)}{\partial t}-\nabla[\kappa(T) \nabla T(\boldsymbol{x}, t)]+\rho_{D}(T) C_{p}(T) v_{S} \nabla T(\boldsymbol{x}, t)  \tag{2.6}\\
&=Q(\boldsymbol{x}, t) .
\end{align*}
$$

Additionally, phase changes with their latent heats of melting and evaporation have to be considered. This is usually done by calculating an enthalpy term $H(\boldsymbol{x}, t)$ from an integration of the product of mass density and specific heat constant with the addition of the latent heat terms. Equation (2.6) then becomes:

$$
\begin{equation*}
\frac{\partial H(\boldsymbol{x}, t)}{\partial t}-\nabla[\kappa(T) \nabla T(\boldsymbol{x}, t)]+\boldsymbol{v}_{s} \nabla H(\boldsymbol{x}, t)=Q(\boldsymbol{x}, t) . \tag{2.7}
\end{equation*}
$$

Equation (2.7) can only be solved numerically. In several models [42, 45, 46] it has been shown, that with increasing laser power, the surface heats up, starts to melt, evaporates and even overheating after evaporation is possible. Additionally and beyond the model, nonlinear effects may occur, when a substantial amount of material evaporates and forms a plasma plume above the surface. Depending on the laser parameters, the interaction of laser might not only be with the material but also with the plasma plume, which then subsequently can interact again with the material.

The heat equation [Eq. (2.7)] only describes heat transfer through heat conduction. Heat convection and heat radiation can be neglected for laser doping with a pulsed (e.g. via Q-switching) laser [47]. Furthermore, melt flow due to the Marangoni effect $[46,48,49]$ is not considered in the model used in this thesis. In general,
fluid flow arising from e.g. the Marangoni effect needs to be considered for a precise modelling of the dopant depth profile [49].

### 2.2.2 Dopant diffusion model

Diffusion is generally described by the 3D diffusion equation based on Fick's second law, where the concentration $C_{A}(\boldsymbol{x}, t)$ is given by:

$$
\begin{equation*}
\frac{\partial C_{A}(\boldsymbol{x}, t)}{\partial t}-D_{l} \Delta C_{A}(\boldsymbol{x}, t)=0, \tag{2.8}
\end{equation*}
$$

with a constant diffusion coefficient $D_{l}$. The respective boundary conditions determine the influence from the source of dopants. In first approximation, Eq. (2.8) holds when it is assumed that diffusion happens into the melt, only. Re-adsorption of evaporated material and diffusion into heat affected areas are not considered and can be neglected in general. Another higher order influence is that the diffusion constant is temperature and phase dependent. Additionally, the convection and fluid flow of the melt enhances mixing of the dopant atoms in the molten Si .

Equation (2.8) has to be solved for the molten area simultaneously with the heat equation. The molten area constantly changes over time so the volume varies, where highly effective diffusion occurs. Both equations (heat equation and diffusion equation) have been solved numerically in [42, 46, 47, 49-52].

Bäuerle [42] showed approximate 1D solutions for the dopant concentration for two different boundary conditions. The boundary conditions are either an infinite source of dopants or a finite source of dopants at the substrate surface. For the fi-
nite source a concentration $C_{A}^{0}$ is assumed at the surface and for the time $t=0$. The 1D solution of Eq. (2.8) for the dopant depth $z$ is given by:

$$
\begin{equation*}
C_{A}(z, t)=C_{A}^{0} \operatorname{erfc}\left(\frac{z}{z_{l i}(t)}\right), \tag{2.9}
\end{equation*}
$$

where $z_{l i}(t)$ is the effective maximal diffusion depth given by $z_{l i}(t)=2 \sqrt{D_{l} t_{l i}}$ and $t_{l i}$ the time during which the substrate stays molten. For an infinite source the boundary condition is a constant surface flux and the solution then becomes:

$$
\begin{equation*}
C_{A}(z, t)=\frac{J_{i n} z_{l i}(t)}{D_{l}}\left(\frac{z_{l i}(\mathrm{t}) \exp \left(-z^{2} / z_{l i}^{2}(t)\right)}{\sqrt{\pi}}-z \operatorname{erfc}\left(\frac{z}{z_{l i}(t)}\right)\right), \tag{2.10}
\end{equation*}
$$

where $J_{\text {in }}$ is the dopant influx on the surface. These solutions are approximated results for the doping efficiency depending on the starting dopant concentration or the dopant flux. The heat influence is indirectly considered by the effective maximal diffusion depth. The alteration of the molten area during a laser pulse is not considered.

### 2.2.3 Relevant model results for the used laser systems

This section summarises relevant model results for laser doping with the lasers and laser parameters used in this thesis. Three lasers were used in this work. The Nanio 532-20-V from InnoLas Laser and the Pyroflex 25 532-OEM-1 from PyroPhotonics Lasers were both Q-switched diode-pumped solid state lasers. Both laser systems are nanosecond pulsed laser. The third laser (Millennia Prime from Spectra-Physics) was a diode-pumped solid state laser system with a CW output. All laser systems used frequency doubling to obtain a 532 nm (green) wavelength. The Nanio and Pyroflex laser were used with laser pulse lengths in the range of 10 - 200 ns full width at half maximum (FWHM) and single pulse laser fluence of 0.1 - $5.5 \mathrm{~J} / \mathrm{cm}^{2}$ for a beam diameter of $\sim 50 \mu \mathrm{~m}$. The laser pulse repetition frequency
ranges were between $10-500 \mathrm{kHz}$ for the laser systems. The Millennia laser was used with a power output of 15 W and a scanning speed of $0.1-10 \mathrm{~m} / \mathrm{s}$. The energy density range was calculated as $10-2000 \mathrm{~J} / \mathrm{cm}^{2}$ for a beam diameter of $\sim 12 \mu \mathrm{~m}$.

Based on the energy densities and the heating model, it is possible to estimate ranges for melting, evaporation and plasma occurrences. General results of the model in [42] show that melting typically occurs when the laser fluence is above $0.1 \mathrm{~J} / \mathrm{cm}^{2}$. Surface evaporation typically occurs for laser fluence above $1 \mathrm{~J} / \mathrm{cm}^{2}$ and plasma occurs for laser fluence above $10 \mathrm{~J} / \mathrm{cm}^{2}$. These results assume interaction times above 10 ns . Therefore, melting and evaporation can be observed for the two pulsed laser systems assuming that the interaction time is given by the laser pulse length. In case of the CW laser system, simulations by the tool by Fell [47] show that melting and evaporation can also be observed. However, plasma is generally not observed during laser doping.

Another important question for the two used pulsed laser systems is if two consecutive laser pulses interact with each other via a residual heat from the preceding laser pulse. A general solution [42] and simulations [47] show that the residual heat from a preceding laser pulse is negligible small for the used repetition frequencies. Therefore, the heat influence of consecutive laser pulses can be treated, separately. However, the absorption of the laser light might change between laser pulses since the surface alters when molten or evaporated.

Other heat influences are that the melt depth and time increases for increasing laser pulse duration and energy densities below the evaporation threshold [53-56] and the heat influence on the surrounding area is roughly in the same range as the area of the laser pulse [47].

Concerning laser doping, it has been shown that longer melt times and deeper melt depths are resulting in higher dopant concentrations and deeper diffusion, respectively. Additionally, increasing the number of laser pulses $N_{p}$ on an area increases the dopant concentration and decreases sheet resistance, which is reflected by defining $z_{l i}(t)$ in Eqs. (2.8) and (2.9) as: $z_{l i}(t) \approx 2 \sqrt{D_{l} N_{p} t_{l i}}$ [42]. Overlapping laser pulses partly also increases dopant concentration and depth [56, 57].

### 2.3 Laser doping techniques

There are various laser doping techniques, which are currently or have been investigated for solar cell applications. They can be differentiated by the method of applying the dopant precursor to the substrate. One method, which was investigated early on, is gas immersion laser doping (GILD), where the gas atmosphere surrounding the substrate is the dopant source [58,59]. This method is not suited for solar cell applications since the need of a low impurity gas atmosphere is not suitable for high throughput low cost manufacturing. Another method is wet film laser doping (WFLD) or also called spin-on doping (SOD), where a dopant source is applied as liquid film on the substrate surface [54, 60]. This method usually uses a scanner system to move the laser beam across the surface. The next method is laser chemical processing (LCP), where a liquid jet is used to guide the laser beam across the substrate surface [61]. The liquid jet also contains the dopant atoms.

Another method that uses a liquid precursor is laser doping in a liquid bath [62], which is similar to WFLD. A fifth method is doping from a solid substrate such as PSG [63, 64], enriched coatings (e.g. phosphorus doped $\operatorname{SiN}_{\mathrm{x}}$ ) [65], sputtered or printed precursors [21, 66]. The WFLD and LCP methods are used in this thesis and are discussed in more detail below.

### 2.3.1 Wet film laser doping (WFLD)

The dopant precursor is applied as liquid film on the surface in case of WFLD. Methods to apply a liquid film include spin-on, spray-on or roll-on of the liquid or immersion the substrate in a liquid bath. The thickness of the liquid film can vary between a few $\mu \mathrm{m}$ up to several mm in case of the immersion in liquid bath. WFLD usually implies a finite dopant source for spin-on, spray-on and roll-on dopant precursors. However, large precursor thicknesses or the immersion in a liquid bath can also be treated as an infinite dopant source.

Figure 2.4 shows an illustration of WFLD as used in this thesis. The laser beam was directed with a galvanometric scanner system across the wafer surface. The applied scanner system (intelliSCAN 20 from SCANLAB) consisted of movable mirrors, which were directed such that the laser beam could be moved anywhere on the sample surface with speeds of a few $\mathrm{mm} / \mathrm{s}$ up to a few $\mathrm{m} / \mathrm{s}$. The laser beam was focused onto the substrate surface with an f -theta lens, which has a barrel distortion such that the laser beam stays in focus at any point on the flat sample. The dopant film consisting of $30 \mathrm{wt} \% \mathrm{H}_{3} \mathrm{PO}_{4}$ was applied with spin-on deposition if not otherwise stated. The film was spun onto the wafer surface for 30 s at a rota-
tional speed of 3000 rpm . The result is a thin dopant film of approximately $2 \mu \mathrm{~m}$ height on the full-area of the wafer.


Fig. 2.4 Schematic illustration of the working principle of WFLD. The laser beam is scanned across the surface by galvanometric movable mirrors and focused onto the wafer surface. The dopant precursor is applied on the substrate surface in a previous step.

The WFLD was mainly employed with a CW laser. The CW laser caused a continuous heat imposing on the substrate surface, which caused a continuous line following the scanning direction. To form large laser-doped areas, several lines were scanned in parallel with a certain hatch. The losses of laser intensity within the optical system were measured to be $\sim 10 \%$. The stated values for average power in the experiments are the average power of the laser corrected by this factor. Individual laser-doped lines had a width of 8-40 $\mu \mathrm{m}$. The surrounding area of the line is also affected by the heat of the laser (heat affected zone).

The main advantage of WFLD is the simplicity of the setup and the flexibility to use different methods to apply the dopant precursor. The main disadvantage is the necessity of accurate focusing over the whole size of the substrate. Furthermore, the dopant precursors are finite for certain deposition methods, which may limit the dose of dopant atoms in the substrate and may lead to lower surface concentrations.

### 2.3.2 Laser chemical processing (LCP)

Laser chemical processing uses a liquid jet in which a laser beam is coupled into via total internal reflection [61, 67]. The liquid jet acts as waveguide for the laser beam (comparable to an optical fibre made of glass) and as dopant source. The dopant atoms are continuously reaching the surface. Therefore, this method has an infinite dopant source. Figure 2.5 shows the working principle of LCP as used in this thesis.


Fig. 2.5 Schematic illustration of the working principle of LCP. The laser beam is focused through a window into a high pressure liquid jet and stays focused inside the jet by total internal reflection. The focussed laser beam and liquid jet hit the surface of the substrate which is moved under the jet. (Image obtained from [37].)

The laser beam, coming from an optical fibre, was focused in the machine (SelectDop LCP, RENA) with a focusing lens through a window into the exit nozzle of a liquid chamber. The liquid was pressed with $\sim 150$ bar through the stainless steel exit nozzle with diameter of $50 \mu \mathrm{~m}$, forming a laminar flowing jet. The laser
beam remained inside the jet by total internal reflection, as long as a laminar flow of the jet was maintained. The liquid used in this thesis was phosphoric acid with concentration of $60 \mathrm{wt} \%$ (if not stated otherwise). A gas flow of $\sim 1$ bar was used to support the liquid jet such that the distance from the nozzle where the laminar jet would break down was increased. The breakdown of the jet also marked the maximum working distance, which was around $5-7 \mathrm{~cm}$ similar as obtained in [68, 69].

The substrate was moved under the jet with a certain speed. The laser beam within the jet hits the surface, melts or even evaporates the surface material, while the liquid flow cools the surrounding area. Dopant atoms from the liquid jet diffuse into the molten area.

A pulsed laser is generally used with the LCP technology. Each laser pulse affects an approximately round-shaped area as shown in [51]. Those areas can be overlapped to form a line (pulse-to-pulse distance). These lines can be overlapped with a certain hatch (line-to-line distance) to form larger areas. The average number of laser pulses within a certain area is described as laser pulse density, which will be discussed in detail in Sec. 3.3.1. The losses of the laser intensity within the optical system used in this thesis were measured to be $\sim 30 \%$. The stated values for single pulse laser fluence in the experiments are the single pulse laser fluence of the laser corrected by this factor.

The nozzle diameter and the laser intensity determined the approximate affected area on the substrate surface. For the used $50 \mu \mathrm{~m}$ nozzle the affected area was 8 -
$60 \mu \mathrm{~m}$ in diameter for a single pulse. The main influence on the surrounding area were melt expulsion, which depends on the laser intensity and can reach even more than $10 \mu \mathrm{~m}$. The heat affected zone is usually less than a few $\mu \mathrm{m}$ [47].

The main advantages of LCP results from the liquid jet, which acts as a continuous supply of dopant atoms, reduces contamination of the surrounding area by removal of ablated material and keeps the laser beam focused inside the water jet over a long distance. On the other side, the coupling of a laser beam into a liquid chemical jet is still challenging and requires extensive engineering efforts.

The LCP machine used extensive safety measures to ensure the safety of the user. The supply of the high pressure liquid chemical jet was enclosed in a double housing and featured automated and manual pressure control. Fumes of the chemical liquid were exhausted through an exhaust piping and the chemical was disposed in dedicated waste disposal container. All moving parts where enclosed behind interlocked gates and electrical hazards were prevented with proper insulation. Additionally, the whole laser system including nozzle was enclosed in a laser safety housing.

### 2.4 Relevant characterisation methods

This section gives a brief overview of the main relevant characterisation methods used in this work. Essentially, only a few characteristics are important for laser doping: the dopant depth profile and the homogeneity of doping, defect density, location and type of defect, geometrical aspects (size and shape of the doped areas), roughness and roughening of the surface as well as material removal.

Measurements of the dopant depth profile can be performed directly by electrochemical capacitance voltage (ECV) or secondary ion mass spectrometry (SIMS) [51, 70]. ECV as well as SIMS measurements are averaging the dopant depth profile over a certain area. In cases where the homogeneity or the lateral distribution of dopant concentration needs to be known, time-of-flight (TOF) SIMS can be used, which is able to measure lateral dopant atom concentrations with a resolution down to a few $\mu \mathrm{m}$ [51]. SIMS measures all incorporated dopant atoms, while ECV measures only substitutionally incorporated dopant atoms but not nonsubstitutionally incorporated dopant atoms like agglomerated or precipitated dopant atoms [71]. However, for laser-doped samples, it is assumed that all dopant atoms are substitutionally incorporated, since the heavily doped layer is formed by crystallisation of molten silicon ('liquid phase epitaxy')[72]. ECV measurements are discussed in detail in Section 2.4.1.

Another method which can be used to estimate the doping efficiency of laser processes are sheet resistance $\left(R_{s h}\right)$ measurements. $R_{s h}$ measurements are much simpler to carry out compared to ECV or SIMS measurements but the dopant depth profile cannot be obtained. However, they can be used to identify interesting process parameters, which could then be tested by ECV or SIMS measurements. $R_{s h}$ measurements are also used to calibrate ECV measurements or to compare to SIMS or spreading resistance measurements [73]. Section 2.4.2 discusses $R_{s h}$ measurements.

Homogeneity of doping can be measured by TOF-SIMS. Another way to measure homogeneity in terms of dopant depth is given by electron beam-induced current (EBIC) measurements. EBIC is discussed in detail in Sec. 2.4.3.

Measurement of defects of laser-doped areas can be carried out in several ways. Good examples of defect studies on laser-doped areas are published in [17, 7477]. In the present work, defect studies of laser-doped areas were done by emitter saturation current density measurements. The used method to obtain emitter saturation current density is discussed in Sec. 2.4.4.

Other characteristics of laser-doped areas such as geometrical aspects and roughness were measured by a confocal optical microscope (LEXT, Olympus).

### 2.4.1 Electrochemical Capacitance-Voltage measurements

ECV measures dopant depth profiles by stepwise etching of material and measuring the capacitance-voltage curve at each step [70, 71, 78-81]. Figure 2.6 shows a schematic of the ECV setup where the electrolyte forms a Schottky-like contact with the sample surface.


Fig. 2.6 Schematic illustration of ECV measurement. The sample is in direct contact with an electrolyte and electrically contacted with a voltage supply and a potentiostat. An ultraviolet (UV) light source can be used to support the etching.

Depending on the sample ( $p$-type or $n$-type doping), different etch methods are used. Figure 2.7 shows a simplified schematic of the etch process. In principle, both etching processes need an injection of holes at the surface (step 1) and a substitution of the open bonds of silicon with a different material (step 2).


Fig. 2.7 Electrochemically etching of $p$-type or $n$-type silicon with ammonium bifluoride solution. The blue colour denotes the electrolyte and pink denotes the Si substrate. Si bonds are shown as black arcs. Black circles denote electrons and green circles denote fluorine ions. Holes are accumulating at the surface, when biased externally. For $n$-type Si , holes may be generated from elec-tron-hole pairs with an external light source (indicated by a yellow line). Eventually, fluorine ions bind to the generated dangling bonds at the surface atoms.

For a p-type doped sample, the injection of holes is performed with applying a potential such that an anodic current flow is observed. The electrons are drawn from the surface into the semiconductor and holes are accumulating at the surface. For $n$-type, the holes are injected by a light source. Additionally, a voltage is applied, putting the Si under reversed bias to support the movement of electrons away from the surface. Eventually, fluorine atoms from the ammonium bifluoride solution will bind to the generated open bonds. When the silicon atom is completely surrounded by flour atoms, it is dissolved from the silicon surface.

The dissolution rate can be obtained by measuring the etch current. Faradays law of electrolysis yields for the etch depth $z_{\text {etch }}$ :

$$
\begin{equation*}
z_{\text {etch }}=\frac{M_{\text {mol }}}{\rho_{D} A v} \frac{\int I d t}{q L} \tag{2.11}
\end{equation*}
$$

where $M_{m o l}$ is the molar mass, $A$ is the etch area, $q$ is the elementary charge, $L$ is the Avogadro constant and $v$ is the valence of the semiconductor (for $\mathrm{Si}: v=4$, however, hydrogen binding, dislocations or grain boundaries reduce the valence of $\mathrm{Si})$. The charge $\int I d t$ is approximately given by the measured current $I$ multiplied with the time interval $\Delta t$.

The carrier concentration is determined from capacitance-voltage measurements after each etch step. Figure 2.8 shows a schematic of the process.


Fig. 2.8 Schematic illustration of a capacitance voltage measurement. Approximated band structure of electrolyte - semiconductor ( $n$-type) contact with conduction band energy $E_{C}$, Fermi level $E_{F}$ and valence band energy $E_{V}$. Superimposed is the space charge density graph, with the depletion region in the semiconductor and an electron layer accumulating at the surface in the electrolyte. In forward bias the width of the depletion region becomes smaller.

A small bias voltage modulated with a frequency signal is applied to the Schottky contact. The change in voltage $V$ causes a change in the width of depletion region, which also changes its capacitance $C$. This is comparable to making capacitor plates in a conventional capacitor larger or smaller. The depletion region also depends on the carrier concentration $N$. Therefore, one can calculate the carrier concentration from the changes in capacitance using the Mott-Schottky equation:

$$
\begin{equation*}
N=-\frac{2}{A^{2} e \epsilon \epsilon_{0} \frac{d\left(1 / C^{2}\right)}{d V}} \tag{2.12}
\end{equation*}
$$

where the constants $\epsilon$ and $\epsilon_{0}$ are the relative permittivity and the vacuum permittivity, respectively. The validity of the Mott-Schottky equation is influenced by many factors, such as the presence of electrically active defects, low dopant concentration, low voltages, stable surfaces and resistances in the circuit but in general applicable for the performed measurements [79, 81, 82].

ECV dopant depth profiles were measured with an automated wafer profiler (CVP21, WEP Control) using a 0.1 M solution of ammonium-bifluoride. The measured dopant depth profiles were calibrated by either an externally measured depth of etching and measured surface area or by $R_{s h}$ measurements as discussed in Appendix A.

### 2.4.2 Sheet resistance measurements

The $R_{s h}$ measurements on c-Si sheets are widely used to evaluate doped areas [73, 83-90]. The $R_{s h}$ is one of the main parameters affecting device performance, and is also commonly used to characterise doping processes such as thermal diffusion, ion implantation, or laser doping. Potential drop (PD) measurements are commonly used to obtain the $R_{s h}$ of a sample [73, 83]. They are either four-point probe (4PP) measurements, or transfer length method (TLM) measurements. The setups for PD measurements such as 4PP and TLM are simple and vastly available. Measurements can be obtained quickly, and a mapping on large areas is possible with a typical 4PP setup.

The $R_{s h}$ can be regarded as the 2-dimensional resistivity of a thin diffused layer with thickness $z_{\max }$ and is obtained from integration over the dopant concentrations and dopant mobilities at different depths $z$ [73]:

$$
\begin{equation*}
R_{s h}=\frac{1}{q \int_{0}^{z_{\max }}\left[n(z) \mu_{n}(n(z))+p(z) \mu_{p}(p(z))\right] d z} \tag{2.13}
\end{equation*}
$$

where, $n(z) \mu_{n}(n(z))$ and $p(z) \mu_{p}(p(z))$ are the concentration of negatively charged carriers times their mobility and positively charged carries times their mobility, respectively. In the case of PD measurements in the dark, it can be assumed that the minority carriers do not add a significant contribution to $R_{s h}$, therefore $n(x) \mu_{n}(n(x))$ or $p(x) \mu_{p}(p(x))$ can be ignored. It is not possible to calculate a dopant depth profile for diffused samples directly from the measured $R_{s h}$. However, comparisons between diffusion processes are possible, when similar processes are used. Evaluations of $R_{s h}$ measurements regarding the diffusion are commonly supported by dopant depth profiles from SIMS measurements, ECV measurements, or simulated dopant depth profiles.

The $R_{s h}$ of a sample can be determined from a PD measurement using four probes (the 4PP setup), where a constant current is applied on the Si surface through two probes ( $I^{+}$and $I$ ) and the generated potential drop (or potential difference) between the two remaining probes ( $V^{+}$and $V$ ) is measured. In a measurement with arbitrarily placed probes on an infinite homogeneously doped sheet $R_{s h}$ can be determined from the following relation [73]:

$$
\begin{equation*}
R_{s h}^{4 P P}=\frac{2 \pi}{\ln \left(s_{2} s_{3} / s_{1} s_{4}\right)} \frac{V}{I}, \tag{2.14}
\end{equation*}
$$

where $s_{1}$ and $s_{2}$ are the distances from current probe $I^{+}$to voltage probe $V^{+}$and voltage probe $V$ and $s_{3}$ and $s_{4}$ are the distances from current probe $I$ to voltage probe $V^{+}$and voltage probe $V$, respectively (see also Fig. 2.9). The term $R_{s h}^{4 P P}$ is used here to reflect that the $R_{s h}$ is obtained from 4PP measurements. In Eq. (2.14) a layer with a non-conducting boundary such as $n$-type doping on $p$-type substrate or vice versa is assumed.


Fig. 2.9 Schematic illustration of potential drop $R_{\text {sh }}$ measurements using four probes with arbitrary distance and placement. The sample is an infinitely wide thin conducting sheet or layer with a nonconducting boundary to the next layer in $z$ direction. The current is applied through the probes $I^{+}$ and $I$ while the voltage is measured through the probes $V^{+}$and $V$. The distances between the probes are shown as $s_{1}-s_{4}$.

When using a collinear arrangement of the probes with $s_{2}=s_{3}=s$ and $s_{1}=s_{4}=2 s$, Eq.
(2.14) simplifies to:

$$
\begin{equation*}
R_{s h}^{4 P P}=\frac{\pi}{\ln (2)} \frac{V}{I} \approx 4.532 \frac{V}{I} . \tag{2.15}
\end{equation*}
$$

When the probe spacing is smaller than 10 times the thickness of the sheet a correction factor for the non-infinitesimal depth needs to be applied. This correction factor requires exact knowledge about the depth of the laser-doped area [91]. Therefore, larger probe spacing - as used in conventional 4PP setups - are pre-
ferred in contrast to micro 4PP measurements [92, 93]. Usual probe spacing of commercially available 4PP desktop setups is in the range of $1-1.59 \mathrm{~mm},{ }^{8}$ which allows a maximum depth of up to $\sim 100 \mu \mathrm{~m}$. The depths of laser-doped areas are in the range of a few $\mu \mathrm{m}[54,60,94]$. Therefore a correction factor regarding the depth of diffusion can be neglected for laser-doped areas.

Measurements of $R_{s h}$ with the 4PP setup are commonly performed by measuring resistance of the sheet twice: Once with the current applied through the outer two probes $\left(R_{l}\right)$ and once with the current applied through one inner and one outer probe ( $R_{2}$ ). Both resistances are used to calculate $R_{s h}$ of the layer by solving the following equation [95, 96]:

$$
\begin{equation*}
\exp \left(\frac{2 \pi R_{1}}{R_{s h}^{\text {dual }}}\right)-\exp \left(\frac{2 \pi R_{2}}{R_{s h}^{\text {dual }}}\right)=1 \tag{2.16}
\end{equation*}
$$

The method is also often referred to as 'dual configuration method' and reduces the influences of boundaries when measuring laterally confined samples. The term $R_{s h}^{\text {dual }}$ is used here to reflect that the $R_{s h}$ is obtained from the dual configuration method.

The 4PP setup (RG100/RT3000, Napson) that was used in this work automatically adjusts the applied current to be within the optimal current-voltage regime. This avoids measurement errors caused by too large currents (which can lead to carrier injection) or noise influence from too low currents. The 4PP setup was equipped with a collinear probe head (TC150u100g, Jandel), with a probe spacing of 1.0

[^3]mm . The resistance was measured in the dark applying the current in both directions (from $I^{+}$to $I$ and conversely).

It is also possible to obtain $R_{s h}$ from TLM measurements, where contact pads with different distances are connected with two or more probes, as shown in Fig. 2.10. The potential drop is measured between two neighbouring contact pads.


Fig. 2.10 Schematic illustration of TLM measurements using rectangular contacting pads with distances $d_{x}$. The width of the whole structure $w$ is identical to the width of the contacts. The current is applied through the probes $I^{+}$and $I$ while the voltage is measured through the probes $V^{+}$and $V$.

The total resistance $\left(R_{T}\right)$ between the neighbouring pads is given as:

$$
\begin{equation*}
R_{T}:=\frac{V}{I}=\frac{R_{s h}}{w} d_{x}+2 R_{c}, \tag{2.17}
\end{equation*}
$$

where $d_{x}$ is the distance between the contact pads, $w$ and $R_{c}$ are the width and the contact resistance of the pads, respectively. The $R_{s h}$ is obtained by measuring $R_{T}$ between contact pads of different distance and calculating the slope. For this calculation rectangular contact pads are assumed, and that the total width of the sample is not larger than the width of the contact pads. Similar results can be obtained with e.g. circular contacting pads [73].

