USE OF THESES

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Capturing the spectra of solar cells

Helmut Mäckel

A thesis submitted for the degree of Doctor of Philosophy of The Australian National University

December, 2004
Physics as art...

ideality factor as a function of voltage at different temperatures
Declaration

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any published or written by another person except where due reference is made in the text. The work in this thesis is my own, except for the contributions made by others as described in the Acknowledgements.

Helmut Mäckel
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My parents deserve a special mention for encouraging me to study in this country on the other side of the globe. Finally, I would like to express my warmest gratitude to my girlfriend Cinthia for providing an invaluable support and for putting up with me over the last few months of being more a phantom than a partner!
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Abstract

In broad terms, this thesis explores unchartered territory in solar cell characterisation and proposes several new techniques based on the spectral, injection and temperature dependence of three measurable parameters: short-circuit current, open-circuit voltage, and photoconductance. The work in this thesis is a thorough study of all facets of these techniques and their comparison to existing diagnostic tools. The thesis proves the validity of these techniques through theoretical derivations and computer simulations, and illustrates their applicability with a broad range of experimental devices.

The spectral response of the short-circuit current has significant explanatory power in disclosing recombination processes. Its measurement is used to reveal some of the most important device characteristics, among them the diffusion length, surface recombination velocity and emitter quantum efficiency. Spectral responsivity measurements are generally performed using a small signal technique and a cost-intensive lock-in detection. In this thesis, a novel approach to spectral response measurements is presented: the quasi-steady-state short-circuit current response (QSS\textsubscript{sc}$\lambda$). It employs large signals and cost-effective data-acquisition. Thus, in technical aspects, it stands out for its very simple design. Measurements of a wide range of different solar cell structures showed an excellent agreement with the conventional method. QSS\textsubscript{sc}$\lambda$ could therefore prove useful as an alternative diagnostic tool to the traditional technique.

The spectral response of the open-circuit voltage is a concept that was not deemed to be important in the past. The surface photovoltage technique (SVP) harnesses the colour sensitivity of the voltage in order to determine the diffusion length. However, the voltage response has only been used as a tool to extract the diffusion length, whilst no importance has been attached to its own meaning. In this work we show analytically, with simulations and also experimentally, that the spectral photovoltage perfectly mimics the characteristics of the spectral photocurrent. The technique devised for this purpose, the quasi-steady-state voltage response (QSSV\textsubscript{oc}$\lambda$), also uses large light intensities and a simple data acquisition. The distinct advantage of the new method over the spectral photocurrent method is its applicability directly after junction formation. It out-competes SPV in the sense that it offers the possibility of studying devices under real operating conditions. The similarity of the current and voltage responses provided the impetus to
extend models used to analyse the spectral photocurrent to the voltage case. In particular, two models not previously employed in the SVP technique, the model of Isenberg and the model for rear-illuminated cells, could gain a great deal of importance in the quest to determine recombination parameters in silicon devices.

By adding temperature variation to the spectral response of the short-circuit current, it becomes a technique for defect identification. This is rooted in the fact that the temperature dependence of the diffusion length can disclose valuable information about defects. The temperature dependent quantum efficiency of the current, $TQE_{J_{sc}}$, takes advantages of this property. We enrich the range of spectroscopic tools by studying the temperature dependent quantum efficiency of the voltage instead ($TQE_{V_{oc}}$). Additionally, this work sounds the potential of the white light QSSV$_{oc}$ method as a spectroscopic tool. The temperature and injection-level dependent voltage spectroscopy (TIVS) is the outcome of this idea. This work demonstrates that $TQE_{V_{oc}}$ is able to unveil defect properties equally as well as $TQE_{J_{sc}}$. TIVS, in contrast, has been found to be hampered by the difficulty of predicting the bulk lifetime from the open-circuit voltage.

The spectral photoconductance is a versatile technique widely employed in the investigation of photodetectors. In solar cell research, the use of two different wavelengths was occasionally used to separate between surface and bulk recombination. This work aims to establish the spectral photoconductance ($QSSPC-\lambda$) as a valuable and powerful tool for device characterisation. The underlying measurement technique to detect the photoconductance, the quasi-steady-state photoconductance ($QSSPC$), outranks similar techniques for its simple design and cost-effective signal detection. In non-diffused silicon wafers, $QSSPC-\lambda$ offers the scope to separate between surface and bulk recombination and to act as a depth resolution of deeply injected defects. In emitter structures, the method promises to widen the realm of characteristic tools that trace the emitter quantum efficiency.
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Thesis motivation and outline

The most successful and beautiful mechanism in nature that uses solar energy is photosynthesis. It is the driving force to supply energy to plants, algae and cyanobacteria. In this process, light strikes a chlorophyll molecule inside the plant, which releases an electron. This electron is used as a source of energy to convert carbon dioxide into sugars. The electron is retrieved from a water molecule and channelled back to the chlorophyll molecule, which closes the cycle. The end products of the water dissociation are oxygen and hydrogen ions. The exciting characteristics of this cycle is the fact that the plant continuously replenishes the electrons that drive the conversion.

What has worked perfectly in nature in many organisms and for such a long time frame is certainly intriguing for any researcher who is seeking to find a source of renewable energy. Artificial photosynthesis has the potential to produce hydrogen or other energy-rich fuels from water in a clean, cheap and limitless way. Nonetheless, the exact nature of the electrochemical reactions behind the photosynthesis has been shrouded in mystery. What puzzled many researchers for a long time is the fact that the energy required to split water is much greater than any biological molecule can provide. Recently, researchers found the spatial arrangement behind the 'catalytic core' that is located in the chloroplast, the heart of the photosynthetic apparatus, and that is responsible for the splitting of water [1]. Still, exact knowledge of the chemistry inside the catalytic core has yet to be unearthed. This chemistry is pivotal in replicating nature's most successful energy conversion mechanism and until this is resolved, artificial photosynthesis will remain a dream.

In the meantime, the most intriguing artificial use of solar energy resides in photovoltaic (PV) and conversion. Together with this form of energy, solar thermal, hydropower, biomass and wind energy rank among the most promising renewable energy sources. The use of renewable energies compared to the world energy demand in 1998 was the following: hydropower ~ 2%, biomass ~ 12%, wind energy ~ 0.03% and solar energy ~ 0.02% [2]. The fraction of PV that contributed to the solar energy share was about 0.01%. Thus in total, clean energy supplies only account for ~ 14–15% of global primary energy use. This seems to be a minor fraction, but considering the small time frame renewable energy technologies have had available to mature, it is only fair to envisage their technical
potential in comparison to world energy utilisation. In this depiction, hydro power and the leading contestant, bio mass, were only able to cover about 12% and 68% of the total energy consumption in 1998 [2]. Wind energy, by contrast, possesses the technical means to provide for over 159% of world energy use. However, the most compelling prospect lies within solar energy: it has the technical potential to produce over 391% of world energy consumption.

![Learning curve of different energy sources comparing the installation costs with the cumulative installation](image.png)

**Figure 1:** Learning curve of different energy sources comparing the installation costs with the cumulative installation [3–8].

Another aspect for comparison is offered by so-called learning curves, which apply when a new product is launched on the market. Figure 1 illustrates the learning curves of renewable energy compared to fossil fuels and nuclear power. An experience curve depicts the fall of the product price as its production volume increases. In this case, it compares the installation costs in kW with the cumulative generation installed. The learning curve usually traverses two stages: Initially, the costs of the start-up of the company and the product development lead to high prices. Additionally, production volume at the beginning is low and the costs are spread over relatively few sold units. In case of photovoltaics, its employment was only financially attractive for niche applications like remote telecommunication transmitters or governmental-sponsored programs (satellites, weather monitoring stations). When the production expands, the costs drop according to economies of scale. The technology is soon within reach of wider markets, the demands grow and people can more easily afford the product. This is the first stage of the learning curve, where prices fall steadily. The second stage is reached, when there is only limited improvement available to lower costs or increase module efficiency. From then on, the re-
duction of prices is slowed down remarkably. This is shown by the kink in the experience curve. The slope of the curve is thus the crucial indicator for the cost reduction for every doubling of cumulative production.

As can be seen in Figure 1, renewable energy sources clearly perform poorer than fossil fuels. However, the decrease in construction costs of nuclear power and super saturated coal plants has almost come to a halt and the development of gas turbines stopped in 1980. The installation cost of wind turbines is clearly less than the costs of nuclear plants and has still potential for improvement even though the progress has slowed down. Solar cells have reached the cost of nuclear power, for both conventional wafers and thin films. Importantly, their development is still in an early stage and the phase of slowing progress might not be reached for a long time (indicated with dashed lines). In the long run, the installation costs of photovoltaics are likely to reach a level similar to wind energy. A further decrease seems possible since new PV technologies are emerging in pilot production or are under investigation: thin film cells, dye and organic cells, to name just a few [2]. The PV market is still expanding with an amazing 30% growth each year. If the operation, transport and waste costs are added to the depiction in Figure 1, the argument for renewables becomes more favourable. Fossil fuels have high operation and transport costs, which makes wind turbines competitive on the free energy market. This is not yet the case for photovoltaics, but as the learning curves indicates, there is plenty room for improvement.

So the market and the potential for photovoltaics certainly exist, but what are the arguments pro and contra for photovoltaics? One argument for PV is obviously the energy source: solar radiation is a vast and infinite energy supply. Within solar energy, solar thermal power plants are restricted to areas with high levels of direct insolation. Standard PV systems, conversely, convert diffuse and direct radiation with approximately the same efficiency and thus are not hampered by such site limitations [2]. Photovoltaics are able to convert sunlight directly into electricity, our most versatile form of energy, whereas solar thermal applications have to go through an indirect route to achieve the same.

PV certainly does not generate any combustion byproducts, radioactive fuel for disposal or noise, and most importantly: a very low CO₂ output [9]. CO₂ emissions of PV systems occur almost entirely during system manufacturing and not during system operation. Consequently, the emission rate depends on the emissions of the energy source supplied for the PV fabrication. At present, grid-connected PV-systems can supply energy at a CO₂ emission rate that constitutes only 5–13% of the emission rate of current fossil energy technologies [10]. This highlights the excellent potential of photovoltaics to reduce greenhouse gas emissions. Moreover, the goals in reducing CO₂ emissions to avoid
irreversible climate changes are so high that they are only socially acceptable if most fuel sources are replaced by PV and only partly by wind energy, biomass and solar thermal power [9].

One further advantage of PV is the energy pay-back time, which is between 2–6 years depending on the average yearly irradiation [10]. Owing to the fact that modules have an expected lifetime of 25–30 years, PV systems have the means to provide an energy surplus for many years. The operation costs of PV systems are low and since they have no moving parts, costs for wear rarely occur. They can be installed quickly, and easily integrated in existing or new buildings. The systems are modular, that is, they exist in small or large sizes from milliwatt application in watches to megawatt producing grid-connected power plants [2].

On the negative side, photovoltaics are haunted by high installation costs and are still 5 to 10 times more expensive than conventional alternatives [9]. PV can not supply a stable source of electricity during the day due to the diffuse nature of sunlight, and is thus mostly employed for high-peak demands in grid-connected applications. A large disadvantage is the fact that no economically efficient storage is in sight that covers low output cycles, especially at nighttime. Finally, PV’s contribution to the world energy demand is minuscule with about 0.01% and increasing this share will require a massive boost in module production.

The initial costs and the low energy conversion efficiency of PV compared to other fuels are the primary barriers preventing it becoming a bigger player in the world energy market. The centre-piece (and at the same time the most costly part) of a photovoltaic module is the solar cell. The semiconductor material, in turn, comprises 65% of the costs involved in fabricating a solar cell [9]. The lion’s share of wafers used in the PV industry are made from silicon with 90% in either single or multicrystalline form. Silicon owes its dominance to the fact that it is one of the most abundant minerals in the earth crust. It has a band gap of 1.13 eV, which is almost optimal for solar conversion. What gave the silicon technology a major head start was certainly the fact that the PV industry could build on an existing wealth of research and technology developed by the microelectronics industry. Moreover, efficiencies of 20–25% for single crystalline cells compared to 10–18% for other technologies (apart from multijunction and concentrator cells) have been reached in the laboratory [10].

Current solar cell research is based on three pillars representing different aspects and strategies to lower costs and improve cell performance: technology, characterisation and simulation. The first field of inquiry encompasses the development of new solar cell con-
cepts that ensure cheaper production (by lowering wafer thickness or cutting down process steps) and new fabrication technologies (e.g. new types of furnaces for the emitter diffusion that allow higher throughput or better emitter quality, implementation of sputtering techniques for the deposition of surface passivation layers). The second research activity seeks to unearth the sources of performance losses, and tries to devise ways of improving energy conversion. The third category engages with a deep physical understanding of the solar cell by modelling it in the best possible way in accordance with the current wealth of knowledge available.

This thesis builds on the second pillar of solar cell research and to be more specific, on mastering electrical losses in silicon solar cells by means of characterisation. The electrical losses in a solar cell can be separated in two categories: recombination and resistivity losses. Herein, the recombination losses out-weigh the resistivity losses by a factor of 4–5. Figure 2 highlights the most important processes, which lead to electrical losses, and their influence on solar cell output parameters. The efficiency of the solar cell is determined by the short-circuit current density $J_{sc}$, the open-circuit current density $V_{oc}$ and the fill factor $FF$. Most recombination processes affect the dark saturation current $J_0$ and thus only the open-circuit voltage (blue signs). At the front and rear surface, recombination via surface defects is expressed by the surface recombination velocity (SRV). In the emitter and base region a high recombination lowers the lifetime of minority charge carriers, which in turn increases the dark saturation current. Recombination can also occur in the depletion region via trapping states. This leads to a dark saturation current $J_{02}$, which places a further limit on the open-circuit voltage. Recombination of charge carriers generated near the $p-n$ junction can also impact on the short-circuit current density [11]. Recombination through trapping levels additionally acts to reduce the fill factor.

In general, solar cells are afflicted with parasitic series and shunt resistance. The series resistance stems from the emitter and base resistance of the semiconductor material, the bulk resistance of the metal contacts and the metal-semiconductor contact resistance (green signs). The shunt resistance is associated with leakage current across the $p-n$ junction. This has its origin in regions, where the front metallisation comes in direct contact with the bulk region, e.g. around the edges of the cell or in the presence of crystal defects or caused by firing of metal contacts through the emitter. Both types of parasitic resistance have an important effect on the fill factor.

Since recombination losses outbalance resistance losses by far, it is of more benefit to delve into the investigation of this class of leakage to enhance device performance. This thesis is thus concerned with the tracing and understanding of recombination. In
broad terms, diagnostic tools that tackle this issue can be split into three categories: first, techniques that measure a global parameter like the voltage or the lifetime. Second, spatially resolved measurement that record a topographical map of a global parameter and third, spectrally resolved measurements that can provide a depth profile of a certain parameter.

The final scanning of the current-voltage characteristic takes a central role in device testing and is, in general, the only process monitoring tool employed in the industry. It reveals the output parameters that determine the efficiency: $J_{sc}$, $V_{oc}$ and $FF$. Additionally, the dark series resistance and shunt resistance can be unearthed by a fit to the $I-V$ curve. But it has a limited value for diagnostic or control during device processing. This gap is filled by other measurement techniques presented below.

Illumination-voltage curves obtained by means of the quasi-steady-state open-circuit voltage ($QSSV_{oc}$) are a viable alternative to standard $I-V$ curves [12]. They can be measured as soon as a junction exists and, when compared with the illuminated current-
voltage curve, can reveal the series resistance. QSSV\textsubscript{oc} uses a steady-state light source that enables the recording of a large range of voltages and intensities in one step. Chapter 2 and 3 explore this useful method in more detail.

The extraction of local $I-V$ curves has been made possible with the tool CELLO [13]. A homogeneously illuminated solar cell, kept at a constant current or voltage, is locally excited by a small modulated laser signal. The global current or voltage response is measured at several points of the global $I-V$ characteristics using a lock-in technique. An advanced model allows the extraction of the local current-voltage curve at each pixel. The global open-circuit voltage, in turn, can be measured with QSSV\textsubscript{oc} or by a transient decay method [14]. Voltage-mapping is achieved with the instrument Corescan [15], where a tungsten probe accompanied by a steady-state light spot scans across the wafer by scratching the surface to penetrate the antireflection coating.

The recombination processes are, in general, examined by detecting the lifetime or the diffusion length of charge carriers. Several mechanisms are usually intermingled in a lifetime measurement and hence an effective lifetime is recorded. Photoconductance based methods allow a contactless and quick assessment of the effective lifetime. Next to the microwave photoconductance decay (MW-PCD), the quasi-steady-state photoconductance (QSSPC) has gained a great deal of importance. These methods will be explored in more detail in this work. Photoluminescence measurements recently appeared on the stage of lifetime characterisation [16]. Here, a suitable sensor detects the spontaneous emission rate sparked by irradiating the sample. The excess carrier density is proportional to the luminescence intensity, which permits the lifetime to be determined.

The separation of a specific lifetime is achieved by mitigating all other recombination activities. The bulk lifetime, as an example, is deduced by passivating the surface recombination channels with a surface coating like silicon nitride [17]. Alternatively, there exists a range of versatile tools that measure the bulk diffusion length. The spectral response of the short-circuit current and the surface photovoltage (SPV) are the major workhorses in semiconductor research laboratories fulfilling this task. Both methods use the spectral response of the current or voltage as a stepping stone to decipher the diffusion length. They will be widely discussed in this thesis, since they have a lot in common with the techniques devised in this work.

The surface recombination can also be extracted by spectral response measurements of the current [18] or the excess photoconductance [19]. A special note is warranted for the latter technique in this work. The emitter lifetime is indirectly assessed by determining the emitter saturation current by means of a photoconductance measurement [20].
Recombination through defects represents a major contribution to the overall electrical losses. A vast range of methods deal with this phenomena. Deep-level transient spectroscopy (DLTS) is the classical method used to determine the nature of defects [14]. It obtains the defect parameters from the capacitance spectroscopy of the charge carrier re-emitted from the defect. Lifetime spectroscopy had a recent advent as a defect diagnostic tool and proves to be very successful. Here, the technique explores the fact that most contaminants respond to a change in carrier density or temperature in a way that betrays their recombinative nature. An indirect insight in the temperature dependence of the carrier lifetime delivers the temperature dependent quantum efficiency of the short-circuit current ($TQE_{J_{sc}}$) [21]. This thesis extends the range of spectroscopic tools with two novel techniques: the temperature dependent quantum efficiency of the open-circuit voltage ($TQE_{V_{oc}}$) and the temperature and injection-level dependent voltage spectroscopy (TIVS).

Spatially resolved lifetime diagnostic tools are widespread in the solar cell community. Indirect methods are the SPV mapping [22] and the extension of the spectral response of the current to two dimensions: the light beam-induced current method (LBIC) [23]. This method maps the short-circuit current of solar cells as a function of wavelength using a laser system that scans the wafer. Direct mappings of the lifetime are performed by the spatially resolved MW-PCD [24, 25]. The scanning via QSSPC is presently limited to several mm\(^2\) resolution as a result of the size of the inductive coil used for the lifetime detection. Novel techniques based on infrared detection of free carrier absorption have made inroads in recent years. Infrared Lifetime Mapping (ILM) [26] and its successor, Carrier Density Imaging (CDI) [27], are fast, spatially resolved lifetime methods, based on the absorption or emission of infrared light by free carriers. A fast CCD camera measures the IR absorption or emission, respectively. The use of lock-in detection leads to highly resolved and largely noise-reduced lifetime images.

Spectrally resolved measurements only exist in the form of the short-circuit current response. Most other techniques, a prominent example is SPV, solely use the spectral dependence for further analysis but do not ascribe any deeper meaning to the spectra itself. As this list of measurement techniques has shown, there exists an abundance of techniques that measure global or spatially resolved parameters, but there is a clear shortage of spectral responsibility tools that detect parameters other than the spectral photocurrent. The core of this thesis is therefore devoted to fill this gap. This sheds light on the spectra of solar cells from more than one angle. The spotlight is moved towards the spectral response of the open-circuit voltage and the excess photoconductance, giving valuable new
information about the sensitivity of semiconductor devices to light of different wavelengths.

The word spectrum has been first used by Sir Isaac Newton in 1666 referring to the Phenomenon of Colours, the diffraction of light by a prism. The Collier's Encyclopedia, for example, lists spectrum as 'a word used in physics to indicate the separation and orderly arrangement of light or other electromagnetic radiation into component colours (i.e. wavelengths)' [28]. Hence, since Newton, the word spectrum has been mostly associated with the different colours of sunlight, including the UV and IR range. Capturing the spectra of solar cells, in this work, refers to the response of the solar cell to the sun spectrum. In brief, this thesis gives an account of the spectra, or the response of solar cells in all facets.

**Thesis outline**

Chapter 1 is concerned with the spectral response of the short-circuit current. The notion of the spectral response and - the easier to grasp - quantum efficiency will be introduced in this chapter. An analytical one-dimensional model will be presented thereafter, which describes not only the sensitivity of the solar cell under short-circuit conditions, but also under open-circuit and intermediate working conditions. Starting from this derivation, the most important approximations of the quantum efficiency will be revised. These conjectures are aimed at extracting the bulk diffusion length in an approximate, but less computing-intensive manner.

The technique that represents the hallmark of spectral responsivity measurements is the conventional 'spectral response of the short-circuit current'. This widespread tool is composed of, among other components, a small light excitation superimposed by a strong bias light and a sophisticated lock-in detection. A novel approach to the measurement of the current response will be launched in this thesis that replaces the steady-state, small-area illumination with a declining light source that produces large signals. Here, we indicate some of its potential advantages: First, it evades a hitch that the conventional methods face: the measurement of differential rather than actual magnitudes. Second, it allows a signal detection without resorting to costly lock-in amplifiers. Finally, it enables the measurement of the spectral response at a broad range of intensities in one single recording, an experiment that would normally entail a series of measurements at different bias light intensities. Both diagnostic tools will be presented and compared in detail. The measurement of a range of test devices will evaluate whether the new technique can keep pace with the traditional contender.
Chapter 2 focuses on the spectral response of the open-circuit voltage. It represents the logical extension of spectral responsivity measurements to the solar cell output parameter that is equally important to the short-circuit current. It has been widely assumed that the voltage does not experience a great sensitivity to light of different wavelengths. This assertion will be scrutinised thoroughly, and proved to be wrong. PC1D calculations will shed light on this question in the first place. Following that, the analytical model developed in Chapter 1 will be extended to the open-circuit case. This will address the issue of a possible link between the spectral photocurrent and the spectral photovoltage.

The novel technique used to detect this quantity will then be inaugurated. It is based on the quasi-steady-state open-circuit voltage method and uses the same set-up as its current analogue. Before giving away too many details, we will hint at just one of its advantages. It is often overlooked that the voltage can be accessed after junction formation. This avoids the lengthy fabrication of a complete solar cell. It thus saves precious processing time and allows the control of the fabrication steps following the emitter formation. The final validation of this method will be attempted by comparing a range of test measurements with the outcome of the spectral response of the current.

Chapter 2 is also considered with the analysis of the spectral photovoltage to determine the bulk diffusion length. The models developed in Chapter 1 that approximate the quantum efficiency of the short-circuit current will be extended to the voltage case. A concise study with PC1D will clarify the theoretical potential of the models and compare it to the analysis of the short-circuit current response. Next, we will appraise the models by applying them to a set of different test structures, and by bringing the findings face to face with the results of the spectral photocurrent.

Chapter 3 will still deal with the spectra of solar cells, but it will partly depart from the classical spectral response. The spectra of devices here is more interpreted as the sensitivity to defects. If the spectral response of the current is carried out at a set of different temperatures, the bulk lifetime can be determined as a function of temperature. Apply this technique to solar cells that are plagued by impurities and it transforms into a spectroscopic tool for defect identification. This is the basic idea behind TQEJ_{sc}. It is only natural to consider the measurement of the spectral response of the voltage instead, which will be addressed in this chapter in form of the TQEV_{sc} method.

It is also possible to extract the bulk lifetime directly from a voltage measurement at white light. The well established ‘quasi-steady-state open-circuit voltage technique’ is predestined for this role as it is also able to simultaneously record the voltage over a wide range of light intensities. The ‘temperature and injection dependent voltage spectroscopy’
developed in Chapter 3 goes one step further by applying the voltage technique at different temperatures. To test the potential of the novel methods, they are applied to solar cells processed on aluminium-doped Czochralski silicon. This material suffers from aluminium-oxygen related defects. The appeal of the new technique will be tested against traditional spectroscopic tools, notably lifetime spectroscopy and DLTS.

Chapter 4 introduces yet another method that may contribute to the existing body of characterisation tools and may find its application in photovoltaics and microelectronics: the spectral response of the photoconductance. The quasi-steady-state photoconductance is the underlying measurement technique that records the photoconductance, whereas the monochromatic irradiation is created with the same set-up as employed by the other method. The theoretical and experimental investigation of the spectral photoconductance will unearth a surprising characteristic that marks it if a high surface recombination velocity is present at the front surface: a hump in the infrared response that is not detected by any other spectral response. The spectral photoconductance will be applied to bare silicon wafers in order to explore their front surface recombination behaviour and to ion implanted silicon to trace any residues due to the implantation. Finally, Chapter 4 is devoted to the measurement of emitter structures with the spectral photoconductance. It tries to corroborate the claim that the spectral response of the photoconductance can deliver the same information as the conventional spectral response, but this already after junction formation.
"The quantum efficiency spectrum of a thin film solar cell reflects both the optical properties and the transport properties, and is therefore a quantity that elucidates more of the device physics than the current voltage curve."

Rolf Brendel, 2001

1.1 Introduction

The spectral response of the photocurrent is a powerful tool for the development and calibration of solar cells. In this technique, monochromatic light illuminates the cell, resulting in a current density that is a measure of its ability to collect charge carriers. As light of different colours is absorbed at different depths in the solar cell, the spectral response provides a depth resolution of the recombination processes that hinder charge carrier collection. The high-energy UV light, on the one hand, is strongly absorbed in the first few micrometres of the device and creates a highly unbalanced generation profile. The IR irradiation on the other hand, is only weakly absorbed and leads to a more homogeneous generation profile. Hence, separate information on the recombination mechanisms in the emitter, depletion and base region as well as on the front surface of the device can be obtained. In addition, the response at long wavelengths indicates the light-trapping capability of the device.

In general, spectral responsivity measurements are performed under short-circuit conditions. In this case, the spectral response can be easily defined and is usually close to the current at maximum power point. Spectral response systems resort to either interference filters, monochromators or interferometers to produce monochromatic light [29, 30]. For single junction solar cells, the device is illuminated with periodic monochromatic light superimposed by a broadband bias light of much higher intensity. The short-circuit current
signal is proportional to the change in the recombination rate and, as a result, the spectral response is a differential parameter [31-33]. The differential spectral response is equal to the absolute spectral response if it is independent of the bias intensity.

Devices with non-linear behaviour, that is, where injection-level dependent recombination processes influence the spectral response, are studied by varying the bias light intensity. A well-known example is the enhancement of the spectral response in the long wavelength range with increased bias light as a result of an injection-level dependent back surface recombination velocity [33]. Amorphous silicon solar cells, in turn, show a noticeable decrease in current response with increasing irradiance [34]. An attractive alternative to the bias light method is to change the carrier density by applying a voltage bias [33]. The determination of the injection level is simplified in this case, since the optical properties of the device do not enter the calculation of the carrier density, as is the case with the first technique. Voltage dependent current collection also occurs in amorphous silicon solar cells, Cadmium-telluride and Cu(Ga,In)(S,Se) material systems [35].

The spectral response of the short-circuit current plays an important role in the calibration of solar cells. When a photovoltaic device is evaluated under a light source with respect to a reference spectrum, there is a spectral mismatch error between the reference spectrum and the test spectrum. The reference spectrum is generally the standard AM1.5G sun spectrum. If the spectral response of the photocurrent of the test and reference cell and the spectral distribution of the light source are known, the error can be corrected for by a 'spectral correction factor' [36, 37].

Spectral responsivity measurements of the current have been extended to spatially resolved techniques in the form of the light-beam-induced current (LBIC) technique [23]. LBIC aims to identify recombination centres in the bulk and at the surface and the existence of crystallographic defects. Its most compelling application is the measurement of a topographical map of the bulk diffusion length. The resolution of the apparatus can be as fine as a tenth of a micron and is mainly determined by the spot size and the diffusion length of the test device. Some set-ups include the whole spectral bandwidth by including a monochromator [38]. Other systems employ laser diodes of several wavelengths as the light source [39]. In general, the solar cell is moved on an x-y-stage below the light spot. The measurement speed can be increased, if several signals are superimposed with different frequencies and if the light spot rather than the solar cell is moved [18, 40].

In the following section, we have a closer look at the definition, the interpretation and the usefulness of the spectral response. This method offers powerful monitoring and predictive properties disclosing electric loss mechanisms of solar cell devices. Not surprisingly,
one of the primary applications of the spectral response technique is the extraction of recombination parameters. In Section 1.3, the theory that is used in the literature to model the spectral response is outlined. The underlying model is the solution of the transport equations of a one-dimensional, homogeneously doped p-n junction. We generalise here the model found in the literature for a generation rate that allows an arbitrary number of multiple reflections.

Thereafter, a literature survey is presented that covers various approximations of the base component of the spectral response, the most well-known being the linear relationship between the inverse internal quantum efficiency and the absorption depth. These models serve to extract the base diffusion length or to separate between bulk and surface recombination. Both possible scenarios, illumination from the front and rear side of the device are envisaged (1.4).

The measurement set-up realised in most laboratories to obtain the spectral response is described in section 1.5. In this thesis, an alternative method has been developed that displays some intriguing innovations. Advantages and inconveniences in comparison to the conventional techniques are discussed in section 1.6 in a technical perspective and taking into account the measurement results.

1.2 Definition and interpretation of the spectral response of the current

The conventional spectral response is defined as the ratio of charge carriers collected under short-circuit conditions in an external circuit and the incident illumination power of photons at a given wavelength:

\[ SR(\lambda) = \frac{J_{sc}(\lambda)}{P_{light}(\lambda)}. \]  

(1.1)

In general, the spectral response is normalised to its maximum possible value, that is, the ideal spectral response \( SR_{ideal} = \lambda \text{ (nm)}/(1240 \text{ eVnm}/\text{C}), \) where \( \lambda \) is the wavelength of illumination expressed in nm and the factor 1240 is the wavelength in vacuum of a 1 eV photon. The normalised spectral response is equal to the external quantum efficiency \( EQE(J_{sc}) \), which is defined as the ratio of the short-circuit current density \( J_{sc} \) to the incident photon flux on the surface of the solar cell \( N_{ph} \):

\[ EQE(J_{sc}, \lambda) = \frac{J_{sc}(\lambda)}{qN_{ph}(\lambda)} = \frac{\hbar c}{q\lambda} SR. \]  

(1.2)
The internal quantum efficiency $IQE(J_{sc})$ is a parameter that allows analysis of the electronic loss mechanisms within the device. As the name suggests, it considers only photons that are absorbed inside the device. If $R(\lambda)$ is the primary reflection at the cell surface, $IQE(J_{sc})$ can thus be deduced from $EQE(J_{sc})$: \[ IQE(J_{sc}, \lambda) = \frac{EQE(J_{sc}, \lambda)}{1 - R(\lambda)}. \] (1.3)

Figure 1.1 depicts an example to illustrate the impact of the reflectance on the different perception of the external and internal quantum efficiency. Deliberately, a cell with a high reflectance has been chosen for the PC1D calculations [41], produced by a 100 nm thick silicon dioxide coating at the front surface. The cell exhibits considerably lower external yield in the low and high wavelength range. This could be misleadingly interpreted as a high recombination rate at the front surface or a low bulk quality. The internal quantum efficiency is therefore the more relevant parameter to attach importance to. To gain more insight into how the various recombination activities affect $IQE(J_{sc})$, a set of calculations has been performed, each with a slight modification to the contributing parameters. The following discussion resumes the finding of Ref. [42]. The influential parameters considered here are the peak density of the emitter dopant $N_{peak}$, the shunt resistance $R_{sh}$, the emitter thickness $W_e$, the front and back surface recombination velocity $S_{front}$ and $S_{back}$ and the minority bulk lifetime $\tau_{bulk}$. The data of the six different cells are given in Table 1.1, while the PC1D simulations are displayed in Figure 1.2.

**Figure 1.1:** Comparison of external and internal quantum efficiency of the short-circuit current as functions of wavelength. Additionally, the primary surface reflectance is also depicted.

**Figure 1.2:** Influence of different material and cell parameters on the internal quantum efficiency. The corresponding cell parameters can be found in Table 1.1 [42].
### 1.3 One-dimensional analytical model of a $p-n$ junction under monochromatic light

Table 1.1: Parameters of the PC1D calculation of six different scenarios of the internal quantum efficiency, shown in Figure 1.2. The internal front reflectance was assumed to be 90% (specular reflectance) and the internal rear reflectance 70% (diffuse reflectance). The thickness was 300 $\mu$m and the base resistivity 1 $\Omega$ cm [42].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cell 1</th>
<th>Cell 2</th>
<th>Cell 3</th>
<th>Cell 4</th>
<th>Cell 5</th>
<th>Cell 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{peak}}$ [cm$^{-3}$]</td>
<td>$3 \times 10^{19}$</td>
<td>$1.4 \times 10^{20}$</td>
<td>$3 \times 10^{19}$</td>
<td>$3 \times 10^{19}$</td>
<td>$3 \times 10^{19}$</td>
<td>$3 \times 10^{19}$</td>
</tr>
<tr>
<td>$R_{\text{sh}}$ [Ω cm$^{-2}$]</td>
<td>120</td>
<td>40</td>
<td>40</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>$W_e$ [$\mu$m]</td>
<td>0.5</td>
<td>0.5</td>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$S_{\text{front}}$ [cm/s]</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>$10^6$</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>$S_{\text{bulk}}$ [cm/s]</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>10</td>
<td>1500</td>
</tr>
<tr>
<td>$S_{\text{back}}$ [cm/s]</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>$10^9$</td>
</tr>
</tbody>
</table>

Starting with the typical IQE of a higher efficiency cell (cell 1), the parameters have been varied one by one, resulting in a degradation of the efficiency. The front region is affected by surface recombination and the emitter characteristics. The highest decrease in the UV range is thereby inflicted by a high recombination rate at the front surface (cell 4). A higher surface doping concentration (cell 2) or a deeper emitter (cell 3) also prove detrimental to the internal carrier collection at low wavelengths. If a low emitter sheet resistance is desirable, a deeper dopant diffusion yields a better performance. The Auger recombination is the main culprit here in limiting the efficiency in highly doped emitters. The rear side of the device, by contrast, is mainly influenced by the bulk lifetime and the back surface recombination, both exhibiting a similar effect on the IR efficiency. The decrease of the internal response is extended to smaller wavelengths in the case of a low minority bulk lifetime (cell 5) than in the case of a high rear surface (cell 6). For both scenarios, a hump appears in the far infrared. This hump is a result of photons that bounce back from the rear side and are absorbed closer to the emitter region, thus contributing to the carrier collection.

### 1.3 One-dimensional analytical model of a $p-n$ junction under monochromatic light

This thesis deals with techniques and experiments that concern the spectral response of various parameters, the most important among them being the short-circuit current and the open-circuit voltage. The measurement of the spectral response is ultimately directed toward the determination of power losses that are caused by bulk and surface recombination and recombination in the emitter and depletion regions. However, the spectral response itself shows only the combined influence of the various parameters involved in
the recombination processes. It is therefore necessary to establish an accurate model that
describes the spectral response in terms of these parameters. The model is aimed at
routine applications of the measurement of the spectral response, hence it should not be
computing intensive. The model derived in this section offers a sufficient solution to this
requirement and has been proved useful in the past: it is the one-dimensional analytical
model of an illuminated, abrupt $p-n$ junction.

This traditional model is based on subdividing the device into separate regions [43].
The most obvious region is the quasi-neutral base, which is usually uniformly doped and
extends practically over the whole thickness of the device. It is common to assume low-
injection conditions, that is, excess carrier densities well below the dopant density. This
assumption permits us to neglect the drift term when calculating the current density,
which thus becomes essentially a carrier diffusion flux. It also allows the use of a simple
expression for carrier recombination, based on the concept of minority carrier lifetime.
Finally, it permits an approximation of the non-equilibrium electron-hole product as the
product of excess carrier density times the dopant density, that is, $n_p \approx \Delta n N_A$. The latter
leads to a relationship between excess carrier density (and subsequently, device current)
and terminal voltage that follows the ideal Shockley equation, that is, has an ideality
factor of 1.

The second device region that needs to be modelled is the emitter, usually formed by
thermal diffusion and having, as a consequence, a non-uniform dopant density. Since most
material parameters depend on doping, the situation we face is that of a quasi-neutral re-
gion in low-injection where the relevant parameters vary with the one-dimensional position
variable $x$. To complicate matters, even the intrinsic carrier density (its effective value,
$n_t^{\text{eff}}$) is position dependent, to reflect the narrowing of the energy band gap that occurs at
high dopant densities. The position dependence of dopant and carrier densities creates a
built-in electric field that makes it necessary to include a drift term in the expression for
the current. Such emitter regions, including possible BSF or floating junction schemes,
may, despite their complexity, be modelled in a quasi-analytical fashion by following an
iterative method that starts from the integral form of the continuity equations [44].