The TLM method can be modified to be able to measure single laser-doped lines directly [97-99]. Previously, two different methods based on the TLM method
were used to extract $R_{s h}$ of single laser-doped lines. Either large laser-doped areas with different distances are connected with a single laser-doped line, or multiple individual laser-doped lines are contacted via metallisation at different distances to assemble a TLM-like pattern. Both methods are not ideal for the characterisation of laser-doped lines for solar cell applications: A single laser-doped line needs to have a very low $R_{s h}$ of less than $15 \Omega /$ sq. to obtain reliable measurements [98] and a metallisation step introduces another possible source of errors.

The TLM patterns in this work were measured with four probes connected to a source meter (model 236, Keithley) delivering a fixed current. The current was set to be within the samples' linear current-voltage regime [73]. The measurement was performed in the dark using forward and reverse currents.

### 2.4.3 Electron beam-induced current (EBIC)

Electron beam-induced current uses the electron beam of a scanning electron microscope (SEM) to induce a current in a sample with an internal electric field, e.g. a $p-n$ junction in a semiconductor. The current is measured by contacting the sample and amplifying the current signal of the probe. The result is an EBIC image of the relative current value at different locations. Figure 2.11 shows a schematic of an EBIC setup.

The current measured with the EBIC system occurs due to the generation of elec-tron-hole pairs, which are separated by the $p-n$ junction. The collection probability depends on the distance to the $p-n$ junction and the electronic quality of the 'illuminated' region (such as the local minority carrier lifetime and surface recombina-
tion velocity)[100]. The generation of electron-hole pairs depends on the SEM interaction volume, which is also influenced by geometrical factors of the sample, such as the material volume especially on rough surfaces [17].


Fig. 2.11 Schematic illustration of an EBIC setup with a semiconductor sample. The electron beam-induced current is generated by the electron beam of an SEM.

In this work, EBIC is used to detect the location of $p-n$ junctions in cross-sectional regions milled into the samples using ions. The left image of Fig. 2.12 is a typical SEM image (grayscale) with a superimposed EBIC image (red) of the crosssection of a sample. The sample is an alkaline-textured, lightly boron-doped $\mathrm{c}-\mathrm{Si}$ wafer with a phosphorus-diffused $\mathrm{n}^{+}$layer along the top surface. The right graph shows a line scan of the EBIC signal starting at the surface. The EBIC signal is maximal at the centre of the $p-n$ junction and decreases with increasing distance from the $p-n$ junction due to the lower collection probability of minority carriers.


Fig. 2.12 Left: Measured SEM image (greyscale) with superimposed EBIC image (red). Right: EBIC image intensity depending on the distance to the surface. The SEM and EBIC images were obtained with a SEM voltage of 3 kV .

The interaction volume of the SEM electron beam is smaller for lower acceleration voltages. Therefore, lower acceleration voltages increase the spatial resolution of the measurements. Furthermore, the SEM electron beam interaction volume with the sample decreases when going closer to the surface. Therefore, the generation rate of electron-hole pairs is reduced, which causes also a lower EBIC current close to the surface. This effect happens in combination with surface recombination and may cause the detection of a deeper $p-n$ junction as actually present in the sample [17]. Detection with different acceleration voltages may be used to unravel this problem, since larger interaction volumes are more affected by this problem.

### 2.4.4 Quasi-Steady-State Photo conductance measurements

Quasi-steady-state photo conductance (QSSPC) measurements determine the effective minority carrier lifetime of a semiconductor sample [101], which can be used to obtain the emitter saturation current density. The emitter saturation current density is a measure of the recombination in the emitter and therefore affects the solar cell efficiency as discussed in Sec. 2.1.1. The sample is placed on an inductor coil, which induces an induction current in the sample. A light source illuminates the sample, such that electron-hole pairs are generated. The generated excess charge carriers increase the conductance, and therefore the induction current, in the sample. The change in induction current is also detected by the inductor coil and measured. Figure 2.13 shows a schematic of the measurement method.


Fig. 2.13 Schematic illustration of the QSSPC setup which measures the effective minority carrier lifetime of a sample. A flash lamp changes the conductance of the sample, which is coupled with an inductor coil. The change in conductance is detected by a change in induction current and measured.

The light source, which is a decaying flash in case of QSSPC, generates excess carriers in the sample. In case of a $p$-type wafer, the effective minority carrier lifetime of the sample ( $\tau_{e f f}$ ) depends on the excess minority carriers ( $\Delta n$ ) and the generation rate ( $G$ ) by [102]:

$$
\begin{equation*}
\tau_{e f f}=\frac{\Delta n}{G-\frac{d \Delta n)}{d t}}, \tag{2.18}
\end{equation*}
$$

Since a decaying flash is used, the variation of $\Delta n$ over time is measured. The generation rate is obtained by measuring the photon-flux at the surface with a calibrated reference solar cell and applying an optical constant as factor to account for absorption losses. The excess minority carrier density is obtained through the change in the induction current, which also depends on the mobility of the carriers. Both quantities ( $G$ and $\Delta n$ ) are spatially averaged over the thickness of the sample.

Equation 2.17 is the generalised analysis of QSSPC measurements by Nagel et al. [102]. In case of a short $\tau_{\text {eff }}$, the light source can be set to a longer illumination
decay time than $\tau_{e f f}$. In this case the sample is in quasi-steady-state. Therefore, $\Delta n$ does not change significantly in the relevant time scale and it is assumed that $d(\Delta n) / d t=0$. In case of a long $\tau_{e f f}$, the flash light can be set up to illuminate the sample with a very short illumination decay time. Here, $\Delta n$ follows an exponential decay (transient mode) and the generation rate can be neglected ( $G=0$ ) during the decay of the light-generated electron-hole pairs.

Under certain conditions, the emitter saturation current density $\left(J_{0 e}\right)$ can be obtained from $\tau_{e f f}$ measurements. Here in this thesis, $\tau_{e f f}$ is measured under highinjection conditions in the bulk of the sample, meaning that the excess carrier density is significantly larger than the bulk dopant density ( $\Delta n \gg N_{d o p}$ ). In this case and by using a symmetrical sample and neglecting radiative recombination, the emitter saturation current density $\left(J_{0 e}\right)$ is related to the inverse effective lifetime by [13]:

$$
\begin{equation*}
\frac{1}{\tau_{e f f}}-\frac{1}{\tau_{\text {Auger }}}=\frac{1}{\tau_{S R H}}+\frac{2 J_{0 e}}{q n_{i}^{2} W} \Delta n, \tag{2.19}
\end{equation*}
$$

with $n_{i}$ is the intrinsic carrier concentration and $W$ is the width (=thickness) of the sample. Under high injection, SRH recombination in the bulk plays no significant role for high lifetime material. In combination with using a suitable parameterisation of the Auger recombination rate in the sample, it is therefore possible to obtain $J_{0 e}$ from the $\tau_{e f f}$ measurements.

## 3 Electrical characterisation of laser-doped silicon

## regions using sheet resistance measurements

This chapter applies potential drop (PD) measurements to laser-doped areas, in order to compare laser doping processes and parameters in terms of their doping efficiency. Laser-doped areas can be split into two groups: micro-scale laserdoped areas such as lines or dots and large-scale laser-doped areas. Large laserdoped areas are formed by overlapping many single lines or by using large beams [59]. Due to their different size, different measurement methods have to be used to study the various groups of laser-doped areas. Lines are commonly measured with a method based on TLM and large-scale laser-doped areas with 4PP measurements [54, 98, 99, 103]. In this chapter, different sources of errors are investigated for each method in order to determine how accurate and reliable $R_{s h}$ measurements of laser-doped structures can be performed.

Section 3.1 introduces a novel characterisation method for lines, where the resistance of multiple laser-doped lines is measured for different distances. The impact of inhomogeneous current distribution on the $R_{s h}$ value extracted by this method is investigated in Section 3.1.2. In Section 3.1.3 the influence of a conductive surface coating which is typically encountered for solar cell applications is discussed. Section 3.2 deals with 4PP measurements and how they can be applied to $R_{s h}$ measurements of laser-doped areas.

Laser-doped areas may feature one or more of the following properties which makes them non-ideal for 4PP measurements:
(a) Small size,
(b) Inhomogeneous depth and resistivity,
(c) Surface roughness,
(d) Presence of a non-conductive or conductive coating.

Sections 3.2.1-3.2.4 deal with each of the cases (a) - (d), respectively. In Section 3.3 the concept of laser pulse density is introduced [104], which allows comparison between PD measurements conducted on arbitrary laser-doped areas including dots, lines or larger areas. This method is experimentally corroborated in Section 3.3.2 for lines and larger areas, and for two different laser doping methods. The results of this chapter are summarised in Section 3.4.

### 3.1 Potential drop measurements on single laser-doped lines

Based on the TLM measurements, two methods were introduced in the literature for measuring the $R_{s h}$ of laser-doped lines [98, 99]. However, both of these measurements are not ideal for the characterisation of these regions as mentioned in Sec. 2.4.2. One method restricts the measurement to lines which show a high conductivity in order to obtain reliable measurements while the other method requires additional metallisation steps which introduces another possible source of errors. In the subsequent section a new method is proposed, which combines the strengths of both methods making it applicable to a wide variety of laser-doped lines. Section 3.1.2 presents a test case in which the main error factor, the inhomogeneous current distribution, is investigated. Section 3.1.3 shows how the
method is influenced by a conductive coating, which is typically encountered for solar cell applications.

### 3.1.1 Introduction of the method

The TLM measurements (see Section 2.4.2) can be modified to allow measurements of single laser-doped lines [97]. In this case the contacting pads are laserdoped areas and connected with identical multiple laser-doped lines as shown in Fig. 3.1.


Fig. 3.1 Schematic of the test structure that can be used to measure laser-doped lines. Contacting pads with different distance $d_{x}$ which are made of large laser-doped areas are connected with multiple laser-doped lines. The test structure has the opposite doping type than the substrate. The resistance is measured between adjacent contact pads and the slope of the distance ( $d_{x}$ ) versus resistance $\left(R_{T}\right)$ curve is given by the $R_{s h}$ divided by the number of lines $\left(N_{L}\right)$ and width of the lines $\left(w_{L}\right)$.

The substrate needs to be of the opposite doping type for $R_{s h}$ measurements such that the laser-doped lines are the only conducting connection between the contacting pads. Under this requirement, the laser-doped lines can be regarded as wire resistors between the contacting pads. The $R_{T}$ of these lines is given by:

$$
\begin{equation*}
R_{T}=\rho_{R} \frac{d_{x}}{A_{c}}+2 R_{c} \tag{3.1}
\end{equation*}
$$

with $\rho_{R}$ is the resistivity of the laser-doped lines and $A_{c}=N_{L} w_{L} z_{\text {max }}$ is the crosssectional area of all lines together with $N_{L}$ is the number of lines and $w_{L}$ is the
width of the lines. Identical lines with rectangular dopant depth profiles are assumed here for simplicity but Eq. (3.1) is also valid for any cross sectional area. The $R_{s h}$ can be calculated from the slope of $R_{T}$ versus distance curve:

$$
\begin{equation*}
R_{s h}=N_{L} w_{L} \frac{\Delta R_{T}}{\Delta d_{x}} . \tag{3.2}
\end{equation*}
$$

Equation (3.2) assumes a uniform resistivity and a rectangular cross sectional area of the laser-doped lines. The contacting pads of the pattern in Fig. 3.1 are made of laser-doped areas. The contact resistance is the lumped resistance consisting of the resistance between the probes and the contacting pads, the resistance of the contacting pad itself and the resistance between the contacting pads and the laserdoped lines.

This method of using multiple lines between laser-doped contacting pads allows accurate measurements of $R_{s h}$ of lines in a wide $R_{s h}$ range. This is an enhancement of the measurement range comparing to a previous method published by Wang et al. [98].

While this modified TLM has similarities to the conventional TLM, the name TLM might be confusing since the transfer length concept is not involved. The modified TLM will be referred to as line resistance measurement (LRM) method in this work as it is in principle a measurement of the resistance of laser-doped lines.

### 3.1.2 Experimental corroboration of method

The question might arise whether the LRM method can be used with multiple lines, since the current distribution may not be homogeneous across the lines but may favour certain lines close to the current probes or with lower resistivity. This effect may be elevated due to the fact that the contacting pads also consist of la-ser-doped areas, which generally have a lower lateral conductance than e.g. evaporated metal contacting pads.

In order to investigate if the LRM method can be used with multiple lines, test structures were prepared that feature two sets of laser-doped lines with a different $R_{s h}$. The samples were prepared on RCA (Radio Corporation of America) cleaned and iso-textured $p$-type multicrystalline Si wafers. Laser-doped patterns were fabricated using LCP with the parameters shown in Table 3.1. The contacting pads for the LRM pattern were of the size $5 \times 20 \mathrm{~mm}^{2}$ with distances $d_{x}$ of $2-12 \mathrm{~mm}$ between them.

Table 3.1 Overview of the used LCP parameters (compare Sec. 2.3.2).

| Frequency <br> $[\mathbf{k H z}]$ | Pulse dura- <br> tion <br> $(\mathbf{F W H M})[\mathbf{n s}]$ | Fluence <br> $\boldsymbol{\Phi}_{\boldsymbol{p}}\left[\mathbf{J} / \mathbf{c m}^{2}\right]$ | Scribing <br> speed <br> $\boldsymbol{v}_{s}[\mathbf{m} / \mathbf{s}]$ | Hatch $\boldsymbol{h}[\boldsymbol{\mu m}]$ | Laser pulse den- <br> sity $\boldsymbol{n}_{\boldsymbol{p}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 100 | 19 | $\mathrm{~L} 1: 1.1$ | 0.5 | Lines: 75 | Lines: 16 |
|  | L2: 1.6 | 0.5 | Contact areas: 10 | Contact areas: 39 |  |

The LRM patterns were prepared using two process variations resulting in lines $L_{l}$ and $L_{2}$ with different $R_{s h, l}$ and $R_{s h, 2}$, respectively. A set of samples as used in this experiment consisted of three modified LRM samples as shown in Fig. 3.2: First, a sample containing $N_{L}$ lines of type $L_{l}$; second, a sample containing $N_{L}$ lines of type $L_{2}$ and third; a sample containing alternately $N_{L}$ lines of type $L_{1}$ and $N_{L}$ lines of type $L_{2}$.


Fig. 3.2 Schematic illustration of one set of LRM samples. Two LRM samples were prepared consisting only of lines $L_{l}$ or $L_{2}$, which results in $R_{s h}$ of the lines $R_{s h, l}$ and $R_{s h, 2}$, respectively. The average $R_{s h}^{\text {calc }}$ is then compared to the measured $R_{s h}^{\text {mes }}$ of a LRM sample with both $L_{1}$ and $L_{2}$ lines.

The measured $R_{s h}$ values from the sample, which were scribed only with lines $L_{l}$ or lines $L_{2}$, were inversed and added to obtain an inversed $R_{s h}^{\text {calc }}$. The $R_{s h}^{\text {calc }}$ represents the $R_{s h}$ which would be expected for the pattern with both lines $L_{1}$ and $L_{2}$. The actual $R_{s h}$ of the patterns with both lines was measured, as well ( $R_{s h}^{m e s}$ ). The $R_{s h}^{c a l c}$ was compared to the measured $R_{s h}^{m e s}$ of the sample with both laser parameters. Several pattern sets were prepared with $N_{L}=15$ or 20 and different number of laser passes along the lines ( $1,2,3,5$, and 10 times). The distribution of the ratios between $R_{s h}^{\text {mes }}$ and $R_{s h}^{\text {calc }}$ is shown in Fig. 3.3.

The ratios between $R_{s h}^{m e s}$ and $R_{s h}^{\text {calc }}$ of the 17 patterns is approximating a normal distribution with the centre at 0.008 and standard deviation of 0.107 . The standard deviation of the fit function is in the same range as expectable from the uncertainty of the TLM method.


Fig. 3.3 Distribution of the ratios between measured sheet resistance ( $R_{s h}^{\text {mes }}$ ) and calculated average sheet resistance $\left(R_{s h}^{c a l c}\right)$ of 17 pattern sets. $R_{s h}^{\text {mes }}$ was obtained from measuring LRM patterns with both lines $L_{l}$ and $L_{2}$ and $R_{s h}^{c a l c}$ was obtained from averaging $R_{s h, l}$ and $R_{s h, 2}$ from separate LRM patterns with only $L_{l}$ or $L_{2}$. The red curve is a Gaussian fit with the fit parameters as shown in the plot.

In summary, $R_{s h}$ of LRM patterns consisting of two different types of lines were obtained in two ways: The $R_{s h}$ of the patterns was measured directly and the $R_{s h}$ of the patterns was calculated from separate $R_{s h}$ measurements of the line types featuring also a different number of lines. It was observed that the ratio between measured and calculated $R_{s h}$ is within the uncertainty of $R_{s h}$ measurements. Therefore, it is concluded that neither the resistivity of lines nor the number of lines does significantly influence the measurement accuracy of the LRM method.

### 3.1.3 Measurements on samples with conductive coatings

So far, $R_{s h}$ measurements of uncoated Si samples were discussed, such as $R_{s h}$ measurements of $n$-type laser-doped areas on $p$-type Si substrates. Under certain circumstances a layer other than the thin native oxide may be present on the sample. A relevant example in the field of silicon photovoltaics is the $\mathrm{SiN}_{\mathrm{x}}$ dielectric film that serves as antireflection coating and surface passivation film in silicon wafer solar cell. In this work, it was observed, that a $\operatorname{SiN}_{\mathrm{x}}$ coating may impact $R_{\text {sh }}$ measurements of laser-doped lines. A $\operatorname{SiN}_{\mathrm{x}}$ coating on $p$-type Si may form an in-
version layer due to fixed positive charges [105], which then acts as conducting layer connecting the LRM contact pads in parallel to the laser-doped lines.

Samples were prepared on RCA cleaned and random pyramid textured p-type Cz Si wafers. A $70 \mathrm{~nm} \mathrm{SiN} \mathrm{N}_{\mathrm{x}}$ film was deposited on the wafers using PECVD. Laserdoped patterns were fabricated by WFLD using the parameters shown in Table 3.2. The contacting pads for the LRM pattern were of the size $0.4 \times 7 \mathrm{~mm}^{2}$ with distances $d_{x}$ of 1-4 mm between them.

Table 3.2 Overview of the used WFLD parameters with a CW laser (compare Sec. 2.3.1).

| Avg. Power <br> $[\mathbf{W}]$ | Scribing <br> speed $\boldsymbol{v}_{s}[\mathbf{m} / \mathbf{s}]$ | Dopant media | Hatch $\boldsymbol{h}[\boldsymbol{\mu m}]$ |
| :---: | :---: | :---: | :---: |
| 13.5 | 2 | $30 \mathrm{wt} \% \mathrm{H}_{3} \mathrm{PO}_{4}$ | Lines: 75 <br> Contact areas: 10 |

The $R_{s h}$ was measured as described in Sec. 3.1.1. Three LRM patterns were fabricated and measured before and after a wet etching of the $\operatorname{SiN}_{\mathrm{x}}$ coating. The $\operatorname{SiN}_{\mathrm{x}}$ coating was removed by etching in buffered hydrofluoric acid until the surface was hydrophobic.

The measurement results of the LRM patterns are shown in Fig. 3.4 with the respective $R_{s h}$, which was calculated to correspond to the $R_{s h}$ of a single line to allow comparison between the patterns. For three and five lines it is observed that the $R_{s h}$ measured with $\operatorname{SiN}_{\mathrm{x}}$ film is approximately $30 \%$ lower than the $R_{s h}$ measured after removal of the $\operatorname{SiN}_{\mathrm{x}}$ film. The change in resistance is indicated with an arrow.


Fig. 3.4 Total resistance measurements as a function of the distance of contacting pads. Circles denote patterns consisting of 3 lines, squares denote 5 lines and stars denote 15 lines. The blue colour and the orange colour are labelled in the legend. The lines are linear fits of the measured values and the indicated $R_{s h}$ is the calculated $R_{s h}$ of a single line. The black arrows indicate the difference between the measurements with and without $\operatorname{SiN}_{\mathrm{x}}$.

For the pattern with 15 lines no change in resistance is observed. In this case the conductance along the laser-doped lines is significantly higher than the conductance of the inversion layer. Therefore, the much higher parallel resistance from the inversion layer in the $\operatorname{SiN}_{\mathrm{x}}$ film can be neglected for low resistance values of the lines. It is possible to calculate the influence of the inversion layer (if its conductivity and the geometry are known) by treating it as parallel resistor to the LRM pattern [106]. The premise is that the sample has the same width as the contacting pads (compare to Fig 2.10), which was unfortunately not the case in this experiment. The $R_{s h}$ of the $\operatorname{SiN}_{\mathrm{x}}$ coating was separately measured to be $10 \pm 1$ $\mathrm{k} \Omega / \mathrm{sq}$. , which would approximately explain the results in Fig. 3.4 and is in a good agreement with previous measurements [107].

### 3.2 4PP measurements on laser-doped sheets

The $R_{\text {sh }}$ measurements with a 4PP setup were introduced in Sec. 2.4.2 and can normally be applied straight-forwardly to diffused areas. However, for laserdoped areas certain precautions need to be considered. One condition, which has
been discussed in Sec. 2.4.2, is the thickness of the doped sheet. Other conditions which are potentially affecting 4PP measurements on laser-doped areas are:
(a) small size of the laser-doped areas,
(b) inhomogeneous depth and resistivity,
(c) surface roughness,
(d) non-conducting coatings.

This section deals with 4PP measurements of laser-doped areas under influence of either one or more of the conditions (a) - (d). The influence of each condition is investigated and discussed in Secs. 3.2.1-3.2.4, respectively. Guidelines are given to obtain accurate measurements of samples under these conditions. The discussion in this section is limited to a collinear 4PP setup; however, it may also be applied to square or other 4PP setups.

### 3.2.1 Small size of laser-doped area

Typical laser-doped features are relatively small and do not straight-forwardly allow measurements by the standard 4PP technique. Thorsteinsson et al. [96] have shown that very small areas (in comparison to the probe spacing) can actually be accurately measured by using the dual configuration method (see Section 2.4.2) and by placing the probes within a certain area in the centre. They validated their simulations with micro 4PP measurements.

In this section a calculation is derived, which results in a correction factor for 4PP dual configuration measurements on square laser-doped areas without the need for device simulations as performed in Ref. [96]. Additionally, a practical limit is ob-
tained from experimental results with a conventional 4PP setup with larger probe tips and probe spacing.

Dual configuration 4PP measurements use two separate (single) 4PP measurements $R_{1}$ and $R_{2}$ as discussed for Eq. (2.16). The $R_{s h}^{\text {dual }}$ can be corrected for small areas with a correction factor $\chi$ to obtain the correct $R_{s h}$ :

$$
\begin{equation*}
R_{s h}^{d a l}=\chi R_{s h} . \tag{3.3}
\end{equation*}
$$

The single 4PP measurements can also be used to calculate $R_{s h}$ when the correction factors $F_{1}$ and $F_{2}$ are applied, which are depending on the location of the probes:

$$
\begin{equation*}
R_{s h}=F_{1} R_{1}=F_{2} R_{2} . \tag{3.4}
\end{equation*}
$$

Equations (3.3) and (3.4) are used in Eq. (2.16) to calculate the correction factor $\chi$ :

$$
\begin{equation*}
\exp \left(\frac{2 \pi}{\chi F_{1}}\right)-\exp \left(\frac{2 \pi}{\chi F_{2}}\right)=1 \tag{3.5}
\end{equation*}
$$

Equation (3.5) can be solved numerically when the correction factors for the single measurements are known. The correction factors for the single measurements can be calculated when the geometry of the sample and the probe locations are known [108-110]. A code was developed in Appendix B, which calculates the correction factors $F_{1}, F_{2}$ and $\chi$ depending on the location of the probes.

Laser-doped areas are investigated in experiments to obtain a practical limit for a conventional 4PP setup with larger probe tips and probe spacing. Additionally, the calculated results are compared to the measured values. Differently sized square laser-doped areas were prepared on textured Cz -Si wafer by WFLD using the parameter as shown in Table 3.3.

Table 3.3 Overview of the used WFLD parameters with a CW laser (compare Sec. 2.3.1).

| Avg. Power <br> $[\mathbf{W}]$ | Scribing speed <br> $\boldsymbol{v}_{\boldsymbol{s}}[\mathbf{m} / \mathbf{s}]$ | Dopant me- <br> dia | Hatch $\boldsymbol{h}[\boldsymbol{\mu m}]$ |
| :---: | :---: | :---: | :---: |
| 13.5 | 2 | $30 \mathrm{wt} \%$ <br> $\mathrm{H}_{3} \mathrm{PO}_{4}$ | 10 |

First, the $R_{s h}$ of the sample was obtained from averaging several single configuration 4PP measurements at different locations within each area. Correction factors were applied regarding sample size and probe placement as discussed above. Second, dual configuration 4PP measurements ( $R_{\text {sh }}^{\text {dual }}$ ) along a line through the center of the areas were carried out. No correction factors were applied for the dual configuration measurements. Figure 3.5 shows the ratio of the measured $R_{s h}^{\text {dual }}$ to $R_{s h}$ for different distances $\left(x_{\text {probe }}\right)$ from the centre of the area ( $\left.x_{\text {centre }}\right)$.


Fig. 3.5 Ratio of dual configuration measured sheet resistance ( $R_{s h}^{\text {dual }}$ ) to the $R_{s h}$ of the samples at different distances ( $x_{\text {probe }}$ ) from the centre ( $x_{\text {centre }}$ ). Yellow stars denote a square with $a_{1}=10 \mathrm{~mm}$ width, green triangles with $a_{2}=7 \mathrm{~mm}$ width, blue circles with $a_{3}=6 \mathrm{~mm}$ width, and red squares with $a_{4}=4 \mathrm{~mm}$ width. The lines denote the calculated correction factor according to Eq. (3.5). A black horizontal line marks the case, where $R_{s h}^{\text {dual }}$ is equal to $R_{s h}$ (the grey area indicates the measured uncertainty).

Squared areas with widths $a_{i}$ of $10,7,6$ and 4 mm were measured by a 4PP setup with 1.0 mm probe spacing. The uncertainty of the $R_{s h}$ measurement was obtained from the standard deviation of the single configuration measurements (shown as grey area). While measurements of the areas with a width of up to $7 \mathrm{~mm}\left(a_{2}-a_{4}\right)$ show a good agreement between $R_{s h}^{d u a l}$ and $R_{s h}$ only in a small range near the cen-
tre, the areas with a width of $a_{l}=10 \mathrm{~mm}$ shows good agreement up to a distance of 3 mm from the centre. Therefore, this work suggests a minimum (square) area size of 10 times the probe spacing for $R_{s h}$ measurements with a 4PP setup on laserdoped areas. The correct $R_{s h}$ can then be obtained by placing the probes within an area of $\pm 3$ times the probe spacing around the centre without the need of a correction factor.

The lines in Fig. 3.5 denote the calculated correction factor for each laser-doped area according to Eq. (3.5). The calculations show a very good agreement with the experimental results. However, in the case of the areas with width of $4 \mathrm{~mm}\left(a_{4}\right)$, a slight mismatch in the centre range is observed. It is assumed that this difference can be attributed to the inaccurate probe placement vertical to the $x$ position.

In this section samples with a non-conducting boundary, such as $n$-type laserdoped areas on a p-type substrate were discussed. When the laser doping is performed on samples with the same polarity, the size of the sample can be significantly decreased without an influence on the 4PP measurements. For instance, $R_{s h}$ of a laser-doped stripe of 2.5 mm width on a substrate with the same polarity was measured to be within the uncertainty of $R_{s h}$ of larger areas.

### 3.2.2 Inhomogeneous depth and resistivity

In general laser-doped lines are inhomogeneous, both laterally and vertically due to inhomogeneous melting and dopant diffusion into the Si substrate, caused by the instability of the laser, shape of the beam and surface conditions [17, 51, 94]. Influences of non-uniformities on resistance measurements were studied previous-
ly using the effective medium theory $[111,112]$. One conclusion from this theory is that the measured resistivity of non-uniform areas can, in first-order approximation, be approximated by the area-weighted average resistivity and by assuming small perturbations from the average resistivity [112]. This theory may also be applied to 4PP measurements. Square laser-doped areas of the size of 10 mm were prepared on textured Cz -Si wafers. Laser doping was performed by means of LCP, WFLD using a pulsed laser and WFLD using a CW laser. Table 3.4 shows the used parameters.

Table 3.4 Overview of the used parameters (compare Sec. 2.3.1 and Sec. 2.3.2).

| Method | Dopant <br> media | Avg. <br> Power <br> $[\mathbf{W}]$ | Fre- <br> quency <br> $[\mathbf{k H z}]$ | Pulse <br> duration <br> (FWHM) <br> $[\mathbf{n s}]$ | Fluence <br> $\boldsymbol{\Phi}_{\boldsymbol{p}}\left[\mathrm{J} / \mathrm{cm}^{2}\right]$ | Scribing <br> speed $\boldsymbol{v}_{s}$ <br> $[\mathbf{m} / \mathbf{s}]$ | Hatch <br> $\boldsymbol{h}[\boldsymbol{\mu \mathrm { m }}]$ | Laser <br> pulse <br> density <br> $\boldsymbol{n}_{p}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (i) $\mathbf{L C P}$ <br> (ii) | $60 \mathrm{wt} \%$ <br> $\mathrm{H}_{3} \mathrm{PO}_{4}$ | 2.1 | 100 | 40 | 1.1 | 0.1 | $5-70$ | $79-6$ |
| WFLD <br> pulsed <br> (iii) | $30 \mathrm{wt} \%$ <br> $\mathrm{H}_{3} \mathrm{PO}_{4}$ | 2.8 | 100 | 40 | $\sim 3.4$ | 0.5 | $5-70$ | $79-6$ |
| WFLD <br> CW | $30 \mathrm{wt} \%$ <br> $\mathrm{H}_{3} \mathrm{PO}_{4}$ | 13.5 | 100 | - | $\sim 12.7$ | 4 | $3-20$ | - |

The $R_{s h}$ in this experiment was measured with the four probes parallel $\left(R_{s h}^{p a r}\right)$ and orthogonal ( $R_{S h}^{o r t h}$ ) to the scribing direction of the laser-doped lines. When there is a significant influence of the dopant inhomogeneities, one would expect that the measured $R_{s h}^{o r t h}$ is much larger than the measured $R_{s h}^{p a r}$ according to the sensitivity of the 4 PP setup [113]. Figure 3.6 shows the ratio of the measured $R_{s h}^{o r t h}$ to $R_{s h}^{p a r}$ for different overlaps or distances between lines, which is given as $h$ divided by $w_{L}$.


Fig. 3.6 Ratio between $R_{s h}$ measured orthogonally to the scribing direction $R_{s h}^{o r t h}$ and parallel to the scribing direction $R_{s h}^{p a r}$ as a function of the hatch to line width ratio $h / w_{L}$. The measurements are shown for Processes (i) - (iii) as labelled in Table 3.4. The black vertical line marks the line width (the grey area indicates the uncertainty). The black horizontal line marks the case where $R_{s h}^{o r t h}$ equals $R_{s h}^{p a r}$. The lines are overlapping when $h<w_{L}$. The solid lines connecting the measurements are given as a guide to the eye.

If $h$ is larger than $w_{L}, R_{s h}^{o r t h}$ becomes significantly larger than the measured $R_{s h}^{\text {par }}$.
When $h$ is smaller than $w_{L}$ (i.e., the lines are overlapping), the difference between $R_{s h}^{o r t h}$ and $R_{s h}^{p a r}$ becomes negligible.

In order to support these findings, cross-sectional SEM and EBIC measurements were performed of selected laser-doped areas with or without overlap. Figure 3.7 shows composite images of SEM (grayscale) and EBIC (red) measurements of laser-doped areas orthogonal to the scribing direction. The EBIC signal shows the location of the $p-n$ junction as discussed in Sec. 2.4.3. The samples for these measurements were prepared similar as the samples for Process (iii) (see Table 3.4) but with a scanning speed of $5 \mathrm{~m} / \mathrm{s}$. In Fig. 3.7(a) an overlap $\left(h / w_{L}=0.75\right)$ of the lines was used. The resulting dopant depth shows lateral inhomogeneities, but no interruptions were detected.


Fig. 3.7 Cross-sectional SEM image (grayscale) with superimposed EBIC image (red) of parallel laser-doped lines with (a) $h / w_{L}=0.75$, (b) $h / w_{L}=1$ and (c) $h / w_{L}=1.25$. The cross-sectional plane is orthogonal to the scribing direction of the laser-doped lines.

The lines in Fig. 3.7(b) were scribed with $h / w_{L}=1$. This will ideally result in parallel lines with the edges just touching, however small vibrations during processing or inhomogeneities may cause local overlap or distance between the lines in certain areas along the line edge. For example, some intact pyramid structures from the wafer texture are visible at irregular positions between the line edges [marked with a white circle in Fig. 3.7(b)]. Comparing Fig. 3.7(b) to Fig. 3.7(a), a higher variation in dopant depth is visible but no interruptions between lines. In Fig. 3.7(c) a distance ( $h / w_{L}=1.25$ ) between the lines was used. There are large intact pyramids visible between the lines (marked with a white circle) and some interruptions of the doped areas may occur.

From the results of the 4PP measurements and the SEM/EBIC images, it is concluded that small variations or inhomogeneities in dopant depth or dopant density do not influence $R_{s h}$ measurements and the first-order approximation of the effective medium theory can be applied. The measured $R_{s h}$ is the average $R_{s h}$ of the
non-homogeneously doped areas. Only when interruptions between lines occur, i.e. when the hatch is set to be around, or larger than, the line width, one needs to apply higher-order approximations of the effective medium theory and the measured $R_{s h}$ does not represent the average $R_{s h}$. The results also indicate that multiple $R_{s h}$ measurements with 4PP at different angles may be used to detect interruptions in laser-doped areas.

### 3.2.3 Surface roughness

Laser doping may result in a rough surface (see e.g. Fig. 3.7), when evaporation or excessive inhomogeneous melting is present. Surface roughness of a thin film has potentially three effects on 4PP measurements as shown in Fig. 3.8.


Fig. 3.8 Schematic illustration of possible effects in $R_{s h}$ measurements resulting from rough surfaces: The contact area between probe and surface may decrease (left), the effective distance between probes may increase (middle) and the probes may damage the surface more easily (right).

The first influence of a decreased contact area affects all four probes in the same way. The additional contact resistance imposed from the rough surface (constriction resistance) becomes only relevant, when the total resistance is in a percentile range of the internal resistance of the voltage measurement device (commonly above $10^{12} \Omega$ ). However, such high resistance at the current probes would cause the 4PP setups to reach their voltage limit even when applying very low currents (typically in the range of nA ). Additionally, contact resistances were meas-
ured on flat silicon surfaces with gold probes to be in the range of $\mathrm{k} \Omega$ while they were approximately only 10 times larger on rough laser-doped surfaces.

In certain cases, only a few probes may be affected by a local increase in contact resistance. If only the voltage probes experience a strong increase in contact resistance, the current probes may still be able to deliver a current without reaching the voltage limit. This may result in a wrongly measured resistance but can be prevented by repeating the measurement at different locations. If the contact resistance is still suspected to affect the measurement, an easy way to test the influence is a measurement with two probes which should be closely spaced on the sample. If the overall resistance is at least two orders of magnitude lower than the internal resistance, it indicates that the contact resistance is not influencing the 4PP measurement.

The second influence of an effective increase of the distance between probes or distance to a non-conducting boundary can be neglected: When the roughness is somewhat homogeneous across the sample, the overall geometry of the $R_{s h}$ measurement is scaled and the scaling has no influence on current distribution. The distance between probes increases by the same factor as the distance to a nonconducting boundary. Additionally, 4PP measurements on large laser-doped areas are independent of the probe spacing [73].

The third influence of increased $R_{s h}$ due to measurement-induced damage on rough surfaces can be observed when measuring repeatedly at the same location. Two textured $p$-type Si wafers were prepared, of which one received a full-area $n$ -
type $\mathrm{POCl}_{3}$ diffusion of $100 \Omega / \mathrm{sq}$. with a dopant depth of approximately 400 nm . The other wafer did not receive diffusion. Figure 3.9 shows the ratio of repeated 4PP measurements on the same position $R_{s h}^{i}$ to the average $R_{s h}^{a v g}$ over all measurements at this position.


Fig. 3.9 Measured ratio of repeated $R_{s h}$ measurements with 4PP $\left(R_{s h}^{i}\right)$ to the average sheet resistance $\left(R_{s h}^{a v g}\right)$ of $R_{s h}^{i}$. The orange circles denote $R_{s h}$ measurements on a textured surface without a diffused layer and the blue squares denote $R_{s h}$ measurements on a textured surface with a diffused layer.

For the wafer with a diffused layer, the $R_{s h}$ increased by roughly $6 \%$ after 120 measurements, showing that the probes are damaging parts of the thin diffused layer and therefore are decreasing the conductivity. It may be noteworthy that the sensitivity of 4PP measurements is larger close to the contacts, as shown by Koon et al. [113]. In comparison to the diffused wafer, the $R_{s h}$ of the undiffused wafer shows no measureable change. Here the whole wafer has the same resistivity and therefore the induced damage to a small area on the surface does not lead to a decrease in conductivity. However, when the wafer is very thin, an increase in the measured $R_{s h}$ may also be obtained, since the wafer thickness will decrease due to the probe-induced abrasion of the sample.

The SEM image in Fig. 3.10 shows exemplarily the damage from 4PP measurements on a random pyramid textured Si wafer. The SEM image indicate an estimated abrasion of up to $2 \mu \mathrm{~m}$ of the pyramid tips after 120 repeated measurements at the same location. This may even lead to contacting the bulk material, which may act as parallel resistor to the diffused layer.


Fig. 3.10 Scanning electron microscope image of a textured Si surface after 120 4PP measurements at the same location.

### 3.2.4 Non-conductive coatings

The $R_{s h}$ measurements of Section 3.2 were carried out on uncoated Si samples, such as $R_{s h}$ measurements of $n$-type laser-doped areas on $p$-type Si substrates. Under certain circumstances a layer other than the thin native $\mathrm{SiO}_{2}$ may be presented on the sample, as was also mentioned in Sec. 3.1.3. Another relevant example besides the discussed $\operatorname{SiN}_{\mathrm{x}}$ film is the PSG layer which is formed during the diffusion process as discussed in Sec. 2.1.2.

In the case of 4PP measurements, an insulating layer, which is covering the measurement area, may be able to significantly increase the contact resistance, such that no current can be applied to the sample within the voltage limits as discussed in the previous section. However, the sharp probes of the 4PP setup may be able to penetrate through the insulating layer, depending on the thickness of this layer
and the applied pressure. It was observed that the probes used in this work (Jandel probes, $150 \mu \mathrm{~m}$ tip radius, tungsten carbide with 100 g load) were able to penetrate through a thermally grown $\mathrm{SiO}_{2}$ film with thickness of roughly 120 nm or PECVD $\operatorname{SiN}_{\mathrm{x}}$ layers with a thickness of $\sim 70 \mathrm{~nm}$. This was observed for both rough and flat surfaces. For flat surfaces, repeated measurements at the same location were used to deteriorate the coating.

### 3.3 Comparing PD measurements of laser-doped areas

Previously, an empirical relation was suggested to correlate the $R_{s h}$ of single lines to overlapping lines for laser doping from a liquid thin film with a CW laser [94]. Here, a method is introduced to obtain properties of micro-scale laser-doped areas formed with a focused beam by relating those to large laser-doped areas [104]. A relation is derived for pulsed laser doping by carefully considering the average number of laser pulses which the sample has received (i.e., the laser pulse density). The average number of passes per area (i.e., the density of passes) is considered for CW laser doping. The $R_{\text {sh }}$ measurements are used to experimentally corroborate the relation for CW and pulsed laser-doped silicon samples. This method allows the extraction of relevant information of arbitrary laser-doped areas from dedicated test structures that can be optimised for the desired metrology method.

### 3.3.1 Introduction of method

To explain the method, the formation of laser-doped areas with a pulsed laser will be examined in detail. As discussed in Sec. 2.3.2 each focused laser pulse melts a thin, small surface region of the substrate (e.g. Si), where dopant atoms diffuse
into the melt. Laser-doped micro-scale areas are usually formed by either a single pulse or a one-dimensional series of laser pulses with certain overlap defined by the pulse-to-pulse distance $d$ (giving a doped line). Large laser-doped areas can be formed by overlapping laser pulses in two dimensions, i.e. overlapping laser pulses to form a line and overlapping lines with a line-to-line distance (or hatch) $h$. In either case, a unit cell with area $A_{u c}$ can be defined by the area between the centres of adjacent laser pulses. Figure 3.11 illustrates unit cells for a line $\left(A_{u c}^{\text {line }}\right)$ and a larger area made from overlapping lines $\left(A_{u c}^{b o x}\right)$ assuming a circular laser pulse area $A$ with a radius $r_{p}$. The laser pulse density $\left(n_{p}\right)$ can be described by the average number of stacked laser pulses within a unit cell. Therefore, the laser pulse density is defined as the ratio between the total stacked area $A_{\text {tot }}$ within a unit cell and the area of a unit cell: $n_{p}=A_{t o t} / A_{u c}$.


Fig. 3.11 Schematic of laser-doped areas assuming circular laser pulse area: (a) single line of laserdoped regions with a laser pulse density $n_{p}^{\text {line }}=2$, (b) larger laser-doped area from overlapping lines ('box') with $n_{p}^{\text {box }}=2$. The scale on the right marks the colour coding used to indicate the number of stacked laser pulses $N$ at each location. The area of a laser pulse $A$ and its radius $r_{p}$, the area of a unit cell $A_{u c}$ and the total stacked area within a unit cell $A_{t o t}$ are marked.

In the case of lines the area of a unit cell is given by $A_{u c}^{\text {line }}=2 r_{p} d$, while in the case of overlapping lines the area is given by $A_{u c}^{b o x}=d h$.

The total stacked area $A_{\text {tot }}$ is the sum of all stacked laser pulse areas within a unit cell and can be calculated from the laser pulse area $A$ : The area of one laser pulse may spread over several unit cells such that the laser pulse area is divided into parts. Since the pattern is repetitive, a single unit cell contains each of those parts from adjacent areas of laser pulses. Therefore, the total stacked area of a unit cell is equal to the laser pulse area: $A_{\text {tot }}=A$. The laser pulse density of a line formed with circular laser pulse areas is then:

$$
\begin{equation*}
n_{p}^{\text {line }}=\frac{A_{\text {tot }}}{A_{u c}}=\frac{A}{2 d r_{p}}=\frac{\pi r_{p}}{2 d} \text {. } \tag{3.6}
\end{equation*}
$$

Figure 3.11(a) illustrates a line pattern of circular laser pulses for $r_{p} / d=1.27$, which results in $n_{p}^{\text {line }}=2$. Note that Eq. (3.6) is based on the average number of laser pulses per unit cell. Some areas within the unit cell receive three laser pulses, while other areas receive only one.

In the case of overlapping lines, the laser pulse density $n_{p}^{b o x}$ is given by:

$$
\begin{equation*}
n_{p}^{b o x}=\frac{A_{t o t}}{A_{u c}}=\frac{A}{d h}=\frac{\pi r_{p}{ }^{2}}{d h} \tag{3.7}
\end{equation*}
$$

Figure 3.11(b) illustrates a large laser-doped area formed from overlapping circular laser pulses in two dimensions with $r_{p} / d=0.83$ and $r_{p} / h=0.77$, resulting in $n_{p}^{b o x}=2$. Both, Eq. (3.6) and Eq. (3.7) also consider areas which are not scribed by laser pulses but are enclosed in the unit cell. Therefore, $n<1$ is possible for laser pulse distances and hatch values in the range of the diameter of the laser pulse.

Laser-doped micro-scale areas can be compared to large laser-doped areas when the laser pulse densities of both areas are approximately the same $\left(n_{p}^{\text {box }} \approx n_{p}^{\text {line }}\right)$. In this case, both patterns have gone through the same average number of melting cycles and dopant diffusions and therefore have a similar dopant depth profile. An identical laser pulse density can be observed by keeping the laser pulse distance constant and using a hatch similar to the laser pulse diameter, which means using parallel lines with the same parameters as a single line. However, this case may not be suitable for all applications due to non-uniformities in line width or where it is not possible to align lines perfectly in parallel (compare to the error range in Fig. 3.6). Another option to obtain $n_{p}^{b o x} \approx n_{p}^{\text {line }}$ is to reduce the pulse-to-pulse overlap to compensate for the line-to-line overlap. This case is less affected by non-uniformities since the laser pulses can be more evenly distributed across the whole area.

### 3.3.2 Experimental validation of method

The $R_{s h}$ measurements were used to experimentally corroborate the proposed relation between laser-doped micro-scale areas and large areas. The $R_{s h}$ can be averaged for non-uniformly doped areas as those shown in Fig. 3.11, by using the effective medium theory [111, 112]. Again, the theory states that when only small deviations from the mean resistivity exist, the resistivity observed in a nonuniform area is, in first-order approximation, equivalent to the mean resistivity.

LRM patterns consisting of 10-40 individual laser-doped lines were used to obtain the $R_{s h}$ of lines. The contacting pads were of the size $5 \times 20 \mathrm{~mm}^{2}$ with distances $d_{x}$ of 2-12 mm between them. The $R_{s h}$ of laser-doped areas formed by overlapping
lines was measured by 4PP measurements on rectangular areas with a size of $5 \times$ $156 \mathrm{~mm}^{2}$. The patterns were fabricated on RCA cleaned and acid-textured $p$-type multicrystalline silicon wafers by means of LCP (see Section 2.3.2) with the parameters shown in Table 3.5.

Table 3.5 Overview of the used LCP parameters (compare Sec. 2.3.2).

| Frequency <br> $[\mathbf{k H z}]$ | Pulse duration <br> $(\mathbf{F W H M})[\mathbf{n s}]$ | Fluence <br> $\boldsymbol{\Phi}_{p}\left[\mathbf{J} / \mathbf{c m}^{2}\right]$ | Scribing <br> speed $\boldsymbol{v}_{\boldsymbol{s}}[\mathbf{m} / \mathbf{s}]$ | Hatch $\boldsymbol{h}[\boldsymbol{\mu m}]$ | Laser pulse den- <br> sity $\boldsymbol{n}_{p}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 100 | 19 | 1.2 | $0.1-1$ | see. Table 3.6 | see. Table 3.6 |

The laser pulse diameter $\left(2 r_{p}\right)$ was obtained from the width of the laser-doped line, which was measured to be $49 \pm 3 \mu \mathrm{~m}$. Several test structures were prepared with varying laser speeds to obtain laser pulse distances $d$ in the $2-10 \mu \mathrm{~m}$ range. For the laser-doped areas formed by overlapping lines, a hatch of 10,20 and $30 \mu \mathrm{~m}$ was used. All structures were scribed twice, to minimise the impact of possible interruptions of lines, which may occur at high-speed processing. The $R_{s h}$ of the lines were measured with the LRM method as shown in Sec. 3.1.1. Six samples were measured for each investigated laser pulse distance. The $R_{s h}$ of the areas with overlapping lines were measured with a 4PP setup (see Sec. 2.4.2) and averaged over seven measurement locations within each sample area.

Table 3.6 shows the measured $R_{s h}$ of lines and of larger areas for different laser pulse densities in case of an identical $n_{p}$. The distance and hatch values for the larger areas and the distance values for lines are also shown. The $R_{s h}$ of both structures are comparable and the mean difference between the $R_{s h}^{\text {box }}$ and $R_{s h}^{\text {line }}$ is 6 $\Omega / \mathrm{sq}$., which is within the error range of most patterns. Only in case of $n_{p}=15$ is a larger mismatch between the $R_{s h}^{b o x}$ and $R_{s h}^{\text {line }}$ observed. One possible explanation are line interruptions, which might be causing an unexpected higher $R_{s h}$ of the
lines. Overall, it can be concluded that properties of single lines can be obtained from large laser-doped areas.

Table 3.6 Laser pulse density and $R_{s h}$ of lines and larger. The laser pulse distance and hatch for larger areas are shown as well.

| $\boldsymbol{n}_{\boldsymbol{p}}$ | $\boldsymbol{R}_{\boldsymbol{s h}}^{\boldsymbol{b o x}}[\mathbf{\Omega} / \mathbf{s q}]$. | $\boldsymbol{d}^{\boldsymbol{b o x}}[\boldsymbol{\mu \mathrm { m } ]}$ | $\boldsymbol{h}[\boldsymbol{\mu \mathrm { m } ]}$ | $\boldsymbol{R}_{\boldsymbol{s h}}^{\text {line }}[\mathbf{\Omega} / \mathbf{s q}]$. | $\boldsymbol{d}^{\text {line }}[\boldsymbol{\mu \mathrm { m }}]$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $9.5 \pm 1$ | $79 \pm 27$ | 10 | 40 | $79 \pm 7$ | 8 |
| $11 \pm 1$ | $68 \pm 21$ | 8 | 40 | $65 \pm 20$ | 7 |
| $13 \pm 1$ | $61 \pm 12$ | 7 | 40 | $52 \pm 6$ | 6 |
| $15 \pm 2$ | $55 \pm 8$ | 8 | 30 | $69 \pm 10$ | 5 |
| $20 \pm 2$ | $50 \pm 7$ | 9 | 20 | $44 \pm 6$ | 4 |
| $25 \pm 3$ | $33 \pm 12$ | 5 | 30 | $32 \pm 6$ | 3 |
| $38 \pm 4$ | $22 \pm 4$ | 10 | 10 | $28 \pm 2$ | 2 |

The uncertainty associated with $R_{s h}$ tends to be larger for lower laser pulse densities and for patterns with a big difference between $d^{b o x}$ and $h$. In these cases the first order approximation of the effective medium theory may not be applicable due to larger resistance differences in certain directions. The uncertainty may be decreased by taking a second order approximation into account, considering the location of the probes in relation to $d^{b o x}$ and $h$. Laser-induced defects may also impact the measurement especially for very high laser pulse densities.

It is also possible to apply the relation between laser-doped micro-scale areas and large areas to a CW laser doping process. Here, micro-scale areas are formed by scanning along lines with a defined speed, therefore the average number of passes per area, or density of passes, is $n_{C W}^{\text {line }}$. Larger areas have to be written with a hatch approximately equal to the line width to obtain a similar density of passes $n_{C W}^{\text {line }} \approx 1$.

Patterns were prepared similar as the above patterns for lines and larger areas to experimentally corroborate the relation for the WFLD process. The substrates
were commercial 1-3 $\Omega \mathrm{cm} \mathrm{Cz}$ grown Si wafers with a random pyramid texture and a PECVD $\operatorname{SiN}_{\mathrm{x}}$ coating with a thickness of 70 nm . The used laser parameters are shown in Table 3.7.

Table 3.7 Overview of the used WFLD parameters with a CW laser (compare Sec. 2.3.1).

| Avg. Power <br> $[\mathbf{W}]$ | Scribing speed <br> $\boldsymbol{v}_{\boldsymbol{s}}[\mathbf{m} / \mathbf{s}]$ | Dopant media | Hatch $\boldsymbol{h}[\boldsymbol{\mu \mathrm { m } ]}$ |
| :---: | :---: | :---: | :---: |
| $8.1 / 13.5$ | $2-5$ | $30 \mathrm{wt} \% \mathrm{H}_{3} \mathrm{PO}_{4}$ | $3-25$ |

For each laser setting, three line patterns and several larger areas with different hatch were prepared. The error was estimated to be $10 \%$ for all $R_{s h}$ measurements and line width measurements. Figure 3.12 presents the ratio of the measured $R_{s h}$ of larger areas $\left(R_{s h}^{b o x}\right)$ and lines $\left(R_{s h}^{\text {line }}\right)$ as a function of $n_{C W}^{b o x}$.


Fig. 3.12 Ratio of measured sheet resistances of larger areas $\left(R_{s h}^{b o x}\right)$ and lines $\left(R_{s h}^{\text {line }}\right)$ as a function of the density of passes $\left(n_{C W}^{b o x}\right)$ for four different laser settings. The lines are a guide to the eye.

The $R_{s h}$ of larger areas and lines are comparable $\left(R_{s h}^{\text {box }} \approx R_{s h}^{\text {line }}\right)$, only when $n_{C W}^{b o x} \approx 1$. For smaller and larger values, the difference between $R_{s h}^{b o x}$ and $R_{s h}^{\text {line }}$ increases strongly. Therefore, it is concluded that the method of comparing the laser pulse density can be extended to WFLD by considering density of passes. Note that the empirically based concept of pseudo $R_{s h}$ described previously [94] does also include the case where $n_{C W}^{b o x}=1$ to obtain $R_{s h}^{b o x} \approx R_{s h}^{\text {line }}$. In this previous study, the $R_{s h}$ of lines is approximated by the pseudo $R_{s h}$ of the larger areas. The
pseudo $R_{s h}$ is defined as multiplying the $R_{s h}$ of larger areas by the ratio of hatch to line width.

In conclusion, it was shown that laser-doped microstructures can be related to large laser-doped areas, when keeping the laser pulse density (or the density of passes) constant. The $R_{s h}$ measurements of laser-doped lines match $R_{s h}$ measurements of laser-doped larger areas for the same laser pulse density (or density of passes). The method allows extracting non-localised properties of micro-scale areas such as $R_{s h}$ and dopant depth profile from test structures, which can be tailormade for the desired metrology method. Using the laser pulse density also allows comparing areas formed with a focused laser beam to areas formed with a beam expander.

### 3.4 Chapter summary

This chapter discusses the electrical characterisation of laser-doped silicon regions with potential drop measurements of sheet resistance. At first laser-doped areas are divided into micro-scale laser-doped areas (i.e. lines) and large laser-doped areas (formed by overlapping lines) due to their different measurement methods.

For lines, a new measurement method is introduced, which measures resistance of multiple laser-doped lines for different length of the lines. This method combines the advantages of two previously developed methods and allows characterisation within a wide conductivity range of the laser-doped lines and using a simple processing scheme of test samples. The method was also tested against the influence of inhomogeneous current distribution across the lines. The results showed that
inhomogeneous current distribution can be neglected within the uncertainty of the measurement.

The sheet resistance measurements of laser-doped lines are influenced by conductive coatings. A conventional $\operatorname{SiN}_{\mathrm{x}}$ coating on $p$-type silicon forms an inversion layer, which acts as parallel resistor for the resistance measurements of the lines. This parallel resistance can be a significant source of error, depending on the sheet resistance of lines and the area ratio between lines and the conductive coating. Nevertheless, it may be possible to calculate sheet resistance of the lines, if the geometry of the pattern is known, precisely.

For the measurement on large laser-doped areas conditions are discussed, which are potentially influencing sheet resistance measurements. The identified conditions are the small size of the laser-doped areas, inhomogeneous depth and resistivity, surface roughness as well as non-conductive coatings.

Firstly, the influence of the small size of laser-doped areas is discussed. It is shown, how the correction factor of dual configuration four-point probe measurements on small areas can be calculated in contrast to state-of-the-art publications, which use 2D device simulations. An experiment is shown, which derives a practical limit of the minimum size of large laser-doped areas for four-point probe measurements. Additionally, the calculation of the dual configuration correction factor is shown to be in a good agreement with the measurements.

Secondly, the influence of inhomogeneous depth and resistivity is investigated. Large laser-doped test structures were prepared with different line-to-line distance (hatch) and were measured parallel and orthogonal to the scribing direction. It is observed that as long as the hatch of the laser-doped areas is smaller than the width of the lines, the sheet resistances measured parallel and orthogonal are matching. This result is in compliance with the effective medium theory, which states that non-uniformities in resistivity can be approximated by the areaweighted average.