It is, nevertheless, common to use the conventional, uniform-doping model for emitter
regions for an approximate analysis. It is in particular adequate for the purpose envisaged
in this investigation, as we will focus on the determination of the bulk recombination of
the base region and the rear surface recombination. It will be shown that in short-circuit
conditions it is then sufficient to consider only the amount of photons absorbed in the
emitter segment. In the case of open-circuit conditions, the impression left by the emitter
region is more complex and requires in principle the knowledge of the emitter recombination. Nevertheless, there exist ways to circumvent this hurdle, which are discussed in detail in chapter 2.

A third region is introduced between the \( n \) and \( p \) side of the device to account for the fact that there exists a region in which the opposing doping concentrations overlap and neutralise each other. This depletion region is, as the name indicates, mostly free of charge carriers, since they are quickly swept out of this segment due to the high electric field that forms between the two opposing sides of the junction. In a first approximation, the contribution to the overall spectral response is therefore simply given by the number of photons absorbed in the space charge region. Considering this approach and the purpose of the model, the depletion region only plays a minor role in the determination of the base recombination parameters.

Although low-injection approximations are indeed useful to visualise the operation of solar cells, the physical reality is that the parameters that characterise carrier recombination and transport, that is, the lifetime, the surface recombination velocity and the mobility, are not constant, even if low-injection conditions prevail. In particular, the effective lifetime can be strongly dependent on the excess carrier density, even when the latter is much lower than the dopant density. Given that the typical carrier density profiles found in solar cells can span several orders of magnitude, it is clear that the traditional analytical expressions for solar cells are not strictly valid, since they are based on the assumption of constant material parameters. It is, therefore, important to keep in mind that they are only an approximation to a complex physical reality.

In this section we will establish the one-dimensional model for a general situation, i.e. a model that is valid for all kinds of operation conditions (if low-injection can be guaranteed at each condition). Later on, we deal, at least in part, with the variability of the fundamental parameters by considering separately the carrier densities that occur at different operating points of the device. As a consequence, we distinguish between the effective lifetime at open-circuit conditions from that at short-circuit, because they can have different values. We also differentiate between the short and open circuit values of global parameters, such as saturation current densities and quantum collection efficiencies. This means that, even if the formal expression for the quantum collection efficiency is identical, the material parameters to be inserted in that expression are, in principle, different for open-circuit, intermediate or short-circuit conditions. The parameter values will also be different depending on the light intensity, because, again, this changes the excess carrier density within the cell. In the ensuing section we briefly consider the situation under
1. Spectral response of the short-circuit current

short-circuit conditions, while the general formulation will pave the way for an analytical model of the spectral response of the voltage (chapter 2).

Another type of carrier density variability is that occurring as a function of the position variable \(x\). For example, the excess carrier density profile in a forward biased diode in the dark is typically given by exponential or hyperbolic functions. So, even a differentiation between operating conditions cannot fully account for the variability of the material parameters. Fortunately, solar cells work under illumination, and this tends to homogenise the carrier profile. Our approach is to represent this position dependence of the physical parameters by considering that they take average values over the thickness of the region under analysis (the thickness of the base region, for example). Numerous investigations that make use of this model demonstrate convincingly that valid information can be drawn from it.

![Figure 1.3: One dimensional electrical model of a solar cell.](image)

We begin the elaboration of the model with a glance at the different regions, depicted in Figure 1.3. \(W_e, W_{scr}\) and \(W_b\) denote the thickness of the emitter, space charge and base regions, respectively, the whole width is denoted with \(W\). In the \(n\) and \(p\)-type regions the behaviour of the minority carrier densities is governed by the appropriate continuity equations. If the two sides of the junction are uniform in doping, then there is no electrical field outside of the depletion region. The hole and electron currents are thus reduced to a diffusive component, which simplifies the continuity equation, first shown for the emitter region, to the following:

\[
D_p \frac{\partial^2 \Delta p}{\partial x^2} (x, \lambda) - \frac{D_p}{L_p^2} \Delta p (x, \lambda) + G(x, \lambda) = 0. \tag{1.4}
\]

\(D_p\) is the hole diffusion constant and \(L_p\) is the minority diffusion length. \(G(x, \lambda)\) is the generation rate, which is composed of the number of photons \(N_{ph}\) that hit the device surface and the probability that these photons are absorbed at a distance \(x\) inside the active area. This probability is described by the absorption coefficient \(\alpha\). When a ray of photons passes through the device, the photon flux subsides exponentially with the
1.3 One-dimensional analytical model of a p-n junction under monochromatic light

distance $x$ and the absorption coefficient $\alpha$. In the simplest case, one considers a planar single-layer structure and a ray of photons that passes the silicon just once. The generation rate is then a mono-exponential function:

$$G(x, \lambda) = N_{ph}(\lambda) (1 - R(\lambda)) \alpha(\lambda) e^{-\alpha(\lambda)x}. \quad (1.5)$$

The fact that photons are reflected at the surface is accounted for with the term $(1 - R)$, where $R$ is the overall reflectance. Equation 1.5 gives only a crude description of the actual generation rate, especially if thin or textured wafers are used. Nevertheless, this approximation is often used for its simplicity. A more accurate approach uses multiple ray passages and includes refraction at textured surfaces [45]. This leads to a generation rate that is the sum of four exponential functions:

$$G(x, \lambda) = \sum_{i=1}^{4} a_i(\lambda) e^{b_i(\lambda)x}. \quad (1.6)$$

The constants $a_i$ and $b_i$ contain the optical information that is imprinted on the absorption fraction at each path. They depend thus on the absorption coefficient and the internal reflectance at the front and rear side of the device. The deduction of the model (known as the optical model of Basore) and the exact composition of the generation rate is outlined in detail in Appendix C.2. In the following we will determine all equations for a general generation rate and will make use of either form whenever it suits best. The general solution for the minority carrier density in the emitter region is:

$$\Delta p(x, \lambda) = A(\lambda) \cosh \frac{x}{L_p} + B(\lambda) \sinh \frac{x}{L_p} + f(x, \lambda). \quad (1.7)$$

The function $f(x, \lambda)$ is related to the generation rate and is consequently a function of the photon flux, the surface reflectance and the absorption coefficient. If we consider Equation 1.5 as part of the continuity equation, $f(x, \lambda)$ is directly proportional to the generation rate:

$$f(x, \lambda) = N_{ph}(\lambda) (1 - R(\lambda)) \frac{L_p^2 / D_p \alpha(\lambda)}{1 - L_p^2 \alpha^2(\lambda)} e^{-\alpha(\lambda)x}. \quad (1.8)$$

The generalisation to more ray passages and thus more exponential terms in the generation rate is easily accomplished (see also Appendix C.2 for more details):

$$f(x, \lambda) = N_{ph}(\lambda) \sum_{i=1}^{4} \frac{L_p^2 / D_p a_i(\lambda)}{1 - L_p^2 b_i^2(\lambda)} e^{b_i(\lambda)x}. \quad (1.9)$$
Note that \( f(x, \lambda) \) is no longer proportional to \( G(x, \lambda) \) of Equation 1.6. With a general formulation in mind, it is thus convenient to use \( f(x, \lambda) \) instead of \( G(x, \lambda) \), as it enters directly into the solution of the minority carrier concentration. All that is now required to obtain a formulation of the minority carrier concentration of the base region, is to exchange the parameters of the emitter region, \( L_p \) and \( D_p \) with \( L_n \) and \( D_n \). The pre-factors \( A \) and \( B \) are fully determined by the boundary conditions at the front surface and the depletion region:

\[
\frac{D_p}{L_p} \frac{\partial \Delta p}{\partial x} \bigg|_{x=0} = S_p \Delta p (x = 0)
\]

and

\[
\Delta p (x = W_e) = \begin{cases} 
0 & \text{short-circuit conditions} \\
\frac{n_e^2}{N_A} (e^{\frac{V}{kT}} - 1) & \text{forward voltage or open-circuit conditions}.
\end{cases}
\]

The excess carrier density is reduced to zero in short-circuit conditions by the electric field in the space charge region. A typical expression linking the minority carrier density and the open-circuit voltage at low-injection is employed in the case of open-circuit circumstances. For the sake of a general description, we will use the term \( \Delta p(W_e) \) (and later on \( \Delta n(W_e + W_{scr}) \)) for arbitrary operation conditions. We are now able to rewrite \( \Delta p (x, \lambda) \) in terms of the emitter region's recombination parameters:

\[
\Delta p (x, \lambda) = (\Delta p(W_e) - f(W_e, \lambda)) \cdot \frac{S_p L_p}{D_p} \frac{\sinh \frac{x}{L_p} + \cosh \frac{x}{L_p}}{\sinh \frac{W_e}{L_p} + \cosh \frac{W_e}{L_p}} + \frac{S_p L_p}{D_p} f(0, \lambda) - L_p f'(0, \lambda) + \frac{W_e - x}{L_p} \sinh \frac{W_e}{L_p} + f(x, \lambda).
\]

Here, \( f' \) denotes the derivative of \( f \). The next step on the way to obtain the spectral response is the hole current density, \( J_p \), at the edge of the junction:

\[
J_p = - q D_p \frac{\partial \Delta p}{\partial x} \bigg|_{x=W_e} = - \frac{D_p}{L_p} \Xi_p (W_e) \cdot (\Delta p(W_e) - f(W_e, \lambda))
\]

\[
- q D_p \frac{S_p L_p}{D_p} \frac{\sinh \frac{W_e}{L_p} + \cosh \frac{W_e}{L_p}}{\sinh \frac{W_e}{L_p} + \cosh \frac{W_e}{L_p}} + q D_p f'(W_e, \lambda),
\]

where \( \Xi_p (x) \) is the geometrical factor, which comes into play when a finite sample thickness is introduced:
1.3 One-dimensional analytical model of a p-n junction under monochromatic light

\[ \Xi_p(W_e) = \frac{S_p L_p \cosh \frac{W_e}{L_p} + \sinh \frac{W_e}{L_p}}{\frac{S_p L_p \sinh \frac{W_e}{L_p} + \cosh \frac{W_e}{L_p}}{D_p}}. \]  

(1.14)

\( \Delta p(x, \lambda) \) and \( J_p \) denote the excess carrier density and hole current of the top side of a p-n junction at a given wavelength for a general generation rate, assuming this region to be uniform in carrier lifetime, mobility and doping level. These equations can be used to describe solar cells with a grown top region and as a first approximation to devices with diffused emitter regions. In Chapter 2 a different formulation of \( J_p \) will be established using the concept of the emitter saturation current. This offers the prospect of describing arbitrary emitter geometries, since all the spatial or injection-level dependent recombination parameters of the front region are united in the emitter saturation current.

The current density contributed by the depletion region is equal to the number of photons absorbed there:

\[ J_{G,scw} = q N_{ph} (1 - R) \left( e^{-\alpha(\lambda) W_e} - e^{-\alpha(\lambda)(W_e + W_{sor})} \right). \]  

(1.15)

The base region can now be described in a similar way as the top region. The continuity equation is given by:

\[ D_n \frac{\partial^2 \Delta n}{\partial x^2}(x, \lambda) - \frac{D_n}{L_n^2} \Delta n(x, \lambda) + G(x, \lambda) = 0, \]  

(1.16)

with the boundary conditions:

\[ -D_n \frac{\partial \Delta n}{\partial x} \bigg|_{x=W} = S_n \Delta n(x = W) \]  

(1.17)

and

\[ \Delta n(x = W_e + W_{sor}) = \begin{cases} 0 & \text{short-circuit conditions} \\ \frac{n_0^2}{N_A} (e^{\frac{eV}{kT}} - 1) & \text{forward voltage or open-circuit conditions.} \end{cases} \]  

(1.18)

Again, we use a carrier density of zero in the case of short-circuit conditions and the low-injection approximation when we face open-circuit situations. Using these boundary conditions, the electron distribution for a uniform p-base is:
\[ \Delta n(x, \lambda) = \left( \Delta n(W_e + W_{scr}) - f(W_e + W_{scr}, \lambda) \right) \times \\
\left( \cosh \frac{x - (W_e + W_{scr})}{L_n} - \Xi_n(W_b) \sinh \frac{x - (W_e + W_{scr})}{L_n} \right) \\
- \frac{S_{P} L_{n} f(W, \lambda) + L_{n} f'(W, \lambda)}{S_{P} L_{n} \sinh \frac{S_{P} L_{n}}{L_{n}} + \cosh \frac{S_{P} L_{n}}{L_{n}}} \sinh \frac{x - (W_e + W_{scr})}{L_n} + f(x, \lambda). \] (1.19)

A similar expression holds for \( \Xi(W_b) \) as for \( \Xi(W_e) \). \( f(x, \lambda) \) is given by Equation 1.8 or Equation 1.9 by exchanging \( L_p, D_p \) with \( L_n, D_n \). The related expression for the electron current at general operation conditions is then:

\[ J_n = qD_n \left. \frac{\partial \Delta p}{\partial x} \right|_{x=W_e} \\
= -q \frac{D_n \Xi_n(W_b)}{L_n} \cdot \left( \Delta n(W_e + W_{scr}) - f(W_e + W_{scr}, \lambda) \right) \\
- qD_n \frac{S_{P} L_{n} f(W, \lambda) + f'(W, \lambda)}{S_{P} L_{n} \sinh \frac{S_{P} L_{n}}{L_{n}} + \cosh \frac{S_{P} L_{n}}{L_{n}}} + qD_n f'(W_e + W_{scr}, \lambda). \] (1.20)

Equation 1.20 is the important formulation upon which the extraction of recombination parameters of the base region for front illumination is built. Note that the influence of the emitter region is only given by \( qD_n f'(W_e + W_{scr}) \) and \( qD_n f'(\lambda, W_e + W_{scr}) \) in short-circuit circumstances. In other words, the current density in the base region is reduced due to the absorption of photons in the top regions.

Finally, an expression for the total photocurrent can be put down:

\[ J = J_p + J_{G,scr} + J_n. \] (1.21)

It is salutary to remember that this equation is valid under any operation conditions and for an arbitrary generation rate. Its implementation is only curtailed due to the simplified geometry and the restriction to low-injection conditions. We come back to this general form in a later chapter, but for the time being we are only interested in the short-circuit application. The external quantum efficiency of the short-circuit current can then be obtained by:

\[ EQE(J_{sc}, \lambda) = \frac{J_{sc}(\lambda)}{qN_{ph}(\lambda)} = EQE_p + EQE_{scr} + EQE_n, \] (1.22)

where \( J_{sc} \) is the total photocurrent in short circuit conditions. \( EQE_p, EQE_{scr} \) and \( EQE_n \) denote the contributions of the three regions to the total external quantum efficiency. All equations can be easily translated from a \( p-n \) junction to a \( n-p \) device by interchanging \( L_p, D_p \) and \( S_p \) with \( L_n, D_n \) and \( S_n \).
1.4 Determination of surface and bulk recombination in the base region

1.4.1 Front illumination

The diffusion length is a fundamental parameter that determines the quality of the semiconductor material used for p-n junctions, bipolar transistors and solar cells. In the semiconductor industry, the diffusion length is an indicator of heavy metal contamination and micro-defects in silicon. It is used to evaluate crystal growth and is an important tool for monitoring contamination introduced during key processing steps in fabrication of integrated circuits [46]. Its value directly affects the performance of the solar cell, both the open-circuit voltage and short-circuit current. A sufficiently high diffusion length is needed to assure that generated carriers reach the junction areas of the solar cell in order to be collected before they recombine. The measurement of this parameter is therefore an elementary part of solar cell characterisation and the aim of several different measurement methods.

The determination of recombination parameters in the base region by means of the spectral response of the short-circuit current has been explored widely in the past [45, 47–56]. First investigations already appeared in the early days of solar cell processing [57]. They have two aims: First, the extraction of the bulk diffusion length of the silicon volume, especially in cases where it dominates the global recombination rate. Second, the separation of the bulk diffusion length and the rear surface recombination velocity, desirable particularly when both parameters impart similar influences. Due to the nature of the equations, the explicit deduction of the surface recombination velocity is not possible. Most models use only a small portion of wavelengths that is purely absorbed in the base region for the extraction of the diffusion length. However, an accurate determination is only possible if a series of restricting approximations are made that are only fulfilled by a handful of devices. In most cases, only an effective diffusion length is measured, i.e. a diffusion length that is influenced by rear surface recombination. The separation of volume and surface parameters of the base region is in general difficult: usually, it is restricted to the determination of an upper limit for the surface recombination velocity and a lower limit for the bulk diffusion length [52]. A second range of wavelengths leading to homogeneous generation in the base is often consulted in addition in order to restrict the range of possible solutions [45].

In this section, we work through the different models beginning with the classical extraction of the diffusion length, the model with the most assumptions, and ending with
the analysis using the least approximations. The aim of this section is the presentation of all models for the short-circuit spectral response available in the literature, keeping in mind the possible novel application to the spectral response of the open-circuit voltage.

The linear model

The first model, based on a linearity between the inverse internal quantum efficiency and the absorption depth of the light [45, 48, 49] involves the following assumptions:

1) Only absorption in the base region is considered, which implies that the absorption length has to be much larger than the thickness of the emitter region. This is usually achieved if $1/\alpha \geq 5\text{–}14 \mu m$ or in terms of wavelength: $\lambda \geq 750\text{–}850 \text{nm}$.

2) Any reflection at the back of the solar cell is neglected, i.e. the penetration depth has to be considerably smaller than the wafer thickness.

3) The generation of carriers is mainly achieved by the first passage of photon rays.

4) Low-injection conditions prevail throughout the base region.

5) If the diffusion length is much larger than the sample thickness, the following assumption is needed, but is in general easily fulfilled: The diffusion length has to be larger than the penetration depth $1/\alpha$ of the light.

Assumptions 1) and 2) essentially limit the wavelength range to $\lambda > 750 \text{ nm}$ and $\lambda \leq 950 \text{ nm}$, depending on the thickness of the emitter and base region. The generation rate can be simplified to Equation 1.5 due to the third condition. Note that a generalisation of this generation rate to textured surfaces is simply achieved by including the angle of refraction, $\phi$, at this surface, i.e. by using $\alpha/cos \phi$ instead of $\alpha$ [45, 53]. Typical values for $\phi$ are $41.7^\circ$ for chemically textured (100)-oriented silicon at $\lambda = 900 \text{ nm}$ [45]. Assumption 4) assures that we can restrict the analysis to the electron current in the base given by Equation 1.20.

Using Equations 1.5 and 1.20 at short-circuit conditions, we obtain:

$$J_n = qN_{ph}(1 - R) \frac{L_n \alpha}{1 - L_n^2 \alpha^2} e^{-\alpha(W_a + W_{sec})} \times$$

$$\left( \Xi_n(W_b) + \frac{L_n \alpha e^{-\alpha W_b}}{S_n L_n \sinh \frac{W_b}{L_n} + \cosh \frac{W_b}{L_n}} - L_n \alpha \right). \quad (1.23)$$

From $J_n$, the internal quantum efficiency of the base region, $IQE_n$, can be deduced:
1.4 Determination of surface and bulk recombination in the base region

\[ IQE_n = \frac{J_n}{qN_{ph}(1 - R)} = \frac{L_n \alpha}{L_n^2 \alpha^2 - 1} e^{-\alpha(W_e + W_{scr})} \left( L_n \alpha - \Xi_n(W_b) - \frac{(L_n \alpha + \frac{S_n L_n}{D_n}) e^{-\alpha W_b} \sinh \frac{W_e}{L_n} + \cosh \frac{W_e}{L_n}}{\frac{S_n L_n}{D_n} \sinh \frac{W_e}{L_n} + \cosh \frac{W_e}{L_n}} \right). \] (1.24)

The absorption depth of light with \( \lambda > 700 \) nm is larger than 5 \( \mu \)m. In this case, the combined width of the emitter and depletion region can be neglected in comparison to the cell thickness. Hence, we can write \( W_b \approx W \). If no light reaches the back of the device,

\[ \exp(-\alpha W_b) \approx 0. \] (1.25)

It is common to define an effective diffusion lengths as follows:

\[ L_{\text{eff}} = L_n/\Xi_n(W). \] (1.26)

Combining these first approximations, Equation 1.24 simplifies to:

\[ IQE_n = \frac{L_n \alpha}{L_n^2 \alpha^2 - 1} (L_n \alpha - L_n/L_{\text{eff}}) e^{-\alpha(W_e + W_{scr})}. \] (1.27)

Equation 1.27 serves as the basis for most of the following approximations. If the analysis is concentrated on wavelengths that are only weakly absorbed in the emitter and depletion region (assumption 1),

\[ \exp(-\alpha(W_e + W_{scr})) \approx 1. \] (1.28)

The analysis is now divided into two cases that are distinguished by the magnitude of the diffusion length:

A) \( W \gg L_n \)

In this case, the effective diffusion lengths is equivalent to the actual diffusion length which gives rise to the well known formula given for example in [48]:

\[ IQE_n \approx \frac{L_n \alpha}{L_n \alpha + 1} \text{ or } 1/IQE_n \approx 1 + \frac{1}{L_n \alpha}. \] (1.29)

The plot of \( 1/IQE_n \) against \( 1/\alpha \) should therefore result in a straight line, at least for the range of wavelength for which the assumptions are valid. This straight line cuts \( 1/IQE_n \) at 1 and intercepts the horizontal axis at \( L_n \). The wavelength range for the fit is in general determined in the lower limit by the assumption \( 1/\alpha \geq 5-14 \mu \)m (\( \lambda \geq 700-800 \) nm) and in the upper limit by \( 1/\alpha \geq W/4 \) (\( \lambda \geq 950-1000 \) nm) [45].
Figure 1.4: Example of the inverse internal quantum efficiency as a function of absorption depth to illustrate the extraction of the diffusion length.

Figure 1.4 illustrates an example of this linear fit for the device RPAL44_A1.2b, where all assumptions can be fulfilled. The range of wavelength used in the linear fit is 750–950 nm. The diffusion length is determined to be \( \sim 7 \, \mu\text{m} \), well below the device thickness of 335 \( \mu\text{m} \). Details of the device and the measurement of the internal quantum efficiency are available in section 1.5.1.

**B) \( W \ll L_n \)**

In this case, the condition that \( L_n \) is larger than the penetration depth implies (assumption 5)):

\[
L_n > 1/\alpha \rightarrow \alpha^2 L_n^2 \gg 1 \rightarrow \frac{L_n \alpha}{L_n^2 \alpha^2 - 1} \approx \frac{1}{L_n \alpha}.
\]  

(1.30)

The internal quantum efficiency is then given by

\[
IQE_n \approx \frac{1}{L_n \alpha} (L_n \alpha - L_n/L_{\text{eff}}) = 1 - \frac{1}{L_{\text{eff}} \alpha}
\]  

(1.31)

and we can again establish a linear relation between the inverse internal quantum efficiency, \( 1/IQE_n \), and the penetration depth \( 1/\alpha \):

\[
1/IQE_n \approx \frac{1}{1 - (L_{\text{eff}} \alpha)^{-1}} \approx 1 + \frac{1}{L_{\text{eff}} \alpha}.
\]  

(1.32)

We pause here to stress the distinction between \( L_{\text{eff}} \) and \( L_n \) and to investigate the
influence of the base surface recombination velocity $S_n$ on $L_{\text{eff}}$. Looking at the definition of $L_{\text{eff}}$ and the origin of the parameter $\Xi_n(W)$ - a geometrical factor marking the difference between a device of finite and infinite dimensions - we can state that: $L_n$ is the (average) minority diffusion length of the base region and thus a fundamental parameter describing the quality of the silicon. It is only affected by intrinsic recombination processes (SRH recombination, Auger recombination, etc.) and the mobility of minority carriers. $L_{\text{eff}}$ in contrast, is also influenced by rear surface recombination. $L_{\text{eff}}$ is thus the more important parameter for the final device performance. In particular, the dark saturation current density is determined by $L_{\text{eff}}$ [45]. For infinite devices or zero surface recombination, $\Xi_n(W)$ vanishes and $L_{\text{eff}}$ equals $L_n$.

Figure 1.5: Effective diffusion length as a function of rear surface recombination rate and actual diffusion length for a 1 $\Omega$ cm wafer with thickness 300 $\mu$m.

Figure 1.5 displays the effective diffusion length as a surface map over a matrix of different values for $L_n$ and $S_n$. The case simulated here is a 300 $\mu$m thick cell of doping density $N_A = 10^{16}$ cm$^{-3}$. The $L_{\text{eff}}$-surface can be broadly divided into three regions. Region 1 is characterised by $L_n < 150$ $\mu$m and expresses a similar behaviour regardless of the surface recombination. In this regime, $L_{\text{eff}}$ and $L_n$ merge and it is likely that any analysis of the internal quantum efficiency will determine the bulk diffusion length
with great accuracy, while it will not reveal $S_n$. Region 2 is classified by a high surface recombination $> 2 \times 10^3 \text{ cm/s}$ and a high bulk diffusion length $\geq 200 \ \mu\text{m}$. The surface is almost flat in the whole region indicating that a broad set of different $L_n$ and $S_n$ will lead to the same effective diffusion length. For very high $L_n$ and $S_n$, $L_{\text{eff}}$ approaches $W$, a fact that is true for any wafer thickness. In most of this region, $L_{\text{eff}}$ is smaller than $L_n$. The impact of either recombination parameter on $L_{\text{eff}}$ is very hard to judge and usually requires the knowledge of one of them. The third regime is distinguished by its strongly ascending gradient. For most of this region, $L_{\text{eff}}$ is much higher than $L_n$, itself being much higher than the thickness. A small increase in $L_n$ or a small drop in $S_n$ brings about a rapid increase in $L_{\text{eff}}$. Effective diffusion lengths of equal magnitude lie on a ring surrounding the ascent, a fact that complicates the interpretation of $L_{\text{eff}}$ in this regime. In summary, the thickness of the sample can serve as an indicator to appraise $L_{\text{eff}}$.

The model of Lagowski-Spiegel

Due to the high degree of approximation in the derivation of Equations 1.29 and 1.32, the application of this equation is limited or can lead to erroneous results [54, 55]. Keller et al. calculated errors in $L_{\text{eff}}$ of 10–20% for certain scenarios of bulk diffusion lengths and surface recombination velocities. The uncertainties in $L_n$ could reach several 10% even if $S_n$ was known exactly. Note that the errors have only been caused by the analytical fitting and do not include any experimental uncertainties.

Several effects cause the limitations of the linear model: the linearity is not obtained for all cell designs, the influence of the emitter regions becomes more important when the cell thickness is decreased, there exists several possible pairs of $L_n$ and $S_n$ to obtain the same $L_{\text{eff}}$ and finally, the influence of the internal back side reflection can not be totally neglected. This effect is aggravated for thinner cells or better rear-side passivation.

Spiegel et al. [55] partly overcame this limitation by omitting the condition that $L_n$ should be larger than the penetration depth (condition 5). Going back to Equation 1.27 and neglecting any absorption in the front section of the device leads to the following derivation:

$$IQE_n \approx \frac{1 - (L_{\text{eff}})^{-1}}{1 - (L_n)^{-2}}. \quad (1.33)$$

A similar derivation has been found by Lagowski et al. for the surface photovoltage method [58]. This derivation is discussed in more detail in Chapter 2. Comparing this approximation with the linear model, Spiegel et al. found out that his model is capable
of predicting the effective diffusion length for a wide range of $L_n$, $W$ and $S_n$. The linear model, in contrast, only gives a high accuracy when $L_n \ll W$. In this case, Equation 1.33 reduces to Equation 1.29 \[55\].

Equation 1.33 has a further advantage in that it enables the separation of bulk and rear surface recombination via Equation 1.26. Spiegel et al. established the following situations in which a high accuracy in either $L_n$ or $S_n$ can be obtained: If the bulk diffusion length is smaller than the sample thickness, $L_n$ can be determined accurately for all $S_n$ values (region 1 in Figure 1.5). In the other case, $S_n$ has to be sufficiently small (i.e. if $L_n > 500 \ \mu m$, $S_n < 1000 \ \text{cm/s}$, region 3). The back surface recombination velocity, in turn, can be extracted with high accuracy if $L_n/W$ is high and $S_n$ is sufficiently small ($< 2000 \ \text{cm/s}$). Unfortunately, due to the pole in Equation 1.33, the analysis is restricted to $\alpha < L_n$. This is illustrated further in Figure 1.6. The total internal quantum efficiency and the contribution of each region has been plotted, using Equation 1.22 with the mono-exponential expression for the generation rate (Equation 1.5). The simulation parameters are: $W_e = 0.5 \ \mu m$, $D_p = 5 \ \text{cm}^2/\text{s}$, $L_p = 15 \ \mu m$, $S_p = 10^4 \ \text{cm/s}$; depletion region: $W_{scr} = 1 \ \mu m$; base: $W_b = 298.5 \ \mu m$, $D_n = 30 \ \text{cm}^2/\text{s}$, $L_n = 1000 \ \mu m$, $S_n = 10^7 \ \text{cm/s}$.

Additionally, the linear model (Equation 1.29) and the model of Lagowski-Spiegel (Equation 1.33) are shown. The graph reveals clearly the impact of the pole for wavelengths as low as 950 nm.

**Including absorption in the emitter and depletion region**

Figure 1.6 unveils another, general problem with the approximations that has been pointed out by Spiegel \[59\]. Surprisingly, both approximations agree very well with the total internal quantum efficiency for $\lambda = 600-1000 \ \text{nm}$, but not with the base contribution, of which they are an approximation. This suits of course the way the models have been used in experiments in the past, where the measured, that is, the total IQE has been employed for the fit. Spiegel realised that the contribution of the emitter and depletion region has to be included in the formulation of the linear model (Figure 1.6). By incorporating absorption (but not recombination) in the emitter and space charge region, he could prove for the linear model with $L_n \ll W$ that it is actually the inverse of the total internal quantum efficiency that obeys a linear relation \[59\]. His findings showed that even for unpassivated front surfaces or deep emitters with $W_e > 1 \ \mu m$, the linear model agrees down to $\lambda = 800 \ \text{nm}$. For all other cases, the range of wavelengths can be extended down to $\lambda = 600 \ \text{nm}$ \[59\].

This deduction is repeated in the following, going one step further and proving the
1. Spectral response of the short-circuit current

![Graph showing spectral response and contributions of different regions as a function of wavelength.](image)

**Figure 1.6:** Internal quantum efficiency and the contributions of the different regions as a function of wavelength. The curves are derived from Equation 1.22 using the mono-exponential expression for the generation rate. Additionally, the linear model and the model of Lagowski-Spiegel are depicted. The following parameter have been taken for the fit: Emitter: $W_e = 0.5 \, \mu\text{m}$, $D_p = 5 \, \text{cm}^2/\text{s}$, $L_p = 15 \, \mu\text{m}$, $S_p = 10^4 \, \text{cm}/\text{s}$; depletion region: $W_{scr} = 1 \, \mu\text{m}$; base: $W_b = 298.5 \, \mu\text{m}$, $D_n = 30 \, \text{cm}^2/\text{s}$, $L_n = 1000 \, \mu\text{m}$, $S_n = 10^7 \, \text{cm}/\text{s}$. Note the singularity of the model of Lagowski-Spiegel in Figure 1.6 due to the pole of Equation 1.33.

same for the model of Lagowski-Spiegel and thus arbitrary $L_n$ and $L_{eff}$. The contribution of absorption in the emitter region is given by:

$$IQE_p = \int_0^{W_e} dx \alpha e^{-\alpha x} = 1 - e^{-\alpha W_e}. \tag{1.34}$$

Going back to Equation 1.27 and including the absorption in the front region (Equation 1.15 and Equation 1.34), leads to the following:

$$IQE(J_{sc}) = 1 - e^{-\alpha(W_e + W_{scr})} + \frac{L_n \alpha}{L_n^2 \alpha^2 - 1} (L_n \alpha - L_n/L_{eff}) e^{-\alpha(W_e + W_{scr})}$$

$$= 1 + \frac{(1 - \alpha L_n^2/L_{eff}) e^{-\alpha(W_e + W_{scr})}}{L_n^2 \alpha^2 - 1}. \tag{1.35}$$

With the assumption $(\alpha (W_e + W_{scr})) \ll 1$, that is, only weak absorption in the front region, Equation 1.35 can be approximated by:

$$IQE(J_{sc}) \approx \frac{L_n^2 \alpha^2 (1 + (W_e + W_{scr})/L_{eff}) - \alpha (L_n^2/L_{eff} + (W_e + W_{scr}))}{L_n^2 \alpha^2 - 1}. \tag{1.36}$$

Finally, the fact that the effective diffusion length is much larger than the thickness of
the front region, allows us to neglect all terms containing \((W_e + W_{scr})\). This results in the same expression as in Equation 1.33, but here for the total \(IQE(J_{sc})\). This is an important result, as the accuracy of the fits for arbitrary cell designs can be increased by the incorporation of more wavelengths.

Fischer et al. realised the inclusion of the emitter region in a simple way by separating the front region into two sections [60, 61]: The first, with thickness \(W_d\), contains the lion share of the loss in the emitter. It is often called a ‘dead layer’, as it does not contribute to the carrier collection: If the absorption depth is much larger than \(W_d\), the amount of electrons generated in the dead layer is small and entirely annihilated by recombination at the front surface and the emitter. The second part encompasses a small section of the emitter region, the depletion region and the first part of the adjacent base region. In terms of wavelength, this segment describes all electrons generated by light in the range 500–700 nm. The loss in the emitter is confined to a few percent and can be described by an exponential pre-factor:

\[
IQE_n \approx e^{-\alpha W_d} \left( \frac{1 - (L_{eff} \alpha)^{-1}}{1 - (L_n \alpha)^{-2}} \right).
\]

In this way, an even better fit of the emitter component can be realised and the wavelength range can be extended down to 500 nm.

The model of Isenberg

The discontinuity of the model of Lagowski-Spiegel at \(1/\alpha = L_n\) hampers the analysis of \(IQE\) with this expression (Figure 1.6), especially for thin wafers [54, 56]. Isenberg et al. circumvented the discontinuity by using the full analytical version of \(IQE_n\) with the optical model of Basore [56]. The only assumption that flows into this model is the requirement that the absorption depth has to be larger than the combined thickness of the emitter and depletion region. It follows that \(f(W_e + W_{scr}) \approx f(0)\), the same for the derivative of \(f\). The model of Isenberg can then be computed from Equation 1.20:

\[
IQE_n = \frac{D_n}{L_n} \frac{f(0)}{(1 - R)N_{ph}} - \frac{D_n}{(1 - R)N_{ph}} \frac{\frac{S_n}{D_n} f(W) + f'(W)}{\frac{S_n}{D_n} \sinh_{L_n} \tanh_{L_n} + \cosh_{L_n}} + q D_n \frac{f'(0)}{(1 - R)N_{ph}}.
\]
Spectral response of the short-circuit current routine gave similar results to the formula of Lagowski-Spiegel [56]. As in the linear model and the model of Lagowski-Spiegel, simulations show that the model of Isenberg is an approximation to the total IQE rather than the base part.

In Figure 1.7 the inverse internal quantum efficiency as a function of the inverse absorption coefficient is displayed, where IQE has been calculated by different models. The analytical model is shown for two different generation rates (Equation 1.5 and 1.6). They are compared to their respective approximations: the linear model, the model of Lagowski-Spiegel and the model of Isenberg. The cell is a 335 µm thick cell with textured front surface and a diffusion length of either 10 µm (left graph) or 1000 µm (right graph). All other material parameters are the same as in Figure 1.6. If $L_n \ll W$, both versions of the analytical model converge for $\lambda \leq 1000$ nm. Carriers generated as a result of multiple reflection recombine before making any difference to the internal quantum efficiency. All approximations agree in the wavelength ranges depicted in the graphs, but they only represent a good fit for $\lambda \leq 900$ nm. The difference in the optical model becomes noticeable for $\lambda \sim 900$ nm in the case of a large diffusion length. Only then carriers generated due to internal reflection contribute to the IQE. The linear model constitutes only a satisfying

![Figure 1.7: Inverse internal quantum efficiency as a function of the inverse absorption coefficient for different models describing the internal quantum efficiency. In red, the analytical model using the mono-exponential expression for the generation (Equation 1.5) and its two approximations: the linear model and the model of Lagowski-Spiegel are shown. In blue, the analytical model with the optical model of Basore (Equation 1.5 for the generation) and its approximation, the model of Isenberg, are represented. For these two evaluations, the optical parameters for a textured front surface have been chosen. On the left side, the bulk diffusion length is smaller than the thickness of 335 µm ($L_n = 10$ µm), on the right side, larger ($L_n = 1000$ µm). The thickness of the depletion region has been chosen to $W_{scr} = 0.25$ µm, all other material parameters are the same as in Figure 1.6.](image)
approximation for wavelengths up to 900 nm, followed by the model of Lagowski-Spiegel (up to \( \sim 970 \) nm). The model of Isenberg is the only fit that describes the full analytical model for all shown wavelengths, if \( L_n \gg W \).