Thirdly, the influence of surface roughness is discussed. Surface roughness may increase the contact resistance of the probes, may increase the distance of the probes or the distance to edge of the sample or may damage the surface. It was identified in experiments that the damage to the surface is the only significant influencing factor for sheet resistance measurements.

Finally, non-conductive coatings are discussed. It was observed that commercially available probes are able to penetrate through non-conductive coatings, when applied repetitively. Reliable measurements were possible for 120 nm thick thermally grown $\mathrm{SiO}_{2}$ layer and 70 nm thick plasma enhanced chemical vapour deposition $\mathrm{SiN}_{\mathrm{x}}$ layer.

The last part of the chapter discusses how the two measurement methods (for mi-cro-scale and large laser-doped areas) can be compared with each other. A method is introduced, which can be used to obtain sheet resistance of micro-scale laserdoped areas by measuring large laser-doped areas or vice versa. This method is
based on the average number of laser pulses which the sample has received or laser pulse density. It allows measurements of test structures, which can be tailored for the desired metrology method. Experimental results are shown to corroborate the proposed method.

The results of this chapter have led to the following publications:

1. M. Heinrich, S. Kluska, Z. Hameiri, B. Hoex and A. G. Aberle, "Extracting physical properties of arbitrarily shaped laser-doped microscale areas in semiconductors," Appl. Phys. Lett., vol. 103, no. 26, p. 262103, 2013.
2. M. Heinrich, S. Kluska, S. Binder, Z. Hameiri, B. Hoex and A.G. Aberle, "Accurate potential drop sheet resistance measurements of laser-doped areas in semiconductors," J.Appl. Phys., vol. 116, no. 13, p. 134505, 2014
3. M. Heinrich, N. Palina, J. Wong, B. Hoex and A. G. Aberle, "Accurate measurement of laser-doped line sheet resistance for silicon wafer solar cell applications," Technical Digest 21st International Photovoltaic Science and Engineering Conference (PVSEC-21), Fukuoka, Japan 2011, p. 4D-1P-29.

## 4 Investigation of laser doping parameters

This chapter investigates laser doping parameters for the optimisation of the doping efficiency. The focus is on laser doping with the LCP system as introduced in Sec. 2.3.2, however the results can be applied to any wet laser doping process. The technology parameters which may impact doping efficiency are: the laser output power or energy, the wavelength, the pulse duration, the pulse frequency, the speed of processing, the overlap of lines, the pulse diameter, the dopant concentration and the pressure of the liquid jet. The laser output power, frequency and pulse diameter determine the single pulse laser fluence. The frequency, the processing speed and the pulse diameter determine the laser pulse density, which was introduced in Sec. 3.3. The dopant concentration of the liquid dopant source and pressure of the jet determine the dopant flux. This chapter will focus on the impact of the single pulse laser fluence and dopant flux in Sec. 4.1 and on the laser pulse density in Sec. 4.2. Section 4.3 summarises the Chapter.

### 4.1 Impact of the single pulse laser fluence and dopant flux on the doping efficiency

The laser fluence (also commonly referred to as laser energy density) describes the photon energy delivered per unit area. The single pulse laser fluence (also commonly referred to as laser pulse energy density) is the integrated photon flux during a single pulse and can be obtained by dividing the measured average power by the repetition frequency and the measured spot area of a laser pulse. The laser fluence directly influences the energy transferred into the substrate, which affects
the amount and time of the substrate in molten phase. As discussed in Section 2.2.3, a longer melt time and deeper melt depth increase the diffusion of dopant atoms into the melt. Therefore, laser fluence is a very relevant parameter for laser doping. The $R_{s h}$ measurements as discussed in Section 2.4.2 are typically used to evaluate and compare the impact of laser fluences on the laser doping efficiency.

The focus in this section is on the dopant incorporation and how it is affected by the laser-induced phase changes of the substrate (i.e. from solid to liquid and from liquid to gas). The influence is discussed using a 1D model in Sec. 4.1.1 and by experimental results in Sec. 4.1.2. The effect of the single pulse laser fluence on the emitter saturation current density is discussed in Sec. 4.1.3.

### 4.1.1 Simulation results

Laser doping was simulated using LCPSim [45, 47, 50, 51, 114], which is an extensive laser processing simulation tool written by Dr. Andreas Fell and available at the Fraunhofer Institute for Solar Energy Systems (ISE). The tool solves the heat equation simultaneously with the diffusion equation (see Sec. 2.2.1 and 2.2.2). Melting and evaporation of the substrate are both considered in LCPSim. LCPSim uses an adaptive grid size and an alternating direction explicit (ADE) method to solve the differential equations. The ADE algorithm solves two finite difference equations both in opposite space directions. Each equation is explicitly solvable. The algorithm is unconditionally stable and has no inherent time step limitation, which allows a fast calculation. The used parameters for the simulations are shown in Table 4.1 (if not otherwise stated).

Table 4.1 Simulation parameters for the LCPSim calculations.

|  | LCPSim parameters |
| :--- | :--- |
| Geometrical dimensions | 1 D |
| Evaporation model | Knudsen |
| Laser pulse shape | Smooth |
| Laser pulse length | 20 ns |
| Wavelength | 532 nm |
| Nozzle diameter | $50 \mu \mathrm{~m}$ |
| Heat transfer coefficient to liquid | $10000 \mathrm{~W} / \mathrm{m}^{2}$ |
| Fluence | $1 \mathrm{~J} / \mathrm{cm}^{2}$ |
| Background doping | Pure Si |
| Diffusion boundary | Infinite flux |
| Surface concentration | $3 \times 10^{20}$ atoms/cm² |
| Si substrate thickness | $180 \mu \mathrm{~m}$ |
| Reflection | Calculated by optical properties |
| Temperature | 300 K |
| Surface | planar |
| Minimum grid size | 10 nm |
| Integration method | ADE (time step param. 5) |
| Initial conditions | Standard (LCPSim 1.1) |
| Number of laser pulses | 1 |
| Frequency | 100 kHz |

LCPSim was used to investigate the influence of the laser fluence of a single laser pulse on the doping efficiency. The generic dopant source was assumed to be infinite meaning that an infinite flux of dopant atoms is available at the surface. This assumption leads to a fixed dopant concentration at the surface independent of the laser fluence.

Figure 4.1 shows how the dopant depth profile changes as a function of the single pulse laser fluence below the evaporation threshold $\left(\sim 2.0 \mathrm{~J} / \mathrm{cm}^{2}\right.$ for the parameters in Table 4.1). Increasing the laser fluence also increases the depth of the dopant depth profiles. The increase in laser fluence causes (a) a longer duration of the molten phase, such that the diffusion into the molten phase occurs for a prolonged time and (b) a deeper melt depth. When increasing the single pulse laser fluences above the evaporation threshold laser fluence, it is observed that the trend is reversed as shown in Fig. 4.2.


Fig. 4.1 Simulated dopant atoms depth profiles for different values of single pulse laser fluence. The laser fluence was below the evaporation threshold.

Figure 4.2 shows the simulated dopant depth profiles for different values of laser fluence above the evaporation threshold. An increase in laser fluence causes the depth of the dopant depth profile to decrease in this case. A higher laser fluence causes evaporation such that the range available for diffusion decreases.


Fig. 4.2 Simulated dopant atoms depth profiles for different values of single pulse laser fluence. In this case the laser fluence was above the evaporation threshold and all other parameters were identically to the ones used for Fig. 4.1.

Table 4.2 summarises the maximum melt depth and maximum evaporation depth for the various simulated dopant depth profiles. The range which is available for diffusion ( $\Delta$ depth) is the range between the maximum depth of the substrate in molten state and the maximum depth where the substrate was evaporated. This range reduces, when increasing the laser fluence further above the evaporation threshold. Additionally, evaporation and diffusion occur simultaneously. At the
beginning of a laser pulse, diffusion may have been already taken place within a few nm; however, these first few nm of the diffused layer may be removed later during the laser pulse via evaporation. Therefore, the diffusion source at the surface is continuously altered such that it becomes more difficult to diffuse deeper into the substrate by increasing the single pulse laser fluence further above the melting threshold.

Table 4.2 Maximum melt depth and maximum evaporation depth (as obtained by heat calculations of LCPSim) and the range available for diffusion ( $\Delta$ depth) for the different laser fluences shown in Fig. 4.2.

|  | $\mathbf{2 . 0 ~ J / c m}$ | $\mathbf{3 . 0 ~ J / c m}$ | $\mathbf{4 . 0 ~ J / c m}$ |  |
| :--- | :--- | :--- | :--- | :--- |
|  |  | $\mathbf{5 . 0 ~ J} / \mathbf{c m}^{2}$ |  |  |
| Max. melt depth | 781 nm | 872 nm | 935 nm | 1054 nm |
| Max. evaporation depth | 17 nm | 116 nm | 248 nm | 380 nm |
| $\boldsymbol{\Delta}$ depth | 764 nm | 756 nm | 687 nm | 674 nm |

Figure 4.3 shows the simulated $R_{s h}$ as function of the single pulse laser fluence for different laser pulse lengths. The values of $R_{s h}$ were obtained from simulating the dopant profile and applying the standard mobility model in Ref. [115] for phosphorous doping.


Fig. 4.3 Simulated $R_{s h}$ as function of laser fluence for different laser pulse durations. The cross marks the approximate evaporation threshold as obtained from the simulations. Other parameters were set at the values summarised in Table 4.1.

The $R_{s h}$ first decreases as a function of the laser fluence before reaching the evaporation threshold. For laser fluences above the evaporation threshold, the $R_{s h}$ in-
creases again. Longer laser pulse lengths result in a lower minimum $R_{s h}$ and a higher evaporation threshold. The reason for the higher evaporation threshold is that the peak power decreases for higher laser pulse durations, which causes a decrease in the maximum temperature of the silicon substrate for an identical laser fluence. Therefore, a higher laser fluence is necessary to increase the temperature of the substrate above the evaporation threshold. The reason for the lower $R_{s h}$ is that the duration of the molten phase increases with increasing laser pulse duration. Therefore, the time available for diffusion |into the molten Si increases. Please note that the evaporation threshold seems to be at slightly higher laser fluences than the minimum $R_{s h}$. It is assumed that this difference can be attributed to the finite space grid, which does only consider evaporation when the evaporation depth is larger than 10 nm .

### 4.1.2 Experimental results

LCP as introduced in Section 2.3.2 was used to prepare samples with various laser fluences. The samples were prepared on RCA cleaned and iso-textured or as-cut p-type multicrystalline Si substrates using the parameters as shown in Table 4.3. Two different laser pulse durations were used to prepare the samples.

Table 4.3 Overview of the used LCP parameters (compare Sec. 2.3.2).

| Frequency <br> $[\mathbf{k H z}]$ | Pulse duration <br> $(\mathbf{F W H M})[\mathbf{n s}]$ | Fluence <br> $\boldsymbol{\Phi}_{p}\left[\mathbf{J} / \mathbf{c m}^{2}\right]$ | Scribing speed <br> $\boldsymbol{v}_{\boldsymbol{s}}[\mathbf{m} / \mathbf{s}]$ | Hatch <br> $\boldsymbol{h}[\boldsymbol{\mu m}]$ | Laser pulse den- <br> sity $\boldsymbol{n}_{\boldsymbol{p}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 100 | 19 or 40 | $1-6$ | 0.5 | 10 | 39 |

The $R_{s h}$ measurements of all samples in this section were carried out with a 4PP setup as described in Sec. 2.4.2. The patterns were of the size $5 \times 156 \mathrm{~mm}^{2}$. The uncertainty of $R_{s h}$ measurements was estimated from the standard deviation of test
structures to be $10 \%$ and the uncertainty of the laser fluence ( $10 \%$ ) was estimated from the uncertainty of the beam radius and the uncertainty in losses between the measured output and the output on the wafer.

Figure 4.4 shows the measured $R_{s h}$ for different single pulse laser fluences and laser pulse durations. The $R_{s h}$ first decreases for increasing laser fluence and increases after reaching a minimum value. Comparing the different laser pulse durations with each other, it is observed that the laser fluence corresponding with the minimum $R_{s h}$ is larger and the obtained minimum $R_{s h}$ is lower for the longer laser pulse duration.


Fig. 4.4 Measured $R_{s h}$ as function of the single pulse laser fluence for different laser pulse durations as shown in the legend. The lines were fitted results of the simulations of Sec. 4.1.1 with the parameters as shown in Table 4.1.

The experimental results were fitted using the model described in Sec. 4.1.1. The laser fluences used in the simulations was adjusted such that the laser fluence value with the minimum $R_{s h}$ matched the experimental results. In case of the sample with laser pulse duration of 19 ns , the laser fluence was reduced by $0.78 \mathrm{~J} / \mathrm{cm}^{2}$ and in case of the sample with laser pulse duration of 40 ns the laser fluence was reduced by $0.25 \mathrm{~J} / \mathrm{cm}^{2}$. The reason for this mismatch in laser fluence can be caused by the fact that the 1D model assume a flat surface, while in the experiment rough
surfaces were used, which have a different reflection coefficient. The different offset between the samples with laser pulse duration of 19 ns and 40 ns is due to the fact that the 19 ns sample was prepared on an iso-textured surface, while the 40 ns sample was prepared on an as-cut sample. The iso-textured surface shows a lower reflection coefficient and therefore the offset with the simulations is largest.

The $R_{s h}$ was fitted in the simulations by adjusting the surface dopant concentration, such that the minimum $R_{s h}$ matches approximately the minimum $R_{s h}$ for both laser pulse durations. The differences in $R_{s h}$ are caused by mainly three factors. First, the experiment was prepared by overlapping many laser pulses within the doped area (39 on average as shown in Table 4.3). However, the model assume only a single laser pulse. Additionally, the 1D model does not account for inhomogeneous melting, evaporation and doping within the laser spot due to speckled laser intensity distribution in the liquid jet [51, 116]. Another influence causing a difference in $R_{s h}$ is the assumption of an infinite dopant flux in the model and will be discussed here in more detail.

ECV measurements (described in detail in Sec. 2.4.1) were performed on the samples prepared with a 19 ns laser pulse duration with certain laser fluences. The ECV measurements in Fig. 4.5 show that the maximum depth of the dopant depth profiles increased for increasing laser fluences until a maximum depth at the laser fluence corresponding with the lowest $R_{s h}$. The depth then decreased for larger laser fluences. This is also observed in the model in Section 4.1.1.


Fig. 4.5 Measured ECV dopant depth profiles for samples which were laser-doped using different laser fluences. The inset shows the measured $R_{s h}$ as a function of the laser fluence. The lowest $R_{s h}$ was obtained for a laser fluence of $(1.9 \pm 0.2) \mathrm{J} / \mathrm{cm}^{2}$. The ECV measurements were calibrated using 4PP measurements as discussed in Appendix A.

The measurements also show that the dopant concentrations at the surface increased for low laser fluences and remained approximately constant for higher laser fluences. This was not observed in the model in Sec. 4.1.1, where the dopant concentration at the surface was the maximum dopant concentration for all laser fluences due to the assumption of an infinite dopant flux. One possible conclusion is that the assumption of an infinite dopant flux may not be valid but a finite dopant flux may need to be assumed. A finite dopant flux would cause an increasing dopant concentration at the surface for e.g. increasing time of silicon in molten phase.

Additionally, the ECV dopant depth profile for the sample that was laser-doped using a laser fluence of $1.5 \mathrm{~J} / \mathrm{cm}^{2}$ (red triangles) indicates that the maximum dopant depth was already reached before reaching the minimum $R_{s h}$. Further investigations with a confocal microscope revealed that the minimum $R_{s h}$ was reached for a laser fluence above the evaporation threshold in contrary to the predictions of the model in Sec. 4.1.1.

The increase of the surface concentration (which corresponds with a decrease in $R_{s h}$ ) for laser fluences below the evaporation threshold was observed in several cases throughout this work. The increase in surface concentration is most likely caused by a non-infinite dopant flux at the surface, which was already suggested earlier [42]. A finite dopant flux can explain an increase in surface concentration for increasing melt time. Other explanations for the observed increase in surface concentration could be due to influence from the inhomogeneous intensity profile of the laser beam. When the evaporation threshold is only locally reached at speckles with high intensity, other areas may still show an increase in melt time and depth. The applied model may also overestimate the surface evaporation or underestimate the melting depth since re-adsorption of evaporated material or convection in the melt are not considered.

To account for the increase in surface concentration, the LCPSim tool was extended to investigate if the introduction of a finite dopant flux as a boundary condition can better represent the obtained $R_{s h}$. Figure 4.6 shows the results of the simulations in comparison with the measured $R_{s h}$ of the samples prepared with a laser pulse of 19 ns . Again, the laser fluence used in the simulations was adjusted such that the laser fluences with the minimum $R_{s h}$ match with the measurement results. The constant surface dopant concentration and the constant dopant fluxes were also adjusted such that the minimum $R_{s h}$ matches with the minimum $R_{s h}$ of the experiment. Both models using a single laser pulse were able to describe the $R_{s h}$ around the evaporation threshold or for laser fluences which are slightly higher. However, they both fail, when going to lower laser fluences or much higher laser fluences. In case of a single laser pulse, both models are essential identical.


Fig. 4.6 Measured $R_{\text {sh }}$ in comparison to fits using LCPSim. The LCPSim simulations used various boundary conditions as shown in the legend. The dopant flux was set to $3 \times 10^{22}$ atoms $/ \mathrm{cm}^{2}$ s for the simulations with one laser pulse and to $6 \times 10^{20}$ atoms $/ \mathrm{cm}^{2}$ s for the simulations using 10 laser pulses. Other parameters were set at the values summarised in Table 4.1.

The fit using 10 laser pulses is slightly better in recognizing the sharp decrease in $R_{s h}$ for laser fluences below the laser fluence corresponding with the minimum $R_{s h}$. The number of laser pulses multiply the effect of a single laser pulse; therefore, enhancing the small differences in time of Si in molten phase between different laser fluences. However, other effects such as a temperature depended dopant flux or a change in surface morphology between laser pulses or the influence of speckles may also help to explain the sharp increase. Also in case of larger laser fluences than the laser fluence corresponding with the minimum $R_{s h}$, secondary effects such as the re-adsorption or melt flow may need to be considered in the model to describe the $R_{s h}$ dependencies.

In conclusion, the introduction of a finite flux instead of a constant surface concentration may better explain the $R_{s h}$ behaviour for laser fluences below the melting threshold than a constant surface concentration. This would also increase the validity of the simulation model for multiple pulses. Other effects such as a temperature dependent diffusion coefficient or 2D effects may need to be considered as well. The results here were obtained for laser doping with the LCP system.

However, they are also applicable for other doping processes which use an infinite source such as WFLD with a thick layer.

### 4.1.3 Impact of laser doping on the emitter saturation current density

This section discusses the influence of single pulse laser fluence on the emitter saturation current density of samples prepared with LCP as shown in Sec. 2.3.2. Samples were prepared on $p$-type CzSi wafers with a $3 \Omega . \mathrm{cm}$ resistivity. They received a SDE followed consecutively by an alkaline pyramid-texturing, a $\mathrm{POCl}_{3}$ diffusion on both sides resulting in a $70 \Omega /$ sq. emitter, a PSG etch and RCA cleaning, a PECVD $\operatorname{SiN}_{\mathrm{x}}$ antireflection coating with the thickness of 70 nm on both sides and a fast-firing step. Laser doping was performed with the parameters shown in Table 4.4.

Table 4.4 Overview of the used LCP parameters (compare Sec. 2.3.2).

| $\begin{gathered} \text { Frequency } \\ {[\mathbf{k H z}]} \\ \hline \end{gathered}$ | Pulse duration (FWHM) [ns] | $\begin{gathered} \text { Fluence } \\ \Phi_{p}\left[\mathrm{~J} / \mathrm{cm}^{2}\right] \\ \hline \end{gathered}$ | $\begin{gathered} \text { Scribing speed } \\ v_{s}[\mathrm{~m} / \mathrm{s}] \\ \hline \end{gathered}$ | $\begin{aligned} & \text { Hatch } \\ & h[\mu \mathrm{~m}] \end{aligned}$ | Laser pulse density $n_{p}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 100 | 40 | 1.4-5.3 | 0.5 | For $R_{s h}: 10$ <br> For $J_{O I, L D}$ : 2000 | For $R_{s h}: 39$ <br> For $J_{O I, L D}: 16$ |

For $R_{s h}$ measurements, areas with a size of $5 \times 156 \mathrm{~mm}^{2}$ were prepared. For measurements of the emitter saturation current $\left(J_{0 e}\right)$, areas of the size of $40 \times 40 \mathrm{~mm}^{2}$ were prepared so they could be measured by the QSSPC method. The samples featured a coverage ratio of roughly $5 \%$ such that the difference in generation due to the different absorption of the laser-doped areas is negligible and that the $J_{0 e}$ values could be obtained in high injection level. The samples were investigated with a confocal microscope and $R_{s h}$ measurements were performed with a 4PP setup as described in Sec. 2.4.2. The values of $J_{o e}$ of the samples were obtained by the QSSPC setup in high injection as described in Sec. 2.4.4 before and after laser
doping. The values of the emitter saturation current densities of the laser -doped patterns $\left(J_{01, L D}\right)$ were calculated from the area weighted differences of $J_{o e}$ before and after laser-doping ${ }^{9}$.

Figure 4.7 shows the results of QSSPC measurements along with $R_{s h}$ measurements. The evaporation threshold in Fig. 4.7 was obtained from confocal microscope images of the laser-doped areas.


Fig. 4.7 Measured $R_{s h}$ (orange) and $J_{01, L D}$ (blue) as function of the single pulse laser fluence. The uncertainties of the laser fluence and of the $R_{s h}$ were estimated as discussed in the previous section. The uncertainty in $J_{01, L D}$ was estimated based on coverage ratio measurements and from the fit to the inverse $\tau_{\text {eff }}$. The evaporation threshold is marked as a black line, with the grey areas marking the laser fluence range where melting but no evaporation occurs.

The $J_{01, L D}$ had a large value around $3000 \mathrm{fA} / \mathrm{cm}^{2}$ for laser fluences at or below the melting threshold but then decreases for increasing laser fluence. The lowest $J_{01, L D}$ of around $1000 \mathrm{fA} / \mathrm{cm}^{2}$ was obtained for the laser fluence corresponding with the lowest $R_{s h}$. The $J_{01, L D}$ values show a general trend to decrease with lower $R_{s h}$ as also previously observed by Kerr et al. on furnace diffused samples [117]. The reason for this trend is due to the lower surface recombination for lower $R_{\text {sh }}$. For very large values of laser fluence (above $4 \mathrm{~J} / \mathrm{cm}^{2}$ ), it seems that the $J_{01, L D}$ increases

[^4]slightly. This can be attributed to the increase in $R_{\text {sh }}$ but also to a larger impact of laser-induced defects which cause a larger SRH recombination. The effect of SRH recombination for values of $J_{01, L D}$ is further investigated.

ECV measurements as shown in Sec. 2.4.1 were performed to obtain the dopant depth profiles of laser-doped areas, which are then used to calculate $J_{01, L D}$ using simulations with 'EDNA' [118]. Table 4.5 compares the calculated $J_{01, L D}$ values to the measured values of Fig. 4.7. The calculations, which were based on the measured ECV dopant depth profiles, show a monotonic decrease of $J_{01, L D}$ for increasing laser fluence. However, this is not observed for the measured values. Additionally, the measured values are much larger than the calculated values. This large difference indicates that SRH recombination within the laser-doped areas is most likely contributing to a large part to the overall recombination rate, which was also observed in [57, 74].

Table 4.5 Calculated $J_{01, L D}$ and measured $J_{01, L D}$ for different laser fluences. The EDNA simulations used the measured ECV dopant depth profiles and an effective surface recombination velocity of $S=1 \times 10^{7} \mathrm{~cm} / \mathrm{s}$, which represents an unpassivated surface. The ECV dopant depth profiles were calibrated using $R_{s h}$ measurements as discussed in Appendix A.

| Fluence [J/cm ${ }^{\mathbf{2}}$ ] | $\boldsymbol{R}_{\text {sh }}[\mathbf{\Omega} / \mathbf{s q}$.] | Calc. $\boldsymbol{J}_{\mathbf{0 1 , L D}}$ <br> $\left[\mathbf{f A} / \mathbf{c m}^{2}\right]$ | Meas. $\boldsymbol{J}_{\mathbf{0 1 , L D}}$ <br> $\left[\mathbf{f A} / \mathbf{c m}^{2}\right.$ ] |
| :---: | :---: | :---: | :---: |
| 1.4 | 61.1 | 550 | 2530 |
| 1.8 | 41.3 | 313 | 2860 |
| 3.6 | 17.6 | 32 | 1120 |
| 4.6 | 25.7 | 25 | 1510 |

SRH recombination can be caused by different types of defects. In this work, defects were investigated with Yang defect etching, electron backscattering diffraction (EBSD), and SIMS. Similar as in previous studies [75], large crystallographic defects induced by lasers due to the re-crystallisation, such as grain boundaries or stacking faults, were not observed. However, the Yang etch revealed a large
amount of localised defects and SIMS measurements show a large amount of oxygen and nitrogen, which were unintentionally incorporated into the substrate during laser diffusion.

Previous studies on different laser doping setups [56,77] show a much lower $J_{01, L D}$ of laser-doped areas as observed here in this section. However, these studies used a completely different setup with much lower laser fluences and used the PSG layer as the dopant source. Additionally, there was no $\operatorname{SiN}_{\mathrm{x}}$ layer present before laser doping. The presence of a $\operatorname{SiN}_{\mathrm{x}}$ layer before laser doping is shown to have a significant negative influence on recombination in the laser-doped areas [75]. Therefore, the laser-induced defects may be reduced and the $J_{01, L D}$ increased by using different setups or different sample types.

### 4.2 Laser pulse density

Here the influence of laser pulse density (Sec. 3.3.1) on the doping efficiency in terms of $R_{s h}$ is investigated. First, the model of laser doping as discussed in Sec. 2.2.2 is extended to contain doping with multiple laser pulses by the laser pulse density and secondly, the model is applied to experimental results of laser doping with different laser pulse densities.

### 4.2.1 Model of dopant diffusion with multiple laser pulses

Section 2.2.2 describes a model for dopant diffusion in Si during laser doping. The model can be also considered with $N_{p}$ laser pulses on the same area by defining
the effective maximal diffusion depth $z_{l i}$, which is used in Eq. (2.9) and Eq. (2.10) as [42]:

$$
\begin{equation*}
z_{l i}=2 \sqrt{D_{l} N_{p} t_{l i}}, \tag{4.1}
\end{equation*}
$$

where $t_{l i}$ is multiplied by the number of laser pulses $\left(N_{p}\right)$. This model assumes that (i) each laser pulse melts the Si laterally uniformly within the area of the laser pulse, (ii) dopant atoms are diffusing only into the liquid Si (which is reasonable as solid phase diffusion can be ignored for these short timescales) and (iii) the diffusion into the molten area is uniform, which applies for infinite dopant sources (gas atmosphere or liquid jet) or for low $N_{p}$.

The laser pulse density can be used to extend the definition of Eq. (4.1) to laser doping where only parts of the doped area between laser pulses are identical. In this case the number of laser pulses is replaced by the laser pulse density $\left(n_{p}\right)$ :

$$
\begin{equation*}
z_{l i}=2 \sqrt{D_{l} n_{p} t_{l i}} . \tag{4.2}
\end{equation*}
$$

Figure 4.8 shows results of the model in Eq. (2.10) depending on the $n_{p}$. A maximum dopant depth $\left(z_{\max }\right)$ is considered in the model, which correlates with the maximum melt depth. At this depth it is assumed that the dopant concentration $C_{A}\left(z>z_{\max }\right)=0$, since solid state diffusion is negligible. Additionally, the solubility limit of phosphorus in liquid $\operatorname{Si}\left(C_{A, \max }^{\text {Sol }}=1.82 \times 10^{21} \mathrm{~cm}^{-3}\right)$ is considered for the model such that dopant influx $J_{i n}$ is reduced when $C_{A}(z)>C_{A, \text { max }}^{\text {Sol }}$ to obtain $\max \left(C_{A}(z)\right)=C_{A, \text { max }}^{s o l}$. Furthermore, the concentration $C_{A}(z)$ is reduced to the maximum active concentration $\left(C_{A, \text { max }}^{a c t}\right)$ when $C_{A}>C_{A, \max }^{a c t}$ for $R_{s h}$ calculations. The values of $R_{s h}$ were obtained by applying the standard mobility model of Ref. [115] to the obtained dopant profiles and assuming phosphorous dopant atoms.


Fig. 4.8 Simulation results of the model as in Eq. (2.10) for different model parameters. The inset shows the change in dopant depth profile for increasing laser pulse density for dopant influx of $J_{\text {in }}=1 \times 10^{22} 1 / \mathrm{cm}^{2}, t_{l i}=50 \mathrm{~ns}, z_{\text {max }}=0.7 \mu \mathrm{~m}$ and $C_{A, \text { max }}^{a}=5 \times 10^{20} \mathrm{~cm}^{-3}$. The black curve in the main graph shows the $R_{s h}$ as function of the laser pulse density for the same parameters. For the red solid curve $J_{\text {in }}$ was reduced to $J_{i n}=1 \times 10^{21} 1 / \mathrm{cm}^{2}$ and for blue solid curve $J_{i n}$ was increased to $J_{i n}=1 \times 10^{23} 1 / \mathrm{cm}^{2}$. For the red dashed curve $t_{l i}$ was reduced to $t_{l i}=10 \mathrm{~ns}$ and for the blue solid curve $t_{l i}$ was increased to $t_{l i}=500 \mathrm{~ns}$. For the red dotted curve $z_{\max }$ was reduced to $z_{\max }=0.5 \mu \mathrm{~m}$ and for the blue dotted curve $z_{\max }$ was increased to $z_{\max }=0.7 \mu \mathrm{~m}$.

Independent of the laser parameters used, the $R_{s h}$ decreases exponentially until a minimal $R_{s h}$ is reached in Fig. 4.8. The reason is shown in the inset. The concentration and depth of the dopant depth profiles increases for increasing $n_{p}$ until the maximum depth and the solubility limit is reached. Further laser pulses do not affect the solubility limit and diffusion depth, therefore, $R_{s h}$ remains constant. A decrease in the melting time $t_{l i}$ or in the dopant influx $J_{\text {in }}$ (red dashed and red solid curves) are both causing the minimum $R_{s h}$ to be reached for higher $n_{p}$, while an increase in $t_{l i}$ or $J_{\text {in }}$ (blue dashed and blue solid curves) are causing the minimum $R_{s h}$ to be reached for lower $n_{p}$. The influence of $t_{l i}$ and $J_{i n}$ on the $R_{s h}$ are in this sense similar. Both parameters describe how many dopant atoms are incorporated within a single laser pulse (comparable to the dose for ion implantation). A larger melt time could thereby compensate for a smaller dopant influx or vice versa.

An increase in maximum dopant depth (blue dotted curve) causes a lower minimum $R_{s h}$ while a decrease in dopant depth (red dotted curve) causes a higher minimum $R_{s h}$.

A change in laser fluence will cause a different dopant depth and a different time of Si in the molten phase. For this reason higher laser fluences which are still below the evaporation threshold laser fluence, will cause a lower minimum $R_{\text {sh }}$. Using higher laser fluences than the evaporation threshold laser fluence causes the minimum $R_{s h}$ to be higher.

### 4.2.2 Experimental results of laser pulse density doping

In order to experimentally corroborate the extension of the model in Eq. (2.10) by $n_{p}$, patterns were prepared with different $n_{p}$ and their $R_{s h}$ was measured. The measured $R_{s h}$ is then fitted by the model of the previous section.

The patterns were prepared identical to the patterns in Section 3.3.2, where $R_{s h}$ measurements of LRM patterns were compared with $R_{s h}$ measurements of 4PP patterns. The used LCP parameters are shown in Table 4.6.

Table 4.6 Overview of the used LCP parameters (compare Sec. 2.3.2).

| Frequency <br> $[\mathbf{k H z}]$ | Pulse duration <br> $(\mathbf{F W H M})[\mathrm{ns}]$ | Fluence <br> $\boldsymbol{\Phi}_{p}\left[\mathbf{J} / \mathbf{c m}^{2}\right]$ | Scribing <br> speed $\boldsymbol{v}_{s}[\mathbf{m} / \mathbf{s}]$ | Hatch $\boldsymbol{h}[\boldsymbol{\mu \mathrm { m } ]}$ | Laser pulse den- <br> sity $\boldsymbol{n}_{p}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 100 | 19 | 1.2 | $0.1-1$ | $10-40$ | $9-189$ |

The laser pulse diameter $\left(2 r_{p}\right)$ was obtained from the width of the laser-doped line, which was measured to be $49 \pm 3 \mu \mathrm{~m}$. Several test structures were prepared with varying laser speeds to obtain laser pulse distances $d$ in the 2-10 $\mu \mathrm{m}$ range. For the laser-doped areas formed by overlapping lines, a hatch of $10,20,30$ and 40
$\mu \mathrm{m}$ was used. All structures were scribed twice, to minimise the impact of possible interruptions of lines which may occur at high-speed processing.

Figure 4.9 shows the measured $R_{s h}$ of LRM patterns and 4PP patterns as function of $n_{p}$. The error bars for $n_{p}$ denote the uncertainty arising from the line width measurements. The error bars for $R_{s h}$ denote the standard deviation of measurements on multiple samples in case of LRM patterns or multiple measurements at different locations and rotations of the probe on one sample in case of 4PP patterns.


Fig. 4.9 Measured $R_{s h}$ as a function of the $n_{p}$ for laser-doped LRM patterns (orange circles) and laser-doped 4PP patterns (blue). The black curve is a fit based on the model in Eq. (2.10) with $J_{\text {in }}=1.8 \times 10^{21} 1 / \mathrm{cm}^{2}, t_{l i}=50 \mathrm{~ns}, z_{\max }=0.4 \mu \mathrm{~m}$ and $C_{A, \text { max }}^{a c t}=1 \times 10^{20} \mathrm{~cm}^{-3}$. The $R_{s h}$ of the fitted phosphorous concentration profiles was calculated using the standard mobility model of Ref. [115].

The black solid line in Fig 4.9 shows a fit of the measured $R_{s h}$ with Eq. (2.10). The fit parameters are shown in the figure caption. The time $t_{l i}$ and depth $z_{\max }$ were comparable to simulation results with LCPSim with similar doping parameters [47]. The maximum active dopant concentration $C_{A, \text { max }}^{a c t}=1 \times 10^{20} \mathrm{~cm}^{-3}$ and $z_{\max }$ are also similar to measured dopant depth profiles as shown in Fig. 4.10. The experimental results were fit very well by the model in Eq. (2.10) with the implementation of $n_{p}$ as in Eq. (4.2). The fit also applies to both kinds of patterns, being
a further corroboration for the method of comparing $R_{s h}$ measurements between these patterns (see Section 3.3). Certain patterns show a larger deviation from the fit then other patterns. Examples are the 4PP patterns with a $n_{p}$ of 19 ( $R_{s h}=61 \pm$ $15 \Omega / \mathrm{sq}$.) and 24 ( $R_{\text {sh }}=50 \pm 6 \Omega / \mathrm{sq}$.). In both cases, the ratio between the line distance and laser pulse distance was large (8 and 10, respectively). In these cases $n_{p}$ may not accurately describe the doped layer since the dopant concentration might be very inhomogeneous within the sample and interruptions may occur.

Figure 4.10 shows ECV dopant profiles of 4PP patterns of the samples discussed above. Samples prepared with $n_{p}$ of 14,21 and 42 and with the respective $R_{s h}$ of $63 \Omega /$ sq., $36 \Omega /$ sq. and $20 \Omega /$ sq. were used.


Fig. 4.10 ECV measurements of the dopant depth profiles of areas prepared with different $n_{p}$. The ECV dopant depth profiles were calibrated with the measured $R_{s h}$ (see Appendix A). The lines are the corresponding model results from the fit as in Fig. 4.9.

As shown in Sec. 4.2.1, with increasing $n_{p}$, the dopant depth as well as the surface concentration increases. The shape of the dopant depth profile becomes increasingly rectangular. Also the dopant depth profiles from the fitted model (as of Fig. 4.9) match the measured dopant depth profiles closely in shape and concentration. When reaching the maximum dopant depth a certain mismatch between the model and the measured dopant depth profiles is observed. This difference in maximum
dopant depth between model and measurements can be attributed to inhomogeneous melting as observed in Fig. 3.7. Lateral inhomogeneities in the laser-doped areas are caused by a non-homogeneous laser beam or by the non-uniform laser pulse overlapping (see e.g. Fig. 3.11). These inhomogeneities are not considered in the 1D model. ECV measurements average the dopant concentration of a certain area for each depth. Therefore, inhomogeneities in depth are reflected by ECV measurements as a decreasing slope in concentration over depth.

### 4.3 Chapter summary

This chapter described the influence of the single pulse laser fluence, laser pulse density and dopant flux on the doping efficiency.

Section 4.1 discussed the sheet resistance and dopant depth profile of laser-doped areas depending on the single pulse laser fluence with a 1D model in combination with experiments. It was observed, that a minimum sheet resistance exists, which correlates with the evaporation threshold laser fluence in case of an infinite dopant flux. However, experimental results suggested that the sheet resistance behaviour for different single pulse laser fluences may be better modelled by a finite dopant flux. Therefore, an existing model was extended to include a finite dopant flux, which showed a better approximation of the measured sheet resistance. The last part of Sec. 4.1 dealt with emitter saturation current density measurements of la-ser-doped areas. It was observed that a lower sheet resistance corresponds with a lower emitter saturation current density and it was concluded that the emitter saturation current density is heavily influenced by SRH recombination.

Section 4.2 discussed the sheet resistance and dopant depth profile of laser-doped areas depending on the laser pulse density. An existing model was extended using the defined laser pulse density of Sec. 3.3.1. Results of the experiment and the model showed that for low laser pulse densities the sheet resistance decreased due to an increase in dopant concentration. In case of high laser pulse densities, the sheet resistance remained constant since the dopant depth profile was approximately rectangular shaped with the maximum melt depth and surface concentration.

## 5 Solar cells featuring selective emitter doping and plated contacts

This chapter discusses the application of laser doping for the formation of selective emitters for Si wafer solar cells. Three batches of solar cells were prepared The first two solar cell batches featured a highly doped thermally diffused homogeneous emitter, which is also suitable for conventional screen-printed contacts. In this case, the only possible beneficial influence of a selective emitter is a reduction of the recombination at the metal-semiconductor interface as discussed in Sec. 5.1. The results indicate that the highly doped selective emitter shows a benefit compared to the lowly doped selective emitter. However, it is also observed that the performed laser doping induces defects, which are potentially limiting the solar cell efficiency. Therefore, a second solar cell batch was designed that focussed on reducing the laser-induced damage and the results are discussed in Sec. 5.2.

Finally, a third solar cell batch was fabricated and discussed in Sec. 5.3 to compare laser-doped and plated to conventional solar cells with screen-printed contacts. The results are summarised and concluded in Sec. 5.4.

### 5.1 Laser-doped solar cells with and without selective emitter

The goal of this experiment was to compare two different LCP recipes on Al-BSF and Al-LBSF silicon wafer solar cells. One recipe resulted in a homogeneous opening of the $\mathrm{SiN}_{\mathrm{x}}$, film without a significant change of the $R_{\text {sh }}$ of the underlying
emitter, therefore no selective emitter was obtained. The other LCP process resulted in a low $R_{s h}$ therefore a selective emitter was obtained.

### 5.1.1 Solar cell fabrication

The substrates used for fabricating the solar cells were $p$-type multicrystalline Si wafers with a size of $156 \times 156 \mathrm{~mm}^{2}$. The processing of the solar cells follows the discussion in Sec. 2.1.2 employing industrial processing tools. The solar cells featured an Al-BSF or an Al-LBSF rear surface and a shallow industrial $70 \Omega / \mathrm{sq}$. emitter on the front side. The plated front contacts of the solar cells featured a plated Ni seed layer and an Ag conducting layer. A capping layer was not necessary in this case since the used Ag conducting layer does not react with the environment such as a Cu conducting layer. After plating, the solar cells were annealed at $300^{\circ} \mathrm{C}$ for 2 min to improve the front contact formation.

The industrial $70 \Omega /$ sq. emitter used in this work was an emitter optimised for screen-printed contacts. Consequently, it had a high surface dopant concentration to ensure low contact resistivity with the screen-printed grid. However, this is not beneficial for solar cells featuring a selective emitter. Here the non-metallised area should be solely optimised for a low emitter saturation current density. Therefore, the solar cell efficiency potential of a selective emitter design could not be fully explored in this experiment. In this thesis an industrial homogeneous emitter had to be used since high quality selective emitter solar cells were not available.

The Al-BSF and Al-LBSF solar cell precursors were processed in two groups. For half of the samples of each group, only the front $\operatorname{SiN}_{\mathrm{x}}$ film was opened and the
laser doping was kept to a minimum. The other half of the samples underwent standard LCP processing resulting in a selective emitter. A schematic of the process flow of the various groups is shown in Fig. 5.1.

| Group (A-O) | Group (A-S) | Group (L-O) | Group (L-S) |
| :---: | :---: | :---: | :---: |
| Al-BSF precursors |  | Al-LBSF precursors |  |
| LCP open | LCP selective emitter | LCP open | LCP selective emitter |
| Ni-Ag plating |  |  |  |
| Annealing |  |  |  |

Fig. 5.1 Process flow of the fabricated solar cells. The groups were split into Al-BSF (A) and AlLBSF (L) solar cells and feature either laser ablation of the $\mathrm{SiN}_{\mathrm{x}}$ film with LCP opening (O) or selective emitter with LCP doping (S), respectively. Afterwards Ni and Ag plating and annealing were applied to metallise the front of the solar cells.

All samples were processed using LCP with the parameters shown in Table 5.1. The parameters were chosen from $R_{s h}$ measurements on test structures, where the (A/L-O) parameter resulted in a negligible change of $R_{s h}$ of the emitter and the (A/L-S) parameter resulted in the lowest obtained $R_{s h}$. The $R_{s h}$ was measured on $5 \times 156 \mathrm{~mm}^{2}$ sized test samples prepared in an identical way as the busbars.

Table 5.1 Overview of the used LCP parameters (compare Sec. 2.3.2).

| Frequency <br> $[\mathbf{k H z}]$ | Pulse duration <br> $(\mathbf{F W H M})[\mathbf{n s}]$ | Fluence <br> $\boldsymbol{\Phi}_{p}\left[\mathbf{J} / \mathbf{c m}^{2}\right]$ | Scribing <br> speed $\boldsymbol{v}_{\boldsymbol{s}}[\mathbf{m} / \mathbf{s}]$ | Hatch $\boldsymbol{h}[\boldsymbol{\mu m}]$ | Laser pulse den- <br> sity $\boldsymbol{n}_{p}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 100 | 40 | $(\mathrm{O}): 0.7$ | $(\mathrm{~S}): 2.5$ | 0.5 | Finger: 1660 |
|  |  |  |  |  |  |
|  |  |  | Busbars: 10 | Busbars: 39 |  |

Group (A-O) and Group (L-O) were processed with a single pulse laser fluence of $0.7 \mathrm{~J} / \mathrm{cm}^{2}$ and Groups (A-S) and (L-S) with a higher single pulse laser fluence of $2.5 \mathrm{~J} / \mathrm{cm}^{2}$. Identical laser parameters were used for fabrication of the Al-BSF and the Al-LBSF solar cells since the front surfaces of the precursors were similar. All solar cells featured 94 fingers with 3 busbars with a width of 1.6 mm .

Figure 5.2 shows the resulting laser-doped lines for the two used single pulse laser fluence. The lines obtained using a laser fluence of $0.7 \mathrm{~J} / \mathrm{cm}^{2}$ are roughly $10 \mu \mathrm{~m}$ thinner than the lines obtained by using a laser fluence of $2.5 \mathrm{~J} / \mathrm{cm}^{2}$. In case of a laser fluence of $0.7 \mathrm{~J} / \mathrm{cm}^{2}$, the $R_{s h}$ of the emitter did not change significantly and was basically equal to the as-diffused value. In case of a laser fluence of $2.5 \mathrm{~J} / \mathrm{cm}^{2}$, the $R_{\text {sh }}$ was significantly reduced. Therefore, it was assumed that the laser fluence of $0.7 \mathrm{~J} / \mathrm{cm}^{2}$ resulted in a merely opening of the $\mathrm{SiN}_{\mathrm{x}}$ film and only when using a laser fluence of $2.5 \mathrm{~J} / \mathrm{cm}^{2}$ a selective emitter was obtained.

| Group (A-O) | Group (L-O) | Group (A-S) | Group (L-S) |
| :---: | :---: | :---: | :---: |
| $\Phi_{p}=0.7 \mathrm{~J} / \mathrm{cm}^{2}$ |  | $\Phi_{p}=2.5 \mathrm{~J} / \mathrm{cm}^{2}$ |  |
|  |  |  |  |
| $w_{L}=43 \pm 2 \mu \mathrm{~m}$ |  | $w_{L}=53 \pm 2 \mu \mathrm{~m}$ |  |
| $R_{\text {sh }}=74 \pm 8 \Omega / \mathrm{sq}$. |  | $R_{\text {sh }}=32 \pm 4 \Omega / \mathrm{sq}$. |  |

Fig. 5.2 Optical microscope images, line width measurements and corresponding $R_{s h}$ of the differently laser processed areas. The scale bars denotes $20 \mu \mathrm{~m}$. The uncertainty in line width is given by the inhomogeneous opening width of the $\operatorname{SiN}_{\mathrm{x}}$ film and the uncertainty in $R_{s h}$ is given by the standard deviation of $R_{s h}$ measurements.

ECV measurements were performed on the areas that were used for the $R_{s h}$ measurements and the dopant depth profiles are shown in Fig. 5.3. The ECV dopant depth profiles show that for both processing parameters a surface concentration above $1 \times 20 \mathrm{~cm}^{-3}$ is obtained. The dopant depth profile obtained with the higher single pulse laser fluence has a higher surface concentration and the $p-n$ junction is at a greater depth.


Fig. 5.3 Dopant depth profiles as measured with ECV. The dopant depth profiles were calibrated according to their $R_{s h}$ as shown in Appendix A.

### 5.1.2 Solar cell results

The results of the one-Sun $I-V$ measurements of the finalised Si wafer solar cells are summarised in Fig. 5.4.

The $V_{O C}$ of the solar cells with a selective emitter (A/L-S) shows a higher value than the $V_{O C}$ of the solar cells without (A/L-O). The $J_{S C}$ of the solar cells with a rear passivation show a roughly $1 \mathrm{~mA} / \mathrm{cm}^{2}$ higher $J_{S C}$. Comparing the groups with and without selective emitter, there is no significant difference in $J_{S C}$. The $F F$ of the solar cells with selective emitter is slightly higher compared to the solar cells with $\mathrm{SiN}_{\mathrm{x}}$ film openings and the $F F$ of the solar cells with rear passivation was found to be slightly lower. The efficiency of the selective emitter solar cells is slightly higher than the efficiency of the solar cells with laser openings. The solar cells with rear passivation show a higher efficiency.


Fig. 5.4 Boxplots of the one-Sun $I-V$ parameters of all solar cell groups.

The champion solar cell of this experiment (16.5\%) is in Group (L-S) and has a rear passivation and a selective emitter laser doping. The subsequent sections analyse in detail the different reasons, which cause the observed losses in voltage, current and fill factor for each group.

### 5.1.3 Open-circuit voltage analysis

The main difference in $V_{O C}$ was observed between the solar cells with laser opening and with selective emitter. The Groups (A/L-O) exhibited a smaller width of the laser affected areas and the dopant depth profile was shallower and with a lower surface concentration as comparing to the Groups (A/L-S) (see Fig. 5.3). Both effects influence the $V_{O C}$ of a solar cell by the emitter saturation current density as discussed in [37]. To verify if these two effects can explain the difference in $V_{O C}$, 2D simulations were performed with the software Quokka [119]. The parameters used in these Quokka simulations are shown in Table 5.2.

Table 5.2 Quokka parameters used for $V_{O C}$ simulations.

| Parameter | Values used in Quokka |
| :--- | :--- |
| Geometrical dimensions | 2 D |
| Mobility model | $\mathrm{Klaassen}[151]$ |
| Temperature | 300 K |
| Bulk material | $p$-type c-Si |
| Bulk resistivity | $2 \Omega . \mathrm{cm}$ |
| Bulk minority carrier lifetime | $57 \mu \mathrm{~s}$ |
| Solar cell thickness | $190 \mu \mathrm{~m}$ |
| Lateral unit cell size | $830 \mu \mathrm{~m}$ |
| Front contact opening width | $w_{L} / 2+29 \mu \mathrm{~m}$ |
| Front contact metal width | $30+29 \mu \mathrm{~m}$ |
| External shunt resistance | $100 \mathrm{k} \Omega . \mathrm{cm}^{2}$ |
| Passivated saturation current density $\left(\boldsymbol{J}_{\mathbf{0 1 , p a s s}}\right)$ | $330 \mathrm{fA} / \mathrm{cm}^{2}$ |
| Passivated saturation current density $\left(\boldsymbol{J}_{\mathbf{0 2} \boldsymbol{p a s s}}\right)$ | $10 \mathrm{nA} / \mathrm{cm}^{2}$ |
| Metallised saturation current density $\left(\mathbf{J}_{\mathbf{0 1 , L \boldsymbol { L }}}\right)$ | $50-3000 \mathrm{fA} / \mathrm{cm}^{2}$ |
| Metallised saturation current density $\left(\boldsymbol{J}_{\mathbf{0 2 , L D}}\right)$ | $10 \mathrm{nA} / \mathrm{cm}^{2}$ |
| Rear BSF saturation current density | $400 \mathrm{fA} / \mathrm{cm}^{2}$ |

The unknown parameters (in particular the bulk resistivity and carrier lifetime) were used to fit the actually obtained $V_{O C}$ values in the experiment. The addition in contact width of $29 \mu \mathrm{~m}$ is to account for the opening and metallisation fraction of the busbars in the 2 D simulations. The values of $w_{L}$ were obtained from Sec. 5.1.1 and the values of $J_{01, L D}$ were obtained from calculations with EDNA [118] using the measured ECV dopant depth profiles shown in Fig. 5.3. Additionally, the measured $J_{01, L D}$ values of Fig. 4.7 were also used in the simulations to account for the high SRH recombination within the laser-doped areas. Table 5.3 summarises the results from the Quokka simulations.

Table 5.3 Quokka results for the simulation parameters given in Table 5.2.

|  | $\begin{aligned} & \hline \text { Measured } \\ & w_{L} / 2[\mu \mathrm{~m}] \end{aligned}$ | $\begin{gathered} \text { Measured } \\ \text { avg. } V_{O C} \\ {[\mathrm{mV}]} \end{gathered}$ | $\begin{gathered} \hline \text { Calculated } \\ J_{01, L D} \\ {\left[\mathbf{f A} / \mathbf{c m}^{2}\right]} \\ (E C V) \end{gathered}$ | $\begin{gathered} \text { Simulated } \\ V_{O C}[\mathrm{mV}] \\ (E C V) \end{gathered}$ | Measured $J_{O I, L D}$ $\left[\mathbf{f A} / \mathbf{c m}^{2}\right]$ (Fig. 4.7) | Simulated <br> $V_{O C}[\mathrm{mV}]$ <br> (Fig. 4.7) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (A-O) | 21.5 | $616 \pm 2$ | 540 | 619 | (~) 3000 | 616 |
| (A-S) | 26.5 | $619 \pm 3$ | 60 | 620 | ( ) 1000 | 619 |

The Quokka simulations show that the difference in $J_{01, L D}$ which was calculated from the dopant depth profiles was not sufficient to explain the difference in
measured $V_{O C}$. However, when using the measured values of $J_{O 1, L D}$ as shown in Fig. 4.7, a difference of 3 mV in $V_{O C}$ can be reproduced. Therefore, the measured difference in $V_{O C}$ between Group (A-O) and Group (A-S) can be motivated by the high $J_{01, L D}$ values, which were also discussed in Sec. 4.1.3.

From the results of the simulations it is apparent that the applied laser doping process introduced defects in the laser treated regions, which increased the recombination and therefore the $J_{0 I, L D}$. However, going to a lower $R_{s h}$ the recombination at the metal-semiconductor interface was reduced by the highly doped selective emitter region such that an overall lower $J_{01, L D}$ was obtained (see also Sec. 4.1.3). This lower $J_{O 1, L D}$ was also observed as a higher $V_{O C}$ of the solar cells with selective emitter in this experiment. The effect of laser-induced defects increasing the recombination will be further investigated for the next solar cell batch in Sec. 5.2.3.

Another effect which influenced the $V_{O C}$ of the investigated solar cell batch was background plating. Background plating was largely influencing the Group (L-S), which therefore does not show a significant benefit in $V_{O C}$ for most of the solar cells. The impact of background plating will also be discussed in more detail for the next solar cell batch in Sec. 5.2. The main reason for the background plating in this solar cell batch was most likely the presence of defects in the $\mathrm{SiN}_{\mathrm{x}}$ layer. These small defects in the $\operatorname{SiN}_{\mathrm{x}}$ film do not deteriorate a screen-printed solar cell. However, they may cause significant background plating. Additionally, sharp edges of the multicrystalline texture and non-optimised $\mathrm{SiN}_{\mathrm{x}}$ processing may also cause severe background plating, especially at grain boundaries [29, 35].

### 5.1.4 Short-circuit current density analysis

The $J_{S C}$ for the solar cells with local rear contacts was significantly larger than the $J_{S C}$ for the solar cells without rear passivation, as shown in Fig. 5.4. This is because of higher internal quantum efficiencies (IQE) for long wavelengths, which means that the electron-hole pairs generated close to the rear surface have a lower chance to recombine due to a higher degree of surface passivation at the rear surface for the Al-LBSF solar cells. Otherwise there was no significant difference observed between the various groups. Figure 5.5 shows exemplary IQE, external quantum efficiencies (EQE) and reflection spectra (R) curves as a function of the wavelength for two typical solar cells of Group (A-O) and Group (L-S). Additionally, the IQE, EQE and R of a solar cell are presented, which was prepared on the same Al-BSF precursors but using screen printing instead of laser doping (SP). The screen-printed solar cell features 84 instead of the 94 fingers of the laser processed solar cell.


Fig. 5.5 Measured IQE, EQE and R of two typical solar cells of Groups (A-O) and (L-S) and a screen-printed solar cell (SP). The IQE is represented by diamond markers, the EQE by square markers and the R by circle markers.

Comparing the IQE between the solar cells of the Group (A-O) and (L-S) it is observed that the (L-S) solar cell showed a similar IQE than the (A-O) solar cell for short wavelengths. A small difference may be attributed to the selective emitter, which had lower recombination losses for the IQE. However, the effect is very minor since the generation in the selective emitter region is almost zero due to the shading [120]. Therefore, there was no significant advantage in $J_{S C}$ observed. The IQE for the SP solar cell was better than the IQE of (L-S) for low wavelengths. This can be due to the negative influence of the defects induced by laser doping. Another possible explanation is the background plating of the laser processed solar cells, which may introduce local recombination centres across the whole area of the solar cells. The SP solar cell also showed overall a lower R , which is due to the lower number of fingers and the absence of background plating.

The increased IQE of the solar cell of group (L-S) for long wavelengths is easily visible in Fig. 5.5. As discussed above, this effect is attributed to the rear surface passivation.

When comparing typical solar cells of Group (L-O) and (L-S) it was observed that for short wavelengths the IQE was also slightly larger for the Group (L-S). However, the reflection of the solar cells of the Group (L-S) was significantly larger, too. Therefore, the possible slight benefit of the selective emitter was outbalanced by the reflection losses due to background plating, which resulted in an overall slightly lower $J_{S C}$. The background plating caused an overall reduced current of all plated solar cells, which will be discussed in more detail in Sec. 5.2.4.