The most advanced model for \( IQE \) has been established by Brendel et al. [53] (Appendix C.2). They refined the optical model of Basore by accounting for partially diffuse reflecting rear surfaces. Another improvement is the distinction between the angle of light propagation in the emitter and base region. In this model, \( IQE \) and reflectance data are fitted with a least squares algorithm in order to maximise the information about electrical and optical parameters. The investigations led to the commercially available software IQElD [53, 62, 63], which also includes a homogenous emitter model and the space charge region (Equation 1.13 and 1.15), as well as a base region that can be subdivided into an electrically active region and a substrate region [64].

In broad terms, this section described three different models that are able to fit the inverse of the internal quantum efficiency of the short-circuit current in the wavelength range of \( \sim 600-1000 \) nm. The linear model, the model of Lagowski-Spiegel and the model of Isenberg. The linear model is most welcome in experiment, since the analysis proves to be simple and straightforward. But the restriction to \( L_n \ll W \) places a limit to its application. This gap is filled by the other two models, but they are more cumbersome, needing a non-linear fit analysis. In Chapter 2, special attention is paid to these three models during the examination of the spectral response of the open-circuit voltage.

### 1.4.2 Rear illumination

A viable alternative to the illumination of the emitter side is the opposite: the case where the base region is exposed to the light source. This applies to bifacial solar cells, to the rear illumination of conventional cells, where the back metallisation has been etched away, or to rear-junction solar cells. This allows, similarly to the evaluation in the last section, the determination of the bulk diffusion length and the surface recombination velocity [65–69]. The surface recombination velocity in this case denotes the velocity of the side exposed to the illumination. This technique will be applied in this thesis to rear-junction cells produced on n-type base material. Hence, we will begin the mathematical treatment with Equation 1.13, from where the internal quantum efficiency of the n-side region can be deduced:

\[
IQE_p = \frac{L_p \alpha}{L_p^2 \alpha^2 - 1} \left( -\Xi_p(W) e^{-\alpha W} + \frac{S_p L_p}{D_p} \sinh \frac{W}{L_p} + \cos h \frac{W}{L_p} + L_p \alpha e^{-\alpha W} \right). \tag{1.39}
\]
Of particular interest is the mid-wavelength region (500-800 µm). The rear-surface IQE significantly deviates from the front-surface IQE in this region. It is basically flat, with a small positive slope towards the longer wavelength. The absolute number of the rear-IQE is very sensitive to \( L_p \) and \( S_p \) and can reach values below 30% for low \( L_p \) or high \( S_p \). This results from the fact that photo-generated carriers have to diffuse across the width of the base in order to be collected at the junction. In the mid-wavelength region, Equation 1.39 can be further approximated using the following assumption: 1) \( \alpha W > 2 \), i.e. the absorption depth has to be much smaller than the thickness. This eliminates all terms with \( \exp(-\alpha W) \). 2) Negligible absorption in the passivation layer of the n-side (e.g. back-surface field). 3) \( L^2_p \alpha^2 \gg 1 \). This implies that the penetration depth is smaller than the average length the charge carriers have to endure before they recombine. This results in the following [66]:

\[
IQE_p = \frac{1 + \frac{S_p}{D_p} \frac{1}{\alpha}}{S_p L_p \frac{W}{D_p} \sinh \frac{W}{L_p} + \cosh \frac{W}{L_p}}.
\]

This equation predicts that a plot of \( IQE_p \) as a function of the absorption depth should yield a linear relationship. The slope divided by the intercept equals \( S_p/D_p \) and a numerical fit using this value allows then access to the diffusion length.

This section completes the description of models that have been successfully applied in the past to determine the bulk diffusion length and the surface recombination from the internal quantum efficiency of the short-circuit current. The challenge will be whether similar models can be derived for the measurement of the spectral response of the open-circuit voltage. These evaluations will indeed prove very useful, as we will see in the next chapter, since the open-circuit spectral response can be described in similar terms to the IQE.

### 1.5 Conventional spectral response of the short-circuit current

In this section, the measurement method to determine the spectral responsivity that is used in most calibration laboratories is presented [70]. It is called ‘conventional’ to distinguish it from the newly developed quasi-steady-state short circuit current response, QSSJ_{sc-\lambda}, that will be introduced in the next section. The characteristic feature of the conventional technique is the light source: a time-modulated low, continuous power beam
for the monochromatic excitation that is superimposed onto a strong bias light. The method can therefore be labelled a ‘small signal’ technique. Figure 1.8 shows a schematic set-up of the measurement tool.

The monochromatic beam is achieved by using a xenon arc lamp (usually 1 kW) or a tungsten halogen light (150 W). A grating monochromator produces the monochromatic light. As an alternative, a set of several wheels containing bandpass filters of different wavelengths with 10 nm bandwidth is often employed. Grating monochromator systems have the advantage of a higher spectral resolution, but suffer from lower optical transmission than filter-based systems. The spectral range extends from 280 nm at the UV end of the spectrum to 1330–1900 nm at the IR end. A filter wheel placed behind the exit slit of the monochromator cuts of higher-order diffractions. Additionally, ‘grey filters’ can be introduced into the beam path to attenuate the strong lines of the Xe lamp that occur in the infrared or stray light because of reflection inside the monochromator. Optical fibre bundles direct the beam towards a monitor device and the sample under investigation. The light beam is homogeneous over approximately $2 \times 2 \text{ cm}^2$. The bias light is used to regulate the injection level of the device and is in general adjusted to 1 sun to simulate a cell under standard operation conditions. The ratio of signal to bias current on a $2 \times 2 \text{ cm}^2$ cell illuminated with one sun bias light is in general $10^{-6}$ to $10^{-4}$. To discriminate between the test-device current resulting from monochromatic light and that from stray and bias light, the small power beam is modulated with a light chopper before entering the monochromator. The periodic monochromatic light produces an AC photocurrent that is converted into an AC voltage. It is filtered out from the DC broadband current by a lock-in amplifier. The operational amplifier maintains the device at a constant voltage. Systems employing a pulsed flash and bandpass filters are not uncommon for $EQE$ measurements of solar cells and modules. The set-ups used for solar modules are usually very large in size: the flash and the test devices are separated by up to 8 m, resulting in an intensity of $\approx 0.01$ suns [71]. Budde et al. scaled down such a system to measure small solar cells of $2 \times 2 \text{ cm}^2$ [72], and used the decaying part of the flash. Their method can be considered quasi-steady-state, but with very weak signals, due to the large distance between light source and test device. A pulsed flash combined with 1 nm narrow bandpass filters has also been used by Ostojia et al. for $EQE$ measurements of solar cells [73].

To determine a device’s spectral responsivity, one must know the power, or irradiance reaching the test device at each wavelength and the current produced by the device at each of those wavelengths. The power is measured by means of a calibrated monitor cell, a photodiode or a pyroelectric radiometer. At the same time the current produced by
the sample device is measured. If $J_{sc, mon}$ and $EQE(J_{sc, mon})$ are the current density and external quantum efficiency of the monitor cell, the external quantum efficiency of the sample cell can be deduced from:

$$EQE(J_{sc, samp}) = \frac{J_{sc, samp}}{J_{sc, mon}} EQE(J_{sc, mon}),$$

where $J_{sc, samp}$ and $EQE(J_{sc, samp})$ denote the analogous sample values. The accuracy of the measurement can be increased if a calibrated reference cell is measured before the measurement of the test device to check the stability of the light source. All measurements of the conventional spectral responsivity in this work have been performed at the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany, with a set-up similar to the one shown in Figure 1.8.

1.6 Quasi-steady-state technique for the spectral response of the short-circuit current

1.6.1 Measurement set-up

The conventional spectral response represents an exciting technique that has since long demonstrated its valuable status, but it has some disadvantages. The small light excitation
ensures a linear relationship between incoming light intensity and output signal, but the
data signals usually have to be amplified with the lock-in technique. The small signals are
far from the high intensities solar cells face in normal operation, which is circumvented by
the use of a bias light in the case of the short-circuit method. However, this leads to the
measurement of differential parameters, which have to be integrated in a subsequent step.

We present in this thesis a direct method employing large signals, avoiding a bias light
and therefore giving the true steady-state, rather than the differential parameters: the
spectral response of the quasi-steady-state short-circuit current (QSS/J_{sc-\lambda}). The method
uses bandpass filters instead of a monochromator and has no lock-in amplification. The
set-up presented here is similar to the design of Budde et al., the main difference being
that the distance between the flash and the test plane is reduced to reach high illumination
intensities. The data quality is also improved by using a fast data acquisition card. The
QSS/J_{sc-\lambda} method avoids some errors common to traditional small signal systems. For
example, errors associated with the electronic instrumentation used for the current-voltage
conversion (e.g. lock-in amplifier) and errors as a consequence of the response-time to
periodic light or the spectral content of the bias light [29]. The photographic flash offers
the advantage that a broad range of light intensities can be measured. Hence, the external
quantum efficiency and, as a consequence, the diffusion length can be investigated as a
function of intensity in one single measurement.

A sketch of the measurement apparatus is shown in Figure 1.9. In addition, Figure 1.10
provides a closer inspection of the experimental set-up. Two different models of photo­
graphic flashes have been employed in this thesis: 1) A Quantum flash with a total power
output of 400 J, a time constant of \sim 1 ms and a maximum pulse time of \sim 8 ms [74]. 2)
A Broncolor flash with a total power rating of 1600 J, a time constant of \sim 3 ms and a
pulse length of \sim 12 ms [75], which is about 5 times longer than the flash used by Budde
et al. [72]. With the latter flash, intensities up to 10 suns of monochromatic illumination
are attainable using 10 nm filters. The pulse of the flashes has a sharp increase and an
approximately exponential decay (see also Figure 1.11). A black tube placed around the
light bulb provides some collimation of light towards the bandpass filter. 16 bandpass
filters with a bandwidth of 10 nm covering the range of 400-1150 nm at intervals of 50 nm
produce the required monochromatic light. The photon flux has been adjusted with grey
filters so that the same range is covered for each wavelength. The range of photon fluxes
in most experiments stretches from approximately \(2\times10^{16}\) to \(8.5 \times 10^{17} \text{s}^{-1}\text{cm}^{-2}\). This is
equivalent, in terms of photons that can be absorbed by silicon, to a white light intensity
of 0.04-3 suns. The illuminated area on the test plane is \(5\times5 \text{cm}^2\).
The samples are placed on a copper stage whose temperature is kept at 25 °C. A mask is used to illuminate only the area of the device. An operational amplifier keeps the test cell under short-circuit conditions. The monitor cell is a back-contact silicon-concentrator cell from SunPower [76]. The monitor device is connected in parallel with a resistor that places the cell near short-circuit operation. This ensures the linearity between the photon flux and the output current. The magnitude of the resistor can be changed according to the light intensity to avoid the monitor cell moving too close to open-circuit conditions. The monitor cell exhibits an excellent linearity with the incident photon flux up to an intensity of ~ 10 suns [77, 78] but performs sub-linearly with intensities higher than ~ 100 suns.

In a first measurement, the photon flux is determined by the monitor cell. Subsequently, the quasi-steady-state short-circuit current of the sample is measured. A stepper motor moves the stage area between the reference and test device. To increase the accuracy of the measurement, the flash pulse can be repeated (usually between 3–5 times). This counteracts possible fluctuations of the light intensity. The data is read out by means of a data acquisition card and analysed in the computer. The total measurement time, employing one flash per wavelength, is about 3 minutes. An additional advantage of this technique is that, by simply omitting the operational amplifier, the test device can be switched to open-circuit conditions and the voltage response can be detected. This allows
a quick analysis of current and voltage response in succession. The voltage method is described in detail in the next chapter.

The measurement set-up is host to a number of various measurement technique beside the spectral response of the short-circuit current. The intensity-current and intensity-voltage curve of a solar cell can be recorded after removing the filter compartment. The second tool is reviewed in Chapter 2 and 3. The temperature of the sample stage can be adjusted between 10–190 °C, permitting defect analysis of bulk material. Three methods are available that rely on the temperature dependence of defect parameters: the temperature dependent internal quantum efficiency of the short-circuit current and the open-circuit voltage ($\text{TQE}_\text{sc}$ and $\text{TQEV}_{\text{oc}}$, respectively) and the temperature and injection-level de-

Figure 1.10: Photograph of the measurement apparatus with which all quasi-steady-state measurements have been performed. This set-up houses the following methods: the quasi-steady-state short-circuit current ($\text{QSS}_\text{sc}$) and its spectral dependent counterpart ($\text{QSS}_\text{sc}\text{ }-\lambda$), the quasi-steady-state open-circuit voltage ($\text{QSS}_\text{oc}$) and its spectral version ($\text{QSS}_\text{oc}\text{ }-\lambda$) (see also Chapter 2). Furthermore three temperature dependent methods: the temperature dependent internal quantum efficiency of the short-circuit current and the open-circuit voltage ($\text{TQE}_\text{sc}$ and $\text{TQEV}_{\text{oc}}$, respectively) and the temperature and injection-level dependent voltage spectroscopy (TIVS, Chapter 3). By placing the photoconductance testing station on top of the sample stage, the spectral response of the photoconductance ($\text{QSSPC}\text{ }-\lambda$) is the final option that can be examined (Chapter 4).
1. Spectral response of the short-circuit current

Figure 1.11: The photon flux and short-circuit current signal corresponding to the photographic flash pulse at 400 nm of the 0.7 Ωcm cell RPAL44_A1.2b.

Figure 1.12: Short-circuit current of the 0.7 Ωcm cell RPAL44_A1.2b versus photon flux for various wavelengths.

ependent voltage spectroscopy (TIVS, Chapter 3). By placing a photoconductance testing station on top of the sample stage, the spectral response of the photoconductance (QSSPC-λ) is the last option that can be examined (Chapter 4). The design and construction of the measurement apparatus and the software for the data acquisition and analysis have been the core work of this thesis.
Coming back to the $Q_{ssJ_{sc}-\lambda}$ technique, let us have a close look at the data analysis. The measured short-circuit current is proportional to the incoming photon flux. This can be seen in Figure 1.11, where the response of the monitor cell and the sample cell to the flash pulse is depicted. The signal of the photon flux and current are usually taken from the maximum of the pulse. The actual units of the photon flux are $s^{-1} \text{cm}^{-2}$, but the typical magnitudes of $10^{16} \times 3 \times 10^{17} s^{-1} \text{cm}^{-2}$ are not very meaningful for most people. Therefore we display the photon flux in ‘suns’, in the sense that 1 sun of monochromatic light at 400 nm corresponds to the number of photons at 1 suns under standard AM1.5G conditions. This can be expressed as: $N_{\text{ph}}[\text{suns}] = N_{\text{ph}}[s^{-1} \text{cm}^{-2}] / 2.814 \times 10^{17} / \text{suns}$. Figure 1.12 illustrates a typical example of a $Q_{ssJ_{sc}-\lambda}$ measurement. The cell investigated here exhibits a very strong sensitivity to monochromatic light of different wavelengths due to a low bulk diffusion length. The external quantum efficiency is extracted from the slope of the photon flux-current curve using the whole illumination range [72]. By virtue of to the longer flash duration in this system compared to Budde et al., a broader range of intensities can be measured and the determination of the slope becomes more precise. To investigate non-linear behaviour in solar cells, the external quantum efficiency can also be determined at a constant current or photon flux.

The measurement errors of the system are due to several factors: The sequential measurement of reference and test device may introduce errors a consequence of the fluctuation of the light intensity between both measurements. This is mitigated by averaging the measurements of several flash pulses at each wavelength. Next, the determination of the photon flux, which has been outlined in detail in Appendix B.1, requires the exact knowledge of the $EQE$ of the monitor cell and the relative photon flux of the flash lamp. The $EQE$ of the monitor cell has been measured at the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany, with a measurement error of $\pm 3\%$ [79]. Concerning the flash spectrum, not only the wavelength dependence but also the time dependence is important, since the spectrum shifts to longer wavelengths with time. However, the time dependence of the flash spectrum is difficult to measure. In most cases, the Broncolor flash has been used for the measurement, where a photon flux spectrum was not available. As discussed for the Quantum flash in Appendix B.1, the error is small, provided the $EQE$ of the monitor cell is known: smaller than $\pm 0.08\%$ for wavelengths between 450 and 950 nm and smaller than $\pm 1.2\%$ for 400, 1000 and 1050 nm. The error for higher wavelengths could not be assessed, since the available data of the flash spectrum is limited.

\[\text{The unity 1 sun is defined as the area under the AM1.5G sun spectrum normalised to 100 mW/cm}^2.\]

For the calculation of 1 suns of photon flux we used the area that contributes to the absorption in silicon. In other words, all photons, whose energy lies above the band-gap of silicon, are used in the calculation. In terms of wavelengths, all photons with $\lambda < 1130 \text{ nm}$.
to wavelength $< 1070$ nm, but is likely to increase with wavelength. We estimate an error of 2% for this spectral mismatch, so that the total error of $EQE$ due to the photon flux determination is approximately ± 4%.

The optical system of the QSS$J_{sc}$-λ apparatus has still room for improvement: the collimation of the light beam is only achieved with a black tube, not with appropriate lenses, meaning that a proportion of the light strikes the filters at an angle. This may lead to a small wavelength shift and a slightly different reflectance at the cell's surface. Additionally, it can not be excluded that some stray white light or background light from the cabin walls may be absorbed in the test device. The uniformity of the light may also vary across the test plane. We estimate an error of 5% for the stray light and the determination of the short-circuit current. The total error at each light intensity amounts to approximately ± 8% (using the root sum square of each error). The linear fit decreases this error to approximately ± 5% due to error propagation. In comparison, by repeating the measurement several times, a maximum deviation smaller than ±5% is observed for most cells.

1.6.2 Comparison between the traditional spectral responsivity method

A range of solar cells with various structures have been tested with both methods for characterising the spectral response. Table 1.2 lists the thickness, doping type, resistivity and cell performance data. These are the test cells examined:

1) FB99.8d, a high-efficiency cell with passivated rear surface and local back surface field. This structure is known under the names PERL (Passivated Emitter and Rear

<table>
<thead>
<tr>
<th>Name</th>
<th>Thickness [µm]</th>
<th>Base Material</th>
<th>Resistivity [Ω cm]</th>
<th>$J_{sc}$ [mA/cm²]</th>
<th>$V_{oc}$ [mV]</th>
<th>$FF$ [%]</th>
<th>$η$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FB99.8d*</td>
<td>385</td>
<td>p-type FZ</td>
<td>1.25</td>
<td>38.8</td>
<td>670</td>
<td>78.4</td>
<td>20.4</td>
</tr>
<tr>
<td>RPAL44.A1.2b*</td>
<td>330</td>
<td>p-type Cz</td>
<td>0.7</td>
<td>29.1</td>
<td>571</td>
<td>79.5</td>
<td>13.2</td>
</tr>
<tr>
<td>RPAL44.A3.1b*</td>
<td>335</td>
<td>p-type Cz</td>
<td>0.15</td>
<td>25.2</td>
<td>585</td>
<td>80.1</td>
<td>11.8</td>
</tr>
<tr>
<td>ULF03.7.5*</td>
<td>99</td>
<td>p-type FZ</td>
<td>0.5</td>
<td>38.3</td>
<td>658</td>
<td>78.2</td>
<td>19.7</td>
</tr>
<tr>
<td>ULF03.10.5*</td>
<td>156</td>
<td>p-type FZ</td>
<td>0.5</td>
<td>37.7</td>
<td>638</td>
<td>76.4</td>
<td>18.8</td>
</tr>
<tr>
<td>FB137.14-20.1*</td>
<td>220</td>
<td>p-type mc</td>
<td>1.25</td>
<td>31.1</td>
<td>584</td>
<td>77.1</td>
<td>14.0</td>
</tr>
<tr>
<td>M31</td>
<td>235</td>
<td>p-type mc</td>
<td>0.3</td>
<td>29.3</td>
<td>620</td>
<td>77.7</td>
<td>14.1</td>
</tr>
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<td>80nza</td>
<td>357</td>
<td>n-type FZ</td>
<td>80</td>
<td>34.5</td>
<td>617</td>
<td>79.2</td>
<td>16.9</td>
</tr>
</tbody>
</table>
1.6 Quasi-steady-state technique for the spectral response of the short-circuit current

Locally diffused Cell [80]) or LBSF cell [81]. This cell type features at the front a MgTi double-layer antireflection coating (ARC) on top of a 105 nm SiO₂ passivation layer and a two-step emitter diffusion. Another SiO₂ layer completes the passivation on the rear side. The local back surface field is achieved by a p⁺ diffusion under the rear point contacts. The cell is characterised by an excellent current, voltage and fill factor, resulting in a high conversion efficiency.

2) RPAL44.A1.2b and RPA144.A3.1b, two Passivated Emitter and Rear Cells (PERC) [82] fabricated on aluminium doped base material. In addition to the previous device, they received a front texture with random pyramids, while they do not benefit from a double-layer ARC. The passivation scheme is the same as for cell 1. No second emitter diffusion under the front grid lines has been performed. The base material is known to have a very low diffusion length due to an aluminium related defect [83]. The low Jsc and Voc reflect the losses in the bulk due to these defects.

3) ULF03.7.5 and ULF03.10.5, two laser-fired contact (LFC) cells with random pyramids processed on thin wafers of thickness 99 and 156 µm [84, 85]. The peculiarity of this cell structure is the rear contact scheme, where a laser fires the contact pattern through the rear side SiO₂ passivation [86]. The front side of the cell is the same as in 2). The wafers have been thinned by mechanical abrasion.

4) FB137.14-20.1, a multi-crystalline solar cell experiencing a high-efficiency structure that is slightly modified from the traditional PERL/LBSF cell. The differences are: honey comb texture at the front surface, gettering diffusion and single step phosphorus emitter [87].

5) M3l, a multi-crystalline device with simplified PERC structure [88]. The simplifications are: no surface texturing and a single step emitter diffusion. The front and rear surfaces are passivated with silicon nitride. This cells is characterised by a high Voc as a result of an excellent SiN passivation quality, the reduced degradation of the bulk material by avoiding high temperature oxidation [88], and, importantly, the use of low resistivity silicon.

6) 80nza, an n-type rear junction cell, where the junction has been made by alloying the full area aluminium contact at the rear side. The front passivation consists of a n⁺n high-low junction followed by a thin silicon oxide passivation that also serves as a crude antireflection coating [89].
The first five cells have been processed at the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany; the last two at the Semiconductor Physics and Devices laboratory at ANU. Some of these cells will accompany us throughout the remainder of the thesis in a variety of applications. Figure 1.13 illustrates the comparison of the measurements with both techniques. Since the quasi-steady-state measurement could not detect any injection-level dependence of the cells investigated here, it is expected that the differential $EQE$ obtained from the conventional technique will agree with the integral $EQE$. The data of the QSS$J_{sc}-\lambda$ measurements is the mean $EQE$ of several repeated measurements. Error bars indicate a deviation of 5% estimated from the measurement errors of the photon flux and the current, the scattered white light and the linear fit, unless the mean deviation from repeated measurements resulted in a higher error. The error of the conventional method is approximately ± 3% [79].

The first two samples show an excellent agreement between both diagnostic tools. The $EQE$ of the PERL cell is a reflection of its high-efficiency design and its corresponding cell characteristics. The low response for wavelengths $> 700$ nm in the aluminium-doped PERC cell on the upper right is a strong indicator of a low diffusion length of the bulk material. Note the high response in the UV for this device, which is a consequence of the reduced reflectance at the textured surface. This strong response can also be seen in the next two examples, ULF03.7.5 and FB137.14-20.1.

The $EQE$ of the thin cell ULF03.7.5 shows the shape of a well designed high-efficiency device. The sample has a lower responsivity between 500 and 900 nm when measured with the conventional method, while the external quantum efficiency measured with QSS$J_{sc}-\lambda$ touches the 100% mark. The latter clearly proves too optimistic, since the reflectance amounts to 6% at 600 nm. Thus, the measurement error for this cell is likely of the same order of magnitude as the value of the reflectance in this range, i.e. 6%. The difference in cell structure compared to the other devices may indicate the source of the overestimated $EQE$, that is, the much lower thickness of the substrate and the laser-fired contacts. Notwithstanding this, both curves agree satisfactorily within the measurement errors.

The device on the middle right, FB137.14-20.1, starts its spectral response with a high yield as can be expected for a well-passivated device with honey comb texturing. But it suffers clearly in the lower energy end of the spectrum, which has its origin in the lower quality of the bulk material. In the 1000 nm region, the two techniques disagree the most, which can not be explained by the measurement errors. Again, we have not been able to detected a significant injection-level dependence in the QSS$J_{sc}-\lambda$ data that could point to a possible explanation. It has to be added that the $IQE$ in the IR is the region most
1.6 Quasi-steady-state technique for the spectral response of the short-circuit current

Figure 1.13: Comparison of the external quantum efficiency of six different cell structures measured by the conventional spectral response technique and by the quasi-steady-state short-circuit current response. Error bars indicate a deviation of 5% estimated from the measurement errors of the photon flux and the current, the scattered white light and the linear fit, unless the mean deviation from repeated measurements resulted in a higher error. The error of the conventional method is approximately ± 3% [79]. The most important parameters of the cells are summarised in Table 1.2.

difficult to measure accurately, which may partly explain the discrepancies. The EQE of the cell on the lower left, M3I, also decreases in the high wavelength range as a result of the low bulk diffusion length of the multicrystalline material. Here, the comparison of both spectral responsivity tools results in an excellent agreement. The measurements of the last cell, the rear-junction cell 80Nza, shows a clear divergence at very high wavelengths. The reason for the discrepancy with the conventional measurement most probably lies in the
fact that the $EQE$ of a rear-junction cell is more sensitive to IR light absorption than front-junction devices.

For the quasi-steady-state measurements, an injection-level dependence of the short-circuit current response at high wavelengths may be expected for devices with rear passivation. However, even for the high lifetime FZ cells no such dependence on the light intensity could be detected. This is most likely rooted in the fact that the measurement is still limited to such low carrier density levels that the injection-level dependence plays a minor role. Note that, although the flash used is capable of producing up to 10 suns of illumination, the device is in short-circuit, which results in a much lower carrier density than what would be expected in open-circuit. Furthermore, for non-linear solar cells, it is likely that the illumination with 1 sun of monochromatic light will result in a different $EQE$ compared to biasing the sample with 1 sun light and measuring the small monochromatic light excitation.

In this section, we presented for the first time measurements of the spectral response using quasi-steady-state monochromatic light of high intensity. For most of the cell types discussed here, the comparison with the conventional spectral response resulted in a good to excellent agreement. Still, two cell structures fall slightly short of this positive outcome: the RP-LFC cells and the multicrystalline cell FB137_14-20.1. An injection-level dependence as the cause can be excluded, the exact reason for the discrepancies is rather suspected to lie in the different optics and bias illuminations used in both measurement set-ups. The conventional $EQE$ has been measured with a system consisting of two monochromators in series, the light beam is therefore very narrow and close to its target wavelength. For the QSS$J_{sc}$-$\lambda$, by contrast, errors may arise from the imperfect light collimation and stray white light. Nonetheless, the measurements demonstrate that the new spectral response technique has successfully passed its examination.

1.7 Conclusion

In this chapter, the notion of the spectral response of the short-circuit current has been reviewed. The concept of the external and internal quantum efficiency has been presented, noting the importance of the latter in revealing the recombination dynamics of the various segments of the solar cell. A mathematical framework has been set up that describes the spectral response in a simplified yet highly meaningful way. The model delineated here leads to a relationship for the total current output as a function of wavelength that is valid for arbitrary operation conditions and generation rates. This generalisation will
prove useful for the understanding of the spectral response of the open-circuit current, described in the next chapter. This derivation has been, furthermore, the starting point to discuss a number of approximations prevalent in the literature that serve to extract important recombination parameters from a spectral response measurement. As such, the well-known linear model, the model of Lagowski-Spiegel and the model of Isenberg received special attention. All models aim to determine one or several of the following bulk properties: the minority diffusion length, the effective diffusion length and the base surface recombination velocity. The detailed deduction and analysis of these models is motivated by the idea to apply them to the spectral response of the voltage, which would contribute to the existing body of knowledge.

The technique that spearheads the suite of characterisation tools for spectral responsivity measurements has been presented. The distinctive attributes of this method are the small light excitation superimposed by a strong bias light and lock-in detection. This tool has been compared with the newly devised quasi-steady-state short-circuit current response. It enjoys large signals and thus can resort to simple data acquisition hardware. As another consequence, the technique measures the true instead of the differential spectral response. The main attraction of the quasi-steady-state current response is the possibility to study the injection dependence of the spectral response, although this needs further experimental verification.

Comparison of measurements performed with both methods show an excellent agreement, underlining the powerful monitoring capabilities of the new diagnostic tool. Slight differences in the spectra have been related to technical issues of the QSS$J_{ac}-\lambda$ apparatus. They are the sequential measurement of monitor and sample cell, fluctuation in the flash intensity and optical errors like stray light and inhomogeneities in the light spot. The samples investigated here showed no injection-level dependent $EQE$, which has been explained by the fact that the excess carrier concentration is still much less than under open-circuit, even if light intensities of up to 10 suns are used to illuminate the device. The spectral response of the voltage, envisaged in the next chapter, is naturally better suited to investigate injection-level dependence.
Spectral response of the open-circuit voltage

"The illumination-V_{oc} curve only requires that the contact to the p^+ and n^+ regions of the cell be much better than the impedance of the measurement tool. This very simple requirement means that in many cases, the illumination-V_{oc} curve can be taken at any point in the process after the emitter diffusion by simply probing the appropriate areas of the silicon."

Ron Sinton, 1999

2.1 Introduction

The open-circuit voltage is one of the most important parameters that determine the performance of solar cells, its significance equalled only by the short-circuit current. However, the spectral response of the voltage has long been ignored as a unique feature of solar cells. The reason for this is, on one hand, the fact that with the spectral response of the short-circuit current, there exists a well established diagnostic tool satisfying all questions about the solar cell's response to light of different wavelengths. On the other hand, the voltage has been assumed to be barely affected by the sun's spectral composition. Besides the fact that this work proves the opposite, there are enough other incentives to delve into this intriguing field of inquiry.

For a start, the conventional short-circuit current method is hindered by the fact that it requires finished solar cells to ensure that series and contact resistance effects do not limit the collection of current carriers. However, voltage measurements can be performed as soon as a junction has been formed in the silicon wafer, offering the advantage of quality control of the subsequent process steps. Next, in the traditional short-circuit current technique, a bias light is used in order to investigate the device at an injection level intended to approach normal operation conditions. Nevertheless, because the device
is maintained at short-circuit, the most important conditions, the maximum power point, remain unexplored. To approach injection levels representative of maximum power while maintaining short-circuit conditions, bias light intensities greater than 10 suns would be needed, which is impractical even with the approach launched in the last chapter. At open-circuit conditions, on the contrary, a bias light is able to establish the carrier concentration, which prevails at the maximum power point, at light intensities that usually lie below 1 sun.

Certainly, there already exists a technique that is based on measuring the spectral response of the voltage: the surface photovoltage technique, or shortly SPV [22, 46]. This technique is widely used to measure the carrier diffusion length. But the spectral photovoltage serves only as a spring board to access the diffusion length, while no importance has been ascribed to its own meaning. It is primarily seen as a 'lifetime testing method' rather than a spectral response technique. The SPV method uses a similar measurement setup to the conventional short-circuit current response, including a light source, a chopper, a monochromator and a lock-in amplifier. The most frequent tactic to inspire the build-up of a voltage is to induce a surface space-charge region by chemically treating the device's surface. In this case no contacts or junctions have to be formed. Solar cell precursors enjoying an emitter diffusion, completed solar cells or Schottky diodes are also suitable. The SPV method measures a voltage in the range of a few mV. This ensures that the voltage is proportional to the irradiance of the light source. However, it is quite different from measuring the real open-circuit voltage of a solar cell. The small photovoltage proves also to be very affected by high surface or depletion recombination, which can lead to incorrect determination of the diffusion length in the constant voltage SPV [90].

The spectral response of the voltage is staging a comeback in this chapter in the form of the quasi-steady-state open-circuit voltage response (QSSV_{oc-λ}). In a sense, it is a melange between SPV and another well acclaimed voltage characterisation tool: the quasi-steady-state open-circuit voltage (QSSV_{oc}). This method uses the same principle as QSSJ_{oc-λ} (chapter 1): a flash lamp provides a broad range of intensities, whose signal is picked up by a monitoring cell. Simultaneously, the voltage change is detected. The result is a (white-light) illumination-voltage curve that can be easily converted into an $I-V$ curve if the short-circuit current at 1 sun is known [12]. The difference between the implied $I-V$ curve and a directly measured one lies in the fact that the voltage measurement does not account for series resistance effects. QSSV_{oc} can be applied at any moment after junction formation, the only requirement being that the contact to the $p$ and $n$ regions of the cell are much better than the input impedance of the measurement set-up [12]. This offers the scope to analyse in detail each processing step that follows the emitter diffusion until the
full completion of the cell.

By implementing bandpass filters into the QSSV\textsubscript{oc} system, it turns into a spectral responsivity method. This is the avenue taken in this work. The voltages reached in the device by performing QSSV\textsubscript{oc}-\lambda measurements are usually in the range 300–750 mV and include the voltage at the maximum power point and the open-circuit voltage at standard 1 sun condition. Thus, contrary to the SPV method, the spectral response of the open-circuit voltage is measured akin to the conditions solar cells face in normal operation. Although short-circuit conditions are not actually explored, they can be approximately inferred from the open-circuit conditions at very low light intensities in the range of 1/20th to 1/10th suns.

This study has shown that the spectral response of the voltage behaves similarly to the spectral response of the short-circuit current, making it a valuable technique in solar cell characterisation. Beyond the similarity between the traditional and new spectral response techniques, the spectral photovoltage allows a new insight into recombination losses of solar cells, based on the different carrier concentrations at short and open-circuit conditions. Moreover, it permits the extraction of spectrally resolved recombination losses at an average injection level that is similar (or representative) to that prevailing at the maximum power point. QSSV\textsubscript{oc}-\lambda provides an improvement to the spectral response of short-circuit current tool in the sense that it does not need fully-fledged solar cells and scores an advantage over SPV in the sense that it delivers a broad range of voltages that reflect the operation conditions between short-circuit and open-circuit boundaries.

This chapter is organised as follows: the next section tackles the most burning issue: what are the characteristics of the spectral response of the voltage? After the introduction of a definition for the voltage response, computer simulations are carried out that help to clarify the impact of recombination and material parameters on the spectral response. Section 2.2 continues as well the work on the one-dimensional analytical model that was started in Section 1.3 for the special case of open-circuit conditions. A link between the spectral response of the voltage and the current is established here. The importance of the SPV technique deserves a special place, hence, Section 2.3 is dedicated to explain the method in more detail and compares it with the new spectral response tool. Next, we proceed to the experimental validation of the new technique. Here, measurements of the spectral response of both the short-circuit current and open-circuit voltage are compared. A new spectral technique can not gain in importance without proving that it is able to extract the base diffusion length. This important matter provides the motivation for the final section.
2. Spectral response of the open-circuit voltage

2.2 Characteristics of the spectral response of the voltage

2.2.1 Definition of the external and internal quantum efficiency of the voltage

The external quantum efficiency of the short-circuit current $EQE(J_{sc})$ compares the incident photocurrent $qN_{ph}$ to the collected current $J_{sc}$. In analogy to this, a suitable definition of the external quantum efficiency of the open-circuit voltage would be to compare the maximum voltage that can be induced by the incident photon flux with the measured open circuit voltage $V_{oc}$. The inherent difficulty with this approach lies in the fact that there exists no straightforward way to deduce a voltage as a function of photon flux that reflects 100% conversion of photons into charge carriers. The voltage is not only determined by the amount of incident photons but as well by the current flow within the cell. In other words by the saturation currents of the emitter and base region, $J_{0e}$ and $J_{0b}$, respectively. If these current flows are known, an upper limit to the voltage may be derived via [11]:

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{qN_{ph}}{J_{0b} + J_{0e}} \right),$$

$$J_{0b} = \frac{qD_n n_f^2}{L_n N_D} \Xi(H).$$

Here, the derivation of $J_{0b}$ of an ideal one-dimensional device in terms of the bulk diffusion length $L_n$, the doping density $N_D$ and the diffusion constant $D_n$ is given as well. The emitter saturation current may be suppressed in an idealised solar cell, but the base saturation current has to be more realistic in order to derive a reasonable ‘100% voltage’. This means that the silicon material and the device structure have to be taken into account. Due to the logarithmic term in Equation 2.1, the upper limit of the voltage is very sensitive to small changes in $J_{0b}$. The most critical of the parameters that determine $J_{0b}$ is the bulk diffusion length. An upper limit to $L_n$ under low-injection conditions is given by Auger recombination. However, this limit may lead to so-defined external quantum efficiencies as low as 35%, even for a high open-circuit voltage output. Other factors like band-gap narrowing and variations of the diffusion coefficient with doping level, to name just a few, contribute as well to the maximum voltage. This makes this approach ambiguous and impractical.

In order to find a better definition of the quantum efficiency of the open-circuit voltage, we resort to the classical relation between current and voltage: $J \propto \exp \left( \frac{qV}{kT} \right) - 1$. Thus, we compare the incident photocurrent $qN_{ph}$ to a magnitude that is proportional to the
2.2 Characteristics of the spectral response of the voltage

current density that flows in an ideal diode if a voltage equal to \( V_{oc} \) is applied:

\[
EQE(V_{oc}) = \exp\left(\frac{qV_{oc}}{kT}\right) - 1
\]

\[
IQE(V_{oc}) = \exp\left(\frac{qV_{oc}}{kT}\right) - 1
\]

The internal quantum efficiency of the open-circuit voltage \( IQE(V_{oc}) \) is then defined analogously to \( IQE(J_{sc}) \). One of the reasons for this definitions is the fact that it will allow us to quantify \( EQE(V_{oc}) \) in terms of the internal quantum efficiency of the short-circuit current (see section 2.5).

Given the fact that this approach takes the ratio of two different magnitudes, the photocurrent and the exponential of the open-circuit voltage, a reference point is needed at which the quantum efficiency at different wavelengths can be compared. Most sensibly, it should be analysed at the same voltage, since this ascertains that the excess carrier density at the junction is the same at each point of the spectral analysis. A second scenario, an evaluation at constant photon flux, is also conceivable. This allows us to unravel intensity dependent effects that may be caused for example by the injection dependence of the surface recombination velocity. The decay of the light source over a broad range of light intensities facilitates the location of a reference point for both approaches.

A significant difference between short-circuit and open-circuit \( EQE \) is that the first is intuitively easier to grasp, because it is expressed as a percentage. A difficulty of the open-circuit response is that its magnitude is not physically intuitive having the units \([\text{cm}^2\text{s}/\text{C}]\). The exponential term in \( EQE(V_{oc}) \) implies that it will shift strongly when changing from one reference point to another (e.g. from 500 to 600 mV) and that it will vary broadly from device to device. Furthermore, the definition implicitly assumes an ideality factor that is unity and voltage-independent. This is certainly not correct, especially at medium illumination levels, where recombination in the space charge region starts to dominate or at low light intensities, where the ideal behaviour may be masked by a shunt resistance.

For the constant voltage method, these dilemmas can be avoided if \( EQE(V_{oc}) \) is normalised to the external quantum efficiency at a reference wavelength. This gives rise to the following relative expressions for the external quantum efficiency of the open-circuit voltage:

\[
EQE(V_{oc})|_{rel, V_{oc}=\text{const}} = \frac{EQE(V_{oc}, \lambda)}{EQE(V_{oc}, \lambda_{ref})}
\]

\[
= \frac{N_{ph}(V_{oc}, \lambda_{ref})}{N_{ph}(V_{oc}, \lambda)}
\]

(2.3)
A similar definition can be established for $IQE(V_{oc})_{rel, V_{oc}=const}$. The advantage of this definition is that it is independent of the ideality factor of the device. In case of an evaluation at a constant photon flux, $EQE(V_{oc})_{rel, N_{ph}=const}$ has to be taken at an illumination, where the ideality factor is close to unity and the same for each wavelength. On page 72 an example is discussed, which highlights the difficulty with the constant photon flux method. Although both approaches will be discussed throughout the thesis, the constant voltage method is recommended, whenever its implementation is possible.

To obtain a fuller picture of the meaning of these parameters, an example of a PC1D calculation is depicted in Figure 2.1. The parameters that entered the PC1D calculations are: ARC coating: 105 nm SiO₂, front surface recombination: 100 cm/s, peak doping density of the emitter region: $3 \times 10^{19}$ cm⁻³, sheet resistance: 120 $\Omega$/cm, diffusion depth: 0.5 $\mu$m, base doping: 1 $\Omega$ cm, low-injection bulk lifetime: 1000 $\mu$s and rear surface recombination: 1000 cm/s. The external quantum efficiency of the current and the voltage and the reflectance $R$ are shown on the left part of Figure 2.1, the internal quantum efficiencies on the right part. The determination of the quantum efficiencies of the voltage are explained in more detail on Section 2.2.3 on page 63.

![Figure 2.1](image)

**Figure 2.1:** Left side: $EQE(J_{sc})$, $EQE(V_{oc})_{rel}$ and reflectance $R$ as a function of wavelength. Right side: $IQE(J_{sc})$ and $IQE(V_{oc})_{rel}$ as a function of wavelength. For the open-circuit quantum efficiencies, the relative measure at a constant voltage and a constant photon flux are depicted.

The reference wavelength is chosen at the maximum of the $EQE(V_{oc})$ curve, in this case at 640 nm. The device described here exhibits low bulk and surface recombination. This results in an $EQE(J_{sc})$ that is mainly affected by the external reflectance and thus in an $IQE(J_{sc})$ that approaches 100% between 300 and 800 nm. The relative quantum efficiencies of the open-circuit voltage are the same, regardless of the exact evaluation.
2.2 Characteristics of the spectral response of the voltage

$\text{EQE}(V_{oc})_{\text{rel}}$ has the same shape as $\text{EQE}(J_{sc})$ but is shifted by the reflectance $\Delta$ at the reference wavelength. This is an inheritance of the definition of $\text{EQE}(V_{oc})_{\text{rel}}$ as a relative measure and narrows its applicability. This divergence can be eschewed if the internal quantum efficiencies is used instead. Apart from minor differences at the high energy end of the sun spectrum, $\text{IQE}(J_{sc})$, $\text{IQE}(V_{oc})_{\text{rel}, V_{oc}=\text{const}}$ and $\text{IQE}(V_{oc})_{\text{rel}, V_{oc}=\text{const}}$ overlap perfectly. It is important to remember that this works only if $\text{IQE}(J_{sc})$ touches the 100% mark at the reference wavelength. In other words, if the solar cell exhibits a low recombination activity in the bulk. If the device additionally benefits from an optimal light trapping scheme (e.g. silicon nitride antireflection coating and surface texturing), then there exist wavelengths in the range 600–800 nm at which $\text{EQE}(J_{sc})$ comes close to 100%. If $\text{EQE}(V_{oc})$ is normalised to one of these wavelengths, the gap $\Delta$ will be minimised for $\text{EQE}(V_{oc})_{\text{rel}}$. In a later part of this section, more device structures are investigated with PC1D, which helps to further understand the meaning of $\text{IQE}(V_{oc})_{\text{rel}}$.

2.2.2 One-dimensional analytical model of the open-circuit quantum efficiency

It is very beneficial to revise the mathematical treatment of the surface photovoltage technique as a first step. The reason is evident, since the problem is comparable to the situation we face in the QSSV$_{oc}$-$\lambda$ method. It turns out that the critical wavelength dependence in all models can be ascribed to a term that is mathematically equivalent to the external quantum efficiency of the short-circuit current in the base, $\text{EQE}_n$. The involvement of this factor is an important result, since all the models used in the SPV technique that serve to extract the diffusion length can be traced back to the models used in the current response.

Theory of the surface photovoltage technique

The surface photovoltage technique is mostly applied to wafers with an induced surface charge region or Schottky contact. Instead of the emitter region, the surface and depletion regions are the predominant zones at the front of the device, where most of the current flow and recombination occurs. The most comprehensive model underlying the surface photovoltage technique has been developed by Choo et al. [90, 91]. Importantly, it includes the impact of surface and depletion region recombination to the overall photovoltage.

The photovoltage is the photo-induced change in the surface potential, $V_{sp}$, that marks the difference in potential between the induced surface charges or the Schottky contact
and the bulk. To further analyse the photovoltage, a relationship has to be found that links it to the incident photon flux. All analytical models are devised by first establishing a relationship between the photovoltage and the splitting of the quasi-Fermi levels

\[ V_F = (\phi_p - \phi_n) \]

The next step is to associate the surface potential with the photon flux; this is accomplished by solving the continuity equation that governs the current flows between surface and volume.

In the surface treatment method, it is assumed that the photo-excitation does not alter the surface charge density. With this approximation in hand, it is possible to link \( V_{sp} \) and \( V_F \) approximately via

\[ \exp\left(\frac{qV_F}{kT}\right) \approx V_{sp} \exp\left(\frac{qV_{sp}}{kT}\right) \]  

(90)

Due to the constant charge condition, the separation of the quasi-Fermi potentials is always much larger than the surface photovoltage. Assuming p-type silicon, the total current in this structure is composed out of a recombination current \( J_s \) at the surface, a recombination and generation current in the depletion region \( (J_{U,scr} \text{ and } J_{G,scr}, \text{ respectively}) \) and a diffusion current at the bulk side of the junction, \( J_n \). The bulk diffusion current follows the superposition principle, that is, it can be separated into a recombination component and a photo-generated part. Instead of the original derivation of reference [90], we express the photocurrents in terms of its respective external quantum efficiencies, e.g. \( EQE_{scr} \) and \( EQE_n \). The surface region is considered too small to have a sizeable photocurrent. The continuity equation implies that

\[ J_s - J_n = J_{G,scr} - J_{U,scr} \]

Implementing the superposition principle and the external quantum efficiencies gives rise to the following [90]:

\[ J_{0s} e^{qV_{sp}/kT} + J_{0U,scr} V_{sp}^{1/2} e^{qV_{sp}/2kT} + J_{0b} V_{sp} e^{qV_{sp}/kT} = qN_{ph}(EQE_{scr} + EQE_n). \]  

(2.4)

\( J_{0s}, J_{0U,scr} \) and \( J_{0b} \) constitute the saturation currents of the surface, depletion and base regions. We refer to reference [90] for further details of \( J_{0s} \) and \( J_{0U,scr} \). The term

\[ qN_{ph}EQE_{scr} \]

is equivalent to the amount of charge carriers generated in the depletion region of a p-n junction (Equation 1.15). Choo et al. used an expression for \( EQE_n \) that is equivalent to the linear approximation of the external quantum efficiency in the bulk, Equation 1.31. Note that the term for \( EQE_n \) solely served as a stepping stone to extract the diffusion length, but no importance has been attributed to its own meaning. The approximation used for \( EQE_n \) usually neglects any absorption due to multiple reflection or any surface recombination at the rear of the wafer. The most advanced model for \( EQE_n \) has been developed by Lagowski et al. [92], which is equivalent to the approximation proposed by Spiegel et al. (see also the later discussion about the determination of the diffusion length in Section 2.5.1 on page 82).

From Equation 2.4 it can be inferred that neither the surface potential nor its expo-
2.2 Characteristics of the spectral response of the voltage

ential is in general linear in the photon flux, unless the surface potential is kept constant at every wavelength. If the photon flux is held constant instead, the linearity is only valid when the material is heavily-doped, has a long carrier lifetime or a very low surface recombination rate [90]. In all other cases, the recombination current at the surface or in the space charge region is likely to strongly influence the relationship between photovoltage and photon flux. Nevertheless, the SPV technique employs such small signals that \( V_{sp} \ll kT/q \). Moreover, for the extraction of the diffusion length, wavelengths that are absorbed away from the surface region become more influential. In this case the recombination in the front surface plays a minor role and \( V_{sp} \propto N_{ph} \).

If a metal-semiconductor contact is used, there exist again three regions of interest: the metal-semiconductor interface, the depletion region between the interface and the bulk and the bulk region itself. The formulation of the current flow envisaged here retraces the train of thoughts of Choo et al. [91], with one simplification. The splitting of the quasi-Fermi levels is nearly equal to the photo-induced voltage, but contrary to the previous case, the assumption of constant quasi-Fermi levels throughout the space charge region can not be upheld anymore. Nevertheless, by neglecting this fact, the currents involved can be more easily split into their recombinative and photo-induced parts.

The balance of the current flow is the same as above. If the base material is p-type, the surface current is given by the recombination of electrons at the metal-semiconductor interface, \( J_{ns} \). Both current contributions from the junction boundaries can again be split into the recombination current and a photocurrent. In this sense, the surface current, as an example, can be expressed by:

\[
J_{ns} = -J_{0ns} \left( e^{\frac{V_{oc}}{kT}} - 1 \right) + qN_{ph} EQ_{Ens},
\]

where the open-circuit voltage \( V_{oc} \) takes the role of the surface potential \( V_{sp} \). The exact form of \( J_{0ns} \) and \( EQ_{Ens} \) can be found in reference [91]. The total balance can then be written in the form:

\[
(J_{0ns} + J_{0b}) \left( e^{\frac{V_{oc}}{kT}} - 1 \right) + J_{U,scr} = qN_{ph} (EQ_{Es} + EQ_{Esr} + EQ_{E}).
\]

Here as well \( EQ_{E} \) stands for the approximate expression for the external quantum efficiency used in the SPV method. The dependence of \( J_{U,scr} \) of the photovoltage is more complicated than in the previous case [91]. If the condition of constant quasi-Fermi levels throughout the depletion region is discarded, the depletion and surface currents can not as easily be separated into their components as shown in Equation 2.6. Nevertheless, the
important outcome to keep in mind is the fact that the relationship between open-circuit voltage and photon flux brings into play the external quantum efficiency of the bulk, $EQEm$. The photovoltage is only linear with the photon flux if it is kept constant. Nevertheless, the recombination in the depletion region can be neglected for light absorption in the base in a good approximation. What follows, is that the exponential of $qVoc$ becomes proportional to $N_{ph}$. In this light, we propose to study the external quantum efficiency of the voltage instead:

$$EQE(Voc) \approx \frac{EQEns + EQE_{scr} + EQEn}{J_{0ns} + J_{0b}}. \quad (2.7)$$

This formulation has the advantage that it is independent of the magnitude of the photon flux and paves the way to study the spectral response of Schottky diodes with $QSSV_{oc} - \lambda$. Through the wavelength dependence of $EQEn$, the external quantum efficiency of the photovoltage is expected to mimic the shape of the short-circuit response.

The SPV method is equally applicable to $p-n$ junction devices. A similar avenue will be pursued to derive an analytical model of the external quantum efficiency of the voltage for such semiconductors. Here, the open-circuit voltage is also equated to the separation of the Fermi levels. However, the generalised formulation of $EQEn$ in this model, which includes internal reflection and rear surface recombination, enables us to improve the extraction of the diffusion length compared to the simplified approach used in the SPV technique. Moreover, it is not restricted to small photovoltages, therefore it can be used in the analysis of the SPV method and $QSSV_{oc} - \lambda$. The model is first described for an abrupt junction, but later generalised to arbitrary emitter structures.

**Abrupt junction**

To bring the external quantum efficiency of the open-circuit voltage of a $p-n$ junction in context with its short-circuit counterpart, we can resort to the the derivation of Chapter 1. The total current flow under arbitrary operation conditions is divided into the emitter, space charge and base component, using the equations 1.13, 1.15 and 1.20. For the emitter and base region, it is again instrumental to divide the current further into an open-circuit and short-circuit part in compliance with the superposition principle. Applying this principle results in the following expression for the total current density:

$$J = J_p + J_{G,scr} + J_n \quad (2.8)$$

$$= \left( \frac{qD_p n_i^2}{L_p N_A} \Sigma(x_p) + \frac{qD_n n_i^2}{L_n N_D} \Sigma(H) \right) (e^{\frac{qVoc}{kT}} - 1) + qN_{ph} (EQEp + EQE_{scr} + EQEn).$$
2.2 Characteristics of the spectral response of the voltage

The recombination current \( J_{U,scr} \) has been neglected here. In open-circuit conditions the total current vanishes: \( J = 0 \). Using the definition of the external quantum efficiency of the open-circuit voltage (Equation 2.2), the following relation can be derived:

\[
EQE(V_{oc}) = \frac{\exp(qV_{oc}/kT) - 1}{qN_{ph}} = \frac{EQE_{p} + EQE_{scr} + EQE_{n}}{q_{D_{p}n_{0}^{2}} \Xi(x_{j}) + q_{D_{n}n_{0}^{2}} \Xi(H)}.
\] (2.9)

The denominator represents the total saturation current \( J_{0} \). Equation 2.9 shows that the definition of the external quantum efficiency of the open-circuit voltage is well founded in hindsight and reveals from where the external quantum efficiency of the open-circuit current takes its wavelength dependence: It is expressed in similar terms as the short-circuit variant. In fact, if we assume that we deal in short-circuit and open-circuit conditions with the same carrier density, or more explicitly: \( S_{p}J_{sc} = S_{p}V_{oc} \) similar for \( S_{n} \), \( \tau_{n} \) and \( \tau_{n} \), as both versions are distinguished from each other only by a constant factor, the total saturation current. This may be achieved by comparing the \( V_{oc} \) measurement at 1/20th to 1/10th suns to \( J_{sc} \) at one sun.

One remark on the analysis of the base component of the external quantum efficiency that has the aim to extract the bulk diffusion length and the base surface recombination velocity: One would assume that a simultaneous fit to \( EQE(J_{oc}) \) and \( EQE(V_{oc}) \) would facilitate this analysis in a mathematical sense (two equations for two unknowns). But in fact, both equations are mathematically the same apart from a constant factor (the total saturation current \( J_{0} \)). Additionally it is worth to note that, despite the similarity of the mathematical expression for the external quantum efficiencies, it can differ strongly under open-circuit conditions, intermediate or short-circuit conditions, as discussed in detail above. In general, we expect higher injection levels under open-circuit than short-circuit operations, which will alter the external quantum efficiency due to the injection dependence of the recombination processes.

**Arbitrary diffusion profiles**

The above evaluation gives a first image and approximation of \( EQE(V_{oc}) \), but for devices with diffused emitter profiles the assumption of an abrupt junction is too far from reality. Rather than de-composing the recombination of the emitter region into its single parts, that is, its surface recombination, bulk lifetime and doping density, it can be treated as an entity. This avoids having to deal with the local dependence of these parameters. Traditionally, the recombination dynamics of each region can be bundled into their respective saturation current densities, \( J_{0x} \) and \( J_{0b} \). For convenience, the space charge
region is absorbed in the emitter region. Hence, instead of drawing a precise line that presents the boundary between emitter and base region, each region can be characterised by two opposing current flows: the saturation current density and the collection current density [93]. This idea is further exemplified with the emitter region. The first current consists of charge carriers from the close-by base region, the space charge region and the emitter segment that are drawn towards the recombination channels of the top region. These channels may be defects at the emitters surface or within the emitter. This current flux can be expressed with the concept of the saturation current density as \( J_0e(e^{\frac{qV_{oc}}{kT}} - 1) \).

The second part consists of the flow of charge carriers that are generated in the emitter region and reach the junction without facing recombination. In short-circuit conditions, this is equal to the amount of charge carriers collected at the junction, represented by \( qN_{ph} EQE_p \). A similar picture can be transferred to the base region. In detail, the hole and electron current of this approach are then given by:

\[
\begin{align*}
J_p &= -J_{0e}(e^{\frac{qV_{oc}}{kT}} - 1) + qN_{ph} EQE_p, \\
J_n &= -J_{0b}(e^{\frac{qV_{oc}}{kT}} - 1) + qN_{ph} EQE_n.
\end{align*}
\]

The local dependence of the base parameters can be neglected in a good approximation. This allows description of the base saturation component with Equation 2.1. Applying the condition of open-circuit, that is, that \( J_p \) and \( J_n \) cancel each other out, we obtain:

\[
EQE(V_{oc}) = \frac{EQE}{J_{0e} + \frac{qD_n\bar{n}^2}{L_N^2 N_D}} \Xi(H).
\]

Note the similarity between this equation and the result of a Schottky contact (Equation 2.7). This equation forecasts that an analysis of \( EQE(V_{oc}) \) at wavelengths that are entirely absorbed in the base region will not only help to extract the bulk diffusion length, but will also predict valuable information about the emitter recombination, epitomised by \( J_{0e} \).

### 2.2.3 Computer simulations

Computer simulations with PC1D [41] have been performed to illustrate the behaviour of the internal quantum efficiency of the open-circuit voltage and to compare it to the traditional spectral response. Six different scenarios are used for typical high-efficiency and industrial silicon solar cells to illustrate the broad application of the new spectral response technique. The parameters used for the computer modelling common to all devices were:
2.2 Characteristics of the spectral response of the voltage

wafer thickness 300 \( \mu \text{m} \), \( p \)-type and resistivity 1 \( \Omega \text{ cm} \). The surface was assumed to be planar and coated with a 70 nm-thick antireflection layer with refractive index 2.1. The front and rear internal reflectance were assumed to be 70 and 90\%. All devices but the industrial cell 5 had a 70 nm-thick passivation layer with refractive index 2.1 on the back side of the cell. The peak doping density, sheet resistance, junction depth, surface recombination and low-injection bulk lifetimes are displayed in Table 2.1.

Table 2.1: Parameters of the PC1D calculations of six different cell devices.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cell 1</th>
<th>Cell 2</th>
<th>Cell 3</th>
<th>Cell 4</th>
<th>Cell 5</th>
<th>Cell 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_{\text{peak}} ) [cm(^{-3})]</td>
<td>( 3 \times 10^{19} )</td>
<td>( 3 \times 10^{19} )</td>
<td>( 3 \times 10^{19} )</td>
<td>( 3 \times 10^{19} )</td>
<td>( 3 \times 10^{20} )</td>
<td>( 3 \times 10^{19} )</td>
</tr>
<tr>
<td>( R_{\text{sh}} ) [( \Omega / \square )]</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>( W_e ) [( \mu \text{m} )]</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>( S_{\text{front}} ) [cm/s]</td>
<td>1000</td>
<td>10(^6)</td>
<td>1000</td>
<td>1000</td>
<td>10(^6)</td>
<td>100</td>
</tr>
<tr>
<td>( \tau_{\text{bulk}} ) [( \mu \text{s} )]</td>
<td>1500</td>
<td>1500</td>
<td>10</td>
<td>1500</td>
<td>10</td>
<td>1500</td>
</tr>
<tr>
<td>( S_{\text{back}} ) [cm/s]</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>10(^6)</td>
<td>1000</td>
<td>1000</td>
</tr>
</tbody>
</table>

The sequence of the voltage simulations proceeded as follows: at each wavelength between 300 and 1200 nm, PC1D calculated a photon flux-voltage curve for a fixed light intensity range between \( 10^{-5} \) and 4 suns. Figure 2.2 shows an example of the PC1D calculation for cell 5. Figure 2.3 elucidates the sequence to obtain the internal quantum efficiency from the photon flux-voltage curve for a constant voltage. The photon flux-voltage curve was interpolated at several constant voltages between \( V_{\text{oc, min}} \) and \( V_{\text{oc, max}} \). At these points, \( IQE(V_{\text{oc}}) \) was calculated and subsequently normalised to the wavelength at which it took its maximum. The reference wavelength was situated around 600 nm as a result of the antireflection coating. This ensured that \( IQE(V_{\text{oc}})|_{\text{rel}} \) was \( \leq 100\% \). Next, the average of \( IQE(V_{\text{oc}})|_{\text{rel}, V_{\text{oc}} = \text{const}} \) of all reference points was calculated. The same procedure was performed for constant photon fluxes.

The concept of the scaled and averaged quantum efficiency helps to mitigate numerical errors that haunt the extraction of the quantum efficiency of the voltage and photoconductance in general, both in simulation or experiment. The photon flux-voltage curves have to be interpolated to access for example the voltage corresponding to a given constant photon flux. This procedure is prone to small numerical errors. The averaging over several relative quantum efficiencies smoothes these errors considerably.

Cell 1 typifies a well passivated high-efficiency solar cell with current output 37.3 mA/cm\(^2\), \( V_{\text{oc}} = 681 \text{ mV} \) and \( \eta = 21.3\% \) under standard conditions (illumination: 0.1 W/cm\(^2\), AM1.5G spectrum; temperature: 300 K). The traditional and the open-circuit \( IQE \) are depicted on the left side of Figure 2.4. The shapes of \( IQE(J_{\text{sc}}) \) and
Figure 2.2: Photon flux-voltage curve of Cell 5 for several wavelengths. $V_{oc, \text{min}}$, $V_{oc, \text{max}}$, $N_{ph, \text{min}}$ and $N_{ph, \text{max}}$ denote the limits for the voltage and photon flux range where the respective internal quantum efficiency has been extracted.

$N_{ph, \text{max}}$ curve

Interpolate at several $V_1$, $V_2$, ..., $V_n$ and extract $IQE(V_{oc})$

Normalise to reference wavelength

Average over all $IQE(V_{oc})_{rel}$

Figure 2.3: Sketch of the sequence of the extraction, normalisation and averaging of the internal quantum efficiency of the open-circuit voltage.

$IQE(V_{oc})_{rel}$ are identical irrespective of the evaluation method of the latter. In cell 2, the front surface recombination velocity has been increased from 100 to $10^6$ cm/s (right graph of Figure 2.4). The de-passivation of the device has two main effects on solar cell performance: first, the higher recombination at the front decreases the voltage output to 615 mV. Second, $IQE(J_{sc})$ at 400 nm decreases from 99 to 48%, which in turn leads to a smaller short-circuit current of 35.4 mA/cm$^2$. Both effects lower the efficiency to 17.9%.

The shape of the curves still remain identical for all wavelengths. Due to the high surface recombination, the highest internal quantum yield in the short-circuit depiction is 98.6%. The normalised measure $IQE(V_{oc})_{rel}$ is not capable of picking up this drop in quantum
2.2 Characteristics of the spectral response of the voltage

Figure 2.4: PC1D calculations of $IQE(J_{sc})$ and $IQE(V_{oc})|_{rel}$, the latter at a constant voltage and photon flux, for a high efficiency device with low front surface recombination (cell 1, left graph) and high front surface recombination (cell 2, right graph).

efficiency, but the error still remains very small.

In the next case, cell 3, we considered a high-efficiency device using low-quality material, e.g. multicrystalline silicon. The surface is well passivated as in cell 1. The low-quality of the base is expressed in a low bulk lifetime of 10 $\mu$s. The diffusion length, $L_{bulk}$, is correspondingly decreased from 2008 to 164 $\mu$m, thus lower than the wafer thickness of 300 $\mu$m. The output parameters are: $J_{sc} = 33.7$ mA/cm$^2$, $V_{oc} = 613$ mV, $\eta = 17.1\%$. This time $IQE(J_{sc})$ is widely affected in the IR (left graph of Figure 2.5), due to the fact

Figure 2.5: PC1D calculations of $IQE(J_{sc})$ and $IQE(V_{oc})|_{rel}$, the latter at a constant voltage and photon flux, for a device with low bulk material (cell 3, left graph) and a device with high rear surface recombination (cell 4, right graph).
that carriers generated at these wavelengths survive only shortly due to the low diffusion lengths. \( IQE(J_{sc}) \) and \( IQE(V_{oc}) \) overlap perfectly by virtue of the fact that \( IQE(J_{sc}) \) still reaches 100% between ~ 500–600 nm.

Following that, the influence of a high rear surface recombination velocity \( S_{rear} \) is studied. Hence, \( S_{rear} \) has been increased to \( 1 \times 10^6 \) cm/s, whereas the front surface recombination velocity remained at 1000 cm/s. This mainly lowers the open-circuit voltage to 627 mV. The short-circuit current is also lowered to 34.3 mA/cm². A comparison of cell 2 and 4 shows that the open-circuit voltage is more affected by high surface recombination on the front surface. This is related to the fact that \( V_{oc} \) depends on the carrier density at the junction. The de-passivation lowers the internal quantum efficiency of the short-circuit current considerably for wavelengths \( \geq 700 \) nm (right graph of Figure 2.5): e.g. for \( \lambda = 1000 \) nm there is an decrease in quantum yield from 94 to 60%. The short-circuit current response and open-circuit voltage response coincide perfectly for this device.

Cell 5 represents a typical industrial silicon solar cell with recombination losses in the short and long wavelengths. We used an emitter dopant profile of a supersaturated phosphorus diffusion with surface concentration of \( 3 \times 10^{20} \) cm⁻³ and a 0.04 \( \mu \)m dead layer, sheet resistance of 50 \( \Omega/\square \), and junction depth of 0.4 \( \mu \)m. The carrier lifetime in the base has been assumed to be 10 \( \mu \)s, the front surface recombination velocity \( 1 \times 10^6 \) cm/s, and the effective surface recombination velocity at the rear \( 10^3 \) cm/s, a value representative of an aluminium alloyed \( p^+ \)-region. The calculated output parameters of this device at standard conditions are \( J_{sc} = 32.3 \) mA/cm², \( V_{oc} = 610 \) mV, \( \eta = 16.2\% \). The maximum of

![Graphs of IQE(Jsc) and IQE(Voc) for Cell 5 and Cell 6](image)

**Figure 2.6:** PC1D calculations of \( IQE(J_{sc}) \) and \( IQE(V_{oc}) \) \( r_{rel} \), the latter at a constant voltage and photon flux, for an industrial solar cell (cell 5, left graph) and a high-efficiency rear-junction cell (cell 6, right graph).
2.3 Comparison of the surface photovoltage technique and QSSV$_{oc}$-$\lambda$

$IQE(J_{sc})$ lies at 96%, below the 100% mark, owing to the high front surface recombination velocity of $1 \times 10^6$ cm/s and the low bulk lifetime (left graph of Figure 2.6). Nonetheless, $IQE(V_{oc})|_{rel}$ mimics the same form as its short-circuit analogue.

PC1D calculations of a high-efficiency sample whose junction is located at the back of the cell round off these theoretical considerations (cell 6 in Figure 2.6 on the right). The internal quantum efficiency of the short-circuit current of a rear-junction device is flat for most of the spectrum and ends with a hump in the IR. Light of these wavelengths are absorbed close to the junction and as a consequence, charge carriers will almost certainly be collected. However, carriers that are generated at the front of the cell have to bridge the whole width of the device in order to contribute to the current. It comes as no surprise that the magnitude and shape of the flat part is strongly affected by front and bulk recombination and never reaches the benchmark of perfect conversion. This example clearly unveils the limits of the voltage response, as it is only able to indicate the relative mismatch between front and rear contribution of charge carriers. Despite this, the shape of $IQE(V_{oc})|_{rel}$ is identical to $IQE(J_{sc})$.

The PC1D calculations underline the potential of the novel voltage responsivity method. If at least one of the two recombination processes, the front surface recombination or the bulk recombination, can be held at bay, the internal quantum efficiency of the voltage of conventional cell structures agrees excellently with its conventional contender. Both forms of evaluation, at a constant voltage or a constant photon flux, prove to be identical apart from minor divergences at the UV end of the spectrum. In the case of a high recombination rate at the front surface and in the volume of the cell, the voltage response gives the same information as that of the short-circuit current, since it identifies the increase of $S_{front}$ with a reduction of the UV response and the decrease of $\tau_{bulk}$ with a drop of the IR yield. The voltage response is also capable of predicting the difference between the impact of $S_{front}$ and the bulk diffusion length on the quantum yield of a rear-junction cell.

2.3 Comparison of the surface photovoltage technique and QSSV$_{oc}$-$\lambda$

The surface photovoltage (SPV) technique is very common in the semiconductor industry for measuring the diffusion length [14, 46, 94]. It’s application ranges from verifying the cleanliness of ovens, clean rooms and processing equipment to monitoring the metal contamination of silicon wafers [95]. SPV is particularly successful in detecting iron-boron
pairs in silicon [96]. For all these purposes, the diffusion length serves as a quality indicator. This versatile method stands out due to the fact that it is fast, nondestructive, contactless and does not require any high temperature step to form an oxide passivation layer, emitter diffusion or metal contact [14]. In photovoltaics, SPV has been additionally used to measure the emitter sheet resistivity [97].

The set-up that produces the monochromatic illumination and the signal detection is exactly the same as in the traditional short-circuit current response. The samples under investigation are in general bare silicon wafers that received a surface treatment to induce a space charge region at the surface (Figure 2.7). The surface space charge region is either in depletion or weak inversion [90]. In some cases no treatment is needed, since a depletion region may form intrinsically due to charges associated with surface or native oxide defects [98]. By illuminating the sample, some charge carriers travel to the surface establishing a surface potential relative to the back of the sample. The surface voltage is a reflection of the excess minority carrier density at the edge of the depletion region and is recorded by a capacitive pick-up probe. The probe consists of a quartz crystal that is coated with a transparent conducting film of indium tin oxide. To avoid edge effects and lateral diffusion to adjacent areas in the dark influencing the surface voltage, the area of illumination is kept larger than the indium tin oxide pick-up area. This ensures that the carrier density profile below the pick-up area is one-dimensional. The wafer chuck serves as the back electrode. In the case of solar cells or Schottky diodes, the device is contacted directly, with the positive side effect of higher voltages.

![Figure 2.7: Above: One dimensional segment of a sample with induced space charge region. The capacitive contact (below) is a transparent, electrically conducting layer allowing light to reach the sample. The pick-up is achieved via an indium tin oxide coating on a quartz substrate.](image-url)
The early version of the SPV method consisted of the measurement at constant voltage. Here, the photon flux is varied until a constant voltage is reached for each light penetration depth [22]. But this method is cumbersome, as sequential measurements have to be carried out at each wavelength. The approach that is presently implemented in commercial SPV tools uses a constant illumination for each point of the spectrum \[46, 99\]. In a first measurement, the surface photovoltage is recorded as a function of photon flux to find the linear regime where the voltage is proportional to the incident photon flux. This is important, since the linear range depends on the diffusion length and front surface recombination of the sample and therefore varies from wafer to wafer. Once a suitable photon flux has been determined, the actual spectral measurement is performed. This implementation of SPV is much faster than the first one, but still not fast enough for high-resolution mappings. In the fast SPV mapping [92], the voltage signal has to be increased to about 10 mV, which entails that the voltage is sub-linear with the photon flux. The preliminary measurement that determines the dependence of the voltage is used to account for this sub-linearity.

The new spectral voltage technique developed here uses the same system as the quasi-steady-state short-circuit current response (Figure 1.9). Instead of the indirect detection of the short-circuit current with an operational amplifier, the open-circuit voltage is picked up directly between the front and rear contacts of the solar cell. Barring this, the procedure of the measurement is exactly the same as in a short-circuit current experiment. There is in principal no limitation to the intensity of the light, as no linear relationship between photon flux and voltage is required. This is rooted in the general formulation of the external quantum efficiency of the open-circuit voltage, where the exponential of the voltage is compared to the photon flux.

As in measurements of the surface photovoltage technique, there exist two implementations: (1) measurement at a constant voltage and (2) at a constant photon flux. The first method has the same practical drawback as the constant voltage SPV method. The open-circuit voltage varies strongly from cell to cell and with wavelength. As a consequence the photon flux has to be adjusted individually for each cell and wavelength, a very undesirable situation for an automatisation of the technique. Fortunately, the flash lamp covers a broad range of intensities, but even so the actual range is limited by the sensitivity of the reference cell and the bandwidth of the filters. It is therefore convenient to keep the range of incident photon flux approximately the same for all wavelengths and cells. Due to the preset photon flux, the $EQE$ at a constant voltage can only be analysed within a relatively small window of injection levels. Still, it is possible to consider $EQE$
Figure 2.8: Photon flux-voltage curve of the 0.15 Ω cm solar cell at white and monochromatic light in the range 400–1150 nm. The minimum and maximum voltage and photon flux show the range in which the $E_{QE}(V_{oc})$ has been evaluated.

at the actual open-circuit voltage and at the maximum power point of the cell in most cases.

A typical measurement of the photon flux-voltage curve at different $\lambda$ is pictured in Figure 2.8. Alongside these curves, a white light measurement is shown (★). The white light as well as the monochromatic light curves have the same shape as a dark $I$-$V$ curve shifted to the first quarter of the x-y plane. In a different perspective, the measurement at 400 nm, for example, is equivalent to the illumination-voltage curve of the solar cell if the sun spectrum consisted only of this particular wavelength. In a sense, the white light curve can then be considered as an ‘averaged’ measurement over the whole spectrum. This figure depicts the recording of the cell RPAL44.A3.1b that suffers from a very low diffusion length (see chapter 1 on page 44 for the details of output parameters and Section 2.5 for the measurement of the diffusion length). It is an excellent example to show a clear wavelength dependence of the $N_{ph}$-$V_{oc}$ curves. For larger penetration depths of the light (which means in this case a lower voltage built-up due to the low diffusion length), the photon flux-voltage curve seems to shift towards the upper left corner of the positive quarter of the x-y plane. This is originated in the fact that at higher wavelengths, the device has to be irradiated with an increased amount of photons to keep a constant voltage.

The external quantum efficiency is evaluated at a constant photon flux and voltage
between the limits indicated in the graph. For each implementation, EQE is determined at several reference points, normalised to a reference wavelength and averaged. The procedure is the same as described for the PCID calculation on page 63. To study non-linear effects, \( EQE(V_{oc})_{rel} \) can be compared at different reference points. This example demonstrates that, with one measurement, both implementations can be studied at a broad range of reference points. As a result to this and the definition of \( EQE(V_{oc}) \), a first measurement to determine the linear regime of the \( N_{ph}-V_{oc} \) curve and any errors due to the sub-linearity at higher voltages can be avoided. In comparison to SPV, where one single value of the diffusion length is extracted, QSS\( V_{oc}-\lambda \) has the ability to determine the diffusion length as a function of voltage (or equivalently carrier density at the junction edge) and photon flux in one measurement. This is an important advantage, since the diffusion length of iron-related defects, to name an example, exhibits a strong dependence on carrier density [100].

The measurement errors of the spectral response of the voltage are the same as for the short-circuit current response mentioned on page 44 apart from the details of the extraction of EQE. In the the spectral photocurrent, fluctuations that appear at different photon fluxes are mitigated by the linear fit over the whole signal range. In the spectral response of the voltage, \( EQE(V_{oc})_{rel} \) is extracted at different photon fluxes or voltages and averaged. We estimated an error of 5% for the stray light and the determination of the open-circuit voltage. The total error at each constant photon flux or voltage amounts to approximately ± 8%. Averaging \( EQE(V_{oc})_{rel} \) at different constant photon fluxes or voltages decreases this error to approximately ± 5% due to error propagation. In comparison, by repeating the measurement several times, a maximum deviation smaller than ±5% is observed for most cells.