### 5.1.5 Pseudo fill factor loss analysis

In this section the pseudo fill factor $(p F F)$ losses are analysed. The $p F F$ is the "series resistance free" $F F$ of the solar cell. The $p F F$ of the solar cells in this batch was generally low as shown in Table 5.4. In order to exclude that the low $p F F$ is caused solely by laser processing, solar cells were prepared with screen printing and the $p F F$ was measured using the Suns- $V_{O C}$ method [101]. The results are also show in Table 5.4. All solar cells featured a $p F F$ below $80 \%$.

Table 5.4 Measured average $p F F$ of the groups.

| (A-O) | (A-S) | (L-O) | (L-S) | Al-BSF SP solar <br> cells |
| :--- | :--- | :--- | :--- | :--- |
| $(78.6 \pm 0.1) \%$ | $(78.4 \pm 0.1) \%$ | $(79.3 \pm 0.1) \%$ | $(79.1 \pm 0.1) \%$ | $(79.7 \pm 0.1) \%$ |

Optical investigations of the solar cells showed that all solar cells had processing related scratches before laser doping. In order to find out if these scratches can account for the $p F F$ loss, test structures were purposely scratched with either tweezers ("soft") or a screw driver ("hard") before laser processing and metallisation. Four test structures were prepared on each wafer. The test structures consisted of a small solar cell pattern of a size of $4 \times 4 \mathrm{~cm}^{2}$ with one busbar with a width of 1 mm and 24 fingers. The laser parameters were identical to the laser parameters used for the Groups (A/L-O). The Suns- $V_{O C}$ curve of these test structures with the obtained $p F F$ values are shown in Fig. 5.6.

The $p F F$ decreases consecutively, after applying a "soft" and a "hard" scratch on the test structure. These scratches are causing non-linear shunts, which are leading to local recombination currents [121]. Therefore, it can be concluded that the observed scratches were possibly reducing the $p F F$ of the investigated solar cell
batch. The $V_{O C}$ was also slightly decreased for the scratched solar cells in this experiment.


Fig. 5.6 Measured Suns- $V_{O C}$ curve of the solar cell without a scratch (green), with a "soft" scratch (blue) and with a "hard" scratch (red).

A further observation in this experiment is that the $p F F$ of the test structures is generally higher than the $p F F$ of the large area solar cells. The reason is that these test structures had a larger distance to the edge. Therefore, the recombination sites at the edges were not within the minority carrier diffusion length of the generated carriers [122]. The influence of the edge was further observed when cutting a few large area solar cells of size $156 \times 156 \mathrm{~mm}^{2}$ at 5 mm distance from the edges. The $p F F$ of these solar cells increased by roughly $0.8 \%$ absolute due to the removal of recombination sides at the edges of the solar cell [123].

The influence from the edges was further investigated with reversed bias electroluminescence (ReBEL) [124] and dark lock-in thermography (DLIT) [125, 126]. Figure 5.7 shows an image of a solar cell with the measured ReBEL signal as overlay.


Fig. 5.7 Image of a solar cell of Group (A-S) as grayscale and measured ReBEL signal at -12 V bias voltage as green overlay.

The image shows that besides a few structures within the wafer, the main ReBEL signal was detected at the edges of the wafer. ReBEL detects pre-breakdown sites, which are local avalanche breakdowns of the $p-n$ junction. These pre-breakdown sites can be non-linear shunts of the solar cell, which would explain a reduction in $p F F$. DLIT measurements with an applied forward and reversed bias of 0.5 V confirmed that there were in fact non-linear shunts at the edges of the solar cell. These non-linear shunts at the edges were generally observed for all groups in this experiment, and even for all cell groups of this thesis. The non-linear shunts are recom-bination-sites at the edges of the solar cells [127]. One possible reason for these recombination sites arises from the non-uniform etching at grain boundaries during chemical edge isolation, where the edges of the solar cell are also in contact with the etching liquid. Even a wrap-around of the etching solution onto the front surface is sometimes observed $[128,129]$. Additionally, plating at the edges is al-
so possible, which might worsen the recombination behaviour. Further studies are necessary to confirm if the chemical edge isolation in combination with plating is causing these shunts at the edges of the wafer, which are limiting the solar cell efficiency.

Another possible influence which was previously suggested to reduce the $p F F$ are the insufficient melting of the grain boundaries [130]. The laser-induced defects may also reduce the $p F F$ due to recombination. Overall, it was not possible to determine an all-embracing explanation for the low $p F F$ of the solar cells fabricated within this thesis. The most probable causes are scratches and non-linear shunts at the edges of the solar cells.

### 5.1.6 Fill factor loss analysis

The $F F$ of the solar cells with Al-LBSF was generally measured to be lower than that of the Al-BSF solar cells. The reason is that the resistance of the bulk material influences the lateral charge carrier transport to the contacts in comparison to the vertical charge transport for a full-area contact. This is generally observed when comparing Al-BSF to Al-LBSF solar cells [131].

The solar cells of Groups (A-S) and (L-S) show a higher FF than the solar cells of Groups (A-O) and (L-O), respectively. Possible reasons are either the contact resistance or the grid resistance at the front surface since the solar cells were processed otherwise identically.

Fig. 5.8 shows the series resistance of the front surface grid $R_{s, \text { front }}$ grid for all groups and the measured $w_{F}$. The $R_{s, \text { front grid }}$ includes only the lateral resistance of the front surface but not the contact resistance between the metal and Si . The $R_{s, \text { front grid }}$ was larger for the Groups ( $\mathrm{A} / \mathrm{L}-\mathrm{O}$ ) compared to the Groups ( $\mathrm{A} / \mathrm{L}-\mathrm{S}$ ), respectively. The reason is the smaller $w_{F}$, which shows that the conductance of the $R_{s, \text { front grid }}$ is limiting the $F F$ of the solar cells. Additionally, conduction within the laser-doped region is also possible, reducing the $R_{s, \text { front grid }}$ further for the Groups (A/L-S).


Fig. 5.8 Boxplots of the measured series resistance of the front surface grid ( $R_{s, \text { front grid }}$ ) for all groups. The measured fingers widths $\left(w_{F}\right)$ of the groups are shown as well.

It is also observed that the Groups (L-O/S) have a lower $R_{s, \text { front } \text { grid }}$ than the Groups (A-O/S). Light-induced plating as discussed in Sec. 2.1.3 shows a higher plating rate on solar cells with a higher $V_{O C}$. The difference in efficiency between the groups could have also resulted in a higher build-up of metal on the front surface of the solar cells of the Groups (L-O/S). However, a difference in plated finger width could not be measured within the error range of the measurement.

A strong correlation between the losses in $F F$ and $R_{S}-R_{s, \text { front }}$ grid was observed as shown in Fig. 5.9. A linear fit function describing the losses in $F F$ depending on $R_{s}-R_{s, \text { front grid }}$ is also shown. There is a strong correlation visible within the groups
and also comparing the groups with each other. For example, the $p F F-F F$ drop is in the range of $4.2 \%-5.9 \%$ for Group (L-S) and in the range of $3.9 \%-4.4 \%$ for Group (L-O). Therefore, it is concluded that the series resistance losses were also influenced by the contact resistance at the front contacts.


Fig. 5.9 Measured difference of $p F F$ and $F F$ for the various solar cell groups as a function of the measured series resistance obtained from comparing light and dark $I-V$ at maximum power point reduced by the series resistance of the front metal grid $\left(R_{s}-R_{s, ~ f r o n t ~ g r i d ~}\right)$. A linear fit was applied, with the fit function shown in the legend.

The contact resistance at the front contacts is influenced by the contact area and the contact resistivity between the Ni and Si . The contact resistivity between Ni and Si is shown to be depending on the dopant concentration at the surface [37, 132]. The dopant concentration at the surface was slightly higher for the Groups (A/L-S) than for the Groups (A/L-S) as shown in Fig. 5.3. Therefore, the lower contact resistance and higher $F F$ can be the result of the selective emitter. Additionally, the contact area between the Groups (A/L-O) and (A/L-S) is different as shown in Fig. 5.2. The contact area of Groups (A/L-S) is even larger than one would expect to be just from the opening width due to the groove of the laserdoped line.

In conclusion, the differences in $F F$ losses between the groups were driven by the grid resistance and by the contact resistance between the plated Ni and Si . The
contact resistance was influenced by the contact resistivity and the contact area.
Further discussions on the contact resistance will be presented in Sec. 5.2.5.

### 5.2 Influence of single pulse laser fluence on solar cell efficiency

The solar cell results of the previous solar cell batch shows that low single pulse laser fluences may cause a significant drop in $V_{O C}$ due to laser-induced defects. This section investigates the influence of single pulse laser fluences below the evaporation threshold on the solar cell efficiency in detail.

### 5.2.1 Solar cell fabrication

The precursors for the solar cells in this section were identical to the Al-BSF precursors of the previous section. Again the solar cells were laser processed by LCP and metallised using Ni and Ag plating. However, no annealing after plating was performed since it did not show a significant effect on the solar cell efficiency.

Laser processing of the solar cells was split in 3 groups, each with a different single pulse laser fluence as shown in Table 5.5.

Table 5.5 Overview of the used LCP parameters (compare Sec. 2.3.2).

| Frequency <br> $[\mathbf{k H z}]$ | Pulse duration <br> $(\mathbf{F W H M})[\mathbf{n s}]$ | Fluence <br> $\boldsymbol{\Phi}_{\boldsymbol{p}}\left[\mathbf{J} / \mathbf{c m}^{2}\right]$ | Scribing speed <br> $\boldsymbol{v}_{\boldsymbol{s}}[\mathbf{m} / \mathbf{s}]$ | Hatch <br> $\boldsymbol{h}[\boldsymbol{\mu} \mathbf{m}]$ | Laser pulse <br> density $\boldsymbol{n}_{\boldsymbol{p}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 200 | 60 | $0.4,0.6$, <br> 1.1 | 0.5 | Finger: 1660 | Finger:16 |
|  |  | Busbars: 10 | Busbars: 39 |  |  |

The solar cells featured 94 fingers with 3 busbars with a width of 1.6 mm . Figure 5.10 shows microscope images of the resulting lines of the groups with the corresponding $w_{L}$ and $R_{s h}$. The $R_{s h}$ was measured on $5 \times 156 \mathrm{~mm}^{2}$ sized test samples
prepared identical as the busbars. The line width is the approximated width of the removed $\operatorname{SiN}_{\mathrm{x}}$.

| Group (A) | Group (B) | Group (C) |
| :---: | :---: | :---: |
| $\Phi_{p}=0.4 \mathrm{~J} / \mathrm{cm}^{2}$ | $\Phi_{p}=0.6 \mathrm{~J} / \mathrm{cm}^{2}$ | $\Phi_{p}=1.1 \mathrm{~J} / \mathrm{cm}^{2}$ |
|  |  |  |
|  |  |  |
|  |  |  |

Fig. 5.10 Optical microscope images, corresponding $R_{s h}$ measurements and line width measurements of the different solar cell groups. The solar cells were fabricated using different single pulse laser fluence during the LCP process. The uncertainty in line width is given by the inhomogeneous opening width of the $\mathrm{SiN}_{\mathrm{x}}$ layer and the uncertainty in $R_{s h}$ is given by the standard deviation of $R_{s h}$ measurements. The scale bar denotes $20 \mu \mathrm{~m}$.

Group (A) was processed with a single pulse laser fluence of $0.4 \mathrm{~J} / \mathrm{cm}^{2}$, which merely melts the first few nm of the substrate and only locally evaporates certain parts of the surface due to the inhomogeneous intensity profile of the jet. Group (B) features a single pulse laser fluence of $0.6 \mathrm{~J} / \mathrm{cm}^{2}$, which results in homogeneously evaporation of the $\mathrm{SiN}_{\mathrm{x}}$ film within the centre of the jet. However, the emitter $R_{s h}$ did not change significantly; therefore it can be concluded that no significant doping of the underlying Si was achieved. The impact of the solar cells in Group (B) due to laser processing is essentially comparable to the impact of Group (A-O) in the previous section. Group (C) featured a lightly doped selective
emitter. The width of the lines, which is the approximate width of the region were $\mathrm{SiN}_{\mathrm{x}}$ was removed, was gradually increasing for increasing laser fluence.

### 5.2.2 Solar cell results

The results of the one-Sun $I-V$ measurements of the finalised Si wafer solar cells are summarised in Figure 5.11. The $V_{O C}$ of the solar cells decreases for increasing single pulse laser fluence, which is identical to the $J_{S C}$ behaviour of the solar cells. The $F F$ increases from Group (A) - (C) and the efficiency decreases from 16.2 to $16.1 \%$ from Group (A) - (C).


Fig. 5.11 Boxplots of the one-Sun $I-V$ parameters of all solar cell groups.

The champion solar cell of this experiment was in Group (A) with the lowest single pulse laser fluence and had an efficiency of $16.5 \%$. Compared to the previous solar cell batch, the average efficiency of Group (A) was $0.3 \%$ absolute higher than the efficiency of the comparable Group (A-S). This can mainly be attributed to the higher $F F$ and higher $V_{O C}$ values. The subsequent sections analyse in detail
the different reasons which could explain the observed losses in voltage, current and fill factor for each group.

Similar as observed in the previous solar cell batch, all solar cells of this experiment featured a large amount of background plating, which was removed in a subsequent etching step as described in the next chapter. This etching step increased the efficiency of the champion solar cell to $16.9 \%$.

### 5.2.3 Open-circuit voltage analysis

When comparing Group (A) and (B) a significant drop in $V_{O C}$ is observed, even though the $R_{s h}$ was quite similar. This drop will again be investigated with Quokka simulations to identify if the difference in opening width can account for the difference in $V_{O C}$. Groups (B) and (C) show no significant difference in $V_{O C}$. It can be argued that the difference between the line width and the influence of the doping cancels each other out.

The Quokka simulations were performed in a similar manner as in Sec. 5.1.3. However, it was much harder to identify the appropriate $J_{01, L D}$ values of the laser treated areas. Therefore, a sweep in $J_{01, L D}$ was performed for the simulations using both line widths. In case of Group (A) the $\mathrm{SiN}_{\mathrm{x}}$ layer was not removed homogeneously. Microscope images were used to measure the fraction of the $\operatorname{SiN}_{\mathrm{x}}$ film that was opened within the laser-doped areas by means of a thresholding algorithm. It was determined that only $\sim 15 \%$ of the $\mathrm{SiN}_{\mathrm{x}}$ film was actually removed. Therefore, only $15 \%$ of the line width was used in the simulations. Figure 5.12
shows the simulated results of $V_{O C}$. The measured average $V_{O C}$ values were $624 \pm$ 2 mV for Group (A) and $620 \pm 2 \mathrm{mV}$ for Group (B).


Fig. 5.12 Simulated $V_{O C}$ as a function of the saturation current density of laser-doped areas for the Groups (A) and (B) as labelled in the legend. Quokka simulation parameters are as given in Table 5.2 with $\tau_{\text {bulk }}=0.83 \mu \mathrm{~s}$ (fitted). The front contact opening width was set to $(13.5+29) \times 0.15$ for Group (A) and to (19.5+29) for Group (B).

In case of Group (A), the $V_{O C}$ decreases only slightly for a large range of $J_{01, L D}$ since the opening areas represented less than $1 \%$ of the solar cell area. Changes in $J_{01, L D}$ in such a small solar cell area need to be huge to affect overall solar cell efficiency significantly, which was also shown in [37]. In case of Group (B), the $V_{O C}$ decreases significantly and one can even observe a better $V_{O C}$ in case of $J_{O I, L D}$ is lower than the $J_{01, \text { pas }}$. In the simulations a $J_{01, L D}$ of $\sim 3500 \mathrm{fA} / \mathrm{cm}^{2}$ was necessary to observe the difference in voltage as observed in the results in Fig. 5.11. This is in good agreement with the results of Sec. 4.1.3 and Sec. 5.1.3, where a $J_{01, L D}$ in this laser fluence range of $\sim 3000 \mathrm{fA} / \mathrm{cm}^{2}$ was obtained.

Comparing the results of this solar cell batch to the results of the previous solar cell batch in Sec. 5.1.3, it is observed that the selective emitter doping is not as beneficial for the solar cell efficiency as minimal openings. The maximum $V_{O C}$ obtained for a selective emitter solar cell in this study was 623 mV , while the maximum $V_{O C}$ for solar cells with minimal openings was 626 mV . This indicates
that the reduction of defects induced by laser doping or a reduction of the contact area (removed $\mathrm{SiN}_{\mathrm{x}}$ film) is more important than the formation of a selective emitter. This only applies to the cases where a selective emitter is not necessary for contacting.

The results of Fig. 5.12 also show that the theoretical benefit of a selective emitter becomes smaller when going to smaller area fractions as also discussed in [37]. Conversely, it means that also the drawbacks of the increased recombination in the laser-doped region may be acceptable in certain cases, where a selective emitter is needed for technological reasons. One reason is the contacting of a very lowly doped homogeneous emitter, which may not be contactable by Ni plating. Another possible reason where a selective emitter may be necessary is when the adhesion of the front contacts is not sufficient [18, 37]. Here an annealing can be used, to obtain adhesion. However, the annealing may cause Ni-silicide spikes which may shunt a shallow homogeneous emitter. A deep diffused selective emitter helps to prevent these annealing-induced shunts.

Another factor which causes $V_{O C}$ losses is background plating, which was also observed on these solar cells. Figure 5.13 shows the $V_{O C}$ depending on the background plating area for the solar cells of Group (A), which exhibit a $V_{O C}$ above 623 mV (green circles). ${ }^{10}$ The background plating area was obtained by measuring the overall metallisation of the solar cell as discussed in Appendix C and subtracting the theoretical metallisation area of the grid, which was obtained from finger width measurements.

[^5]

Fig. 5.13 Measured $V_{O C}$ of Group (A) as function of the relative background plating area [ $A_{B P}$, as percentage of the solar cell area $\left(A_{\text {cell }}\right)$ ]. The $V_{O C}$ was obtained before (green circles) and after (blue squares) etching of the background plating as discussed in Sec. 6.2.2. A linear fit (black line) was applied.

A tendency for lower $V_{O C}$ values for larger plated areas can be observed. To corroborate this tendency, the background plating was etched from all of these solar cells as discussed in Sec. 6.2.2, which resulted in a significant increase in $V_{O C}$ (as shown in Fig. 5.13). The fit shows that without background plating the solar cells would have an average $V_{O C}$ of 627 mV . The $V_{O C}$ was influenced by shading of the solar cells due to lateral balancing currents into the shaded areas [133]. It should be noted that the etching of the background plating does only decrease the shading by removal of the Ag-plated layer. The Ni-plated layer is still present and in contact with the front surface, hence, possible recombination centres are not removed.

### 5.2.4 Short-circuit current loss analysis

The short-circuit current density decreased slightly from Group (A) to Group (C). This effect can be attributed to the increased shading due to the increased finger width. Table 5.6 shows the difference in $J_{S C}$ between the groups and the difference in theoretical metallisation of the grid as calculated from the difference in finger width.

Table 5.6 Difference in $J_{S C}$ as percentage of the average $J_{S C}$ and difference in the theoretical metallised area as percentage of the total metallised area, which was calculated based on the finger width.

|  | $\Delta J_{S C} / J_{S C}[\%]$ | $\Delta A_{\text {Grid }}[\%]$ |
| :--- | :--- | :--- |
| Group (A) - Group (B) | 0.2 | 0.2 |
| Group (A) - Group (C) | 0.4 | 0.3 |
| Group (B) - Group (C) | 0.1 | 0.2 |

Table 5.6 shows that the relative differences in $J_{S C}$ were similar to the relative differences of the metallised areas. Therefore the small differences in $J_{S C}$ are well explained by the different ratio of the metallised areas [134].

Another factor limiting the $J s c$ is background plating. Figure 5.14 shows the measured $J_{S C}$ as function of the background plating area. Again, the background plating area was obtained by measuring the overall metallisation of the solar cell as discussed in Appendix C and subtracting the theoretical metallisation area of the grid, which was obtained from finger width measurements. A linear correlation between background plating and $J_{S C}$ was observed. Therefore, background plating limits the $J_{S C}$ of the solar cells of all solar cell groups. Background plating increases the metal shading of solar cells, which increases the reflection of the solar cells [134, 135]. Following the applied linear fit of Fig. 5.14, the average $J_{S C}$ would be at $34.3 \mathrm{~mA} / \mathrm{cm}^{2}$ without background plating for these solar cells.


Fig. 5.14 Measured $J_{S C}$ depending on the background plating area as percentage of the solar cell area. The groups are labelled as shown in the legend. A linear fit is shown as black line.

### 5.2.5 Fill Factor loss analysis

As discussed for the previous solar cell batch in Sec. 5.1.5, losses in $p F F$ occur due to scratches and shunts at the edges of the solar cells. The fill factors of the solar cells increase consecutively from Group (A) to Group (C).

Table 5.7 shows the $F F$ losses resulting from series resistance for all groups. The difference in series resistance between the groups is mainly caused by the contact resistance. The losses in $F F$ due to series resistance decrease with increasing line width. Even in the case of a similar $R_{s h}$ as for Group (A) and (B), the $F F$ losses due to series resistance decrease, which corroborates the influence of the contact area on the contact resistance. However, an influence of contact resistivity cannot be ruled out by this experiment. It appears that the series resistance losses increase when the difference between Group (C) and (B) are compared to the difference in Group (B) and (A). This apparent increase can be driven by the contact resistivity.

Table 5.7 FF losses corrected by $p F F$ losses $(p F F-F F), w_{L}$ and $R_{s h}$ of laser-doped areas for Groups (A) - (C).

|  | $\boldsymbol{p F F} \mathbf{F} \mathbf{F F}[\%]$ | $\boldsymbol{w}_{\boldsymbol{L}}[\boldsymbol{\mu \mathrm { m }}]$ | $\boldsymbol{R}_{\text {sh }}[\mathbf{\Omega} / \mathbf{s q}]$. |
| :--- | :--- | :--- | :--- |
| Group (A) | $3.6 \pm 0.7$ | $27 \pm 2$ | $77 \pm 7$ |
| Group (B) | $3.3 \pm 0.1$ | $40 \pm 2$ | $75 \pm 3$ |
| Group (C) | $2.8 \pm 0.3$ | $48 \pm 2$ | $66 \pm 14$ |

Compared to the solar cell batch in Sec. 5.1, the $F F$ of these solar cells is in generally higher by $\sim 2 \%$ absolute. The reason is that plating of these solar cells was optimised to result in a lower series resistance of the front grid. Further plating of the solar cells did not increase the $F F$, significantly.

### 5.3 Solar cells with different metallisation methods

The goal of this study was to compare laser-doped selective emitter solar cells to standard screen-printed solar cells. An industrially applicable optimised emitter with a high $R_{s h}$ [56] was chosen for the diffusion of the laser-doped solar cells, while a standard industrial emitter (low $R_{s h}$ ) was used for the screen-printed solar cells.

From theoretical considerations and the results of previous experiments, it was found that the high $R_{s h}$ emitter is still contactable with Ni plating. Therefore, the goal for laser processing was to minimise the impact of laser damage instead of enabling to contact the lowly doped emitter or reduction of recombination at the Si-metal interface. An optimised parameter set for laser processing of the solar cells was chosen based on the previous studies as shown in Sections 5.1 and 5.2. These parameters resulted in minimal openings instead of selective emitter diffusion.

### 5.3.1 Solar cell fabrication

The processing of the solar cells follows Sec. 2.1.2 and the steps are shown in Fig. 5.15. The precursors were $156 \times 156 \mathrm{~mm}^{2}$ multicrystalline silicon wafers with a thickness of $190 \mu \mathrm{~m}$.

| Group (LCP) | Group (SP) |
| :---: | :---: |
| Acid texturing |  |
| HF-dip |  |
| High $R_{\text {sh }}$ emitter diffusion | Low $R_{\text {sh }}$ emitter diffusion |
| Chemical edge isolation |  |
| PSG etching |  |
| $\mathrm{SiN}_{\mathrm{x}}$ coating of front surface |  |
| Screen printing rear side |  |
|  | Screen printing front side |
| Firing at $860^{\circ} \mathrm{C}$ | Co-Firing at $880^{\circ} \mathrm{C}$ |
| LCP processing |  |
| HF-dip |  |
| Ni plating |  |
| Ag plating |  |

Fig. 5.15 Processing flow of the solar cell groups with LCP laser processing and plated front contacts [Group (LCP)], and screen-printed metal contacts [Group (SP)].

The Photovoltaic Technology Evaluation Centre (PV-TEC) at the Fraunhofer Institute for Solar Energy Systems (ISE) in Germany was used for the solar cell precursor processing until the LCP step. Two different diffusions were carried out: the high $R_{s h}$ emitter was targeted to an $R_{s h}$ of $110 \Omega /$ sq. and the low $R_{s h}$ was targeted to an $R_{s h}$ of $75 \Omega / \mathrm{sq}$. However, the diffusion of the high $R_{s h}$ emitter was optimised for mono-crystalline Si solar cells. An application to multicrystalline Si wafers resulted in a lower $R_{s h}$, due to enhanced diffusion at defects [136] and the influence of the different surface morphology. The resulting $R_{s h}$ was measured to be in the range of $100 \Omega / \mathrm{sq}$. Screen printing was tested on two samples with the high $R_{s h}$ emitter. The $F F$ of these solar cells were below $74.5 \%$. Therefore, the emitter can be regarded as non-contactable with the typically used industrial screen printing paste.

The screen printing of the front side was carried out with an optimised "tapered" grid such that the finger width is wider at the busbars ( $\sim 100 \mu \mathrm{~m}$ ) and smaller at the finger location furthest away from the busbar ( $\sim 50 \mu \mathrm{~m}$ ). LCP processing was performed with the parameters shown in Table 5.8.

Table 5.8 Overview of the used LCP parameters (compare Sec. 2.3.2).

| Frequency <br> $[\mathbf{k H z}]$ | Pulse duration <br> $(\mathbf{F W H M})[\mathrm{ns}]$ | Fluence <br> $\boldsymbol{\Phi}_{\boldsymbol{p}}\left[\mathbf{J} / \mathbf{c m}^{2}\right]$ | Scribing <br> speed $\boldsymbol{v}_{\boldsymbol{s}}[\mathbf{m} / \mathbf{s}]$ | Hatch $\boldsymbol{h}[\boldsymbol{\mu \mathrm { m } ]}$ | Laser pulse <br> density $\boldsymbol{n}_{p}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 200 | 60 | 0.7 | 0.5 | Finger: 1857 <br> Busbars: 10 | Finger:16 <br> Busbars: 39 |

Both solar cell groups featured a front metallisation with 84 fingers with 3 busbars with a width of 1.6 mm . The laser fluence was set to $0.7 \mathrm{~J} / \mathrm{cm}^{2}$, which resulted in an opening pattern similar as the pattern shown for Group (A) in Fig. 5.10 on these precursors. The opening width was measured to be $34 \pm 2 \mu \mathrm{~m}$ with the ratio of removed $\mathrm{SiN}_{\mathrm{x}}$ layer to be at $25 \%$. The subsequent plating resulted in an overall finger width of $55 \pm 3 \mu \mathrm{~m}$.

### 5.3.2 Solar cell results

The results of the one-Sun $I-V$ measurements of the finalised Si wafer solar cells are summarised in Fig. 5.16. It can be seen that all median one-Sun $I-V$ parameters of the Group (SP) are higher than those of the Group (LCP). However, in certain cases individual solar cells of the Group (LCP) show a slight benefit, such as in $V_{O C}$ and in $F F$.