The fact that the photon flux-voltage curve at each \( \lambda \) represents a solar cell performance curve in itself means that they are also influenced by the same phenomena that undermine the voltage output of its white light correspondent. In detail, these are shunting effects and depletion region recombination for the low voltage range and Schottky contacts for high voltage output. Figure 2.9 illustrates this with cell FB137.14-20.1, which is plagued by shunting. Owing to the fact that at wavelengths in the IR a higher photon flux is needed to reach the same voltage that is observed at lower wavelengths, the onset of the shunt appears earlier in the photon flux-voltage curve. Figure 2.10 shows the determination of \( EQE(V_{oc})_{rel} \) for \( N_{ph,1} = 1.3 \) suns and \( N_{ph,2} = 0.05 \) suns (shunted region) normalised at 700 nm. If the spectral response is evaluated at \( N_{ph,2} \), the effect of the shunt lowers \( EQE(V_{oc})_{rel} \) considerably in comparison to the analysis at \( N_{ph,1} \). This might lead to the misconception that the shunt resistance is wavelength dependent.
2. Spectral response of the open-circuit voltage

**Figure 2.9:** $N_{\text{ph}}-V_{oc}$ curve at monochromatic light for the cell FB137_14-20.1. $N_{\text{ph},1}$ and $N_{\text{ph},2}$ denote two different reference points at which $EQE(V_{oc})|_{\text{rel}}$ has been derived.

**Figure 2.10:** $EQE(V_{oc})|_{\text{rel}}$ as a function of wavelength extracted at the reference points $N_{\text{ph},1}$ and $N_{\text{ph},2}$.

Alternatively, this behaviour might be misconstrued as a sign of low bulk quality or high rear surface recombination. More specifically, if the spectral response is analysed with the model of Isenberg, the resulting bulk diffusion length at $N_{\text{ph},2}$ is 11.4 $\mu$m, much lower than the 81.8 $\mu$m evaluated at $N_{\text{ph},1}$.

It is important to remember that the definition of $EQE(V_{oc})$ compares the exponen-
2.4 Experimental validation of the spectral response of the voltage

2.4.1 External and internal quantum efficiency of the voltage

The experimental validation of the spectral response of the voltage is demonstrated via a comparison between the relative quantum efficiency of the open-circuit voltage and the conventional quantum efficiency of the short-circuit current. The same devices are used as in Section 1.6, the output parameter can be found accordingly in Table 1.2 on page 44. In the first graph, Figure 2.11, \( EQE(V_{oc})_{rel} \) is compared to \( EQE(J_{sc}) \). For each cell, the y-axis of \( EQE(V_{oc})_{rel} \) is situated on the right, while the y-axis of \( EQE(J_{sc}) \) is displayed on the left. \( EQE(V_{oc})_{rel} \) is pictured with lines and symbols, \( EQE(J_{sc}) \) is shown with a continuous line. The y-axis corresponding to \( EQE(V_{oc})_{rel} \) has been shifted until a perfect overlap can be found for all curves. \( EQE(V_{oc})_{rel} \) has been normalised to the maximum value of \( EQE(V_{oc}) \), the reference wavelengths being situated between 500-
Figure 2.11: \( EQE(J_{sc}) \) and \( EQE(V_{oc})_{rel} \) of a range of different cell structures. \( EQE(J_{sc}) \) is shown as a solid line and its y-axis is located on the left side of each graph. \( EQE(V_{oc})_{rel} \) is shown as a combination of lines and symbols and its y-axis is situated on the right side of each graph. The \( EQE(V_{oc})_{rel} \) have been adjusted until an optimum overlap could be found. The data of the QSSV_{oc-\lambda} measurements is the mean \( EQE \) of several repeated measurements. For the constant voltage method, error bars are included that indicate a deviation of 5% estimated from the measurement errors of the photon flux and the voltage, the scattered white light and averaging over the \( EQE \) at several constant voltages. The error of \( EQE(J_{sc}) \) is approximately ± 3% [79].

700 nm. The data of the QSSV_{oc-\lambda} measurements is the mean \( EQE \) of several repeated measurements. As an example, error bars are included for the constant voltage method. They indicate a deviation of 5% estimated from the measurement errors of the photon flux, voltage, scattered white light and averaging over \( EQE \) at several constant voltages. The error of the constant photon flux methods are of the same magnitude. The error of
2.4 Experimental validation of the spectral response of the voltage

Figure 2.12: \(IQE(J_{sc})\) and \(IQE(V_{oc})\)\textsubscript{rel} of a range of different cell structures. The data of the QSSV\textsubscript{oc}-\textsubscript{A} measurements is the mean IQE of several repeated measurements. For the constant voltage method, error bars are included that indicate a mean deviation of \(6\%\) estimated from the measurement errors of the external quantum efficiency of the voltage and the reflectance. The error of \(IQE(J_{sc})\) is approximately \(\pm 4\%\) [79].

The first two cells, the PERL cell FB99.8d and the PERC cell RPA144.A3.1b, express the same behaviour for all spectral measurements. Importantly, the voltage response of the PERC cell discloses the clear drop in quantum yield in the IR equally as well as its short-circuit analogue. For both cells, there is no difference between the evaluation at constant voltage and photon flux nor between different reference points. The next device in Figure 2.11 is the LFC cell ULF03.7.5 fabricated on a thin wafer of thickness 99 \(\mu\text{m}\). The
external quantum efficiency for the two implementations of the voltage technique are in perfect agreement. However, there exists a visible difference between the short-circuit and open-circuit response. It is not clear if the divergence occurs in the long wavelength range, like it is shown in the graph, or in the mid-wavelength regime. Certainly, one can state that the ratio between visible and IR yield is higher in the spectral response of the voltage. A similar discrepancy has been observed in the comparison between the quasi-steady-state short-circuit current response and its conventional correspondent (Figure 1.13) in Section 1.6.

Next on the list is the high-efficiency structure produced on a multicrystalline wafer, FB137.14-20.1 (on the middle-right of Figure 1.13). The short-circuit and open-circuit response differ slightly in shape. Here as well, one can only conclude that the ratio between UV and IR efficiency diverge slightly between both methods. For this particular cell, a very high photon flux of 2.2 suns had to be employed to reach the range of ideal diode behaviour. Considering the next multicrystalline device, M31, only small differences between all curves in the UV and IR catch the eye. In the last cell, the back-junction device 80nza, \( EQE(V_{oc}) \mid_{rel} \) at a constant voltage perfectly mimics the shape of the short-circuit response. \( EQE(V_{oc}) \mid_{rel} \) evaluated at a constant photon flux, in contrast, shows slight differences. This can be explained by the fact that the illumination-voltage curve at high photon flux is still influenced by non-linear behaviour.

The external quantum efficiency of the open-circuit voltage constitutes only a relative measure of the quantum yield. Nevertheless, it senses qualitatively the impact of low bulk lifetime and rear surface recombination. To get a quantitatively better picture of the quantum efficiency, the relative internal quantum efficiency of the open-circuit voltage should be considered, as mentioned above. This task is performed in Figure 2.12 with the same devices as in the discussion above. The reflectance needed to calculate \( IQE \) has been obtained by a spectrophotometer. The error of the reflectance measurement has been estimated to ± 3%. This leads to a mean deviation of approximately ± 5% for \( IQE(J_{sc}) \) and of approximately ± 6% for \( IQE(V_{oc}) \) due to error propagation. In the case of the thin cell ULF03.7.5, the wafer was too fragile to measure the reflectance. The results of the test structure FB137.14-20.1 have been used instead, in light of the same optical front characteristics as the sample ULF03.7.5. This leads to higher errors in the IR regime of \( IQE \) owing to the fact that the proportion of the light reflected at the rear side is sensitive to the wafer thickness. As a consequence, we estimated an error of ± 5% for the reflectance for \( \lambda \geq 1000 \) nm for this cell.

In all segments of Figure 2.12, the two competing techniques have been displayed on
the same scale. Naturally, the internal quantum efficiencies portray the same divergences as alluded to above. Apart from this, the results fall into two categories: the high efficiency cells that are more or less immune to recombination activities on the one hand (namely FB99.8d, ULF03.7.5 and 80nza) and the cell designs that are subject to quality-degrading bulk effects on the other (RPAL44.A3.1b, FB137.14-20.1 and M31). The reason that drives the two groups apart is the fact that in the first, \(IQE(J_{sc})\) approaches 1 while in the second, the lower bulk lifetime inflicts a downgrading of \(IQE(J_{sc})\) to \(\sim 0.95\). This means that in the first group, \(IQE(V_{oc})\) quantitatively predicts the quantum yield while in the second, \(IQE(V_{oc})\) is overestimated by a few percentage points. The averaged differences between \(IQE(J_{sc})\) and \(IQE(V_{oc})\) for each cell of the second group are about 2%. If the measurement errors are taken into account, the relative internal quantum efficiency of the voltages agrees well with the internal quantum efficiency of the current.

### 2.4.2 Effect of front surface recombination on \(EQE(V_{oc})\)

High front surface recombination has a strong impact on both the external quantum efficiency of the short-circuit current and the external quantum efficiency of the open-circuit voltage. To demonstrate this, two cells have been de-passivated after the first measurement and measured again to show the effect of a high front surface recombination rate on the voltage response. The two samples are an Al-BSF-PERC cell (1Pca) and a rear-junction (RJ) cell made from mc-material (47cb). The characteristics are listed in Table 2.2. The PERC cell received a light phosphorus diffusion (carried out at 875 °C for 35 min) of \(\sim 280 \Omega/\Box\) followed by an oxidation in TCA at 1050 °C for 20 min. This resulted in a SiO\(_2\) layer of approximately 50 nm. The metal fraction of the rear point contact was 6%, the separation between dots was 1 mm. After the contact formation the samples were alloyed at 1000 °C in N\(_2\) for 60 min. This ensures the formation of an aluminium doped \(p^+\) region above the rear point contacts. The RJ cells were phosphorus gettered at 870 °C for 1 h and received a light phosphorus diffusion as above. The full area rear junction has been achieved by evaporating and subsequently annealing aluminium in forming gas at 900 °C for 1 h.

#### Table 2.2: Resistivity, type and output parameter of the cells used in the investigation of the effect of front surface recombination.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Base Material</th>
<th>Resistivity ([\Omega \text{ cm}])</th>
<th>(J_{sc}) ([\text{mA/cm}^2])</th>
<th>(V_{oc}) ([\text{mV}])</th>
<th>(FF) ([%])</th>
<th>(\eta) ([%])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Pca</td>
<td>(p)-type FZ</td>
<td>1</td>
<td>28.9</td>
<td>651</td>
<td>78.7</td>
<td>12.5</td>
</tr>
<tr>
<td>47cb</td>
<td>(n)-type mc</td>
<td>0.4</td>
<td>13.9</td>
<td>554</td>
<td>77.4</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Figure 2.13: \(E_{\text{Q}}E(V_{\text{oc}})|_{\text{rel}}\) at a constant voltage of the cells 1Pca and 47cb before and after de-passivation of the front surface.

Figure 2.13 presents the change in \(E_{\text{Q}}E(V_{\text{oc}})|_{\text{rel}}\) (normalised to its value at 1000 nm). In the PERC cell, the de-passivation decreases the UV response very strongly, even wavelengths up to 800 nm are affected by it. \(E_{\text{Q}}E(V_{\text{oc}})|_{\text{rel}}\) of the rear junction cells have similarities to \(E_{\text{Q}}E(J_{\text{sc}})\) of a bifacial cell illuminated from the rear: the hump in the IR is characteristic for rear junction devices with low diffusion length. Recombination of IR-generated carriers is limited by diffusion to the front surface. After de-passivation, the divergence between the response to wavelengths near the junction at the rear and the front surface is aggravated. In summary, this technique is very sensitive to recombination losses.

2.4.3 Comparing \(I_{\text{Q}}E(V_{\text{oc}})\) at open-circuit voltage and maximum power point

In a previous section, the problem of non-ideal diode behaviour has been raised. Owing to the fact that these effects do not appear at a certain constant voltage or photon flux for all wavelengths, the quantum efficiency of the voltage seems to suffer from a spectral dependent non-ideal phenomenon. To compare short-circuit and open-circuit response, it is therefore necessary to use high photon fluxes in the range of 0.5–2 suns to reach the quasi-ideal range of the photon flux-voltage curve. In some cases, as for the device FB137.14-20.1, even higher irradiation of 2.2 suns was necessary to extract \(E_{\text{Q}}E(V_{\text{oc}})\) outside a disturbed range. As alluded to above, what, if ignored, is a source of error, can be converted into a useful way of characterising the impact of non-linear effects.

Admittedly, the illumination of a device with 1 sun of photons of one single wavelength
is far from real operation conditions (as is the small light excitation in the conventional spectral response). But the fact remains that, for example, if a shunt resistor decreases the voltage output at a certain monochromatic illumination, say at 0.1 suns at $\lambda = 800$ nm, it is likely that this drop contributes to the overall losses under real operation conditions. An evaluation of $EQE(V_{oc})$ at lower photon fluxes or voltages similar to the one occurring

![Figure 2.14](image1.png)

**Figure 2.14**: Photon flux-voltage curve for the device FB137_14-20.1 taken with two flashes in order to cover a range of several orders of magnitudes. The dark lines indicate the constant photon fluxes and voltages at which $EQE(V_{oc})|_{rel}$ has been extracted.

![Figure 2.15](image2.png)

**Figure 2.15**: $EQE(V_{oc})|_{rel}$ versus wavelength for the constant photon fluxes and voltages indicated in Figure 2.14.
during operation, should therefore give precise information about where the shunt will hurt the cell performance the most.

This outline is further illustrated with the device FB137.14-20.1. Figure 2.14 highlights the photon flux-voltage curve obtained by two flashes. The quasi-ideal range is located above 550 mV, whereas a shunt sets in below 500 mV. \( EQE(V_{oc}) \mid_{rel} \) has been evaluated at a constant photon flux of 1 and 0.1 suns and at two constant voltages that are equivalent to the overall open-circuit voltage and the voltage at the maximum power point \( V_{MPP} \). Figure 2.15 shows the result of \( EQE(V_{oc}) \mid_{rel} \). The short-circuit current yield is displayed to facilitate the comparison.

The quantum efficiency of the voltage at white-light open-circuit conditions diverge only slightly from the short-circuit response. However, at the maximum power point a remarkable decrease in output can be seen. From there, the drop in quantum yield can be imagined if the solar cell’s operation point shifts to even lower voltages. If \( EQE(V_{oc}) \mid_{rel} \) is considered at a constant photon flux of 1 sun, the decrease in the IR is aggravated. A light intensity of 0.1 suns corresponds approximately to the average light irradiation under operation conditions. Figure 2.15 indicates that the efficiency at each wavelength falls by up to 50% compared to the 1 sun response if the photon flux irradiance only reaches this level.

To sum up the results of this section, the investigation shows that the spectral response of the open-circuit voltage gives the same information as the conventional spectral response. Qualitatively, the external quantum efficiency of the voltage follows the trend of its short-circuit counterpart and can be used to pinpoint losses within the device relative to its maximum yield. The relative internal quantum efficiency of the voltage mimics the yield quantitatively extremely well, unless the base material suffers from high recombination. Furthermore, the spectral response offers valuable clues as to the amount of degradation inflicted by non-ideal effects like shunting or depletion region losses.

### 2.5 Determination of surface and bulk recombination from the spectral photovoltage

#### 2.5.1 Extension of the analytical models from the short-circuit to the open-circuit case

In the previous chapters, computer simulations and experiments have demonstrated that the spectral photovoltage broadcasts the same information as the spectral response of
the short-circuit current. Furthermore, the external quantum efficiency of the open-circuit voltage can be written analytically in a similar form to the external quantum efficiency of the short-circuit current (Equation 2.11). This suggests strongly that the analysis of the long-wavelength response of the voltage will succeed equally as well as the conventional method for extracting the diffusion length and the base SRV. Even more, this predicts that the same models can be transferred one-to-one to the novel spectral tool.

As in the traditional analysis, it makes sense to consider only the internal processes, in other words to work directly with the internal quantum efficiency of the voltage $IQE(V_{oc})$. Starting with the definition of $IQE(V_{oc})$ and combining it with Equation 2.11, we end up with the following:

$$IQE(V_{oc}) = \frac{\exp\left(\frac{qV_{oc}}{kT}\right) - 1}{qN_{ph}(1 - R)} = \left(\frac{J_{oc}}{q} + \frac{D_n n_i^2}{L_n N_D} \Xi(H)\right)^{-1} \cdot IQE.$$  \hspace{1cm} (2.12)

Here, the term $IQE$ takes the place of $EQE/(1 - R)$. It is the proportionality between $IQE(V_{oc})$ and $IQE$ that offers the scope to use the models developed in Chapter 1 to extract the recombination parameters of the base region.

**Front illumination**

It is useful to split the analysis of $IQE$ into an evaluation at constant voltage and constant photon flux. In the first case, the wavelength dependent variables that are accessible through measurement are the photon flux $N_{ph}$ and the reflectance $R$. In the second case, the wavelength dependence is expressed in the terms $\exp(qV_{oc}/kT)$ and $R$. Rearranging Equation 2.12 so that the measured wavelength dependent parameters appear on one side gives rise to the following expressions for the two implementations:

$$N_{ph}(1 - R) = \left(\frac{J_{oc}}{q} + \frac{D_n n_i^2}{L_n N_D} \Xi(H)\right) (e^{\frac{qV_{oc}}{kT}} - 1) \cdot IQE^{-1} = c_1 \cdot IQE^{-1},$$

$$\frac{1 - R}{e^{\frac{qV_{oc}}{kT}} - 1} = \left(\frac{J_{oc}}{q} + \frac{D_n n_i^2}{L_n N_D} \Xi(H)\right) / N_{ph} \cdot IQE^{-1} = c_2 \cdot IQE^{-1}.$$  \hspace{1cm} (2.13)

The parameters $c_1$ and $c_2$ are approximately constant under low-injection conditions in terms of their wavelength dependence. A special case of the first equation has been derived in [101] for a mono-exponential generation and wafers that are so thick that the unilluminated surface is not disturbed by the incident light. The formulation here, by contrast, is valid for any wafer thickness, diffusion length, open-circuit voltage and generation profile.

If the light source is facing the junction side of the device, there exist three models
to approximate IQE, introduced in Chapter 1: the linear model, the model of Lagowski-Spiegel and the model of Isenberg. For most of these models, there exists an analogy devised for the SPV technique. Introducing the linear model into Equation 2.13 leads to the classical methods applied in the SPV technique: the constant photon flux SPV and the constant voltage SPV. With the help of Equation 1.29 we obtain:

\[
N_{ph}(1 - R) \approx c_1 \cdot \left(1 + \frac{1}{L_n \alpha}\right),
\]
\[
\frac{1 - R}{e^{-\frac{qV_0}{kT}} - 1} \approx c_2 \cdot \left(1 + \frac{1}{L_n \alpha}\right). \tag{2.14}
\]

Note that the exponential term in Equation 2.14 reduces to \(qV_0/kT\) in the SPV technique due to the small light intensities employed. A plot of the left side of Equation 2.14 against the inverse absorption coefficient predicts that the intercept with the horizontal axis yields either \(c_1\) or \(c_2\) and the ratio of the slope and the intercept equals the diffusion length. New to this method is the bonus that an analysis of \(c_1\) and \(c_2\) unveils the emitter saturation current. The constants \(c_1\) and \(c_2\) can also be used to access IQE indirectly from the spectral response of the voltage. Naturally, the same constraints apply here to the linear model as in the spectral response of the short-circuit current.

The more sophisticated model that Spiegel concocted for the analysis of the short-circuit response has its counterpart in the model that Lagowski et al. conceived earlier for SPV [58]. Adopting this approach to Equation 2.13 leads to the following approximation:

\[
N_{ph}(1 - R) \approx c_1 \cdot \frac{1 - (L_{eff} \alpha)^{-1}}{1 - (L_n \alpha)^{-2}},
\]
\[
\frac{1 - R}{e^{-\frac{qV_0}{kT}} - 1} \approx c_2 \cdot \frac{1 - (L_{eff} \alpha)^{-1}}{1 - (L_n \alpha)^{-2}}. \tag{2.15}
\]

This amendment was the guarantor that diffusion lengths 2.5–3 times larger than the wafer thickness could be correctly measured by SPV [58]. An important result of the work of Lagowski et al. is the finding that the front surface recombination reduces the constant voltage signal by the same ratio for all light penetration depths. This underlines that at constant voltage of a few mV, \(c_1\) can be considered as nearly constant, regardless of the quality of the top region. The real test of whether this statement can be maintained, comes when the device experiences voltages of several 100 mV.

The transfer of the model of Isenberg to the spectral photovoltage represents a novel aspect of this work and happens in the same way as above. The last two adaptations have in common that they require a non-linear fit to three variables. The constant \(c_1\) or \(c_2\) is added to the other two that already feature in the non-linear fit of IQE(J_sc) (that
is, \( L_n \) and \( L_{\text{eff}} \) in the model of Lagowski-Spiegel and \( L_n \) and \( S \) in the model of Iseenberg, respectively). A non-linear fit to three parameters is problematic and often results in the determination of only two of them, the third one keeping its initial value. Not surprisingly, the end-product is prone to errors. Two possible ways out are discussed in this work. The first one makes usage of the linear fit as a first approximation to attain the constants \( c_1 \) and \( c_2 \). If the measurement diverges from a straight line, there exists the likelihood that small errors creep into \( c_1 \) and \( c_2 \). Notwithstanding this, computer simulations highlighted that this approach is the most encouraging of the two.

The other back-door consists of neglecting the emitter saturation current in \( c_1 \) and \( c_2 \) and fitting the measurement with only two free parameters. The emitter saturation current of SiO\(_2\)-passivated \( p\)-type FZ silicon with phosphorus diffusion is situated between 10–500 fA/cm\(^2\) [102]. \( J_{\text{be}} \) is hereby strongly dependent on the emitter sheet resistance in the sense that, the heavier the diffusion, the higher the emitter recombination. The upper limit for other passivation schemes, in particular SiN coating, annealed thin oxide passivations or oxide/SiN stacks is found to be even lower, \( \sim 200 \) fA/cm\(^2\) [103]. For lightly diffused devices, the front surface recombination velocity plays a major role in containing the emitter saturation current. Thus, the increased SRV below the grid fingers in finished devices will drive the emitter recombination current to higher values. However, the front surface loses its grip on \( J_{\text{be}} \) for heavily doped emitters.

In order to estimate an upper limit for \( J_{\text{be}} \), the base saturation current \( J_{\text{bb}} = \frac{qD_n n_B^2}{(L_{\text{eff}} N_D)} \) has been plotted as function of the diffusion length \( L_n \) and the rear surface recombination velocity \( S_n \) (Figure 2.16). \( J_{\text{bb}} \) is proportional to the inverse of \( L_{\text{eff}} \); hence, the \( J_{\text{bb}} \) matrix reveals the same map as \( L_{\text{eff}} \) in Figure 1.5, but upside down. In particular, the \( J_{\text{bb}} \) topography can be divided into the same three regions. If the cell’s recombination activity pins the base saturation current into the first two regions, the high value of \( J_{\text{bb}} > 1000 \) fA/cm\(^2\) will most certainly out weigh the emitter saturation current easily, a fact that corroborates neglecting \( J_{\text{be}} \). However, region 3 is an area of concern, since the base saturation current plummets towards very low values, in which case it will be difficult to ignore the emitter saturation current. The base saturation current is shifted to lower values when the doping density is increased, which implies that the region in which \( J_{\text{bb}} \) converges with or drops below \( J_{\text{be}} \), widens.

High-efficiency devices benefit from a bulk and rear surface passivation quality, which places their \( J_{\text{bb}} \) into region 3. Nonetheless, they tend to have very lowly-doped emitter diffusions with a sheet resistance between 100–120 \( \Omega/\square \). The corresponding emitter saturation current is likely to stay below 50 fA/cm\(^2\). In industrial-type devices the situation
is reversed. Low bulk material and higher back SRVs will rocket \( J_{0b} \) into higher levels (region 1 or 2). This trend is followed by \( J_{0e} \) due to the low emitter sheet resistance used in industrial devices. In both cases, it is decided by the base doping density if \( J_{0e} \ll J_{0b} \).

This discussion may lead to the conclusion that \( J_{0e} \) can by disregarded with ease in most cases. Nevertheless, it turned out that the use of the constants \( c_1 \) and \( c_2 \) obtained from the linear fit always gave better results than including the constants in the fit. This may be rooted in the fact that the picture of the constants \( c_1 \) and \( c_2 \) being solely defined by the base and emitter saturation current is too oversimplified. If \( c_1 \) and \( c_2 \), calculated by the linear fit, are used to determine the emitter saturation current, it is mostly not small enough to be neglect vis-a-vis the base recombination current. The introduction of the emitter saturation current into these constants was based on a model that united the front surface, emitter and depletion recombination into the emitter saturation current. Additionally, the model describing the voltage response assumes an ideal relationship between current and voltage. Any divergence from this picture, an ideality factor greater than one or a two-diode relationship, will alter the contribution to \( c_1 \) and \( c_2 \). This explains why the recombination current related to the base component is in most scenarios much higher than the emitter saturation current alone. The simulations in the following section...
concentrate therefore only on the first method to obtain the constants $c_1$ and $c_2$.

Rear illumination

The application of the model to rear illumination derived in Section 1.4 will proceed in the same manner as above. No analogy exists in this case with the SPV technology. This time, we rearrange the wavelength dependent parameters that are obtained from the measurement in a way so that they face $IQE$ instead of $IQE^{-1}$. Substituting $IQE$ with Equation 1.39 gives rise to the following:

$$\frac{1}{N_{ph}(1 - R)} \approx \frac{1}{c_1} \cdot \frac{1 + \frac{S_p}{D_p} \frac{1}{\alpha}}{\frac{S_p L_p}{D_p} \sinh \frac{W}{L_p} + \cosh \frac{W}{L_p}}$$

A plot of the left side against $1/\alpha$ is supposed to give a straight line, with the ratio of the slope and the intercept yielding $S_p/D_p$. Consequently, this model is positioned to predict the surface recombination velocity that is facing the light source exactly in the same way as its short-circuit counterpart. The minority carrier diffusion length, by contrast, can not be deduced subsequently by fitting the intercept, since it contains the additional constant $1/c_1$ or $1/c_2$, respectively. Nevertheless, we can resort to the same trick as above, neglect the emitter saturation current in $1/c_1$ and $1/c_2$ and use the intercept for the extraction of $L_p$. With the help of computer simulations, we will estimate the applicability of such an approach in the ensuing section.

2.5.2 Computer simulations to compare the analysis of the current and voltage response

Models only describe physical phenomena in an approximate way and thus inherently introduce errors on top of the experimental error. Some of the models require a non-linear fit, which is in most cases a least-square calculation, producing an additional error. Naturally, the more assumptions needed for the applicability of the model, the more discrepancies will creep into the fitting results. The best way to assess these errors is to compare the models to a numerical simulation program that is closest to reality. In this case, PC1D was employed as a base to create the ‘measurement data’, that is, the spectral response of the short-circuit current and the voltage. PC1D is a computer program, which solves the fully coupled nonlinear equations for the one-dimensional transport of electrons
and holes in silicon. This model is far more sophisticated than the ones encountered in this investigation; the data generated with its help therefore represent real devices far better and serves as a benchmark. The goal of the models devised in this work is now to reproduce the input recombination parameters that enter the PClD calculation. The following is a thorough study of all facets of electrical losses a solar cell can face and sheds light on how well the models of the spectral response of the voltage compare with its short-circuit equivalents and ultimately, PClD.

Fitting procedure

PClD has been used to calculate the internal quantum efficiency of the short-circuit current and spectrally resolved illumination-voltage curves. In each case, the total wavelength range was 300–1200 nm with a step size of 10 nm. The wavelength dependent parameters of the voltage response have been extracted between certain upper and lower limits for the photon flux and the voltage. Instead of performing a fit at each constant voltage or photon flux and averaging the resulting recombination parameters, it has been found that the fit to the scaled and averaged internal quantum efficiency of the voltage proves to be numerically better. When the wavelength dependent parameters of the left-hand side of the expressions derived earlier are plotted versus $1/\alpha$, the resulting slope contains small errors due to the interpolation. These errors are abated by the averaging of $IQE(V_{oc})|_{rel}$. The linear fit to the inverse of the averaged $IQE(V_{oc})|_{rel}$ will yield an intercept that is different from $c_1$ and $c_2$, of course. But since they will not be included in the fit directly, this does not change the outcome. Only when the emitter saturation current is of interest, the absolute values have been taken for the fit.

The parameters that are common to all simulations are: thickness 300 $\mu$m, internal reflectance: 70% at the front, 90% at the rear side. The fitting to both the short-circuit and open-circuit expressions proceeded in the same way. The wavelength range used for the linear model and the model of Lagowski-Spiegel was 750–950 nm according to the conditions of these models. The range was extended to 1100 nm for the model of Isenberg. The noise level of the least square fits was adjusted to 10% to mimic reasonable experimental error margins. First, the linear fit was carried out determining the effective diffusion length $L_{eff}$. This value was used in the input for the model of Lagowski-Spiegel for the effective and the actual diffusion length. A contour plot that mapped the error $\chi$ of the least square fit in the $L_{eff}-L_n$ plane indicated that there exists nearly always a clear minimum. The fit with the model of Lagowski-Spiegel is thus always very concise and unambiguous. This certainly has its origin in the simple form of the model and the fact that
the back reflection is excluded. The inclusion of the latter is prone to more ambiguities given the fact that the exact nature of the back reflection can only be approximated.

From the resulting effective and actual diffusion lengths, the rear SRV $S_n$ can be deduced via the Equations 1.26 and 1.14. $L_n$ and $S_n$ are then conferred to the fitting with the model of Isenberg. These simulations where much more ambiguous. The fit of $S_n$ is in general the same as the input value. If the latter is far from the actual value, the resulting fit of $L_n$ therefore only represents a best case scenario for this particular surface recombination rate. A contour plot of $\chi$ in the $L_n$ - $S_n$ plane usually gives valuable clues to the right location of both parameters. Additionally, in a final step, a confidence plot is created that reveals the area in which the solution is most likely located. Imagine the fit delivers the pair $L_n, S_n$. The confidence plot now highlights all possible pairs $L_n$ and $S_n$ that comply with the condition $\chi(L_n, S_n) < 5 \times \chi(L_{n, \text{fit}}, S_{n, \text{fit}})$ [64]. An example of such a confidence plot is shown in Figure 2.17. In general, this permits to corroborate the fit. Nevertheless, there is a hitch to this.

The minimum of the least square error does not always point to the best fit. The reason lies in the fact that the inverse of the internal quantum efficiencies traverses two linear regimes. The first one is situated between $\sim 700$ and $1000$ nm and represents the

![Figure 2.17](image-url)

Figure 2.17: Confidence plot of the least square error $\chi$ as a function of $L_n$ and $S_n$. The area enclosed by the red field represents solutions that comply with the condition $\chi(L_n, S_n) < 5 \times \chi(L_{n, \text{fit}}, S_{n, \text{fit}})$. The point A corresponds to the pair $(L_{n, \text{fit}}, S_{n, \text{fit}})$. The point B indicates the location of the best fit according to the confidence plot.
range where the linear model and the model of Lagowski-Spiegel apply (Figure 2.18, left side). The second linear regime appears for $\lambda \sim 1050$ nm. The fitting procedure and the confidence plot often locate the best fit at a minimum least square error (point B in Figure 2.17) that is a compromise between the two linear regimes. This can lead to strong divergences between fit and measurement in one of the linear regimes, as shown on the left of Figure 2.18.

![Graph](image)

**Figure 2.18:** Inverse internal quantum efficiency of the short-circuit current versus absorption depth. Included in the graph are the initial calculation of PC1D (■), the linear fit (straight black line), the model of Lagowski-Spiegel (dashed black line), and two solutions for the model of Isenberg (blue lines). The symbols ◦ indicate the wavelength limits for the fits. The left graph is an expanded view of the right.

A solution to this is to use the plot of $1/IQE$ versus $1/\alpha$ as a guide until a satisfactory overlap is found between fit and measurement. Basore determined that the slope of the second linear part is only determined by the optical properties of the device, mainly the back reflection [45]. Hence, a close fit to the first linear part is the acknowledged priority. A possible better solution is shown in Figure 2.18 as a straight blue line (solution A). In the confidence plot, this solution has a significantly higher least-square error, but nevertheless gives better results.

If the bulk lifetime is very high, the best fit of the diffusion length by the model of Isenberg is given by the highest possible value, which often physically makes no sense. This problem afflicts the current and voltage response alike. In this case, the contour plot helps to choose an upper limit. Naturally, the minimum of the least square error only provides a rough guide to the exact location of the diffusion length. Despite that, the forecast of the contour plot and the confidence plot agreed well with the PC1D inputs.
In summary, the fit with the model of Isenberg is not as straight-forward as the other two. Nonetheless, using the graphical approach to find a best fit renders it much less ambiguous. In particular, the determination of the diffusion length is very successful. Still, due to the fact that the input for the SRV is normally not altered in the fit, it has to be adjusted in advance using Figure 2.18; the final SRV is therefore prone to a wider error margin. Despite this, the model of Isenberg often leads to better results than the model of Lagowski-Spiegel, which has its root in the fact that it includes more wavelengths.

Front illumination

The first simulations are concerned with a device whose junction is facing the illumination. It has a lightly doped emitter with peak density of $3 \times 10^{19}$ cm$^{-3}$, doping depth 0.5 µm and sheet resistance 120 Ω/□ and Gaussian-type diffusion. The base doping density amounts to $1.5 \times 10^{16}$ cm$^{-3}$ (1 Ω cm). The front surface recombination has been kept constant at 1000 cm/s resulting in an emitter saturation current of 35–88 fA/cm², depending on the bulk lifetime.

A) Determination of the diffusion length

To begin with, we are interested in the determination of the actual bulk diffusion length $L_n$. Hence, the bulk lifetime has been varied fixing the rear surface recombination rate at either 100 or $10^6$ cm/s. The bulk lifetime traversed the values 1, 10, 100 and 1000 µs. The corresponding diffusion lengths calculated by PC1D are 52, 164, 518 and 1640 µm. The Figures 2.19 and 2.20 present the results in a plane that compares the PC1D input of $L_n$ to the fitted one. The first two graphs consider cases where the diffusion length is smaller than the device thickness, in the next two the roles are reversed. The diagonal line in each figure represents the target line. In addition, a dotted line marks the location of the effective diffusion length $L_{\text{eff}}$. The scattered symbols always stand for the same model and analysis method. The symbol ■ represents the linear model, ● the model of Lagowski-Spiegel and ▲ the model of Isenberg. The colour black displays the results of the short-circuit current response, white the open-circuit response at a constant voltage. Before looking at the findings in detail, it can be stated that the findings for the spectral response of the voltage agree very well with each other for most of the simulations, regardless if deduced at a constant voltage or photon flux. To keep a more concise representation, the results at a constant photon flux have therefore been left out in this evaluation.

The lowest diffusion length of 52 µm stays well below the thickness of the cell (Fig-
Figure 2.19: Fitted bulk diffusion length versus PC1D input for a diffusion length that is smaller than the device thickness. The diagonal line indicates the target line. The rear surface recombination is 100 (left graph) or $10^6$ cm/s (right graph). The dotted line shows the effective diffusion length according to PC1D. In some cases the results overlap each other. The input value has then been slightly changed for better representation.

According to the theory developed in Chapter 1, this is the range where the linear model finds its applicability. The outcome confirms this strikingly. All models lead to the same diffusion length and the effective and actual ones are equal within the numerical error. The diffusion length of 164 $\mu$m marks the departing line for $L_n$ and $L_{\text{eff}}$. If the rear surface recombination rate can be held at bay, $L_n$ and $L_{\text{eff}}$ still agree very well and all extractions deliver the same result (Figure 2.19 on the left). For excessive surface recombination, there is already a visible split between results that predict the effective rather than the actual bulk diffusion length (Figure 2.19 on the right).

Secondly, let us shift the focus to diffusion lengths that exceed the wafer thickness (Figure 2.20). If the rear SRV is equal to 100 cm/s, the forecasts of both measurement techniques are quite similar. The linear model determines the effective diffusion length, as predicted by the theory. The model of Lagowski-Spiegel and the model of Isenberg still predict the actual diffusion length for $L_n = 518$ $\mu$m, although the results lie close to $L_{\text{eff}}$ for higher $L_n$.

If a high SRV at the rear inflicts on the cell performance, the situation changes drastically. After $L_n$ and $L_{\text{eff}}$ diverge, only the models of Lagowski-Spiegel and Isenberg reveal the actual diffusion length when carried out with the spectral response of the current. The model of Isenberg applied to the voltage response unveils a diffusion length that shows visible discrepancies from the target values but still to an acceptable level. In all other cases, the outcomes forecast the effective diffusion length. It is assumed that the error
Figure 2.20: Fitted bulk diffusion length versus PC1D input for a diffusion length that is larger than the device thickness. The diagonal line indicates the target line. The rear surface recombination is 100 (left graph) or $10^6$ cm/s (right graph). The dotted line shows the effective diffusion length according to PC1D. In some cases the results overlap each other. The input value has then been slightly changed for better representation.

originates in the constants $c_1$ and $c_2$. For these conditions, the functions plotted versus the absorption depth diverge strongly from a straight line in the meaningful wavelength range introducing errors in the calculation of $c_1$ and $c_2$. The reason for the better fit of the voltage response with the model of Isenberg lies in the fact that wavelengths above 950 nm become more important at very high diffusion length. As the chance of resisting the high recombination current towards the rear surface increases, charge carriers absorbed at this part of the spectrum contribute to a greater extent to the quantum yield. This effect passes unnoticed in the models that stop their analysis at 950 nm, but has its impact on the model of Isenberg.

B) Determination of the rear surface recombination rate

The second round of simulations is concerned with the determination of the rear surface recombination rate $S_n$. Here, the bulk lifetime has been kept at either 1500 or 10 $\mu$s, $S_n$ takes the values 100, 1000, $10^4$, $10^5$ and $10^6$ cm/s. Figure 2.21 shows the fitted recombination rate as a function of the input values of $S_n$ for the PC1D calculation. The diagonal line indicates the surface recombination rate that has to be met. The models that are able to forecast the surface recombination rate are the models of Lagowski-Spiegel and Isenberg. As alluded to above, the surface recombination velocity fitted with the model of Isenberg can sometimes only be adjusted graphically, this is especially true when $S_n$ exceeds $10^5$ cm/s. In this case, error bars indicate the (approximate) interval of possible
2. Spectral response of the open-circuit voltage

solutions.

Firstly, let us consider a device that exhibits a high bulk lifetime of 1500 \( \mu \text{s} \) (Figures 2.21 on the left). The analysis of the spectral response of the short-circuit current reveals excellent results for either model for \( S_n \leq 10^4 \text{ cm/s} \). For higher surface recombination, by contrast, both models can only predict a lower limit to \( S_n \). These limits diverge more from the original input values, the higher \( S_n \) becomes. The determination of \( S_n \) via the spectral photovoltage and the model of Isenberg is equally successful as long as \( S_n \) does not transgress 10^4 cm/s. For \( S_n > 10^4 \text{ cm/s} \), the model of Isenberg forecasts \( S_n \) in an interval that stretches 10–15% around its middle value. Admittedly, this interval is situated far below the actual surface recombination velocity. The model of Lagowski-Spiegel applied to the spectral photovoltage is only able to fit satisfying values for the surface recombination rate for \( S_n \leq 1000 \text{ cm/s} \). If the surface recombination rate rises above this, the predictions lie one to two orders of magnitudes below its actual values.

![Figure 2.21: Fitted values of the rear surface recombination rate versus its PC1D input. The diagonal line indicates the target line. The bulk diffusion length amounts to either 1500 (left graph) or 10 \( \mu \text{s} \) (right graph). In most cases, the results of the voltage response at constant voltage or photon flux are equal.](image)

Secondly, the spotlight is turned to devices that suffer from high losses in the bulk (Figures 2.21 on the right). The analysis of the short-circuit response with the model of Isenberg gives the best predictions of \( S_n \) throughout the whole surface recombination range. For \( S_n \leq 10^4 \text{ cm/s} \), the application of this model to the voltage response proves to be the closest to reality, but fails to detect higher surface recombination rates accurately. This model has the advantage that it evaluates two linear regimes instead of one, explaining the better results regardless of the spectral response involved. However, the model of Lagowski-Spiegel faces the difficulty that the effective and actual bulk diffusion length
only diverge slightly. The analysis of the spectral photocurrent with this model still leads to reasonable values for the range \( S_n = 10^3 - 10^4 \) cm/s. But its results are considerably too high for the lowest surface recombination rate. It even fails to determine any value if \( S_n \) exceeds \( 10^4 \) cm/s. If applied to the spectral response of the voltage, the resulting effective and actual diffusion length come so close that the fitted \( S_n \) always stays in the range \( \sim 1000 - 3000 \) cm/s, regardless of the initial input value.

C) Summary

In brief, the model of Isenberg delivers the best predictions of the bulk diffusion length and the surface recombination rate. The analysis of the spectral response of the short-circuit current gives globally better results for this model. However, when applied to the voltage response, the results are equally accurate under the condition that \( S_n \) does not surpass \( 10^4 \) cm/s. If \( S_n \) transgresses this limit, the model still predicts accurately the bulk diffusion length, provided the latter stays below the device thickness. This is an important result, particularly for the application of the SPV technique. With the model of Isenberg, there exists now a new fitting procedure for the voltage response that allows extraction of the diffusion length more accurately, even if \( L_n \) exceeds the sample thickness by far, or a high \( S_n \) up to \( 10^4 \) cm/s plagues the device.

The linear model is only applicable if the diffusion length is much smaller than the sample thickness, as expected. Under these circumstances, all models deliver the same result regardless of the spectral response method used. The model of Lagowski-Spiegel performs as well as the model of Isenberg when employed with the short-circuit response to extract the diffusion length. The determination of the rear surface recombination rate is equally successful provided the bulk quality is high. When applied to the spectral photocurrent, it predicts \( L_n \) accurately if the latter is smaller than the wafer thickness or \( S_n \) below \( 10^3 \) cm/s. The determination of \( S_n \) is only successful when both the bulk and the surface recombination are restrained.

Emitter saturation current

The linear fit to the spectral photovoltage permits determination of the constants \( c_1 \) and \( c_2 \) that appear in Equation 2.13. These constants carry the impact of the emitter losses, which can be assessed by subtracting the base saturation current. In the next simulation, the emitter saturation current \( J_{0e} \) has been determined via \( c_1 \) and \( c_2 \) and compared to the PC1D inputs. Instead of fitting the averaged \( IQE(V_{oc}) \) \( |_{rel} \), the wavelength
dependent parameters, which form the left-hand side of Equation 2.13 have been modelled for a range of constant voltages and photon fluxes. The base saturation current depends of the effective diffusion length, a parameter obtained by any of the models described earlier. The simulations above revealed that the model of Isenberg is able to predict $L_{\text{eff}}$ most accurately. Hence, the results of this model were used to calculate the base saturation current and ultimately $J_{\text{oc}}$.

Figure 2.22: Recombination current densities calculated by PC1D and from the constants $c_1$ and $c_2$ as a function of bulk lifetime. The left graph compares the PC1D calculation to the analysis of the spectral response of the voltage at constant voltages. The right graph shows the same at constant photon fluxes.

Figure 2.22 shows the so-deduced emitter saturation current $J_{\text{oe}}$ as a function of the bulk lifetime with fixed rear SRV of either 100 cm/s and $10^6$ cm/s. The simulation parameters and fitting results correspond to the Figures 2.19 and 2.20. The graph on the left compares the PC1D inputs to the results for constant voltages, the right graph does the same for constant photon fluxes. The PC1D current densities are obtained from the hole current densities at the junction edge and are thus prone to small errors due to the fact that there does not exist a clear definition of the junction borders. In detail, the following inputs are presented in the graphs: 1) the emitter saturation current $J_{\text{oe}}$ obtained from the hole current density at the emitter side of the junction and 2) the combined emitter and depletion recombination current obtained from the hole current density at the p-side edge of the junction. Note that the rear surface recombination does not impact on the PC1D calculations. The fitting results, in turn, are the average value over the fits at several constant voltages or photon fluxes. The standard deviation to this average is included in the form of error bars.

$J_{\text{oe}}$ calculated by PC1D only varies slightly with the bulk lifetime. In fact, the recom-
bination current only shows an increase for the lowest bulk lifetime. The depletion current is negligible compared to $J_{oe}$ for high lifetimes in the base region, but outweighs it if the base region suffers from very high recombination. $J_{oe}$ deduced from $c_1$ and $c_2$ is in most cases significantly higher than the PC1D calculations. Only at the highest bulk lifetime the fit results agree with PC1D. Conversely, they converge better with the combined recombination current densities $J_{oe} + J_{U,scr}$. Among the fit results, the ones obtained at a constant photon flux are considerably closer to the PC1D values. A high rear surface recombination velocity complicates the analysis of the spectral response. This leads to high error margins as encountered in Figure 2.22.

As already indicated in the discussion about whether it is wise to neglect $J_{oe}$ in the constants $c_1$ and $c_2$ (page 85), the depiction of these constants in terms of $J_{oe}$ and $J_{ob}$ alone is too simplistic. Firstly, the one-dimensional model that introduced these recombination currents into the spectral response of the voltage combined the depletion region with the emitter region (see discussion on page 62 and Equation 2.11). Secondly, this model assumes a linear relationship between the current and the exponential of the voltage, in other words an ideal diode. High bulk recombination certainly implies a high depletion recombination and therefore non-ideal effects. The recombination currents that determine $c_1$ and $c_2$ in these circumstances are not only given by $J_{oe} + J_{U,scr}$, but as well by a contribution of the bulk. This is corroborated by the simulations in Figure 2.22. The fit results follow a similar trend to the combined recombination current of $J_{oe} + J_{U,scr}$, but still exceed it significantly. In conclusion, it is better to talk about an effective emitter saturation current.

The next simulations consider a front region whose emitter saturation current has been altered either by changing the front surface recombination velocity or the emitter diffusion. In all cases, the bulk lifetime has been kept at 1000 $\mu$s and the rear surface recombination rate at 100 cm/s. The high lifetime ensures that the effective emitter saturation current is close to the actual one. The doping density of the bulk region is $1.5 \times 10^{16}$ cm$^{-3}$ (1 $\Omega$ cm). In the first part of these simulations, the emitter diffusion was the same as in the previous simulations and $S_{front}$ traversed the values 100, 1000, $10^4$, $10^5$ and $10^6$ cm/s. In the second part, the emitter diffusion was tailored by varying the peak surface concentration and the sheet resistance of the emitter. The diffusion profile was a Gaussian one. The details of the different emitter configurations for the second part are summarised in Table 2.3.

Figure 2.23 illustrates the calculation of the emitter saturation current by PC1D and the analysis of the spectral response of the voltage. Both simulations reveal that the PC1D input values and the analysis of the base part of the spectral response agree very well for
Table 2.3: Six variations of peak surface doping concentration $N_{\text{peak}}$, sheet resistance $R_{\text{sheet}}$ and junction depth $W_e$ resulting in different emitter configurations used for the simulations in Figure 2.23.

<table>
<thead>
<tr>
<th></th>
<th>Cell 1</th>
<th>Cell 2</th>
<th>Cell 3</th>
<th>Cell 4</th>
<th>Cell 5</th>
<th>Cell 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{peak}}$ [cm$^{-3}$]</td>
<td>$10^{18}$</td>
<td>$5 \times 10^{18}$</td>
<td>$10^{19}$</td>
<td>$5 \times 10^{19}$</td>
<td>$10^{20}$</td>
<td>$5 \times 10^{20}$</td>
</tr>
<tr>
<td>$R_{\text{sheet}}$ [Ω/□]</td>
<td>376</td>
<td>241</td>
<td>156</td>
<td>75</td>
<td>49</td>
<td>21</td>
</tr>
<tr>
<td>$W_e$ [µm]</td>
<td>1.02</td>
<td>0.7</td>
<td>0.76</td>
<td>0.57</td>
<td>0.52</td>
<td>0.32</td>
</tr>
</tbody>
</table>

![Graph of Figure 2.23](image)

**Figure 2.23:** Emitter saturation current calculated by PC1D and from the constants $c_1$ and $c_2$. The graph on the left shows the emitter saturation current as a result of the variation of the front surface recombination velocity.

all type of emitters considered here. The agreement and the error margin improves when the emitter saturation current increases.

To sum up, the last simulations underline impressively the potential of the spectral response of the voltage. By measuring the voltage instead of the current, the dark saturation current of the front region is accessible through a detailed analysis of the base spectral response. This illuminates the path for rigorous process control of the emitter quality from its early diffusion to the final metallization step.

**Rear illumination**

The rear illumination of conventionally structured solar cells or the front illumination of back junction cells represents another interesting topic that is considered next. A linear fit to the resulting spectral response of the short-circuit current enables deduction of the surface recombination velocity of the surface facing the light source. The actual and effective diffusion length can then be numerically extracted using $S$ and the intercept.
of the linear fit. The analysis of the spectral photovoltage promises to deliver a similar outcome for $S$ using essentially the same linear fit. Still, the deduction of the other two parameters can only proceed by neglecting the emitter saturation current in the constant that determines the slope and the intercept of the linear fit.

In the next simulations, two different situations have been studied. First, the bulk lifetime remained at 1500 $\mu$s, while the SRV has been varied between 100 and $10^6$ cm/s. In the second case, the SRV was kept at 100 cm/s, whereas the bulk lifetime traversed the values 1, 10, 100 and 1000 $\mu$s. The rear junction diffusion was a Gaussian type emitter with peak surface concentration $3 \times 10^{19}$ cm$^{-3}$, doping depth 0.5 $\mu$m and sheet resistance $120 \Omega/\square$. The base doping density was kept at $1.5 \times 10^{16}$ cm$^{-3}$ (1 $\Omega$ cm), the cell thickness stayed at 300 $\mu$m. The wavelength range envisaged for the analysis stretched from 500 to 800 nm in all cases but one. This range corresponds to the flat part that is so typical for the rear-illumination spectral response. The only exception was when the cell device had a bulk lifetime of 1 $\mu$s. $IQE$ as a function of $1/\alpha$ is then highly non-linear apart from the region between 400 and 600 nm. The findings for the constant voltage and constant photon flux method were the same. The following evaluation will therefore concentrate on the constant voltage case.

The results of the simulation are shown in Figure 2.24. The linear fit to the spectral response is very successful in reproducing the initial PC1D surface recombination velocities (left graph of Figure 2.24). Both measurement methods handle this task equally well; the

![Figure 2.24](image-url)

**Figure 2.24:** Fitted SRV of the surface facing the light source compared to the PC1D input SRV for a rear-junction cell or rear-illuminated cell with bulk lifetime 1500 $\mu$s (left graph). Fitted diffusion length compared to the PC1D input for the same device structure with fixed SRV of 100 cm/s.
fitted values diverge only for very high surface recombination visibly from the target with \( \sim 6.5 \times 10^5 \) instead of \( 10^6 \) cm/s. In comparison, the fitted diffusion lengths that correspond to these simulations are widespread and different for each method. The target value is 2008 \( \mu m \). The fit to the spectral response of the current forecasts values that are too high if the SRV does not exceed \( 10^4 \) cm/s. In detail, \( L_n = 5000 \mu m \) if \( S = 100 \) and 1000 cm/s and \( L_n = 3120 \mu m \) if \( S = 10^4 \) cm/s. For higher SRV, the prediction approaches the input value with \( L_n \) around 1350 \( \mu m \). The analysis of the spectral response of the voltage predicts values that are too low in most cases. To be exact, if \( S = 100 \) cm/s, the fit delivers \( L_n = 2658 \mu m \) (constant voltage) and 1390 \( \mu m \) (constant photon flux). For higher \( S \), both extraction method forecast similar values that decrease from \( \sim 890 \) to \( \sim 550 \mu m \) when \( S \) increases from 1000 to \( 10^6 \) cm/s.

The fitted bulk diffusion length at a constant SRV of 100 cm/s are similarly convincing (right graph of Figure 2.24). If \( L_n \) remains lower than the wafer thickness, the fit reproduces the input values perfectly, irrespective of the extraction method. For higher \( L_n \), the linear fit to the spectral response of the current forecasts values that are closer to the effective diffusion length, but still reasonably good. The outcome of the analysis of the voltage response, by contrast, still delivers an excellent prediction at a bulk lifetime of 100 \( \mu s \). At the highest bulk lifetime investigated here, the fit result differs from the PCID value to the same extent as its short-circuit analogue. Nonetheless, the target value remains within the numerical error margin. This supports the idea of suppressing the emitter saturation current in the analysis of the spectral photovoltage for rear illuminations.

The analysis of each method unveils approximately the same fit results for the surface recombination rates. At a low bulk lifetime of 1 \( \mu s \), the findings are with \( \sim 430 \) cm/s much higher than the initial value. At \( \tau_{\text{bulk}} = 10 \mu s \), it yields 270 cm/s for the current response and 120-256 cm/s for the voltage response. Finally, the results for higher bulk lifetimes are very close to 100 cm/s.

\[ 2.5.3 \quad \text{Experimental analysis of the external quantum efficiency in terms of recombination in the base} \]

The linear model

The linear model is the natural choice to demonstrate the ability of the new spectral response technique to extract recombination parameters, since the interpretation of the fitted parameters is as straightforward as in the analysis of the short-circuit current response. The linear model is demonstrated with solar cells based on aluminium-doped
Czochralski silicon wafers with two different doping densities: 0.7 (RPAL44_A1.2b) and 0.15 Ω cm (RPAL44_A3.1b). Throughout this experiment, we found very similar results for both cells and will therefore restrict the visual presentation to the 0.15 Ω cm cell.

The inverse of $IQE$ of the spectral photocurrent has been plotted as a function of the absorption depth $1/\alpha$, for all wavelengths (Figure 2.25). For $1/\alpha$ up to 160 µm ($\lambda = 1000$ nm), the measured points lie on a straight line. Higher wavelengths deviate from the linear fit, since back reflection cannot be neglected anymore. From the linear fit to the voltage response data, the constants $c_1$ and $c_2$ have been determined and $IQE$

![Figure 2.25](attachment:2.5.png)

**Figure 2.25:** Inverse internal quantum efficiency $1/IQE$ as a function of absorption depth $1/\alpha$. $1/IQE$ of the current response has been obtained directly from the spectral response measurement of the short-circuit current. $1/IQE$ of the spectral photocurrent has been determined indirectly by the linear fit to Equation 2.14. The lines denote the linear fit to $1/IQE$.

**Table 2.4:** Extraction of the diffusion length of the aluminium-doped CZ cells RPAL44.A3.1b and RPA144.A2.1a.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$\rho$ [Ω cm]</th>
<th>W [µm]</th>
<th>Diffusion length [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$IQE(J_{sc})$</td>
<td>$IQE(V_{oc})$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Conv. QSSJ_{sc}</td>
<td>SR $\lambda$</td>
<td>$V_{oc}=N_{ph}=\text{const}$</td>
</tr>
<tr>
<td>RPAL44_A3.1b</td>
<td>0.7</td>
<td>330</td>
<td>14.4</td>
</tr>
<tr>
<td>RPAL44_A2.1a</td>
<td>0.15</td>
<td>335</td>
<td>6.6</td>
</tr>
</tbody>
</table>
has been calculated for all $\lambda$. As an example, Figure 2.25 shows the results of the inverse IQE at a constant voltage of 530 mV and at a constant photon flux of 1 sun as a function of $1/\alpha$. The data form a straight line for $1/\alpha > 70$ $\mu$m ($\lambda > 950$ nm). Table 2.4 shows the diffusion length determined by the short-circuit and open-circuit spectral response. An excellent agreement is found between the different techniques. The extraction of $L_n$ at a constant photon flux is slightly lower, which can be explained by the fact that the diffusion length has a strong injection dependence. $L_n$ is significantly lower than the cell thickness, which validates the linear model.

Application of the models of Lagowski-Spiegel and Isenberg to the voltage response

The linear model is very illustrative and convincing if it is applied to devices that fulfill all conditions as was the case for the defect-rich aluminium doped samples. Most devices benefit from higher diffusion lengths that come close to or are much larger than the wafer thickness. The more sophisticated models of Lagowski-Spiegel and Isenberg then represent a far better approach, a fact that has been additionally supported by the computer simulations in the previous section. We will encounter again some of the devices studied in Chapter 1 and 2 with the spectral response of the short-circuit current and the open-circuit voltage. Their device characteristics can be consulted in Table 1.2 on page 44.

The first cell investigated is the high efficiency cell FB99.8d. The prediction of the three different models applied to several techniques are compared to PC1D calculations. In PC1D, the input parameters have been chosen to match the measured output variables, that is, $J_{sc}$, $V_{oc}$, $EQE(J_{sc})$ and $IQE(J_{sc})$. The techniques are the conventional and the quasi-steady state spectral response of the short-circuit current and the spectral response of the open-circuit voltage, the latter evaluated either at a constant voltage or photon flux. The results of the QSS$J_{sc}$-$\lambda$ method help to assess the disadvantage of having measurement points only every 50 nm instead of 20 nm, as is the case for the conventional tool employed here. Table 2.5 displays the PC1D and the fitted values. The forecasted parameters are $L_{eff}$ for the linear model and $L_{eff}$, $L_n$ and $S_n$ for both the model of Lagowski-Spiegel and the model of Isenberg. The errors shown for the voltage response are derived from the simultaneous analysis at a broad range of constant voltages or photon fluxes. A graphical solution is often employed to improve the prediction of the model of Isenberg for the voltage response. As a consequence, its outcomes have a wider error margin than the ones indicated for the other models.

For this cell, the PC1D calculations revealed an incongruity of the output parameters
2.5 Determination of surface and bulk recombination from the spectral photovoltage

Table 2.5: PC1D calculations and fitting results of $L_{eff}$, $L_n$ and $S_n$ of the device FB99_8d.

<table>
<thead>
<tr>
<th>Method</th>
<th>Linear</th>
<th>Lagowski-Spiegel</th>
<th>Isenberg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L_{eff}$ [µm]</td>
<td>$L_{eff}$ [µm]</td>
<td>$L_{eff}$ [µm]</td>
</tr>
<tr>
<td>PC1D²</td>
<td>462</td>
<td>462</td>
<td>400</td>
</tr>
<tr>
<td>PC1D²</td>
<td>882</td>
<td>882</td>
<td>1830</td>
</tr>
<tr>
<td>Conv. SR</td>
<td>838</td>
<td>502</td>
<td>400</td>
</tr>
<tr>
<td>QSS$J_{sc}$-λ</td>
<td>756</td>
<td>817</td>
<td>1609</td>
</tr>
<tr>
<td>QSSV$<em>{oc}$-λ, $V</em>{oc}$</td>
<td>464±24</td>
<td>408±19</td>
<td>304±20</td>
</tr>
<tr>
<td>QSSV$<em>{oc}$-λ, $N</em>{ph}$</td>
<td>408±32</td>
<td>365±26</td>
<td>288±18</td>
</tr>
</tbody>
</table>

² Adjusted to the measured spectral response
² Adjusted to $V_{oc}$ and $J_{sc}$
* Graphical solution

$J_{sc}$ and $V_{oc}$ on one side and $EQE(J_{sc})$ on the other side. The best fit to the short-circuit current and the open-circuit voltage overestimate $EQE(J_{sc})$ measured with the conventional technique by 2% in the range 700–900 nm. If the PC1D input is adjusted to match the spectral response, $J_{sc}$ is lowered to 37.3 mA/cm$^2$ and $V_{oc}$ to 648 mV, which does not agree well with the measured data of 38.8 mA/cm$^2$ and 670 mV. In Table 2.5, both results are listed. The spectral response is in any event the more sensitive method, and so more weight has been ascribed to its corresponding PC1D results.

The linear model reveals values that diverge strongly from method to method. The current based techniques predict values that are closer to the PC1D simulations adjusted to the standard output parameters. The spectral photovoltage, in turn, delivers an effective diffusion length according to the linear model that rather matches the PC1D results adjusted to the spectral response. The model of Lagowski-Spiegel divides the results again in several groups: The conventional spectral response forecasts values that agree well with the more trustworthy PC1D results. The voltage response discloses an effective and actual diffusion length that is much smaller than $L_{eff}$ deduced from the linear model and the PC1D results that are fitted to the spectral response. The quasi-steady-state current technique, in turn, gives the PC1D simulations that agree better with $J_{sc}$ and $V_{oc}$ more credibility. The prediction of the model of Isenberg is very consistent for all measurement techniques. Most notably, they are in excellent agreement with the PC1D input values that give rise to the correct spectral output.

The next device studied is the high-efficiency cell FB137_14-20.1 fabricated on multicrystalline material. Its output parameters of $J_{sc}=31.1$ mA/cm$^2$ and $V_{oc}=584$ mV are considerably lower than the previous example. Its external quantum efficiency, more-
over, indicates strong losses in the IR due to a low bulk quality of the silicon. The PC1D simulations and the recombination parameter derived from the spectral analysis are given in Table 2.6. PC1D indicates $L_{\text{eff}}$ and $L_n$ equal to 80 $\mu$m, much lower than the device thickness of 250 $\mu$m. Consequently, the linear model already predicts values that are close to this, between 67 and 101 $\mu$m. The outcomes of the model of Lagowski-Spiegel and Isenberg agree convincingly with the PC1D simulations. In particular, the quasi-steady-state techniques overlap well with the PC1D results if the model of Isenberg is used.

Table 2.6: PC1D calculations and fitting results of $L_{\text{eff}}$, $L_n$ and $S_n$ of the device FB137.14-20.l.

<table>
<thead>
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<th>Method</th>
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<th>Lagowski-Spiegel</th>
<th>Isenberg</th>
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<td></td>
<td>$L_{\text{eff}}$</td>
<td>$L_{\text{eff}}$</td>
<td>$L_n$</td>
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<tr>
<td>PC1D</td>
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<tr>
<td>Conv. SR</td>
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<td>87</td>
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<tr>
<td>$QSSJ_{sc-\lambda}$</td>
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<td>72</td>
<td>78</td>
</tr>
<tr>
<td>$QSSV_{oc-\lambda}$, $V_{oc}$</td>
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<td>97±3</td>
<td>97±3</td>
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<tr>
<td>$QSSV_{oc-\lambda}$, $N_{ph}$</td>
<td>96±0.1</td>
<td>98±0.1</td>
<td>99±0.1</td>
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</table>

* Graphical solution

The base recombination is clearly dominated by the low diffusion length. This limits the determination of the rear surface recombination velocity. The spectral analysis of the current response does not allow specification of $S_n$. In most other cases, like for the PC1D calculation and the model of Isenberg applied to the voltage yield, it permits to narrow the range of possible $S_n$. The values shown in Table 2.6 thus only give a crude match to the exact surface recombination rate.

In conclusion, the extraction of the diffusion length for front illumination show very similar results for either spectral responsivity technique. The discrepancies between the conventional methods and the spectral photovoltage can be partly explained by the smaller numbers of wavelengths used in the latter. If the diffusion length determined by the model of Isenberg is taken as an example, the values predicted by $QSSJ_{sc-\lambda}$ differ by 5–17% from the ones obtained from the traditional spectral response. $L_n$ deduced by $QSSV_{oc-\lambda}$, in turn, differs by 7–33% from the outcomes of the conventional technique. This shows that the accuracy can be increased by using more wavelengths.

**Voltage response of rear-illuminated cells**

In a previous section, a rear-junction device fabricated on FZ silicon has been studied with the spectral response of the current and the voltage (device 80nza). The illumination-
2.5 Determination of surface and bulk recombination from the spectral photovoltage

Voltage curves indicate that this cell suffers from non-linearity effects, most likely as a result of an enhanced recombination in the depletion region. This non-linearity decreases the response of $IQE(V_{oc})$ in the IR even for very high constant voltages or photon fluxes (Figure 2.12 on page 75). Ultimately, this causes the slope of $IQE(V_{oc})$ to be negative in the range of interest for the linear model of rear-illuminated cells. Hence, two other devices have been chosen for the test of the linear model. These cells stem from the same batch as the cell 80nza, but were produced on mc-silicon. The inherent smaller diffusion length of mc material ensures that any non-linear effects will be vastly superseded by bulk recombination.

The device characteristics of the two n-type cells with continuous aluminium-doped rear junctions are displayed in Table 2.7. Note that the open-circuit voltages of the solar cells are quite low. The dopant profile and a highly recombinative $p^+$ region of the alloyed and diffused aluminium may place serious limitations on the cell performance. Another factor may be the variability of the diffusion length within the wafer or edge effects due to the small wafer size of 4 cm$^2$ [89].

Table 2.7: Thickness, resistivity and performance data of two multicrystalline rear-junction solar cells.

<table>
<thead>
<tr>
<th>Name</th>
<th>Thickness [µm]</th>
<th>Base Material</th>
<th>Resistivity [Ω cm]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [mV]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5bb</td>
<td>325</td>
<td>n-type mc</td>
<td>2.9</td>
<td>30.3</td>
<td>584</td>
<td>78.0</td>
<td>13.8</td>
</tr>
<tr>
<td>47ca</td>
<td>325</td>
<td>n-type mc</td>
<td>0.4</td>
<td>16.3</td>
<td>564</td>
<td>79.4</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Figure 2.26 illustrates the external quantum efficiency of the short-circuit current and the voltage of the cells 5bb (left graph) and 47ca (right graph). The device 5bb expresses a similar quantum yield to the single crystalline rear junction cell 80nza. $IQE(J_{sc})$ and $IQE(V_{oc})|_{rel, V_{oc} = const}$ overlap perfectly, whereas $IQE(V_{oc})|_{rel, N_{ph} = const}$ shows a slightly lower response in the IR. For the lower doped cell 47ca, the spectral response agrees well regardless of the extraction method. Most notably, the quantum yield exhibits the characteristic hump in the IR that underlines the limited flow of charge carriers from the front region towards the back junction.

The attempt to fit the output characteristics and the short-circuit current response in PCID with a simple $p^+$ region at the rear failed to reproduce the measurement data. The quality of the rear junction, the front surface recombination and the diffusion length is crucial to reach high voltages. The output voltage and the nature of the junction formation all point to a highly recombinative zone either within the emitter or the depletion region. By including a highly recombinative, 2 µm thin region between the aluminium
Figure 2.26: External quantum efficiency of the short-circuit current and the voltage, the latter extracted at a constant voltage and photon flux, for the rear junction cells 5bb (left graph) and 47ca (right graph).

emitter and the n-type base region, the PC1D simulations matched the measurements successfully [104]. The diffusion length of this region was adjusted to 25 and 8 µm, respectively.

The PC1D results suggest a very low front surface recombination rate of 70 cm/s and a very high diffusion length of 5000 µm for the device 5bb (Table 2.8). $S_p$ is significantly higher than the values obtained by the spectral analysis, lying between 200–280 cm/s. The high diffusion length is only matched by the findings of the QSSJ$_{sc-\lambda}$. The low value of $\sim 310–370$ µm predicted by the voltage response is indeed unrealistic, as it would decrease the quantum yield substantially. In the next device, $S_p$ is forecasted very accurately by all method compared to PC1D. Here as well, only the short-circuit current response approximately reflects the right diffusion length. Remember that, in order to obtain the

Table 2.8: Results of the spectral analysis of the quasi-steady-state short-circuit current and open-circuit voltage of the devices 5bb and 47ca.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Method</th>
<th>$L_{eff}$</th>
<th>$L_p$</th>
<th>$S_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[µm]</td>
<td>[µm]</td>
<td>[cm/s]</td>
</tr>
<tr>
<td>5bb</td>
<td>PC1D</td>
<td>2034</td>
<td>5000</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>QSSJ$_{sc-\lambda}$</td>
<td>758</td>
<td>5000</td>
<td>273</td>
</tr>
<tr>
<td></td>
<td>QSSV$<em>{sc-\lambda}$, \ $V</em>{oc}$</td>
<td>324±27</td>
<td>312±27</td>
<td>278±27</td>
</tr>
<tr>
<td></td>
<td>QSSV$<em>{sc-\lambda}$, \ $N</em>{ph}$</td>
<td>367±19</td>
<td>341±19</td>
<td>206±27</td>
</tr>
<tr>
<td>47ca</td>
<td>PC1D</td>
<td>459</td>
<td>500</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>QSSJ$_{sc-\lambda}$</td>
<td>498</td>
<td>674</td>
<td>373</td>
</tr>
<tr>
<td></td>
<td>QSSV$<em>{sc-\lambda}$, \ $V</em>{oc}$</td>
<td>104±4</td>
<td>104±4</td>
<td>355±59</td>
</tr>
<tr>
<td></td>
<td>QSSV$<em>{sc-\lambda}$, \ $N</em>{ph}$</td>
<td>108±4</td>
<td>108±4</td>
<td>351±85</td>
</tr>
</tbody>
</table>
actual diffusion length from a voltage measurement, the impact of the emitter saturation current has to be suppressed. This contradicts the apparent high recombination activity of the aluminium-doped junction region.

It has to be concluded that the emitter saturation current can not so easily be ignored in the analysis of the spectral response of the voltage. Note that this approach failed also for front-illuminated traditional cell structures. In the PC1D calculations of rear-illuminated cells in Section 2.5.2, the recombination in the emitter was small. This may explain the fact that neglecting the emitter saturation current still lead to a correct determination of the diffusion length in the simulations. Still, the linear model predicts the same outcome for the front surface recombination velocity when applied to the current or voltage response.

**Extraction of the diffusion length and \( S_{eff} \) as a function of carrier density**

The spectral response of the open-circuit voltage offers scope for extracting the bulk recombination parameters as a function of excess carrier density at the junction edge. The solar cells investigated for this purpose are multicrystalline solar cells from the same batch as the device M31 (see also Table 1.2 on page 44). They are expected to have a strongly injection-level dependent bulk lifetime and surface recombination, the latter as a result of the SiN passivation layer [105]. Including cell M31, four devices of different doping density have been analysed. Table 2.9 summaries the output parameters of the solar cells.

**Table 2.9:** Thickness, resistivity and performance data of the multicrystalline solar cells with all-silicon nitride passivation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Thickness ( \mu m )</th>
<th>Base Material</th>
<th>Resistivity ( \Omega \ cm )</th>
<th>( J_{sc} ) ( \text{mA/cm}^2 )</th>
<th>( V_{oc} ) ( \text{mV} )</th>
<th>FF ( % )</th>
<th>( \eta ) ( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>M11</td>
<td>265</td>
<td>p-type mc</td>
<td>0.2</td>
<td>30.4</td>
<td>649</td>
<td>80.4</td>
<td>15.8</td>
</tr>
<tr>
<td>M31</td>
<td>235</td>
<td>p-type mc</td>
<td>0.3</td>
<td>29.3</td>
<td>620</td>
<td>77.7</td>
<td>14.1</td>
</tr>
<tr>
<td>M61</td>
<td>300</td>
<td>p-type mc</td>
<td>0.4</td>
<td>30.5</td>
<td>626</td>
<td>76.2</td>
<td>14.5</td>
</tr>
<tr>
<td>M81</td>
<td>255</td>
<td>p-type mc</td>
<td>0.5</td>
<td>30.8</td>
<td>620</td>
<td>79.1</td>
<td>15.1</td>
</tr>
</tbody>
</table>

An injection-level dependence is expected from the minority carrier diffusion length if the ideality factor is greater than unity at higher voltages [106]. In Figure 2.27 the photon flux-voltage curves of the spectral photovoltage measurement of device M31 are plotted alongside two lines whose slope corresponds to the ideality factors of 1 and 2. It can be seen that the ideality factor of the curves is slightly higher than unity in the high voltage range and slowly converges to 2 at around 500 mV. The external quantum efficiency \( EQE(V_{oc})_{rel} \) has been extracted at several constant voltages between the minimum and maximum voltages indicated in Figure 2.27. Figure 2.28 displays \( EQE(V_{oc})_{rel} \) determined
Figure 2.27: Photon flux-voltage curves of the cell M3l to show the limits between which the external quantum efficiency of the voltage has been extracted.

Figure 2.28: External quantum efficiency of the open-circuit voltage of cell M3l at different constant voltages. Note that for some voltages, the extraction was limited to wavelengths below 1050 and 1000 nm due to the upper limit of the illumination that can be achieved with the measurement set-up. A clear decrease in relative quantum yield can be observed between 650 and 1050 nm when the voltage decreases. This was the highest change in quantum efficiency observed in the four multicrystalline cells, a fact that can be explained in the following by a strong injection-level dependence of the diffusion length.
and the rear surface recombination velocity.

Next to the spectral photovoltage, the spectral response of the short-circuit current has been measured with the traditional method and \( \text{QSS}_\text{sc-}\lambda \). From the spectral response, the effective and actual bulk diffusion length and the rear surface recombination velocity have been extracted and compared to PC1D calculations. The spectral photovoltage has been analysed for a wide range of voltages that are effected by recombination in the base region and at the rear surface. Table 2.10 presents the results of the spectral analysis.

**Table 2.10:** PC1D calculation and fitting results of \( L_{\text{eff}} \), \( L_n \) and \( S_n \) of the devices M11, M31, M61 and M81.