The solar cells of Group (SP) show a $V_{O C}$ of around 620 mV , which is lower than expected from the potential of the diffused emitter. No firing optimisation was used for this solar cell batch. Therefore it can be assumed that the firing tempera-
ture was not set at an optimal value for this solar cell batch. The solar cells of Group (LCP) show strongly varying values of $V_{O C}$ between 608 and 624 mV . The same variation pattern of the individual solar cells is also visible in the $J_{S C}$ plot in Fig. 5.16. Therefore it is suspected that the background plating influences the voltage of the solar cells in a similar way as described in Sec. 5.2.3. The cases with a higher $V_{O C}$ than the Group (SP) can be explained by the potential of the high $R_{s h}$ emitter and the smaller contact area between the fingers and the Si .


Fig. 5.16 Boxplots of the one-Sun I-V parameters of the solar cell Groups (LCP) and (SP).

The difference in $J_{S C}$ between the two groups is due to background plating as discussed in Sec. 5.2.4, which is only observed for Group (LCP). Both groups show a low $F F$. In case of the Group (SP), the $F F$ was mainly limited by the series resistance of the front surface grid. The front surface metal grid was printed twice on one solar cell, which resulted in a $F F$ of $79.2 \%$. The $F F$ of the Group (LCP) is mainly limited by the contact resistance as discussed in Sec. 5.1.6 and Sec. 5.2.5. Another factor influencing the $F F$ is the low $p F F$ of both groups, which is sus-
pected to be from the non-ohmic shunts at the edges (as described in Sec. 5.1.5) or from substantial background plating at grain boundaries in case of Group (LCP).

The results also show that the standard deviations in case of the Group (SP) are much smaller than those of the Group (LCP). This can be attributed to the fact that for Group (SP) an optimised industrial process was used for metallisation of the front surface.

The champion solar cell was in Group (SP), with an efficiency of $16.8 \%$. However, with a background plating removal and re-plating as shown in Sec. 6.2.2, the efficiency of the best solar cell of the Group (LCP) was raised by $+0.6 \%$ absolute to $16.9 \%$. The voltage of this solar cell was 626 mV , which is $\sim 6 \mathrm{mV}$ higher than the maximum voltage of Group (SP). Therefore, the efficiency of the solar cells was limited by background plating. Only by eliminating background plating as the main limiting factor, the potential of the lowly doped homogeneous emitter becomes visible.

### 5.4 Chapter summary and conclusions

The application of laser doping with LCP for selective emitter solar cells was investigated in this chapter. Section 5.1 compared a solar cell batch with two laser processes: one resulting in a selective emitter with heavy doping and one resulting in homogeneous openings of the $\operatorname{SiN}_{\mathrm{x}}$ film but with negligible doping. The $R_{s h}$ measurements helped to identify the doping parameter according to their doping efficiency. The results showed that the sample with higher sheet resistance has slightly lower solar cell efficiency than the samples with lower sheet resistance.

However, this influence could not be unambiguously attributed to the sheet resistance but the damage induced by laser doping also needed to be considered. A detailed loss analysis showed that laser doping with LCP featured severe laserinduced damage, which limits the solar cell efficiency in both cases. Other factors which reduced the overall solar cell efficiency are due to scratches, non-linear shunts at the edges of the solar cells and background plating.

Based on the results of Sec. 5.1 a solar cell batch was designed and investigated in Sec. 5.2 to minimise the influence of laser-induced defects on similar solar cell precursors as in Sec. 5.1. This was only possible because the used processing scheme did not require any selective emitter doping for e.g. contacting or prevention of annealing-induced shunts. Laser doping parameters were used to obtain a gradual increase of the laser doping impact. The solar cells with the lowest impact showed the best solar cell efficiency overall, even in comparison to the selective emitter solar cells of the batch shown in Sec. 5.1. It is concluded that the minimisation of the laser damage due to LCP should be the key factor for optimisation of solar cells if a selective emitter is not required for contacting a lowly doped homogeneous emitter or for other technological reasons.

Section 5.3 compared a group with screen-printed contacts with a group with LCP openings of $\mathrm{SiN}_{\mathrm{x}}$ film and subsequent plating. The two groups featured two different emitters: the screen-printed group featured a highly doped emitter, while the LCP group featured a lowly doped emitter. The results showed that the efficiency of the LCP group was severely limited by background plating. The potential of the lowly doped emitter became visible only after eliminating background plating as
the main limiting factor. The main reason for the background plating was that the $\mathrm{SiN}_{\mathrm{x}}$ layer deposition was non-optimised.

From this chapter it can be concluded that the advantage of a laser-doped selective emitter with LCP lies not in the reduction of recombination at the semiconductormetal interface. The laser-induced damage causes high recombination of the LCP laser-doped selective emitter. Additionally, a homogeneous emitter, which can still be contacted by e.g. Ni plating does not require a selective emitter. In this case, the opening of the $\operatorname{SiN}_{\mathrm{x}}$ layer should be optimised to reduce the laserinduced defects instead of diffusion of a highly doped selective emitter with LCP. However, the LCP laser-doped selective emitter may be beneficial for process integration. It was discussed that selective emitter doping could be beneficial in cases where the homogeneous emitter is not contactable with Ni plating or to prevent annealing-induced shunts. In these cases the laser-induced defects may be acceptable due to the technological necessity of a selective emitter. The $R_{s h}$ measurements can then be used to identify the optimised processing parameters.

## 6 Etching of background plating on silicon solar cells

Various results in the previous chapter showed that background plating can significantly deteriorate the solar cell efficiency. It was shown that the $J_{S C}$ is influenced by background plating due to the shading of the solar cell (see Sec. 5.2.4) and the $V_{O C}$ is influenced due to lateral current flows into the shaded areas (see Sec. 5.2.3). Therefore it is of high importance to avoid, or remove background plating. In this chapter a method is developed for removing background plating after the plating process by a simple wet etching step that is easy to integrate into the solar cell fabrication process. The background plating is selectively etched, while the undesired etching on the plated metal grid is minimised. The selective etching is solely based on the different geometries of background plating and the metal grid. Selective etching of background plating may eliminate background plating completely, and can also be used in combination with other methods which avoid background plating.

Section 6.1 describes a model of etching for the different geometries that exist after the plating process. These are a half-spherical geometry for typical background plating, a half-cylindrical geometry for a plated finger and a flat (Cartesian) geometry for the busbars. Section 6.2 compares the model of Sec. 6.1 to experiments conducted on plated Si wafer solar cells and applies the etching of background plating for solar cell processing. Section 6.3 summarises and concludes the chapter.

### 6.1 Theory of etching for different geometries

The selective etching of background plating is based on the different geometries of background plating and the metal grid. Background plating is typically caused by the presence of defects in the dielectric film. These defects can be considered as point sources for the metal deposition during the plating process. It is assumed that the plating occurs isotropically, therefore the resulting background plating consists of half spheres on the surface of the solar cell with a radius $\delta_{0}$ as shown in Fig. 6.1(a) [11].


Fig. 6.1 Schematic illustration of plated areas on solar cells. (a) Cross section of background plating with radius $\delta_{0}$ on a defect in the dielectric coating. (b) Cross section of metal grid (finger or busbar) with dielectric opening with width $w_{L}$. Since plating is assumed to be isotropic the plated metal grows homogeneous at the edges resulting in an arc with the radius $\delta_{0}$ at the edges.

In contrast, the metal grid is plated on a 2 D seed layer or opening in the dielectric with a certain width $w_{L}$ as shown in Fig. 6.1(b). The metal grid is then a bar with the width $w_{L}$ and rounded corners with radius $\delta_{0}$. The length of the bar is approximately the length of the solar cell. For simplicity, it is assumed that the fingers consist of infinite half cylinders with a radius $\delta_{0}$ for ( $w_{L} \rightarrow 0$ ). In this case the seed layer or dielectric opening is assumed to be an infinitesimal thin line across the wafer surface. This assumption would lead to the smallest impact on the $V_{O C}$ of the solar cell as discussed in Sec. 5.2.3. The busbars have a very wide opening
or seed layer width $w_{L}$ in comparison to the fingers. Therefore, the busbars are regarded as infinite flat surface in this analysis. Following these assumptions, plating of solar cells results in structures with a spherical, cylindrical or Cartesian geometry which will be discussed according to their respective coordinate system. For the model it is also assumed that the solar cell surface with the plated structures is immersed in an infinitely large etchant bath regarding the size of the structures.

Wet-chemical etching of metal structures involves (i) the transport of the active etchant species to the structure surface, (ii) an oxidisation reaction of the metal on the structure surface and (iii) the transport of the dissolved metal ions away from the structure surface [137]. The etch rate depends on the rates of processes (i)-(iii). When the rate-limiting step is the surface reaction (ii), the etching is referred to as reaction-limited. If the rate-limiting steps are either one or both of the transport steps (i) and (iii), the etching is referred to as diffusion-limited. In the following, the diffusion-limited case will be discussed and later extended to include the reac-tion-limited case.

### 6.1.1 Diffusion-limited etching

Here, only process (i) will be described, where the active etchant species with concentration $c$ diffuses (without convection) to the surface area at $r=\delta(t)$, where it reacts with the metal and the surface moves outwards (see Fig. 6.2).


Fig. 6.2 Illustration of diffusion-limited etching in one dimension. The metal structure with thickness $\delta(t)$ is etched, while the etchant solution is located between $\delta(t)$ and $r \rightarrow \infty$.

The diffusion of the dissolved metal ions away from the surface [process (iii)] can be discussed in a similar way. The etching process can be described by the diffusion equation, where the etched surface is a moving boundary [137-139]. The diffusion equation for the flat infinite surface of the busbars is:

$$
\begin{equation*}
\frac{\partial c}{\partial t}=D\left[\frac{\alpha_{G}}{r} \frac{\partial c}{\partial r}+\frac{\partial^{2} c}{\partial r^{2}}\right] \quad, t \geq 0, \delta(t)<r<\infty, \tag{6.1}
\end{equation*}
$$

where $D$ is the diffusion coefficient and the geometry factor $\alpha_{G}=0$ for Cartesian geometry. In case of etching of the half-cylindrical finger, the diffusion is radially symmetric along the cylinder. Therefore, the diffusion equation for cylindrical geometries needs to be applied, were $\alpha_{G}=1$. In case of the half-spherical background plating the diffusion equation for spherical geometries needs to be applied were $\alpha_{G}=2$. Initially, the concentration of the active etchant species in the liquid is identical everywhere $\left[r>\delta(t)\right.$ ] and the location of the surface is at $\delta_{0}$. This leads to the starting conditions:

$$
\begin{equation*}
c[0, r>\delta(t)]=c_{0}, \quad \delta(0)=\delta_{0} . \tag{6.2}
\end{equation*}
$$

For $t>0$ the etchant concentration remains $c_{0}$ for $r \rightarrow \infty$ :

$$
\begin{equation*}
c(t, r \rightarrow \infty)=c_{0} . \tag{6.3}
\end{equation*}
$$

At the surface it is assumed that the reaction is instantaneous and the concentration of the etchant is zero:

$$
\begin{equation*}
c[t, x=\delta(t)]=0 . \tag{6.4}
\end{equation*}
$$

Additionally, the velocity at which the surface moves is proportional to the flux of the active etchant species at the surface[138]:

$$
\begin{equation*}
\frac{d s}{d t}=\left.\frac{D M_{m o l}}{m \rho_{D}} \frac{\partial c}{\partial r}\right|_{\{r=\delta(t)\}}, \tag{6.5}
\end{equation*}
$$

where $M_{m o l}$ is the molar mass of the solid, which is etched, $\rho_{D}$ is the mass density of the solid, and $m$ is the number of active etching molecules, which are necessary to dissolve one molecule of the solid. The system of Eqs. (6.1) - (6.5) is commonly referred to as Stefan problem and often encountered in diffusion or heat problems, such as melting ice [140]. Equation (6.5) is called the Stefan condition.

The 1D Stefan problem for a flat infinite surface [Eq. (6.1) with $\alpha_{G}=0$ ] with initial and boundary conditions [Eqs. (6.2) - (6.5)] can be solved semi-analytically. The solution yields that the location of the surface is proportional to the square root of $D t$ :

$$
\begin{equation*}
\delta(t)=2 \gamma(D t)^{1 / 2} . \tag{6.6}
\end{equation*}
$$

The factor $\gamma$ is given by a transcendental equation, which cannot be solved analytically [138].

In case of etching of fingers or background plating, which show a cylindrical or spherical symmetry, no analytically or semi-analytically solution is shown so far. Here, a numerical model will be developed to observe how etching is influenced by the different geometries. Two coordinate transformations will be used to simplify the equation systems. Firstly, a scaling is introduced to arrive at dimensionless equations and secondly the coordinate systems will be defined such that the
moving boundary of the Stefan problem is immobilised [boundary immobilisation (BIM)].

### 6.1.2 Scaling

For the scaling the following transformation of variables will be used:

$$
\begin{align*}
c^{\prime} & :=c / c_{o} \\
t^{\prime} & :=t \times D / \delta_{0}^{2}  \tag{6.7}\\
\delta^{\prime} & :=\delta / \delta_{0}
\end{align*}
$$

and for the $r$ coordinate:

$$
\begin{equation*}
r^{\prime}:=r / \delta_{0} . \tag{6.8}
\end{equation*}
$$

Implementing the defined scaling in the diffusion equation [Eq. (6.1)] leads to:

$$
\begin{equation*}
\frac{\partial c^{\prime}}{\partial t^{\prime}}=\left[\frac{\alpha_{G}}{r^{\prime}} \frac{\partial c^{\prime}}{\partial r^{\prime}}+\frac{\partial^{2} c^{\prime}}{\partial r^{\prime 2}}\right] \tag{6.9}
\end{equation*}
$$

with the initial condition:

$$
\begin{equation*}
c^{\prime}\left[0, r^{\prime}>\delta^{\prime}\left(t^{\prime}\right)\right]=1, \delta(0)=1 \tag{6.10}
\end{equation*}
$$

and the boundary conditions for $r^{\prime} \rightarrow \infty$ :

$$
\begin{equation*}
c^{\prime}\left(t^{\prime}, r \rightarrow \infty\right)=1, \tag{6.11}
\end{equation*}
$$

as well as for $r^{\prime}=\delta^{\prime}(t)$ :

$$
\begin{equation*}
c^{\prime}\left[t^{\prime}, r^{\prime}=\delta^{\prime}\left(t^{\prime}\right)\right]=0, \tag{6.12}
\end{equation*}
$$

and with the Stefan condition:

$$
\begin{equation*}
\frac{d \delta^{\prime}}{d t^{\prime}}=-\left.\frac{1}{\beta} \frac{\partial c^{\prime}}{\partial r^{\prime}}\right|_{r^{\prime}=\delta^{\prime}\left(t^{\prime}\right)} \tag{6.13}
\end{equation*}
$$

with $\beta=m \rho_{D} / M_{m o l} c_{0}$. Therefore the equation system (6.9) - (6.13) contains $\beta$ as the only parameter. The notation of $1 / \beta$ was chosen such that it matches the definition of $\beta$ in Kuiken et al. [138], where values of $\beta$ are given for certain structure and etchant combinations.

### 6.1.3 Boundary immobilisation

The immobilisation of the boundary is one of the methods to solve a moving boundary problem [141-143]. This method was chosen for its simplicity and easy application to 1D problems. The coordinate is defined as:

$$
\begin{equation*}
r^{*}:=\delta^{\prime}\left(t^{\prime}\right) / r^{\prime} \tag{6.14}
\end{equation*}
$$

Therefore, the location interval of the equation system (6.9) - (6.13) are not $r^{\prime} \in\left[\delta^{\prime}\left(t^{\prime}\right), \infty\right)$ but $r^{*} \in(0,1]$. Equation (6.9) then becomes:

$$
\begin{equation*}
\frac{\partial c^{\prime}}{\partial t^{\prime}}=\left[\frac{\left(2-\alpha_{G}\right) r^{* 3}}{\delta^{\prime 2}}-\frac{r^{*} \dot{\delta}^{\prime}}{\delta^{\prime}}\right] \frac{\partial c^{\prime}}{\partial r^{\prime}}+\frac{r^{* 4}}{\delta^{\prime 2}} \frac{\partial^{2} c^{\prime}}{\partial r^{\prime 2}} \tag{6.15}
\end{equation*}
$$

The boundary conditions are then:

$$
\begin{equation*}
c^{\prime}\left(t^{\prime}, r^{*} \rightarrow 0\right)=1, \tag{6.16}
\end{equation*}
$$

for $r^{*}>\infty$ and for $r^{*}=1$ :

$$
\begin{equation*}
c^{\prime}\left(t^{\prime}, r^{*}=1\right)=0, \tag{6.17}
\end{equation*}
$$

with the Stefan condition:

$$
\begin{equation*}
\dot{\delta}^{\prime}:=\frac{d \delta^{\prime}}{d t^{\prime}}=-\left.\frac{1}{\beta} \frac{r^{* 2}}{\delta^{\prime}} \frac{\partial c^{\prime}}{\partial r^{\prime}}\right|_{r^{\prime}=1} \tag{6.18}
\end{equation*}
$$

The equation system (6.15) - (6.18) can be solved with a finite difference approximation in space and a Crank-Nicolson approximation in time [144]. The value of $\dot{\delta}^{\prime}$ is approximated for each time step from the previous time step. The only parameter remaining in the equation system is $\beta$, which is independent of the diffusion constant and can be calculated for arbitrary combinations of etching solutions and structures. However, to obtain the true etch rate, one still needs to apply the scaling of the time [Eq. (6.7)], which also includes the diffusion constant.

### 6.1.4 Results of the model

Simulations were performed for all three geometries (Cartesian, cylindrical and spherical) using the model developed in the previous section. The calculations were tested by using a higher precision in space and time steps for all geometries and for selected parameter values. The results of the model were also tested against the semi-analytical results for the Cartesian geometry, which is described in Eq. (6.6). The results of the model agreed very well with the semi-analytical results. The number of steps in space was chosen to be $r_{\text {step }}=80$ and the number of steps in time was calculated as $t_{\text {step }}=\delta / 2\left[1 /\left(r_{\text {step }}+1\right)^{2}\right]$ according to the accuracy limit of the BIM method [142]. These values were chosen for all calculations in this chapter.

Figure 6.3 shows the general trend of the location of the boundary $\delta^{\prime}$ depending on the etch time $t^{\prime}$ for all three geometries. In case of the Cartesian geometry the etching described by the displacement of the surface is slowest compared to cylindrical and spherical geometries. In spherical geometries, the etching of the surface is fastest and with increasing etching time the difference between spherical and cylindrical etching becomes larger. The inset of Fig. 6.3 shows the concentration at different etching times for spherical geometry. The concentration approaches a linear slope while the boundary is moving towards 0 . The results in Fig. 6.3 show, that a longer etching time $t^{\prime}$ increases the difference in $\delta^{\prime}$ between spherical, cylindrical and Cartesian geometry. This increase in time $t^{\prime}$ can be caused by an increase in $D$ or a decrease in $\delta_{0}$, which is the plated radius of the structures before etching as shown in Fig. 6.1.


Fig. 6.3 Simulated results of the location of the boundary $\delta^{\prime}=\delta / \delta_{0}$ depending on the etch time $t^{\prime}$. The green line denotes Cartesian geometry, the red line cylindrical geometry and the blue line spherical geometry. The inset shows the concentration $c^{\prime}=c / c_{0}$ depending on the location $r^{\prime}=r / \delta_{0}$ for spherical symmetries at different times, which are marked as black circles. The location of the boundary for each time is marked as black line in the inset. The used parameter is $\beta=1$.

The etch rates for different geometries are compared by choosing a specific displacement of the boundary ( $\delta^{\prime}$ end $=0.1$ ) and investigating the time, which is necessary to etch this displacement for each geometries $\left(t^{\prime}{ }_{C}, t^{\prime}{ }_{c y}, t^{\prime}{ }_{s}\right)$.

Figure 6.4 shows the etching time required to etch the structures down to $10 \%$ of their initial size or radius. The difference in etching time becomes larger for increasing values of $\beta$, which is also shown in the inset by the ratio between etching times for cylindrical $\left(t^{\prime}{ }_{c y}\right)$ and spherical $\left(t{ }_{s}{ }_{s}\right)$ geometries. Therefore, increasing $\beta$ is beneficial to increase the selectivity between the etching of half-cylindrical fingers and half-spherical background plating. An increase in $\beta$ can be achieved simply by decreasing the concentration of the active etchant species.


Fig. 6.4 Simulated results of the etching time $t^{\prime}$, to obtain $\delta_{\text {end }}^{\prime}=0.1$ depending on $\beta$. The green line denotes Cartesian geometry, red line cylindrical geometry and blue line spherical geometry. The inset shows the ratio between the etch time for cylindrical and spherical symmetry depending on $\beta$.

### 6.1.5 Inclusion of reaction limited etching

In case the etching system is neither diffusion-limited nor reaction-limited, the surface reaction rate [process (ii)] as well as the transport process (i) are both influencing the etch rate. In this case the constant boundary condition at the surface [Eq. (6.4)] is not valid anymore. Instead, the rate of the surface reaction needs to be considered, which is proportional to the flux of the active etching component at the surface:

$$
\begin{equation*}
\left.D \frac{\partial c}{\partial r}\right|_{r=\delta(t)}=k_{s} c \tag{6.19}
\end{equation*}
$$

where $k_{s}$ is the rate constant of the etchant-metal reaction. The rate constant is generally depending on the temperature of the system and other parameters (e.g. crystal orientation) [137]. In case of a large $k_{s}$, the surface reaction happens very quickly and the active etchant species reacts almost instantaneously at the surface. Therefore, large $k_{s}$ reassemble the case of diffusion-limited reactions with boundary condition defined by Eq. (6.4). In case of a very small $k_{s}$ the reaction is reac-tion-limited.

Using the scaling of Eqs. (6.7) and (6.8) as well as the boundary immobilisation of Eq. (6.14), the boundary condition [Eq. (6.19)] becomes:

$$
\begin{equation*}
\left.\frac{\partial c^{\prime}}{\partial r^{*}}\right|_{r^{*}=1}=k_{s}^{\prime} \frac{\delta^{\prime}}{r^{* 2}} c^{\prime} \tag{6.20}
\end{equation*}
$$

with $k_{s}^{\prime}=k_{s} \delta_{0} / D$. In this case the equation system consisting of Eqs. (6.15), (6.16), (6.18) and (6.20) contains the two parameters $\beta$ and $k_{s}^{\prime}$.

Again, simulations were performed for cylindrical and spherical geometries to obtain the ratio of the etch rates. Figure 6.5 shows the contour plot of the relative time required to reduce the radius of cylindrical and spherical geometries by a factor of ten as a function of $\beta$ and $k^{\prime}$.


Fig. 6.5 Contour plot of the relative etching time required for obtaining $\delta_{\text {end }}^{\prime}=0.1$ for cylindrical geometries $\left(t_{c y}^{\prime}\right)$ versus spherical geometries $\left(t_{s}^{\prime}\right)$ as function of $\beta$ and $k_{s}^{\prime}$.

The results in Fig. 6.5 show that the relative difference is largest for large values of $k_{s}$ and large values of $\beta$. This indicates that it is beneficial to choose an etching solution that is diffusion-limited in order to achieve the maximum selectivity in etching of background plating over etching of the metal grid i.e. a low etchant concentration and a fast surface reaction. The reaction-limited case with small
values of $k_{s}$ and small values of $\beta$ does not show any selectivity and thus cannot be used for selective removal of background plating.

### 6.2 Experimental results

In this section the model of the previous section is compared to experiments conducted on plated Si wafer solar cells (Sec. 6.2.1). The removal of background plating will be demonstrated for the application on finished solar cells with silver (Sec. 6.2.2) or copper (Sec. 6.2.3) plated metallisation.

### 6.2.1 Removal of background plating compared to the model

Solar cells identical to those of Sec. 5.2 were prepared. The solar cells featured background plating distributed across the whole wafer. The dimensions of background plating and fingers were measured with a confocal microscope (LEXT, Olympus). The model assumes half-cylindrical geometries for the fingers, however the true geometry of the finger is an intermediate geometry between halfcylindrical and Cartesian due to the opening width $w_{L}$. For example, the width of the fingers was measured to be $60 \pm 2 \mu \mathrm{~m}$ but the height was measured to be only $12 \pm 1 \mu \mathrm{~m}$. Therefore, the height was used to compare the etching of the structures at different etching times, since it better resembles the radius.

One solar cell was cut into small pieces which were etched in two nitric acid $\left(\mathrm{HNO}_{3}\right)$ solutions containing $60 \mathrm{wt} \% \mathrm{HNO}_{3}$ or $30 \mathrm{wt} \% \mathrm{HNO}_{3}$. The etching reaction of Ag in a $\mathrm{HNO}_{3}$ solution is described as follows:

$$
\begin{equation*}
3 \mathrm{Ag}+4 \mathrm{HNO}_{3} \rightarrow 3 \mathrm{AgNO}_{3}+\mathrm{NO}+2 \mathrm{H}_{2} \mathrm{O} \tag{6.21}
\end{equation*}
$$

The pieces were immersed in the solutions at room temperature. After each time step the samples were taken out of the solution, rinsed with DIW, and measured with a confocal microscope. This was repeated until most of the background plating was not visible anymore with the bare eye. Figure 6.6 shows the measured height of the fingers and background plating for $60 \mathrm{wt} \% \mathrm{HNO}_{3}$ and $30 \mathrm{wt} \% \mathrm{HNO}_{3}$ solutions after each time step.


Fig. 6.6 Measured heights $\delta$ normalised to the starting height $\delta_{0}$ of plated structures as a function of the etching time $t$ for different $\mathrm{HNO}_{3}$ concentrations. Blue denotes fingers and orange denotes background plating. The solid lines were fitted based on the model in Sec. 6.1.3 and the dashed lines based on the model in Sec. 6.1.5. The parameters are shown in Table 6.1.

The heights were normalised to the respective starting height in Fig. 6.6. The etching rate in $60 \mathrm{wt} \% \mathrm{HNO}_{3}$ was much faster as the etching rate in $30 \mathrm{wt} \% \mathrm{HNO}_{3}$. The difference between the height of background plating and height of fingers increased more strongly for the $30 \mathrm{wt} \% \mathrm{HNO}_{3}$ and the difference in height at the last time step was largest. The ratio between normalised height of finger and height of background plating at the last step was $\sim 4$ for the $30 \mathrm{wt} \% \mathrm{HNO}_{3}$ and $\sim 2$ for the $60 \mathrm{wt} \% \mathrm{HNO}_{3}$. The values of $\beta$ for these structure and etchant combinations were calculated using the molar concentrations of $\mathrm{HNO}_{3}$, the molar mass of Ag and the density of Ag , see Table 6.1 . The table also shows the fitting parameters used for the fits in Fig. 6.6.

Table 6.1 Molar concentration and fitting parameters for the fits in Fig. 6.6. $\left(M_{m o l, A g}=108\right.$ $\mathrm{g} / \mathrm{mol}, \rho_{D, A g}=10.5 \mathrm{~g} / \mathrm{cm}^{-3}, \mathrm{~m}=3$ ).

|  | $\boldsymbol{C}_{0, \mathrm{HNO}}^{3}$ <br> [ $\mathrm{mol} / \mathrm{L}$ ] | $\boldsymbol{\beta}$ | $D / \delta_{0}^{2}[\mathrm{~s}]$ | $\boldsymbol{k}_{s}^{\prime}$ |
| :---: | :---: | :---: | :---: | :---: |
| $30 \mathrm{wt} \% \mathrm{HNO}_{3}$ (solid lines) | $5.6 \mathrm{~mol} / \mathrm{L}$ | 50 (calc.) | 0.15 (fitted) | - |
| $60 \mathrm{wt} \% \mathrm{HNO}_{3}$ (solid lines) | $13 \mathrm{~mol} / \mathrm{L}$ | 25 (calc.) | 1.1 (fitted) | - |
| $60 \mathrm{wt} \% \mathrm{HNO}_{3}$ (dashed lines) | $13 \mathrm{~mol} / \mathrm{L}$ | 25 (calc.) | 17 (fixed) | 0.12 (fitted) |

The time scaling factor $\left(D / \delta_{0}^{2}\right)$ was used as fitting parameter for the solid lines. The fits were not able to represent the measured data for $60 \mathrm{wt} \% \mathrm{HNO}_{3}$ well, i.e. a significant difference remained between measured and simulated values. Additionally, the diffusion coefficient of $\mathrm{HNO}_{3}$ in water is reported to be around $3 \times$ $10^{-5} \mathrm{~cm}^{2} / \mathrm{s}$ [145]. This would lead to a time scaling factor of 30 s for these experiments, which is much longer than the values extracted from the experiment. Therefore, it is assumed that the etching process is not diffusion-limited in this case. Instead the transport of etching products from the surface may be the limiting step.