<table>
<thead>
<tr>
<th>Method</th>
<th>Linear</th>
<th>Lagowski-Spiegel</th>
<th>Isenberg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( L_{\text{eff}} )</td>
<td>( L_{\text{eff}} )</td>
<td>( L_n )</td>
</tr>
<tr>
<td>M11: PC1D</td>
<td>98</td>
<td>98</td>
<td>97</td>
</tr>
<tr>
<td>Conv. SR</td>
<td>114</td>
<td>100</td>
<td>96</td>
</tr>
<tr>
<td>( \text{QSS}_{\text{sc-}\lambda} )</td>
<td>155</td>
<td>106</td>
<td>98</td>
</tr>
<tr>
<td>( \text{QSS}<em>\text{sc-}\lambda ), ( V</em>{\text{oc}} )</td>
<td>174±14</td>
<td>164±13</td>
<td>157±12</td>
</tr>
<tr>
<td>M31: PC1D</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Conv. SR</td>
<td>91</td>
<td>80</td>
<td>78</td>
</tr>
<tr>
<td>( \text{QSS}_{\text{sc-}\lambda} )</td>
<td>87</td>
<td>76</td>
<td>75</td>
</tr>
<tr>
<td>( \text{QSS}<em>\text{sc-}\lambda ), ( V</em>{\text{oc}} )</td>
<td>104±18</td>
<td>100±16</td>
<td>100±15</td>
</tr>
<tr>
<td>Conv. SR</td>
<td>119</td>
<td>113</td>
<td>111</td>
</tr>
<tr>
<td>( \text{QSS}_{\text{sc-}\lambda} )</td>
<td>87</td>
<td>93</td>
<td>95</td>
</tr>
<tr>
<td>( \text{QSS}<em>\text{sc-}\lambda ), ( V</em>{\text{oc}} )</td>
<td>89±4</td>
<td>89±3</td>
<td>89±3</td>
</tr>
<tr>
<td>M81: PC1D</td>
<td>131-135</td>
<td>131-135</td>
<td>130</td>
</tr>
<tr>
<td>Conv. SR</td>
<td>157</td>
<td>146</td>
<td>143</td>
</tr>
<tr>
<td>( \text{QSS}_{\text{sc-}\lambda} )</td>
<td>132</td>
<td>121</td>
<td>112</td>
</tr>
<tr>
<td>( \text{QSS}<em>\text{sc-}\lambda ), ( V</em>{\text{oc}} )</td>
<td>190±10</td>
<td>185±10</td>
<td>179±9</td>
</tr>
</tbody>
</table>

Provided the cell structure is identical for all cells, the theory predicts that the voltage decreases, while the diffusion length increases with decreasing base doping density. There is one cell that breaks this trend: The device M31. The measured \( V_{\text{oc}} \) and the diffusion length according to PC1D are lower than expected from the results of the other cells. A likely reason is that this device is afflicted with more low quality grains than the other samples. All analysis methods deliver very similar values for the effective and actual diffusion length for a given measurement tool. This reflects the fact that \( L_n \) is smaller than the device thickness in all cases. The spectral analysis of the current based diagnostic tools agree well with PC1D. The findings for the diffusion length by \( \text{QSS}_\text{sc-}\lambda \), by contrast, are only in satisfying agreement with PC1D for the device M61. For all other samples, the diffusion lengths are clearly higher than expected from the PC1D findings. They also show a fairly large standard deviation compared to cell M61. The results of the model of
Isenberg is in general the option that comes closest to the PC1D results.

The simulations with PC1D can only give a coarse measure of \( S_n \), whereas the analysis of the short-circuit current response fails to produce any prediction. In comparison, the analysis of the voltage response is always successful in forecasting \( S_n \) using either the model of Lagowski-Spiegel or the model of Isenberg. For the cells M11 and M81, the predictions agree well with the PC1D findings. For the other two devices, the experimental determination results in much higher surface recombination velocities than predicted by PC1D. A very high error of the same magnitude as the actual values is also reported for these two devices.

The discrepancy between the PC1D calculations and the results of the current response on one side and the findings of the voltage response on the other side can be explained by having a close look at the injection-level dependence of \( L_n \) and \( S_n \). Figure 2.29 highlights the bulk diffusion length as a function of the excess carrier density obtained from the open-circuit voltage for all devices. The results of the model of Lagowski-Spiegel have been chosen here to obtain a larger voltage range. The model of Isenberg performs in general better than the model of Lagowski-Spiegel, but it requires wavelengths higher than 950 nm. However, the flash intensity in this wavelength range is limited, which in turn limits the voltage output that can be reached.

All devices apart from the cell M61 experience a strong decrease in diffusion length when the carrier concentration at the junction edge decreases. This perfectly explains the higher values obtained from the voltage measurements for the cells M11, M31 and M81, since at open-circuit conditions a much higher excess carrier density prevails in the bulk than at short-circuit. As the decrease in diffusion length is expected to continue towards the lower carrier densities present at short-circuit, the diffusion length most certainly reaches the value measured by the spectral photocurrent methods. In cell M61, by contrast, no such injection-level dependence has been unveiled, which explains the observation that the bulk diffusion length at short-circuit and open-circuit are nearly the same.

In Figure 2.30, the surface recombination velocity \( S_n \) is plotted against the excess carrier density. Cell M11 and M81 did not show any noticeable injection-level dependence as would be expected from the results of Table 2.10. Conversely, the devices M31 and M61 stand out by their remarkable dependence on carrier concentration. For both solar cells, \( S_n \) increases with decreasing carrier density. The strong injection-level dependence accounts for divergences between the findings of PC1D and the analysis of the spectral response of the voltage. It can be related to the silicon nitride passivation layer on the rear side. The effective surface recombination velocity \( S_{eff} \) of SiN coated, lowly doped silicon
2.5 Determination of surface and bulk recombination from the spectral photovoltage

Figure 2.29: Diffusion length extracted from the external quantum efficiency of the voltage as a function of excess carrier density at the junction edge of the silicon nitride passivated multicrystalline solar cells.

Figure 2.30: Surface recombination velocity $S_n$ as a function of the excess carrier density at the junction edge of silicon nitride passivated multicrystalline solar cells. The lines are guides to the eye.

usually expresses a strong dependence on the injection level [105]. Conversely, the values of $S_n$ measured here are much higher than $S_{eff}$ observed for this SiN on Cz silicon wafers. This may be rooted in the fact that the highly irregular crystal structure of multicrystalline silicon is more difficult to passivate than Cz silicon. The combined effect of the increase in
$S_n$ and the decrease in bulk diffusion length explains the strongest change in the external quantum efficiency of the voltage of cell M31 (Figure 2.28).

In summary, it has been demonstrated in this section that the spectral response of the voltages is capable of detecting changes in bulk and rear surface recombination rates due to a change in carrier concentration. This clearly proves to be an advantage over the spectral response of the current.

2.6 Conclusion

The spectral response of the open-circuit voltage has been introduced in this chapter. A new measure, the external quantum efficiency of the open-circuit voltage, has been inaugurated, that captures the essential characteristic of this response. This parameter is defined as the ratio between the exponential of the open-circuit voltage and the incident photon flux. The voltage, and consequently its exponential, are not magnitudes like the current that can be easily quantified in terms of electrons. This implies that the comparison of the output versus the input is not well-defined. This creates first the need for a suitable reference point, e.g. a constant voltage or photon flux, respectively. Second, the external quantum efficiency has to be normalised to a reference wavelength. The end product is therefore a relative measure. To avoid inequalities in the optical losses that mark the relative external quantum efficiency of the voltage, the internal quantum efficiency of the voltage proves to be a better alternative.

A one-dimensional and lowly-injected depiction of a p-n junction helped to forge the link between the external quantum efficiency of the voltage and the external quantum efficiency of the current. The relationship between the two is approximately linear if the recombination parameters like the surface recombination rate or the bulk lifetime are independent of the minority carrier concentration. In comparison, the depiction developed in this investigation is not tied to abrupt junctions since it does not need any assumption about the exact nature of the emitter profile. The predominant analytical models in the SPV technique, the photovoltage of an induced surface region or a metal-semiconductor contact, have been reviewed. This demonstrated that the external quantum efficiency of the bulk region, which contains the crucial information about the diffusion length, constitutes the important element between the photo-induced voltage and the photon flux in any voltage response technique. This paves the way to improve the diffusion length determination by using more sophisticated models for the external quantum efficiency of the bulk than currently employed in the SPV method.
Despite the handicap that a relative measure brings, PC1D calculations performed in this work show impressively the potential of the new technique. Even if the solar cell is subject to various recombination mechanisms at the front surface, in the bulk or the rear surface, the fact remains that the shape of $IQE(V_{oc})|_{rel}$ is identical to $IQE(J_{sc})$. If $IQE(J_{sc})$ touches the 100% benchmark, the relative parameter $IQE(V_{oc})|_{rel}$ overlaps perfectly with its short-circuit counterpart. In all other cases, $IQE(V_{oc})|_{rel}$ is able to indicate the relative loss mechanism, for example the front surface compared to the bulk performance.

The newly devised spectral response tool holds some resemblance to the surface photovoltage technique. The differences to SPV are at the same time its clear advantages: it does not need a calibration for each sample to find the point where the voltage increases linearly with the photon flux. Next, both implementations, the constant photon flux and the constant voltage, can be studied with one single measurement. Moreover, we deal with voltages that are encountered in solar cells under standard illumination and not just a few millivolts.

The comparison of spectrally resolved measurements of the short-circuit current and the open-circuit voltage confirm the findings predicted by the PC1D simulations. $IQE(V_{oc})|_{rel}$ mimics the behaviour of $IQE(J_{sc})$ for a broad range of different solar cell structures. Furthermore, the spectral response of the voltage offers the prospect of assessing the damage of shunts and depletion region recombination on the overall performance of the device. Both methods of evaluation, $IQE(V_{oc})|_{rel}$ at constant voltage or photon flux, deliver the same outcomes for the solar cells studied in this thesis. However, they will certainly not yield the same results in general, because the injection-level dependence of the recombination lifetimes will usually lead to different conditions at constant voltage or constant photon flux. The constant voltage method is definitively the approach that makes physically more sense, since it ensures that the carrier concentration at the junction will be the same for each wavelength. The constant photon flux approach, by contrast, assumes a constant ideality factor for all wavelengths, a situation that is rarely found in real devices.

The proportionality between the external quantum efficiency of the voltage and the current offered scope for transferring the models developed in Chapter 1 for the analysis of the base region to the voltage regime. For front illuminated devices, these are the linear model, the model of Lagowski-Spiegel and the model of Isenberg. As it turned out, there exist analogue models for the first two, which have been traditionally applied in the SPV technique. The model of Isenberg, by contrast, has been employed in this work for the
first time for the analysis of the voltage response. This ties up some loose ends, as the models traditionally used in the SPV method are hampered by many assumptions. Most importantly, the diffusion length of the wafer under investigation is limited by the pole that appears in the model of Lagowski-Spiegel. This assumption can be brushed aside when using the model of Isenberg. For rear illumination, the transfer of the linear model to deduce the base surface recombination constitutes another new analysis tool for the voltage response.

These models for the spectral photovoltage have been tested against PC1D and the conventional models of the spectral response of the current. The simulations demonstrate that the model of Isenberg predicts the bulk diffusion length and the base surface recombination rate the best. The analysis of the voltage response proves to be equally as accurate as the current response, provided that the surface recombination velocity stays below $10^4$ cm/s. Importantly, it performs better than the model of Lagowski-Spiegel if the diffusion length exceeds the wafer thickness.

The parameters that relate the spectral response of the voltage and the current allow the extraction of an effective emitter saturation current regardless of the emitter structure. This is supported by the comparison of PC1D simulations and the analysis of the voltage response. The effective emitter saturation current includes in general a contribution of the depletion and the bulk region, but is very close to the actual $J_{0e}$, the higher the quality of the bulk material. This highlights another facet of the voltage response: the ability to diagnose and control the quality of the emitter region from the first diffusion step until the completion of the solar cell. Finally, the comparison between PC1D calculations and analysis of the spectral response of a rear-illuminated cell foreshadowed that both spectral responsivity methods are able to predict the base surface recombination rate and the bulk diffusion length equally well.

The findings of the theoretical potential of the $IQE$ models are confirmed by the measurement of various devices. First, the analysis of solar cells fabricated on defect-rich aluminium-doped silicon material demonstrates that the linear model concludes in the same bulk diffusion length for both measurement techniques. Second, the transfer of the model of Lagowski-Spiegel and Isenberg to the voltage response proves to be a success. The models deduce recombination parameters that agree well with PC1D simulations and $IQE$ analysis of the spectral response of the current. On top of this, the analysis of the voltage response is often able to forecast the base surface recombination rate, where the current version fails to produce any prediction.

The linear model that enables prediction of the front surface recombination of rear
junction cells has also been transferred to the spectral response of the open-circuit voltage. The results of the linear fits to the voltage response agree perfectly with the findings of its current analogue. Unfortunately, the remedy to deduce the minority bulk diffusion length from the fit - neglecting emitter recombination - gave rise to substantially lower values than in the short-circuit current response. It is thus unwise to use this approach in cells where a high emitter recombination prevails.

One of the main advantages of the spectral response of the voltage is the capability to detect the injection-level dependence of recombination parameters. A detailed study of multicrystalline silicon solar cells with the spectral photovoltage could convincingly unearth the injection-level dependence of the bulk diffusion length and the rear surface recombination velocity. The dependence on carrier concentration could also perfectly explain differences with PC1D results and the analysis of the spectral response of the current, which both deal with much lower injection ranges than present at open-circuit.

To come to a conclusion, the spectral response of the open-circuit voltage presents itself as a viable alternative to the traditional spectral response of the short-circuit current and the surface photovoltage technique. Major breakthroughs of this study are the application of the model of Isenberg to the new technique, the potential of emitter monitoring during device fabrication, a new linear model to extract recombination parameters of rear-illuminated or back-junction solar cells and the ability to scan recombination parameters over a broad range of injection levels.
Chapter 3

Temperature and injection-level dependent voltage spectroscopy

"A versatile alternative to detect directly the presence and the nature of recombination-active defects are temperature or injection dependent lifetime measurements, the so-called lifetime spectroscopy"

Stefan Rein, 2000

3.1 Introduction

If semiconductor devices struggle in their performance, there is almost always something wrong with the material itself that can be named with one word: defects. Metallic impurities can make life miserable for integrated circuits, degrading the yield and the functional efficiency [107]. The recombination activity of defects is one of the major contributions to losses in silicon solar cells [108, 109]. One classical example of a metallic contaminant is iron, responsible for leakage currents and premature breakdown in semiconductor chips [107, 110, 111]. Another common lifetime-killer is copper, used in interconnections in integrated circuits. It enters solar cells unintentionally during wire-cutting of Czochralski silicon or cast mc-silicon wafers, since the wire saws often contain copper [112]. Next on the list are the non-metallic impurities, the most prominent among them the boron-oxygen complexes and oxygen precipitates in boron-doped Cz Si [113–115]. Other accomplices are aluminium-oxygen related defects in aluminium doped Cz Si. Crystallographic defects such as dislocations, vacancies, silicon interstitials and grain boundaries, prevalent especially in poly- and multicrystalline wafers, round off the enumeration. It comes as no surprise that there exists a strong motivation for developing measurement techniques capable of detecting those defects.

The parameter that delicately senses the recombination dynamics of the defects is
the carrier lifetime. The theory behind it is described by the Shockley-Read-Hall (SRH) model [116–118]. It quotes four basic factors as the main influence on the SRH lifetime: the density of the recombination centres, \( N_T \), the energy level, \( E_T \) and the electron and hole capture cross sections, \( \sigma_n \) and \( \sigma_p \), respectively. Several diagnostic tools address the crucially important issue of measuring one or several of these parameters. Among those, deep-level-transient spectroscopy (DLTS) [14] has occupied for long a central role. It helped to create a wealth of data of the energetic positions of metal impurities. But the problems start when it comes to measure the capture cross sections. Since the method avails of an extended temperature range, usually from 77 K to room temperature, it cannot account for temperature-related changes in the capture cross sections or in the defect density. Photoluminescence, in turn, is only sensitive to radiative recombination, hence of limited interest for silicon.

Lifetime spectroscopy has been added to the list of successful diagnostic tools, as it is a very sensitive technique that detects only centres that are important in recombination processes. It delivers outcomes where even the highly sensitive DLTS fails: it perceives defects below the detection limit of the DLTS, since already very small traces of impurities are able to harm the carrier lifetime. Moreover, it fulfilled its promise to accurately detect the electron and hole capture cross section. Two different forms of lifetime techniques, have been established in the past, injection-level dependent lifetime spectroscopy (IDLS) [113–115, 119–121] and temperature dependent lifetime spectroscopy (TDLS) [115, 119, 121–123]. The underlying measurement tools are standard techniques for measuring the lifetime of silicon: the microwave photo conductance decay [124] and the quasi-steady-state photoconductance (QSSPC) [125].

IDLS allows the measurement of the capture cross section and the energy level, since both induce a change in carrier density. However, an unambiguous determination of the energy level is only possible if samples of different doping densities are studied. The defect density does not affect the injection-level dependence of the lifetime, but can be extracted using the measured SRH lifetime and the fitted capture cross section and the energy level. TDLS takes advantages of the fact that the SRH lifetime is inherently dependent of material parameters that vary with temperature: These are the effective densities of states in the conduction and valence band, \( N_C \) and \( N_V \), the thermal velocity of the charge carriers \( v_{th} \) and the Boltzmann factor describing the probability that the energy level \( E_T \) is occupied. TDLS is found to provide good sensitivity in measuring the energy level over the whole band-gap and not just for majority defects (i.e. in the lower half in \( p \)-type Si), as is the case for DLTS. Nevertheless, TDLS cannot decide in which
half of the band-gap the defect does its mischief. The two forms of lifetime spectroscopy have been recently combined into one: temperature and injection-level dependent lifetime spectroscopy (TIDLS) [83]. Here, the carrier lifetime is measured over a broad range of injection levels and a set of temperatures. The analysis consists now of a simultaneous fit of all curves. This method is able to distinguish between deep and shallow recombination centres and is sensitive to the temperature dependence of their capture cross-sections.

Although strong in its applications, lifetime spectroscopy has certain limitations: the effective lifetime can only be measured for carrier concentrations higher than approx. $10^{14}$ cm$^{-3}$, since a phenomenon called ‘trapping’ artificially alters the lifetime for lower concentrations [126] (see also Section 3.3). As a consequence, lifetime spectroscopy is restricted to well-passivated and reasonable good quality silicon. Wagner et al. introduced the temperature dependent measurement of the quantum efficiency, TQE$J_{sc}$ [21]. This technique uses completed solar cells and thus is applicable to poorly passivated devices. The core of this tool is the measurement of the spectral response at each temperature and the subsequent extraction of the bulk diffusion length. This parameter is then converted into bulk lifetime meaning that the actually analysis is a form of TDLS. The inconvenience of this method is that it is cumbersome: it requires the fabrication of a fully processed solar cell and a spectral responsivity measurement at each temperature.

We introduce here two new methods, which can be equally applied to diffused wafers or fully processed solar cells. Both determine the recombination lifetime indirectly via the open-circuit voltage. As such, these techniques rely as well on lifetime spectroscopy as the analysing body. Both techniques employ the quasi-steady-state open-circuit voltage technique. The first, TQE$V_{oc}$, resorts to the spectral response of the open-circuit voltage, introduced in the last chapter. It is the complementary tool to TQE$J_{sc}$, undergoing exactly the same evaluation procedure. If successful, it would prove advantageous over TQE$J_{sc}$ in the sense that it only requires a junction to be formed. TQE$J_{sc}$ measurements have been performed in comparison to underpin the validity of TQE$V_{oc}$. The second, the temperature and injection-level dependent voltage spectroscopy (TIVS), is strongly affiliated with TIDLS. It records the open-circuit voltage for a broad range of intensities and converts it into a recombination lifetime-carrier density depiction. It is capable of attaining very low carrier densities, since the measurement is not affected by trapping. Both techniques promise to widen the realm of possibilities to detect recombination centres.

Since the new diagnostic tools are inherently based on lifetime spectroscopy, we are bound to introduce the fundamental equations that underly this technique. This is tackled in the next section. Following that, the voltage spectroscopy is introduced. One has to be
cautious when translating from open-circuit voltage to the other figure of merit, sometimes referred to as *implicit* lifetime [127]. A large fraction of the second section is thus devoted to the interpretation of the voltage signal and the prediction of the lifetime thereof. The measurement apparatus has been specially designed to master the challenge of measuring the voltage at elevated temperatures. This is approached in Section 3.3.2 followed by the results of the TQE,$I_{ac}$, TQE$V_{ac}$ and TIVS measurements.

### 3.2 Lifetime spectroscopy

The experimental accessible parameter in lifetime spectroscopy is an effective lifetime, generally composed of a surface and bulk contribution in a non-diffused silicon wafer. The surface lifetime is usually suppressed by a passivating layer. The bulk lifetime itself is a composition of several independent mechanisms, the SRH, the Auger and the radiative lifetime:

$$\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{SRH}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{rad}}}. \quad (3.1)$$

The Auger and the radiative part can be easily computed with appropriate models. Appendix D.1 contains more details of the models used in this work. This clears the way to engage directly with the SRH recombination. For a $p$-type silicon wafer with dopant density $N_A$, a single defect with energy $E_T$ and capture cross sections for electrons and holes, $\sigma_n$ and $\sigma_p$, the SRH lifetime can be expressed by [116–118]:

$$\tau_{\text{SRH}} = \frac{\tau_{n0}(N_A + p_1 + \Delta n) + \tau_{p0}(n_1 + \Delta n)}{N_A + \Delta n}. \quad (3.2)$$

Here, $\Delta n = \Delta p$ is the excess carrier density, $\tau_{n0}$ and $\tau_{p0}$ are the capture time constants of electrons and holes. The SRH densities $n_1$ and $p_1$ are the statistical factors when the Fermi level coincides with the energetic positions of the defect:

$$p_1 = N_V \exp\left(-\frac{E_T - E_V}{kT}\right), \quad n_1 = N_C \exp\left(-\frac{E_C - E_T}{kT}\right). \quad (3.3)$$

$N_C$ and $N_V$ represent the effective densities of states in the conduction and valence band and $E_C$ and $E_V$ the energy level of the conduction and valence band edge. The fundamental electron and hole lifetimes, $\tau_{n0}$ and $\tau_{p0}$, are closely related to the capture cross sections of electrons and holes and the thermal velocity via:

$$\tau_{n0} = \frac{1}{v_{th} \sigma_n N_V}, \quad \tau_{p0} = \frac{1}{v_{th} \sigma_p N_T}. \quad (3.4)$$
If more than one dominant defect is present in the silicon, the inverse of the total SRH lifetime is equal to the sum of the inverse of the lifetime of the different contributions:

\[
\frac{1}{\tau_{SRH}} = \sum_{i=1}^{n} \frac{1}{\tau_{SRH,i}}.
\]

As a result, the SRH recombination is dominated by the defect with the lowest lifetime.

### 3.2.1 Injection-level dependent lifetime spectroscopy

Let us consider now in detail the key factors that form the shape of the SRH lifetime as a function of excess carrier density. The starting point for the following discussion is a single defect being active in a p-type silicon wafer, i.e. Equation 3.2. First of all, since the defect density appears in both fundamental lifetimes, \( \tau_{n0} \) and \( \tau_{p0} \), via Equation 3.4, the SRH lifetime is linear in this parameter. This implies that a change in the defect density results solely in a scaling of \( \tau_{SRH} \). Conversely, \( \tau_{n0} \) and \( \tau_{p0} \) themselves and the energy level of the defects are non-linear inputs into the SRH lifetime. This means that they will determine the form and shape of \( \tau_{SRH} \), while on the other hand this complicates the extraction of these parameters. At a given doping density and energy level, it can be expected from Equation 3.2 that the highest variation in \( \Delta n \) can be evoked if \( \tau_{n0} \) and \( \tau_{p0} \) are at extremes. Hence, it is useful to define a symmetry factor \( k \) that describes the ratio between the electron and hole capture sections:

\[
k = \frac{\tau_{p0}}{\tau_{n0}} = \frac{\sigma_n}{\sigma_p}.
\]

In a sense, \( k \) indicates whether the capture of charge carriers is in favour of electrons or holes.

To obtain a fuller picture, the effect of \( k \) is illustrated in Figure 3.1 for a shallow \((E_T = 0.1 \text{ eV})\) and deep energy level \((E_T = 0.55 \text{ eV})\). The doping density has been chosen to be \( N_A = 10^{16} \text{ cm}^{-3} \). It can be stated that, no matter at which energy level the defect is situated, the SRH lifetime experiences the highest change if the balance between electron and hole capture swings strongly towards electron trapping. For a deep level, this leads to an increase in lifetime with increasing injection level, whereas the opposite is the case for a shallow level. For equalised carrier capture, energy levels close to mid-gap prove most effective for SRH recombination. In Figure 3.2, the role of \( k \) and \( E_T \) have been inverted. For two typical asymmetries of carrier capture, \( k = 0.1 \) and 10, the impact of deep, intermediate and near-band-gap levels are studied. For both ratios of cross sections
3. Temperature and injection-level dependent voltage spectroscopy

**Figure 3.1:** Simulation of the SRH lifetime as a function of excess carrier density for several ratios of electron and hole cross sections and two different energy levels. The other parameters needed for these simulations are: p-type doping density $N_A = 10^{16} \text{ cm}^{-3}$, defect density $N_T = 10^{12} \text{ cm}^{-3}$, capture lifetime of the electrons $\tau_{no} = 10 \mu\text{s}$ and temperature $T = 25 ^\circ\text{C}$.

**Figure 3.2:** Simulation of the SRH lifetime as a function of excess carrier density for shallow, intermediate and deep energy levels and two different symmetry factors, $k$. The other parameters chosen for these simulations are: p-type doping density $N_A = 10^{16} \text{ cm}^{-3}$, defect density $N_T = 10^{12} \text{ cm}^{-3}$, capture lifetime of the electrons $\tau_{no} = 10 \mu\text{s}$ and temperature $T = 25 ^\circ\text{C}$.

It can be seen that deep levels entail an increase, shallow levels a decrease in SRH lifetime with increasing carrier concentration, while intermediate levels may cause either of these trends [128].

In fact, two key factors that effectively influence the behaviour of the energy levels are the doping density and the temperature [119]. This is demonstrated in the following graphs (Figure 3.3 and 3.4). Here, the cross sections have been chosen to slightly favour electron capture ($k = 10$). The influence of the doping density on the SRH lifetime of a deep centre is rather modest compared to that of a shallow level (Figure 3.3). By increasing the doping concentration, the trend of an increasing lifetime can not be reversed, only the onset of the increase is shifted towards higher injection levels. The shallow level, by contrast, is highly sensitive to the doping dose, showing that a high doping density is able to change the trend of the SRH lifetime. Regardless of the energy level, a high doping concentration is detrimental to the SRH lifetime. In the other scenario, Figure 3.4, a low sample temperature replaces the harmful action of a high dopant concentration. The shallow level is again heavily affected by a decrease in temperature, while the deep centre stays unmoved. These evident differences offer scope to distinguish between the energy levels by measuring the injection dependence of $\tau_{SRH}$ for different doping densities or at
3.2 Lifetime spectroscopy

different temperatures. The first idea is the basis for the injection-level dependent lifetime spectroscopy, IDLS, while the second path lays the foundation for the temperature and injection-level dependent lifetime spectroscopy, TIDLS. In both methods, a non-linear fit with \( E_T \), \( k \) and \( N_T \) as free parameter is performed simultaneously for all lifetime curves.

\[
N = 10^{14} \cdots 10^{15} \nonumber
\]

\[
E_c - E_T = 0.55 \text{ eV} \nonumber
\]

\[
E_c - E_T = 0.1 \text{ eV} \nonumber
\]

\[
\begin{align*}
10^{12} & - 10^{13} - 10^{14} - 10^{15} - 10^{16} - 10^{17} - 10^{18} \\
\text{Excess carrier density} \Delta n \text{ [cm}^{-3}\text{]} \\
\end{align*}
\]

\[
\begin{align*}
10^{12} & - 10^{13} - 10^{14} - 10^{15} - 10^{16} - 10^{17} - 10^{18} \\
\text{Excess carrier density} \Delta n \text{ [cm}^{-3}\text{]} \\
\end{align*}
\]

\[
\tau_{SRH} \text{ [µs]} \nonumber
\]

\[
\tau_{SRH} \text{ [µs]} \nonumber
\]

Figure 3.3: Theoretical values of the SRH lifetime as a function of excess carrier concentration showing the impact of the doping density. The simulations are based on a p-type wafer with defect density \( N_T = 10^{12} \text{ cm}^{-3} \), ratio of cross sections \( k = 10 \), capture lifetime for electrons \( \tau_{n_0} = 10 \mu s \) and temperature \( T = 25 \text{ °C} \).

Figure 3.4: Theoretical values of the SRH lifetime as a function of excess carrier concentration showing the impact of substrate temperature. The simulations are based on a p-type wafer with doping density \( N_A = 10^{16} \text{ cm}^{-3} \), defect density \( N_T = 10^{12} \text{ cm}^{-3} \), ratio of cross sections \( k = 10 \) and capture lifetime for electrons \( \tau_{n_0} = 10 \mu s \).

So when can \( k \) and \( E_T \) be accurately determined? It turns out that it is only possible for intermediate energy levels, where a transition in the shape of \( \tau_{SRH} \) can be induced by either a change in doping density or substrate temperature [119]. Unfortunately, the product of \( N_T \) and capture cross section can not be separated, but this drawback actually comprises the reason for the high sensitivity of the lifetime spectroscopy: it does not depend directly on the defect density, unlike DLTS.

3.2.2 Temperature dependent lifetime spectroscopy

The temperature dependent lifetime spectroscopy takes a different approach from the two others. It tackles a carrier injection range that is fairly insensitive to small changes in the excess carrier concentration. As can be easily seen in the four previous depictions of the SRH lifetime, a suitable candidate is the low-injection range between \( 10^{12} - 10^{13} \text{ cm}^{-3} \). This carrier concentration can be easily reached with the MW-PCD or QSSPC technique for
well passivated samples. In this particular situation, the carrier density can be neglected vis-a-vis the doping density and Equation 3.2 be written as:

\[
\tau_{\text{SRH}}^{\text{LLI}}(T) = \tau_{n0}(T) \left[ 1 + \frac{p_1(T)}{N_A} + k \frac{n_1(T)}{N_A} \right].
\] (3.7)

If the recombination centre is located in the upper half of the band-gap, the impact of the statistical term \( p_1 \) disappears resulting in the following:

\[
\tau_{\text{SRH}}^{\text{LLI}}(T) = \tau_{n0}(T) \left[ 1 + k \frac{n_1(T)}{N_A} \right].
\] (3.8)

It is instructive to consider the low and high temperature range in a first glance at Equations 3.7 and 3.8, since it helps to unveil the dominant participant that shapes \( \tau_{\text{SRH}}^{\text{LLI}} \). At low temperatures, the energy distributions \( p_1 \) and \( n_1 \) can be neglected compared to the doping density and the low-injection lifetime merges with \( \tau_{n0} \). The fundamental electron lifetime is only slightly temperature dependent, which has its origin in the temperature dependence of the thermal velocity: \( v_{th}(T) = \sqrt{8kT/m^*} \). Here, \( m^* \) is the effective mass [129] (see also Appendix D.3). Certainly, we have disregarded any possible dependence of the electron cross section, which is in general a good approximation. In order to ease the understanding of \( \tau_{\text{SRH}}^{\text{LLI}} \) at high temperatures, it is useful to express all temperature dependent parameters in terms of their counterparts at 300 K [130]:

\[
\tau_{n0}(T) = \tau_{n0}^{300K} \left( \frac{T}{300 \text{ K}} \right)^{-1/2},
\]

\[
N_C(T) = N_C^{300K} \left( \frac{T}{300 \text{ K}} \right)^{3/2}.
\] (3.9)

The same expressions hold for \( \tau_{n0} \) and \( N_C \). At elevated temperatures, either \( p_1 \) or \( n_1 \) gets the upper hand and \( \tau_{\text{SRH}}^{\text{LLI}}(T) \) becomes thermally activated with an activation energy of \( E_a = E_T - E_V \) or \( E_a = E_C - E_T \), respectively. This gives rise to the following expression in this temperature range:

\[
\frac{\tau_{\text{SRH}}^{\text{LLI}}(T)}{T} = \frac{\tau_{n0}^{300K}}{300 \text{ K}} \left[ \left( \frac{T}{300 \text{ K}} \right)^{-3/2} + \kappa \exp \left( -\frac{E_a}{kT} \right) \right].
\] (3.10)

Here, \( \kappa \) denotes either \( N_V^{300K}/N_A \) (energy level in the upper half of the band-gap) or \( \tau_{\text{LP}}^{300K}/\tau_{n0}^{300K} \cdot N_C^{300K}/N_A \) (lower half). This predicts that an Arrhenius plot of \( \ln(\tau_{\text{SRH}}^{\text{LLI}}/T) \) versus 1000/T yields a linear increase for rising temperatures, where the slope is governed by the activation energy. This is illustrated in Figure 3.5 for an assembly of different defect energies.
3.2 Lifetime spectroscopy

Figure 3.5: SRH lifetime in low-injection versus temperature for several defects that are located in the upper half of the band-gap. The following parameters have been used in the simulation: $N_A = 10^{16}$ cm$^{-3}$, defect density $N_T = 10^{12}$ cm$^{-3}$, ratio of cross sections $k = 10$ and capture lifetime of the electrons $\tau_{n0} = 10$ µs.

It is important to highlight that a linear fit to the high-temperature range can not discern between an energy level in the lower or upper half. The mid-temperature range is best characterised by the temperature onset of the linear part. The shallower the position of the defect, the lower the onset. In case of a position in the upper half of the band-gap, the onset is additionally shifted by $\tau_{p0}^{300K}/\tau_{n0}^{300K}$. Note that this represents the only distinction between defects in the lower and upper half. For mid-gap states, the most important, there is almost no temperature dependence (no rapid increase of the lifetime at high temperatures). Nevertheless, even in that case TDLS can be used to determine $E_T$ by exclusion, that is, by detecting that the temperature does not change.

In all other cases, a fit to the whole temperature range will disclose if the position of the recombination centre is located in the lower or upper half. A high doping density or a high activation energy often complicates the analysis, as the linear increase may be shifted out of the experimentally accessible temperature range. TDLS cannot deliver precise outcomes if the defect changes its state during heating, as happens for boron-oxygen or iron-boron pairs. In the same way, the application of TLDS is limited if the low-temperature range is masked by a dependence of the carrier cross sections. Notwithstanding, the simplicity of TDLS outweighs its imperfections and has made this technique a valuable tool in extracting the energy levels of various contaminants [115, 121].
3. Temperature and injection-level dependent voltage spectroscopy

3.3 Voltage spectroscopy

Voltage spectroscopy addresses some flaws that haunt the lifetime spectroscopy as well as the TQE $J_{sc}$ method. First of all, the lifetime spectroscopy measures an effective lifetime, where the surface component is the most important unknown. Surface recombination can be quite successfully held at bay by low-temperature deposition of silicon nitride passivation. Nevertheless, there is always a small residual contribution to the overall lifetime. Even if the surface recombination can be successfully minimised, there is a limit to the usable data that is set by the quality of the silicon bulk material. It is not difficult to imagine that the poorer the base material becomes in terms of lifetime, the harder it gets to establish a high excess carrier concentration. This is not a major inconvenience in principle, but it happens that the low injection lifetime can be screened by an effect that is described as ‘trapping’.

Several competing theories try to describe this phenomena. One of the most widely accepted ones devises trapping as a bulk effect [126]. The Shockley-Read-hall mechanism predicts that recombination at low excess carrier concentration occurs through localised states in the band-gap interacting with carriers from the valence and conduction band. However, these states can act as a ‘trap’ for charge carriers from one band and eject it back into the same band [118]. Their contribution to the recombination can be neglected, because one of the capture cross sections is assumed to be very small. At high intensities, the trap density is insignificant compared to the excess carrier density, even if all trap states are filled. The trap concentration becomes noticeable, by contrast, at lower intensities as an additional factor side by side to the free excess minority carrier density. This is electrostatically counterbalanced by an increased excess majority carrier density, giving rise to an increased photoconductance [126]. In a QSSPC lifetime measurement, this effect is manifested as a ‘tail’ in the lifetime-injection-level curve at low intensities (see also Figure 3.7). It is visible in a wide range of materials, in particular in cast mc-Si [128] and Cz Si [114]. In mc-Si, dislocations and boron-impurity pairs are thought to be the major causes of trapping [131]. There exists a method that corrects the ‘apparent’ lifetime and is able to extend the range of usable data by up to an order of magnitude, but the improvement is equivocal [131]. Another mechanism relates trapping to the presence of a $p$-$n$ junction or field effect passivation, the latter being active if a SiN$_x$ or SiO$_2$ surface passivation has been applied. It is often referred to as depletion region modulation. When light is shone on a wafer, the resulting excess carrier concentration induces a voltage across the depletion region, reducing its width. This increases the bulk region and hence the contribution to the excess conductivity [132, 133].
Apart from trapping effects, lifetime measurements appear to be problematic for materials that are not as comprehensively characterised as crystalline silicon. In amorphous silicon, only a product of lifetime and mobility can be determined [127]. Another disadvantage of lifetime techniques is the fact that it is unable to handle finished devices. The rear metallisation of the solar cell is the reason for this handicap. In the MW-PCD method, the micro-wave signal is reflected at the rear side before being able to enter the device. Thus it does not carry any information about the excess photoconductance created within the sample. The dark conductance of the metal also drives the detection signal out of range in the case of the QSSPC method, and it is questionable if a small deviation from this underlying conductance due to the light illumination would be detectable. This creates the need for a new type of spectroscopy applicable to finished devices, of which TQE$/mathrm{J_{sc}}$ is one of the successful solutions.