The simulations were repeated for $60 \mathrm{wt} \% \mathrm{HNO}_{3}$ considering the surface reaction rate and the transport of etching products from the surface. The diffusion rate of $\mathrm{AgNO}_{3}$ in aqueous $\mathrm{HNO}_{3}$ is reported to be $1.71 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}$ at room temperature [146], which leads to a time scaling factor of 17 s . The application of these parameters to the simulations resulted in a better fit of the measured data for $60 \mathrm{wt} \%$ $\mathrm{HNO}_{3}$. Here, the reaction rate at the surface was used as fitting parameter as shown in Table 6.1. Overall a good agreement between the measurements and the simulations was obtained, considering the very complex process of metal etching (e.g. re-adsorption of the metal at the surface or gas formation during etching).

The experiment was repeated for a $30 \mathrm{wt} \% \mathrm{HNO}_{3}$ solution which was heated up to $40^{\circ} \mathrm{C}$. In this case the ratio between height of finger and height of background plating increased even faster and was measured to be 4.8 at the end of the experiment. The higher temperature increases both the surface reaction rate as well as the diffusion rate. However, the increase in surface reaction rate was stronger, resulting in a higher selectivity for etching the background plating.

### 6.2.2 Removal of background Ag plating for multicrystalline Si wafer solar cells

Solar cells similar to those of Sec. 5.2 were used for this experiment. A water based metal etch solution containing $38 \mathrm{wt} \%$ phosphoric acid, $24 \mathrm{wt} \%$ nitric acid and $9 \mathrm{wt} \%$ acetic acid was prepared for the etching of the background plating of the full-area solar cells. Of all solutions investigated in this work, this solution resulted in the best results concerning etch time and selectivity. The front surface of each solar cell was immersed in the solution for 90 s at room temperature. The one-Sun solar cell $I-V$ parameters were measured before and after etching.

Figure 6.7 shows that the etching of background plating increased the $J_{S C}$ (by $0.9 \mathrm{~mA} / \mathrm{cm}^{2}$ ) but reduced the $F F$ (by $0.9 \%$ absolute) of the solar cells. Overall, the median efficiency of these 8 solar cells increased by $0.2 \%$ absolute. A linear correlation between the $J_{S C}$ and the metallised area is observed as also discussed in in Sec. 5.2.4.


Fig. 6.7 Boxplots of the measured $J_{S C}$ and $F F$ at one-Sun condition of all solar cells, as a function of the metallised area $A_{m}$ as percentage of the solar cell area, before and after etching of background plating. The metallised area was determined by the method described in Appendix C.

Figure 6.8 shows an image of a typical solar cell before and after application of the etching process. Large parts of the background plating (especially at grain boundaries) were removed. However, the metal fingers were also attacked by the etching solution.


Fig. 6.8 Images of a typical solar cell (a) before $A_{m}=(12 \pm 2) \%$ and (b) after $A_{m}=(7 \pm 2) \%$ etching of the background plating. The image was obtained using a standard flatbed scanner.

Table 6.2 shows a comparison of the one-Sun solar cell $I-V$ parameters as well as the finger geometries, grid and background plating area of the solar cell of Fig. 6.8 before and after etching. The grid area $\left(A_{G r i d}\right)$ as percentage of the solar cell area was calculated from the finger width and the background plating area $\left(A_{B P}\right)$ as
percentage of the solar cell area was calculated by the difference between meas$\operatorname{ured} A_{m}$ and $A_{\text {Grid }}$.

Table 6.2 Finger width, finger height, calculated grid area, area of background plating and oneSun solar cell $I-V$ parameters of the solar cell of Fig. 6.8 before and after etching of the background plating.

|  | $\begin{aligned} & \begin{array}{l} w_{F} \\ {[\mu \mathrm{~m}]} \end{array} \\ & \hline \end{aligned}$ | $\begin{aligned} & \begin{array}{l} \delta_{0} \\ {[\mu \mathrm{~m}]} \end{array} \\ & \hline \end{aligned}$ | $A_{\text {Grid }}[\%]$ | $A_{B P}[\%]$ | $\begin{aligned} & \begin{array}{l} V_{o C} \\ {[\mathrm{mV}]} \end{array} \\ & \hline \end{aligned}$ | $\begin{aligned} & \begin{array}{l} J_{S C}[\mathrm{~mA} / \\ \left.\mathbf{c m}^{2}\right] \end{array} \\ & \hline \end{aligned}$ | FF [\%] | $\eta$ [\%] |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Before | $56 \pm 2$ | $8 \pm 1$ | $6.5 \pm 0.2$ | $6 \pm 2$ | 618 | 33.0 | 77.0 | 15.7 |
| After | $47 \pm 2$ | $7 \pm 1$ | $6 \pm 0.2$ | $1 \pm 2$ | 619 | 34.3 | 75.8 | 16.1 |

The increase in $J_{S C}$ of $1.3 \mathrm{~mA} / \mathrm{cm}^{2}$ is mainly due to the decrease in $A_{B P}$ of $\sim 5 \%$ absolute. The finger width decreased by roughly $9 \mu \mathrm{~m}$, and the finger height by 1 $\mu \mathrm{m}$. This decrease accounted for the full $F F$ loss of $1.2 \%$ absolute as determined from simulations using the programme Gridmaster [147]. The $V_{O C}$ did increase by 1 mV . Overall, the efficiency of the solar increased by $0.4 \%$ absolute, mainly due to the increase in $J_{S C}$.

Figure 6.9 shows outlines of the metallised structures obtained from microscope images after different etch times. After an etch time of 30 s most of the background plating was already removed. Only larger particles or connected areas of background plating remained. The width of the finger decreased from $59 \mu \mathrm{~m}$ to 55 $\mu \mathrm{m}$, and the height of the finger decreased slightly from $6 \mu \mathrm{~m}$ to $5.7 \mu \mathrm{~m}$. After etching for another 30 s the background plating had vanished completely for this particular area. At this time the finger width was measured to be $50 \mu \mathrm{~m}$, while the finger height was measured to be $4.8 \mu \mathrm{~m}$. Further etching of another 30 s or 60 s reduced the finger width and height further. The average etch rate was measured to be about $10 \mu \mathrm{~m} / \mathrm{min}$ for the width and $1 \mu \mathrm{~m} / \mathrm{min}$ for the height of the metal fingers.


Fig. 6.9 Outlines of a finger and background plating as determined from microscope images. The colour of the lines indicates the etching time as shown in the image.

### 6.2.3 Removal of background Cu plating for multicrystalline Si wafer solar cells

A multicrystalline p-type Si solar cell precursor with an Al-LBSF on the rear surface and with a size of $156 \times 156 \mathrm{~mm}^{2}$ was used for this experiment. The solar cell precursor was obtained from a different source which used different materials and processes, resulting in a higher efficiency of the solar cells. Laser openings were performed by means of LCP , which was followed by inline Ni and Cu plating at the plating facility at Fraunhofer ISE.

After plating, the solar cell was immersed in an etching solution containing $38 \mathrm{wt} \%$ phosphoric acid, $24 \mathrm{wt} \%$ nitric acid and $9 \mathrm{wt} \%$ acetic acid (as also used for the Ag etching in the previous section). However, Cu is etched faster than Ag ; therefore, the etching time was adjusted to 18 s (at room temperature). An Ag capping layer was plated onto the Cu after the removal of the background plating, to avoid corrosion of the Cu . Table 6.3 shows the one-Sun solar cell $I-V$ parameters before etching, after etching, and after plating of the capping layer.

Table 6.3 One-Sun solar cell $I-V$ parameters before and after etching of background plating and after plating of the Ag capping layer.

|  | $\boldsymbol{V o c}[\mathrm{mV}]$ | $\boldsymbol{J}_{\boldsymbol{S C}}\left[\mathbf{m A} / \mathbf{c m}^{2}\right]$ | $\boldsymbol{F F}[\%]$ | $\boldsymbol{\eta}[\%]$ |
| :---: | :---: | :---: | :---: | :---: |
| Before etching | 644.5 | 36.0 | 76.7 | 17.8 |
| After etching | 644.0 | 36.5 | 74.3 | 17.5 |
| After Ag capping | 646.2 | 36.4 | 76.6 | 18.0 |

Before etching, the $J_{S C}$ of the solar cell was relatively low due to the presence of background plating. Removal of (most of) the background plating increased the $J_{S C}$ by $0.5 \mathrm{~mA} / \mathrm{cm}^{2}$; however, the $F F$ decreased by $2.4 \%$ absolute as large parts of the metal grid were removed by the etching process. It is evident, that the etching process was not optimised for Cu . However, the subsequent plating of the Ag capping layer increased the conductance of the fingers again and consequently also the $F F$. The $J_{S C}$ did not increase significantly after the capping layer plating. Apparently, a sufficient amount of background plating was etched off, such that also the re-occurrence of background plating was reduced. This could be due to e.g. a possible lower plating rate of Ag on Ni than on Cu . Overall the $J_{S C}$ was increased by $0.4 \mathrm{~mA} / \mathrm{cm}^{2}$ while the $F F$ was reduced by $0.1 \%$ absolute, resulting in an efficiency gain of $0.2 \%$ absolute in this experiment. It seems that the $V_{O C}$ of the solar cell was also increased during plating of the capping layer. The underlying reason for this $V_{O C}$ improvement is still unknown.

### 6.3 Chapter summary

This chapter introduced a new method for removing background plating after a plating process. The removal of background plating is based on a wet-chemical etching process, for which a 1D diffusion model was derived. Simulation results of the model showed that background plating can be etched selectively due to the half-spherical geometry of the background plating in comparison to the half-
cylindrical geometry of the fingers or the flat geometry of the busbars. An increase in etching time or decrease in etchant concentration can be used to increase the selectivity of the etching of background plating. Additionally, the influence of the reaction rate at the etchant-metal surface was considered in the model. A faster reaction at the surface increased the selectivity of background plating. Experiments were carried out with nitric acid solutions and silver. The results of the model were fitted to the measurements and showed, overall, good agreement.

Two possible applications of the background plating removal process were shown. Firstly, background plating was removed from finished solar cells with Ag plated front contacts. These solar cells, which had a significant level of background plating, exhibited a median increase in short-circuit current density of $0.9 \mathrm{~mA} / \mathrm{cm}^{2}$ due to the removal of the background plating. This increase in short-circuit current density yielded an increase of the median efficiency by $0.2 \%$ absolute.

Secondly, the etching of background plating was applied after an intermediate plating step. A similar improvement in $J_{S C}$ was observed (and which was not negated by the subsequent plating of the capping layer). Overall, the efficiency of the large-area multicrystalline Si solar cell was improved from $17.8 \%$ to $18.0 \%$ by application of the intermediate background plating removal process.

The results of this chapter have led to the following patent:
M. Heinrich, M. Lieder, M. Kamp, M. Glatthaar and A. Kraft, "Verfahren zur selektiven Entfernung von Ghostplating auf Siliziumsolarzellen" (Method for the selective removal of ghostplating on silicon solar cells); German patent application: DE102014211227.3, June 2014

## 7 Summary and Outlook

### 7.1 Summary

The aim of this work was a thorough investigation of the fabrication and characterisation of laser-doped regions relevant for crystalline silicon wafer solar cells.

The first focus was on the accurate characterisation of laser-doped areas by potential drop sheet resistance measurements. A new method, the line resistance measurement method, was proposed to obtain sheet resistance measurements on smallscale laser-doped areas. This new method enables measurements of the sheet resistance of laser-doped lines in a wide sheet resistance range.

The application of four-point probe sheet resistance measurements was investigated for different "non-ideal" conditions of the laser-doped areas that could potentially affect the accuracy of the measurements. "Non-ideal" conditions mean samples with a small size, inhomogeneous depth and resistivity, surface roughness, and the presence of a non-conductive coating. It was shown that each of these conditions can be a source of error for sheet resistance measurements. However, the error can be overcome if certain precautions are met, as described in Chapter 3.

It was also shown that sheet resistance measurements of large-scale laser-doped areas can be used to obtain the sheet resistance value of small-scale laser-doped
areas, and vice versa. This is possible by considering the method of laser pulse density for a pulsed laser, and the density of passes for a continuous-wave laser.

The second part of the thesis investigated the laser doping efficiency as a function of the single pulse laser fluence, dopant flux and laser pulse density. It was shown that an infinite dopant flux does not suffice to describe the sheet resistance as a function of the single pulse laser fluence. The introduction of a finite dopant flux significantly reduced the differences between the simulations and the experimental results. It was also suggested that higher-order effects, such as the temperature dependant diffusion coefficients, need to be considered in the model to obtain accurate values for the sheet resistance for different single pulse laser fluences.

The laser pulse density was included in another model describing the dopant depth profile or sheet resistance as a function of the number of laser pulses. It was shown that this extended model accurately describes the sheet resistance and dopant depth profiles as a function of the laser pulse density.

The influences of the laser doping parameters on the one-Sun solar cell efficiency were investigated for an industrially feasible process flow, which included an industrial feasible emitter and plating as metallisation method. The influence of a selective emitter structure was investigated for different laser doping parameters. It was found that the laser-induced damage leads to high recombination within the laser-doped regions, which reduces the solar cell efficiency. Therefore, the laser doping in this work was not optimised in order to obtain a more highly doped se-
lective emitter, but to reduce the laser-induced damage. This was possible because plating is able to form an ohmic contact with lowly doped emitters which are not contactable with the screen printing method. An increase in open-circuit voltage of 6 mV was obtained compared with conventional screen-printed solar cells, by using laser doping with minimised damage on an industrially relevant lowly doped homogeneous emitter. However, the overall efficiencies of all laser doped samples fabricated in this thesis were reduced by background plating.

In the final part of the thesis, a new method was developed to remove background plating. The method is based on the different etching rates for different geometries. Background plating on c-Si solar cells is usually a half-sphere, while the metal fingers are approximately described by a half-cylinder. This difference in geometry has a significant influence on the etching time required for complete removal of the structure. A model was developed which shows that spherical geometries can be etched more than three times faster than cylindrical geometries. The developed etching process was successfully applied to several solar cell samples, resulting in a significant efficiency increase.

### 7.2 Outlook

Sheet resistance measurements can be developed further, by considering inhomogeneous areas. In the case of line resistance measurements, it may be possible to obtain the sheet resistance of the laser-doped lines even when a parallel conductor -such as a doped layer or a conductive coating - is present. The key factor for this method is a precise knowledge of the measurement geometry. Another possible
development is the detection of interruptions of a large-scale pattern by using four-point probe measurements at different rotational angles.

In addition to the sheet resistance, the method of laser pulse density may be used to indirectly measure other properties of small-scale laser-doped areas. Nonlocalised properties such as the dopant depth profile or the defect densities may also be expressed in terms of the laser pulse density.

Future work on the relevant parameters influencing laser doping may focus on the dopant flux. So far only macroscopic models for diffusion into liquid silicon during laser doping exist. However, a microscopic model describing how dopant atoms such as phosphorous, boron or other atoms are incorporated into a substrate during laser doping is still missing.

The minimisation of laser-induced damage in solar cell processing can also be achieved by using a different laser setup. Future work may employ different laser systems such as an ultraviolet picosecond or femtosecond laser, which are able to ablate the dielectric on the front surface without significantly affecting the underlying silicon. However, a selective emitter may still be beneficial - or even necessary - in cases where the metallisation method is not able to form an ohmic contact with the emitter. In these cases a heavily doped emitter, which can be optimised by employing sheet resistance measurements, can be used. Additionally, certain technological restrictions may require deep diffused selective emitters such as the adhesion of plated contacts. The prevention of annealing-induced shunts may be necessary to achieve sufficient contact adhesion for photovoltaics module
manufacturing using plated solar cells. These annealing-induced shunts can be prevented by using a deep-diffused selective emitter.

The etching solutions for the removal of background plating could be improved regarding their selectivity in future work. The development of an etching solution could be optimized regarding a fast surface reaction, low diffusivity, and the prevention of the re-attachment of the etched metal to the surface.

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## Appendix A: Accurate dopant depth profile measurements with ECV

The ECV method as introduced in Sec. 2.4.1 measures the dopant depth profile by stepwise etching of material and subsequently measuring the capacitance-voltage curve at each etching step. Both, the etch rate as well as the capacitance-voltage measurement depend on the contact area between sample surface and electrolyte. The contact area is influenced by the sealing ring geometry and the surface morphology of the sample. Furthermore, the etch rate is influenced by the number of valence electrons (i.e. the valence) of the sample material. The valence is the number of open bonds for an atom of the material and is equal to 4 in the case of single-atom Si . However, in a Si crystal the valence is highly affected by the presence of defects such as dislocations and grain boundaries and it is generally $v<4$.

A common method to consider the influences from the contact area and the valence is to calibrate the ECV measurement with the $R_{s h}$ determined by the 4PP technique. The $R_{s h}$ is inversely proportional to the concentration of dopants in the volume measured by the ECV. The conversion between $R_{s h}$ and dopant concentration is done by a standard mobility model [115]. The values for contact area or valence are then adjusted to obtain the measured sheet resistance from the ECV dopant profile. However, dopant inhomogeneities and defects can lead to a deviation between $R_{s h}$ and ECV measurement of up to 10-20\% [148]. Additionally, 4PP
measures only the electrically active dopant atoms, while ECV measures electrically active and inactive substitutionally incorporated dopant atoms [71].

Another well-known method to calibrate ECV measurements is to directly measure both the contact area and the total depth of etching. However, this can be challenging on uneven surfaces, as commonly observed after LCP laser doping. Figure A. 1 shows a scanning electron microscope (SEM) image of a typical LCP laserdoped area on an acid-textured multi-Si wafer. The surface morphology of the la-ser-doped area is clearly different from the original surface, due to local melting and recrystallisation of Si .


Fig. A. 1 SEM micrograph of a LCP laser-doped area on an acid textured multi-Si wafer.

To calibrate the ECV dopant depth profiles, the following quantities should be known:

- Geometrical area: The geometrical area is the area enclosed by the sealant ring. For perfectly flat samples it determines the contact area between electrolyte and sample.
- Surface area factor: The surface area factor (SAF) describes the effective increase of the surface area for uneven samples. For example the SAF is 1.73 in the case of alkali-textured monocrystalline (100) Si. However,
multi-Si wafers have an irregular surface texture, thus the SAF needs to be measured experimentally before ECV etching. The SAF also changes during the etching due to the rounding of sharp corners.
- Etch depth: The etch depth is the total depth of the ECV etch cone. In order to obtain the overall depth on uneven surfaces, height profiles are measured before and after etching with a stylus profiler. The "after etching" height profile was aligned to the "before etching" height profile by adjusting the location and direction of profiling according to marks on the sample surface with the help of a microscope. The difference between the two profiles reveals the actual etch depth as shown in Fig. A.2. To improve the accuracy of this method, an average of multiple measurements were used. This method was found to be crucial in obtaining an accurate etching depth for wavy or uneven surfaces, especially if the etching depth is in similar range as of the surface roughness.


Fig. A. 2 Height profiles obtained before and after an ECV measurement (upper part). For clarity the difference $\Delta$ between the two measurements is plotted in the lower part. The red lines represent the average height of each section. The etch depth is measured as difference between the red lines.

ECV measurements can give accurate dopant depth profiles in excellent agreement with SIMS on laser-doped multi-Si samples, provided an appropriate calibration method is used such as using the surface area and the etched depth. Calibrations using 4PP measurements were shown to have an uncertainty of up to 10 20\%.

The results of this section have led to the following publication:

1. M. Heinrich, H. Hidayat, Z. Hameiri, B. Hoex and A. G. Aberle, "Dopant profiles of laser-doped multicrystalline silicon wafers from electrochemical capacitance-voltage measurements," Proc. 27th European Photovoltaic Solar Energy Conference and Exhibition, Frankfurt, Germany 2012, vol. 2, pp. 1285-1288.

## Appendix B: Calculation of dual configuration

## correction factors

The correction factors for the $R_{s h}$ measurements using a 4PP in single mode can be calculated when the geometry of the sample and the probe locations are known. The calculation of these corrections factors was extensively studied previously [108-110]. In principal it is based on the method of image charges, where a virtual current source (or sink) of the same polarity and value is introduced at the same distance from a border as the actual current source (or sink). The resulting potential field will act as if there is a straight border at half way between the virtual and actual current sources (or sinks). This border resembles the boundary of the sample. A conformal coordinate transformation is used to obtain a single straight boundary for rectangular laser-doped areas. Here, the laser-doped area is mapped onto the upper half of the complex plane, with the real axis being the former outline of the area. Figure B. 1 shows an illustration of the conformal mapping in this case.


Fig. B. 1 Illustration of conformal mapping of a rectangular area onto the upper half plane of the complex plane. Certain points on the outline are marked to indicate the mapping.

Based on conformal mapping, a Python ${ }^{\text {tm }}$ code was written, which calculates the area correction factor for a rectangular area of arbitrary size and with any possible
probe location and rotation. First, a coordinate transformation is carried out, which performs the conformal mapping as illustrated in Fig. B. 1 for the coordinates of the probes and the rectangular area. Then the method of image charges is used to calculate current flow between the probes. The correction factor is obtained by using that a change in voltage is invariant under conformal transformation.

The written script offers a large freedom to vary the size of the sheet, probe placement and probe distance. Figure B. 2 shows one case study, where the probes are located in the centre of a square sample with varying size. The red line marks the calculated correction factors from the Python ${ }^{\text {tm }}$ code, while blue dots and black crosses mark the correction factors obtained in Ref. [108] and [149], respectively.


Fig. B. 2 Calculated $R_{s h}$ correction factor $\left(f_{l}\right)$ depending on the size $a$ of a square sample. The probe location, probe distance ( $s$ ) and sample geometry is shown in the inset. Red lines is the obtained correction factor from the code, blue dots denote the obtained correction factors of Ref. [108] and black crosses denote the obtained correction factors of Ref. [149]. The factor $f_{l}$ is given such that $f_{1}=F_{1} \ln (2) / \pi$ can be multiplied to $R_{s h}^{4 P P}$ to obtain the correct $R_{s h}$.

Figure B. 2 shows an excellent agreement between the results of the model and those from the references, therefore the code can be regarded as validated. The output of a 4PP setup already contains a correction factor for infinite areas $\left[\pi / \ln (2)\right.$, see Eq. (2.15)]. Therefore, the correction factor $f_{l}$ (with the voltage
probes are the inner two probes) is given such that it can be multiplied directly to the output of the 4PP to obtain the correct $R_{s h}$.

The code of the script was also extended to solve Eq. (3.5) to obtain the correction factor for dual configuration measurements on rectangular samples. Figure B. 3 shows an example of the results for a sample of the size $5 \times 156 \mathrm{~mm}^{2}$, which is typically used in this thesis.


Fig. B. 3 Calculated correction factors for sheet measurements depending on the rotation angle of a 4 PP , which has the probe distance of $s=1 \mathrm{~mm}$ and is set in the centre of a sample of the size $5 \times$ $156 \mathrm{~mm}^{2}$. Red lines denote the correction factor $1 / \chi$, green lines denote the correction factor $f_{l}$ (the voltage probes are the inner two probes) and blue lines denote the correction factor $f_{2}$ (voltage probes are one inner and one outer probe).

The results show that when using the dual configuration measurement method, the measured $R_{s h}$ is approximately the correct sheet resistance and the correction factor is not necessarily needed. However, using a single probe configuration on this sample type a correction factor needs to be applied according to the probe rotation. Again, the correction factors $1 / \chi, f_{1}$ and $f_{2}$ are given such that they can be multiplied directly to the output of the 4PP to obtain the correct $R_{s h}$.

## Appendix C: Determination of metallised area

To evaluate background plating over a large area, a digital image of the front surface of a solar cell was obtained by scanning the solar cell with a high resolution scanner. The image was then processed with an image processing algorithm yielding the ratio of metallised area to the full-area of the cell.

The image processing algorithm was developed using a Python ${ }^{\text {tm }}$ script. The algorithm used only the red colour channel of the image to detect metallisation since it offers the highest contrast between the $\mathrm{SiN}_{\mathrm{x}}$ dielectric coating and the metallised areas. The outline of the cell was detected in order to calculate the full-area of the cell. An adaptive thresholding algorithm was used to remove slight inhomogeneities in the scanned image from non-homogeneous lightning or non-homogeneous colour of the $\mathrm{SiN}_{\mathrm{x}}$ film e.g. from different grains on multicrystalline Si. The adaptive thresholding algorithm calculated the local mean value of a neighbourhood area. The neighbourhood was then subtracted by the local mean value. The result was an image, where isolated bright spots were enlarged but small differences in the background were reduced. A fixed threshold was then applied to differentiate between the areas with $\operatorname{SiN}_{\mathrm{x}}$ and the metallised areas. The metallised areas were then used to calculate the ratio between metallised areas and full-area of the cell.

Figure C. 1 compares a scanned image including an overlay of a detected image (left) and a microscope image (right) at the same location. The scanned image results in a blurred version of the microscope image due to the lower resolution. However, the detection algorithm is able to detect most of the background plating,
correctly. Overall background plating can be detected with a diameter of $10 \mu \mathrm{~m}$ or above. Only very small or darker background plating are not always detected, correctly.


Fig. C. 1 A scanned image including an overlay of a detected image (left) is compared to a microscope image (right). Both images were obtained at the same location of the wafer.


[^0]:    ${ }^{1}$ Proven reserves are considering reserves which are recoverable under existing economic and operating conditions and with existing technology. Unconventional oil such as tar sands or shale oil, are mainly unproven reserves. When the oil price increases more and more unconventional oil reserves become proven reserves since a higher operational break-even price can be maintained [150].

[^1]:    ${ }^{2}$ The work of Prof. Michael Klare may be named as an example here. In various books such as The Race for What's Left (2012) or Resource Wars (2001) he analyses conflicts in perspective of securing natural resources.
    ${ }^{3}$ The more and more challenging search for oil has created larger risks for humanity as observed in a recent example: The Deepwater Horizon oil spill caused extensive damage to nature in the Gulf of Mexico (http://www.oilspillcommission.gov).
    ${ }^{4}$ Nuclear power generation has a very high risk for humanity, e.g., the Chernobyl disaster is widely considered as worst nuclear power accident to date. The catastrophe exposed people as well as the surrounding area to high amounts of radiation, causing deaths and widespread contamination

[^2]:    (http://chernobyl.info). A more recent example is the disaster in Fukushima (http://www.world-nuclear.org/info/safety-and-security/safety-of-plants/fukushima-accident/).
    ${ }^{5}$ To name a few examples: Office of Energy Efficiency and Renewable Energy from the US Department of Energy (http://www.eere.energy.gov), the Desertec Foundation (http://www.desertec.org), the Golden Sun project from the national energy board of the People's Republic of China (http://www.china.com.cn/policy/txt/2009-07/23/content_18186602.htm).
    ${ }^{6} \mathrm{http}: / / w w w . a g-e n e r g i e b i l a n z e n . d e ~$
    ${ }^{7}$ http://www.bmwi.de/DE/Themen/Energie/Erneuerbare-Energien/eeg-reform.html

[^3]:    ${ }^{8}$ http://www.jandel.co.uk/products/four-point-probes.html

[^4]:    ${ }^{9}$ The sample is not symmetrical anymore after laser doping, which is a necessary assumption for Eq. (2.19). However, since the treated area was less than $5 \%$ of the total area, the assumption of a symmetrical sample may still be used.

[^5]:    ${ }^{10}$ One solar cell exhibited a $V_{O C}$ of 619 mV . This solar cell featured severe scratches on the front surface, which caused an overall lower $V_{O C}$.