We will pursue a slightly different route by contemplating a voltage instead of a current measurement. The advantage is that voltage and lifetime are interchangeable and complementary quantities [125, 134]. Moreover, it is often overlooked that the voltage can already be obtained after junction formation. The technique of choice is QSSV$_{oc}$, rather than the open-circuit voltage decay, since the junction capacitance can mask lifetime measurement at low injection levels in the latter [135]. Most importantly, trapping is not an issue when measuring the voltage. As alluded to above, trapping is caused by an increase in excess majority carriers. This will not influence the free minority carrier population significantly, hence it does not affect the device voltage. This is demonstrated in Fig-

![Figure 3.6](image1.png)  
**Figure 3.6:** Measured and implied intensity-voltage curves for a 0.35 Ω cm mc-Si cell precursor [128].

![Figure 3.7](image2.png)  
**Figure 3.7:** Implied and measured lifetime-carrier density curves for a 0.35 Ω cm mc-Si cell precursor [128].
ure 3.6, where the measured and implied voltage obtained from a lifetime measurement is shown [128]. The transformation of voltage to lifetime and vice versa is explained in the next chapter. The two curves coincide above \( \sim 4 \) suns but diverge below that point. The 'true' illumination-voltage curve continues unchanged until the effect of a shunt sets in at \( \sim 0.05 \) sun. Conversely, the implied voltage bends into a direction that indicates an ideality factor below one. The graph on the right, Figure 3.7, depicts the corresponding lifetime curves. It shows that the data above 4 suns \( (\Delta n \sim 10^{15} \text{ cm}^{-3}) \) reflects indeed the effective lifetime, whereas the 'true' lifetime measurement is screened by trapping below that intensity. Conversely, the implied lifetime represents the actual minority carrier recombination at least until the impact of the shunt becomes apparent. In conclusion, a voltage measurement therefore allows access to very low excess carrier densities.

### 3.3.1 Prediction of the lifetime obtained from the quasi-steady-state open-circuit voltage with white light

**Conversion of open-circuit voltage to bulk lifetime**

By measuring the voltage we avoid some shortcomings of the lifetime spectroscopy but it will soon become clear that not everything looks bright. The reason lies in the fact that the conversion of the illumination-voltage curve to the lifetime-carrier concentration depiction has to be handled with care. The desired figure of merit, the bulk lifetime, can be defined as follows:

\[
\tau_{\text{bulk}} = \frac{\Delta n_{\text{av}} W_b}{U_{\text{bulk, av}}}.
\]

(3.11)

\( \Delta n_{\text{av}} \) is the average excess carrier density of the base region, \( W_b \) the thickness of the base region and \( U_{\text{bulk, av}} \) the integrated average bulk recombination rate. The bulk lifetime, as it is defined here, constitutes therefore a minority carrier lifetime that is averaged over the base thickness. The measurement, by contrast, delivers the open-circuit voltage and the photon flux. The voltage can be converted into the excess carrier density at the boundary of the \( p-n \) junction via a relation, which implies that the separation of the quasi Fermi levels is equal to the open-circuit voltage:

\[
\Delta n(W_e) [N_A + \Delta n(W_e)] = n_0^2 \exp \left( \frac{qV_{oc}}{kT} \right).
\]

(3.12)

This formulation assumes that the excess carrier density is much higher than the equilibrium electron concentration, \( \Delta n(W_e) \gg n_0 \). Besides this, it is valid for arbitrary injection levels. The photon flux can be transformed into the total integrated generation rate \( G_{\text{tot}} \).
by deducting the optical losses of the device under investigation. The total thickness of the device, in turn, is nearly identical to \( W_b \). From this, we are in principle able to extract an ‘implied’ lifetime via:

\[
\tau_{\text{impl}} = \frac{\Delta n(W_e)W}{G_{\text{tot}}}.
\]  

(3.13)

This expression is frequently used to predict an effective lifetime from a QSSV\(_{\text{oc}}\) measurement that is comparable to the effective lifetime measured in a quasi-steady-state photoconductance experiment. The reverse application of Equations 3.13 and Equations 3.12 is also conceivable. In this case the aim is to convert the effective lifetime obtained from a QSSPC measurement into an open-circuit voltage. As Cuevas et al. pointed out [127], the successful conversion hinges on the condition that the excess carrier density at the junction edge \( \Delta n(W_e) \) equals the average excess carrier concentration \( \Delta n_{\text{av}} \) in the bulk region.

Cuevas et al. investigated three situations for the transfer from the quasi-steady-state photoconductance to the open-circuit voltage. They can be differentiated by their carrier density profile in the base region. The first situation considers samples that present a high bulk lifetime and a low rear surface recombination. In this case, the minority carrier distribution is approximately uniform and \( \Delta n(W_e) \approx \Delta n_{\text{av}} \). If the samples become electronically thick, that is, their diffusion length \( L \) becomes smaller than the wafer thickness, the simple calculation of Equations 3.13 is found to be erroneous. The reason is rooted in the strongly non-uniform carrier profile. \( \Delta n \) in this circumstance has a nearly exponential shape and it can be shown analytically that its integral has approximately the value \( \Delta n(W_e)L \). Hence, Cuevas et al. showed that a better estimate for \( \Delta n_{\text{av}} \) is given by \( \Delta n(W_e)L/W \) [127]. The third situation deals with a high rear surface recombination. Here, the carrier distribution drops approximately linearly from the junction towards the rear surface. For reasonable rear surface recombination velocities, the assumption \( \Delta n(W_e) \approx \Delta n_{\text{av}} \) is still acceptable. However, it becomes unsustainable for very high surface recombination rates. In this case, the effective diffusion length \( L_{\text{eff}} \) turns out to be much smaller than the thickness. A better approximation of \( \Delta n_{\text{av}} \) can then be found in \( \Delta n(W_e)L_{\text{eff}}/W \) [127].

The conversion from open-circuit voltage to effective lifetime and vice versa has been applied successfully in the past to QSSV\(_{\text{oc}}\) and QSSPC measurements [12, 127, 134, 136]. The aim in this work is different, since we are interested in the bulk lifetime and not the effective lifetime. The prediction of the bulk lifetime does not only depend on the excess carrier profile in the base region, but also on the right assumption for the bulk recom-
Temperature and injection-level dependent voltage spectroscopy

Combination rate. In open-circuit conditions and at (quasi-) steady-state illumination, the total generation and recombination rates are balanced. However, the latter encompasses not only the recombination in the bulk but also recombination in the emitter and at the surfaces. In general, it is therefore almost impossible to forecast the bulk recombination rate from the total generation rate. Nonetheless, we have to keep in mind that voltage spectroscopy is aimed at situations where lifetime spectroscopy fails to deliver satisfying outcomes. These are mainly cases where the material quality is so low that the bulk lifetime obtained from a QSSPC measurements is overshadowed by trapping effects. In this circumstance, the bulk recombination rate dominates the other recombination channels. Owing to this, the total generation rate projects a good estimate of $U_{\text{bulk,av}}$. Substituting $W$ with $L$ in Equation 3.13 allows therefore a realistic prediction of the bulk lifetime.

To back this approach with numbers, PC1D calculations have been performed to highlight the difference between the 'true' bulk lifetime and the implied one. These are the material parameters that underly all simulations: emitter saturation current $J_{\text{sc}} = 9.5 \times 10^{-15}$ A/cm$^2$, base doping concentration $N_A = 10^{16}$ cm$^{-3}$ and wafer thickness $W = 300 \mu$m. At an illumination of 1 sun, the open-circuit voltage has been calculated alongside the bulk recombination, cumulative generation and the excess carrier density. The bulk lifetime has been accessed via Equation 3.11, while the open-circuit voltage and the cumulative generation served as the input to $\tau_{\text{impl}} = \Delta n(W_e)L/G$. The outcomes of these simulations are presented in Table 3.1 for several configurations of $\tau_{\text{bulk}}$ and $S_{\text{back}}$. Additionally, the implied lifetime using $W$ instead of $L$ has been displayed to stress the errors that can arise using this path.

The PC1D calculations demonstrate that, if the diffusion length stays below the sample

<table>
<thead>
<tr>
<th>$\tau_{\text{bulk}}$</th>
<th>$S_{\text{back}}$</th>
<th>$L_{\text{bulk}}$</th>
<th>$\Delta n(W_e)L/G$</th>
<th>$\Delta n(W_e)W/G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[µs]</td>
<td>[cm/s]</td>
<td>[µs]</td>
<td>[µs]</td>
<td>[µs]</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>53</td>
<td>0.8</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>169</td>
<td>8.9</td>
<td>15.8</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
<td>378</td>
<td>60.5</td>
<td>48.0</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>535</td>
<td>139.1</td>
<td>78.0</td>
</tr>
<tr>
<td>1</td>
<td>$10^6$</td>
<td>53</td>
<td>0.8</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>$10^6$</td>
<td>169</td>
<td>7.8</td>
<td>13.8</td>
</tr>
<tr>
<td>50</td>
<td>$10^6$</td>
<td>378</td>
<td>27.4</td>
<td>21.7</td>
</tr>
<tr>
<td>100</td>
<td>$10^6$</td>
<td>535</td>
<td>42.2</td>
<td>23.7</td>
</tr>
</tbody>
</table>

Table 3.1: Comparison of the PC1D input values for the bulk lifetime and the calculated implied lifetime.
thickness, the approach using $L$ proves very accurate, even if a high rear surface recombination rate is hampering the cell performance (see bold numbers). Above the threshold of the wafer thickness the implied lifetime using $L$ begins to show a strong deviation from the bulk lifetime. As long as $S_{\text{back}}$ is reasonably low, the thickness is a better alternative to obtain the bulk lifetime (italic numbers). In all other cases, the implied lifetime does not match the bulk lifetime.

The use of $L$ is crucial in another sense, as it ensures that its temperature dependence enters into the derivation of $\tau_{\text{impl}}$. The dilemma is that $L$ is not known initially, which makes a trial and error procedure necessary. An additional complication is that for white light the average absorption length is $\sim 10 \, \mu\text{m}$. If the diffusion length is smaller than this, a detailed simulation of the carrier density profile, for example using PC1D, is advisable. The use of IR light instead of white light would also have the effect to move $\tau_{\text{impl}} = \Delta n(W_c) W/G$ closer to the bulk lifetime.

The voltage spectroscopy technique is demonstrated with solar cells based on aluminium doped Czochralski silicon with two different doping densities: 0.7 and 0.15 $\Omega \, \text{cm}$. These cells, RPA44_A1.2b and RPA44_A3.1b, have been described in detail in Chapter 1 (page 44). Due to the aluminium-induced defects, the bulk diffusion length is very low: $\sim 7$ and $\sim 15 \, \mu\text{m}$, respectively (see the extraction of the diffusion length in Section 2.5.3 on page 99). This indicates that the approach contrived here to predict the bulk lifetime is appropriate. In a succeeding section, the temperature dependence of the low-injection lifetime will be analysed. The results using the implied lifetime will be compared to the bulk lifetime obtained by the temperature dependent spectral response measurements. This comparison will illustrate further the applicability of voltage spectroscopy. In the discussion that follows next, the implied lifetime is calculated using the diffusion length.

**Capacitive effects in the bulk and space charge region**

When extracting the implied lifetime from the intensity-voltage curve, it is important to ensure that the latter is equivalent to the static $I-V$ characteristics. However, the time dependence of the excess carrier density leads to capacitive effects in the base and junction region that can significantly distort the intensity-voltage data [136, 137]. These capacitive effects are attributed to a change in excess charges with time that influences the balance between generation and recombination of excess charges. The effects can significantly dominate the device characteristics if the carrier lifetime is larger than the decay constant of the light source, especially if the light generation changes abruptly with time, as is the case in transient voltage and lifetime measurements.
In the base, the capacitive effect is associated with the excess charges that accumulate if the recombination rate decreases slower than the generation range [136]. This results into a time-dependent charge rate that is proportional to the change in photo-induced voltage. Its impact is more noticeable in high resistivity devices and can significantly alter the device characteristic at mid and high voltages. In the junction, the photo-generated change in voltages leads to a change of the junction width and thus to a change in excess charges in the junction region [137]. This change is proportional to the junction capacitance and the change in voltage. It is more pronounced in low resistivity devices and can considerably influence the intensity-voltage curve at low voltages. Both charge rates have to be added to the generation rate so that the corresponding light intensity accounts for the excess charges in the device. Appendix D.2 explains the mathematical treatment of the capacitance effect and the correction of the intensity-voltage data in detail.

In this study, devices fabricated on 0.15 and 0.7 Ωcm silicon have been used. Hence, the influence of the base capacitance is minimal, but the junction capacitance strongly affects the intensity-voltage curve. This is illustrated with the temperature dependent measurement of the intensity-voltage curve of the 0.7 Ωcm cell RPAL44_A1.2b (Figure 3.8). Both, the apparent and corrected curves, move to the top-left corner with increasing temperatures. As a rule of thumb, the open-circuit voltage drops $\sim 2$ mV per °C. This requires a higher intensity to gain the same voltage output if the temperature is raised. For the apparent data, a shunt-like kink is clearly visible at the lowest $T$ but smoothes out towards higher $T$. One intriguing observation is the fact that the voltage does not seem to drop towards zero for very low light illuminations. This clearly represents a deviation from the well-known static $I$-$V$ characteristics. The correction of the capacitive effect in the junction leads to an increase in intensities at low voltages compared to the apparent data. As Cuevas et al. demonstrated [137], this correction corresponds well to the dark $I$-$V$ characteristics of the device and also ensures that the voltages converge towards zero for zero light intensities. The impact of the junction capacitance decreases with increasing temperature in view of the fact that the influence of the base parameters becomes more important at higher temperatures.

The corresponding apparent and corrected lifetime data is displayed in Figure 3.9. Since the voltage decreases with temperature, the excess carrier density and thus the implied lifetime decrease as well. The apparent lifetime shows a kink at low injection levels that has similarities to the trapping effect described in Figure 3.7. Note however, that at these low carrier densities, the kink is caused by the junction capacitance, as has been shown by computer simulations [137]. Its onset moves towards smaller carrier
concentrations for higher temperatures and is eventually replaced by a drop in implied lifetime at 110 °C. The junction correction increases the range of usable data by an order of magnitude for the lowest temperatures. Nevertheless, the voltage corresponding to this region has an ideality factor that clearly diverges from unity. For the voltage spectroscopy, it is therefore advisable to use only data that is affected by bulk recombination, that is, where the ideality factor is close to one.

Shunt and Schottky effects

Another difficulty arises from the fact that shunting and Schottky effects can lead to a misinterpretation of the results. As an example of this, Figure 3.10 shows the white light measurements for the 0.7 Ω cm cell RP44_A1.2b at 10 °C over seven decades of light intensity. Two effects can be seen that distort the intensity-voltage curve from its ideal pattern. At voltages < 500 mV (Δn < 10^11 cm^-3) a kink occurs leading into the characteristic shape of a shunt resistance. At high voltages the curve shows another indication of a Schottky contact. In the first case, the resulting apparent lifetime decreases strongly with decreasing Δn, contrary to the constant behaviour predicted by the Shockley-Read-Hall model. Still, it could be construed as depletion region or SRH recombination. In the second case, a sharp turn in the lifetime is observed that could be misinterpreted as Auger or emitter recombination. The sharpness of the bend and the low carrier density at which it occurs compared to the base doping of 2.23 x 10^16 cm^-3, by contrast, suggest strongly
that these can be excluded, and that a Schottky contact is the cause.

This and the previous evaluation shows clearly that the voltage ranges affected by junction recombination, shunts or Schottky contacts have to be excluded from the voltage-lifetime-conversion. In conclusion, the analysis of the implied lifetime has been restricted to carrier concentrations between $10^{12}$ cm$^{-3}$ and $10^{15}$ cm$^{-3}$.

3.3.2 Features of the experimental set-up and the temperature dependent data-analysis

Special sample stages that permit a controlled heating of the test devices have been constructed as part of this thesis. Two different methods of temperature regulation are employed: for the temperature range below room temperature, a Peltier element is used for cooling. Above room temperature, a silicone rubber element has been chosen to heat the samples. A total temperature range of 5–190 °C can thus be accessed. Figures 3.11 and 3.12 depict the schematic design of both approaches. The first stage is used for routine measurements and is a classic temperature-controlled set-up. It uses a Peltier element combined with a heat sink and fan to regulate the temperature by cooling and heating. The second temperature stage has been developed to accommodate temperatures up to 190 °C. The temperatures are achieved by a circular wire pattern inside a silicone rubber that is neatly packed between the aluminium backing and the copper stage. The temperature is controlled automatically by switching on and off the current flow through the heater.
This unit is placed inside a box that can be sealed off with a removable lid consisting of a double-glass structure. The Pyrex® glass type used exhibits an excellent transmission over the entire sun spectrum. Figure 3.13 allows a closer look at the high-temperature stage. The accuracy of the temperature lies at \( \sim 2 \, ^\circ\text{C} \). With both set-ups, the external quantum efficiency and the intensity-voltage curve have been measured at 10 \(^\circ\text{C}\) steps.
3. Temperature and injection-level dependent voltage spectroscopy

between 10 and 190 °C. The TQEJ_sc, TQEVeoc and the TDLS methods have been applied to the cell fabricated on 0.7 Ω cm aluminium-doped Cz-Si. RPA144_A1.2b. The TIVS method is performed for both aluminium-doped cells, RPA144_A1.2b and RPA144_A3.1b.

The change in temperature affects a wide range of silicon material parameters. The exact models used for the TQE measurements and the voltage spectroscopy are discussed in Appendix D.3. Here, the temperature dependent variables are listed shortly. The extraction of the bulk lifetime from a TQE measurement requires knowledge of the temperature dependence of the absorption coefficient and the diffusion constant. The temperature dependent variables that enter into the calculation of the Shockley-Read-Hall-lifetime are: the band-gap of silicon, the density of states of the conduction and valence band, the intrinsic carrier density and the thermal velocity. The extraction of the SRH lifetime from the implied lifetime makes use of several models that describe the other recombination mechanisms active in the bulk: these are the Auger and radiative lifetime (Appendix D.1). The implied lifetime deduced from the voltage is affected not only by bulk processes, but as well by the emitter saturation current and the saturation current associated with the local BSF of the rear contacts. These currents are also susceptible to temperature changes, as explained further in Appendix D.1. In our examples, both saturation currents are small in comparison to the base recombination current and can be disregarded.

3.3.3 Results of the various voltage-based spectroscopic tools

Temperature dependent analysis

The internal quantum efficiency of the cell RPA144_A1.2b measured with TQEJ_sc and TQEVeoc is displayed in Figure 3.14 for the long-wavelength range and four different temperatures: 10, 70, 130 and 190 °C. In the voltage case, the relative internal quantum efficiency \( IQE(V_{oc})_{rel} \) is depicted. For better visual comparison, the y-axis of the voltage measurements has been adjusted until a good overlap could be found with its current counterpart. The spectral photocurrent and photovoltage both show a similarly strong drop in responsivity towards longer wavelengths. A clear increase in quantum yield with temperature is manifested for both measurement methods. This stems on one hand from the increase in absorption, which itself is rooted in the decrease of the band-gap energy \( E_g \) (Appendix C.1). On the other hand, the diffusion length improves with increasing temperature.

The long-wavelength range has been fitted with the linear model in order to extract the diffusion length. Since the diffusion length is very low in this sample, the linear fit to \( IQE \)
Figure 3.14: Internal quantum efficiency of the current and voltage as a function of wavelength for several temperatures.

Figure 3.15: Internal quantum efficiency of the current and voltage as a function of wavelength for several temperatures.

The analysis of the spectral photovoltage is able to determine the diffusion length over one to two orders of magnitude of carrier concentration. This is demonstrated in Figure 3.15, where the diffusion length extracted by the spectral photovoltage at various temperatures as a function of excess carrier density.

Figure 3.15: Diffusion length extracted from the spectral response of the voltage at different temperatures as a function of excess carrier density.
temperatures is plotted as a function of carrier density. The diffusion length is fairly constant over the carrier density range and reveals only slight changes in shape due to the increase in temperature. Thus, to facilitate the data analysis, the average of the diffusion length has been converted to the minority carrier lifetime.

Subsequently, the temperature dependent carrier lifetime obtained from both TQE methods has been analysed with the SRH model. Figure 3.16 presents the Arrhenius plot of the low-injection carrier lifetime $\tau$ divided by the temperature $T$ as a function of $1000/T$. Several measurements are shown in this graph: First, the temperature dependent implied lifetime $\tau_{\text{impl}}^{\text{L-L}}$. It has been deduced from the intensity-voltage measurements at a carrier density of $2.5 \times 10^{13}$ cm$^{-3}$ using the temperature dependent diffusion length (●). Second, the bulk lifetime $\tau_b^{\text{L-L}}$ from the various TQE measurements: TQE of the short-circuit current (v), the open-circuit TQE at a constant voltage (●) and at a constant photon flux (△). The linear part at higher temperatures as well as the full temperature range of all data sets have been fitted with the SRH model using one defect level. In all simulations, the defect energy $E_C - E_T$, the capture cross sections $\sigma_n/\sigma_p$ and the low-injection lifetime $\tau_{n0}$ have been taken as fitting parameters. An example of the linear and full SRH fit for the implied lifetime $\tau_{\text{impl}}^{\text{L-L}}$ are included in Figure 3.16. Note that the linear fit can not distinguish between levels situated in the lower or upper half of the band-gap. Only the full SRH model can pin-point the exact defect location [121].

Table 3.2 summarises the resulting energy levels. The defect energies of the fits to
the spectral response measurements agree very well with each other. The energy levels determined from the full SRH fit lie about 0.37–0.41 eV below the conduction band. The ratio of the capture cross sections, $\sigma_n/\sigma_p$, is in the range 300–1000, which implies that the probability of the centre capturing carriers is much higher for electrons than for holes. A correct interpretation of the QSS$V_{oc}$ data (using $L$ rather than $W$) results in a good agreement with the TQE measurements, as shown in the first column.

**Table 3.2:** Energy levels that resulted from a linear and full SRH fit to the temperature dependent low-injection lifetime. Several methods have been used to access the implied or bulk lifetime.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Methods</th>
<th>Defect energy $E_G - E_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPAL44_A1.2b, linear fit *</td>
<td>QSS$V_{oc}$, using $L(T)$</td>
<td>0.45</td>
</tr>
<tr>
<td>RPAL44_A1.2b, full SRH fit</td>
<td>TQEJ$_{sc}$</td>
<td>0.41</td>
</tr>
</tbody>
</table>

*The linear fit can not determine if the energy level is located in the lower or upper half

Schmidt et al. used the TDLS method to analyse a more lightly doped Cz Si sample with a doping density of $7.2 \times 10^{15}$ cm$^{-3}$ [83]. The linear fit revealed an energy level of 0.36 eV in the upper or lower half of the band-gap while the fit with the full SRH model pinned the energy level into the upper half of the band-gap. These results are reasonably consistent with our measurements.

DLTS studies have revealed that aluminium-doped wafers that underwent a heat-treatment at 1170 °C in oxygen showed two dominant defects at $E_T - E_V = 0.31$ eV and 0.41 eV related to Al-O pairs [138, 139]. In another study, two deep levels at $E_T - E_V = 0.43$ eV and 0.47 eV due to Al incorporated into silicon during Czochralski growth have been determined [140]. In that study, the aluminium had been co-doped with either boron or phosphorus and had a concentration of $6 \times 10^{16}$ cm$^{-3}$. This is significantly higher than the concentration of the co-dopant boron ($10^{16}$ cm$^{-3}$) or phosphorus ($3.5 \times 10^{15}$ cm$^{-3}$). Comparing the two studies, it cannot be excluded that the oxygen heat treatment led to the creation of aluminium-oxygen pairs. Hence, samples that have not been subjected to this high temperature step may suffer from Al rather than Al-O recombination centres. Furthermore, several metals have been detected that form metal-aluminium donor-acceptor pairs, where the metal occupies an interstitial and the aluminium a substitutional site.
Some examples are: Fe ($E_T - E_V = 0.19$ eV) and Mn ($E_C - E_T = 0.45$ eV).

Despite the good agreement observed among the TQE methods and their agreement with the results of Schmidt et al., the measured energy levels lie well above the ones reported in the DLTS literature for aluminium related defects, the closest being the Al-Mn pair at $E_T - E_V = 0.45$ eV. Nevertheless, we exclude this possibility, as this pair has not been detected in aluminium-doped silicon, unless intentionally contaminated with manganese. In the following section we explore the TIVS method based on the additional information contained in the injection-level dependence of the lifetime.

Temperature and injection-level dependent analysis

The full set of temperature and injection-level dependent voltage spectroscopy measurements have been performed for the 0.7 and 0.15 $\Omega$ cm cells. The outcome of the full TIDLS fit to the measurements of both cells are very similar. Hence, the analysis is restricted to the device fabricated on 0.7 $\Omega$ cm material. The first statement which can be made is that none of the injection-level dependent lifetime curves can be modelled with a single defect level. On the other hand, various combinations of two energy levels can be fitted to the data equally well. This is not surprising, given the high number of fitting parameters available. Still, it is possible to state that one of the two energy levels has a relatively low fundamental electron lifetime $\tau_{n0}$, close to the measured $\tau_{impl}$, and a small ratio $\sigma_n/\sigma_p$ of 1–40, while the other energy level has a strong mismatch between electron and hole capture ($\sigma_n/\sigma_p \sim 1000$) and a significantly higher $\tau_{n0}$. In a first step, the data have been fitted with the two sets of defect levels for Al and Al-O related centres, respectively. The energy levels were kept constant for all temperatures, leaving $\sigma_n/\sigma_p$ and $\tau_{n0}$ as free parameters. The data could be modelled equally well for both pairs of defects or by interchanging the deep and shallow energy level. As an example, Figure 3.17 shows the fit with the Al-O related energy level, were the deep level occupies the higher $\sigma_n/\sigma_p$ and $\tau_{n0}$. The modelled SRH lifetime is depicted as well. In this case, the diffusion length has been used to obtain the bulk lifetime.

In a second step, we performed least square fit calculations, where the energy level and the ratio of the capture cross sections, $\sigma_n/\sigma_p$, have been varied. The two remaining parameters, $\tau_{n0}$, of each defect, are fitted and the least square error obtained for each pair of energy levels. The resulting contour plot of the two defect levels reveals a broad band of energies for which a satisfactory agreement with the measurement can be found: for one centre, the energy can take the values $E_C - E_T = 0.45–0.85$ eV and the other one, $E_C - E_T = 0.1–1.0$ eV. A wide range of energy levels for the deep defect level has also been
3.3 Voltage spectroscopy

![Figure 3.17: Implied lifetime as a function of carrier density measured at different temperatures between 10 and 190 °C. Included is an example of a fit with a deep energy level at $E_T - E_V = 0.41$ eV and a shallow energy level at $E_T - E_V = 0.31$ eV. The SRH lifetime of the latter level at 190 °C has been added to show its impact on the lifetime.](image)

found by Schmidt et al. [83]: $E_C - E_T = 0.45$–0.95 eV, while the shallow level is either located 0.14 eV below the conduction band or 0.14 eV above the valence band.

Similarly to TIDLS [83], TIVS is capable of finding the temperature dependence of the 

![Figure 3.18: Temperature dependence of the product of electron and hole capture cross section $\sigma_{n,p}$ and defect concentration $N_T$ of the two defects for the 0.7 Ω cm cell. The fits indicate the exponential increase of the capture cross sections.](image)
capture cross sections. Neither technique can separate the effects of capture cross section and defect concentration, but can only determine their product. Figure 3.18 shows the temperature dependence of the product of electron and hole capture cross section $\sigma_{n,p}$ and defect concentration $N_T$ of the two defects. Again, the diffusion length has been taken to deduce the bulk lifetime. The TIVS data was fitted with the aluminium-oxygen related defects with $E_T - E_V = 0.31$ eV and $E_T - E_V = 0.41$ eV. The result is a dependence of $\sigma_{n,p} \propto \exp(\Delta E/kT)$ with $\Delta E = 0.26-0.32$ eV for both doping densities and combinations of energy levels, respectively.

3.4 Conclusion

In this chapter, new defect spectroscopy techniques for semiconductor materials have been presented: the temperature dependent quantum efficiency of the voltage (TQEV$_{oc}$) and the temperature and injection-level dependent voltage spectroscopy (TIVS). TQEV$_{oc}$ is based on the spectral response of the open-circuit voltage introduced in Chapter 2. Here, the diffusion length is extracted from an analysis of the spectral response and converted into minority carrier bulk lifetime. The underlying measurement tool of TIVS is the quasi-steady-state open-circuit voltage method, able to measure the voltage output over several orders of intensity under white light.

The benchmark of defect spectroscopy in terms of the recombination activity of impurities is lifetime spectroscopy. There exist several versions: Either the low-injection lifetime is measured as a function of temperature (TLDS), or the injection-level dependence of the lifetime is investigated, preferably for wafers with different doping densities (IDLS). Both tools can be merged into one: the temperature and injection-level dependent lifetime spectroscopy (TIDLS). Despite its great success, lifetime spectroscopy is hampered in low-material quality, notably because of trapping effects. As another disadvantage, it is limited to devices without metallisation. This gap is filled by the temperature dependent quantum efficiency, TQE$_{J_s}$. This work demonstrated that TQEV$_{oc}$ holds the same appeal as TQE$_{J_s}$, as it showed a good consensus with TDLS and TQE$_{J_s}$. It even out-competes TQE$_{J_s}$ in the sense that it is applicable already after junction formation. Moreover, it is capable of detecting the bulk lifetime over one to two orders of magnitude. But for all these methods, TDLS, TQE$_{J_s}$ and the new method, TQEV$_{oc}$, we have to resign ourselves to the fact that they only analyse the lifetime at low-injection levels. As could be seen in the example explored in this chapter, in some cases the true behaviour of the defects lie beyond their detection
capabilities. The measurements of the aluminium-doped solar cells with TQE$J_{sc}$ and TQE$V_{oc}$ revealed an energy level at 0.37–0.41 eV below the conduction band. The most likely defects that are active in this material, by contrast, have defect states between 0.31 and 0.47 eV above the valence band.

By transferring the white light open-circuit voltage from a TIVS measurement to the minority carrier density, a larger range of injection levels can be obtained. This has the advantage that voltage measurements are not influenced by trapping effects. Junction capacitance effects and Schottky and shunt contacts can narrow the range of voltage data that can be converted into lifetime, but still a wide range of two orders of magnitudes can be achieved. Most importantly, the carrier concentration reaches far higher levels than possible with TQE$V_{oc}$. However, the biggest inconvenience stems from the fact that QSS$V_{oc}$ measurements require a careful approach to calculate the bulk lifetime. PC1D calculations proved that the diffusion length has to be taken as the 'virtual' thickness of the device to deduce the bulk lifetime. Since the diffusion length is in fact the figure of interest, we have to revert to other diagnostic tools to obtain it, for example by combining TQE$V_{oc}$ and TIVS. Unfortunately, this makes the voltage spectroscopy very cumbersome.

Despite this, the combination of the two voltage based spectroscopic tools revealed a satisfactory agreement with DLTS and TIDLS measurements found in the literature. The measurements exposed two main energy levels originating from a deep and a shallow defect. The energy levels could be narrowed down to $E_C - E_T = 0.45$–0.85 eV and $E_C - E_T = 0.1$–1.0 eV. The observation of a very broad range of possible defect states coincides well with the TIDLS measurement by Schmidt et al. Furthermore, the techniques allowed the determination of the temperature dependence of the product of the defect concentration with either the electron or hole capture cross section, respectively, in good agreement with the findings of TIDLS.

To sum up, the temperature dependent spectral response of the voltage proves to be the most promising of the new voltage methods. The analysis is as straightforward as in TQE$J_{sc}$ and the results agree well with the latter and TIDLS. But the biggest bonus of the novel technique stems from the fact that it can be performed directly after junction formation and provides a broad range of diffusion lengths.
Spectral response of the photoconductance

"The main advantages of the spectral response of the steady-state photoconductance are that it is fast, contactless and can be used immediately after junction formation before metallisation"

Andrés Cuevas, 2000

4.1 Introduction

The photoconductivity is an elementary parameter of semiconductors describing the effect of incident radiation on the conductivity of the device. The investigation of the photoconductance, that is, the photoconductivity multiplied by the thickness of the sample, is extremely valuable for process control and device optimisation in semiconductors. Its most important application is the determination of the minority carrier lifetime in silicon wafers. There exist several methods that aim to measure the carrier lifetime via photoconductance measurements. All are contactless techniques and work on the principle that optical excitation creates a surplus of carriers that gives rise to an excess photoconductance on top of the dark conductance of the sample. This excess photoconductance is a measure of the excess carrier density and of its temporal behaviour, thus of the minority carrier lifetime.

The transient photoconductance decay (PCD) employs a sharp pulse for the illumination [14]. After it is turned off, the decay of charge carriers created by this pulse is monitored as a function of time via the photoconductance. There exist two widespread PCD-techniques that distinguish each other by their detection methods: the inductively-coupled PCD [14] and the microwave-detected PCD (MW-PCD) [24, 25]. The first one uses an inductive coil that senses the increase of excess carriers by means of a voltage induced in the coil. It is particularly successful in measuring long lifetimes and is able to
record the lifetime over a large range of injection levels in one flash.

The second method detects the photoconductance via the reflectivity of microwaves directed at the sample surface. The reflectivity is far from being a linear function of the photoconductance, which curtails MW-PCD to a small-signal method. There is no barrier to sense low lifetimes, the challenge is rather to establish high carrier concentrations. To achieve this goal, the small laser pulse is usually superimposed on a bias light. This makes it a differential technique in the same sense as the traditional spectral response of the short-circuit current. As a consequence, the extraction of the lifetime as a function of carrier concentration involves measurements at several bias light intensities and a subsequent integration of the differential lifetimes [33, 141, 142].

The quasi-steady-state photoconductance (QSSPC) encompasses most of the advantages of both PCD methods without taking along the inconvenience of a small signal technique [134]. In particular, it handles short and long lifetimes equally well. In fact, transient and steady-state PC are only two extreme cases of time dependence of the photoconductance decay that can be united in a general analysis independent of light pulse duration and carrier lifetime [143]. Properly speaking, the name quasi-steady-state photoconductance refers to the generic situation. For low lifetimes, the method is essentially steady-state, that is, a perfect balance occurs between recombination and generation of charge carriers. For high lifetimes, this assumption becomes increasingly difficult to uphold. The introduction of the contactless and low-cost QSSPC testing equipment by Sinton has made this technique the most frequently used system for routine lifetime measurements in the solar cell community.

Spectral photoconductance measurements are very widespread in the semiconductor research in the form of the spectral photoconductivity method (SPC). The method is widely employed to investigate the spectral sensitivity of photodetectors [144]. Moreover, it is commonly involved in studying the absorption edge [145, 146] and light trapping [147, 148] in amorphous silicon films. This is a contact method: a pair of electrodes is evaporated on the sample and a voltage or current is applied between these electrodes. The incident light produces a photocurrent or photovoltage that is a reflection of the conductance of the wafer. The excess photoconductance is extracted from the difference between dark and illuminated signals. Commonly, monochromatic light is produced by modulating the light of a halogen lamp and focusing it on a grating monochromator [144]. The modulated signal is separated from the dark signal by a lock-in amplifier. There are several competing techniques to ascertain a linear relationship between photon flux and photocurrent: the first two methods maintain a constant photocurrent or photovoltage by
varying the illumination level [144, 145]. A third tool makes use of an additional bias light at a wavelength that is uniformly absorbed [149]. SPC is very beneficial in studying solids that are hampered by a very low minority carrier lifetime in the ns range, as is the case of gallium arsenide or amorphous silicon. Notwithstanding this, it is a contact-based, and thus destructive, method.

The use of light of various wavelengths in a contactless photocconductance measurement has been first reported by Bail et al. They employed two different wavelength regimes, one in the UV and one in the IR, with the aim to separate the bulk and surface recombination in bare silicon. The technique became known as the two-wavelength method. The idea behind this methodology is that ultra-violet light is absorbed close to the surface, while infrared light is consumed mainly within the silicon volume. If the surface of the bare silicon is devoid of any passivation, the resulting total recombination rates are very distinct from each other. In the first case, the recombination rate is dominated by the front surface recombination. In the second situation, the bulk recombination retains control over the total recombination. This enabled Bail et al. to discern both recombination processes in unpassivated EFG Si-wafers.

Brody et al. systematically investigated the two-wavelength method for a broad range of conditions [150]. His work unearthed some serious limitations on the applicability of the tool. In detail, only a lower bound can be placed on the bulk lifetime for \( \tau_{\text{bulk}} \) greater than \( \sim 10 \, \mu\text{s} \); similarly, only an upper limit can be determined for the surface recombination rate if \( S \) drops below \( \sim 1000 \, \text{cm/s} \).

The introduction of the two-wavelength method sparked a range of applications for different silicon materials, wafers and blocks alike. The reason for this is the particular interest in measuring the bulk lifetime in bare silicon for industrial purposes without any sample preparation. IC and solar cell companies often buy as cut wafers; the possibility to appraise the quality of the material before processing thus has a huge potential to avoid waste of production capacity. To mention one example, Sinton et al. used three broad band filters to measure bulk lifetimes in mc-Si wafers and boules [151]. In 300 \( \mu\text{m} \) thick wafers, lifetimes up to 10 \( \mu\text{s} \) could be discriminated, while in blocks, larger lifetimes could be accessed, since the rear surface does not contribute to the recombination. The technique has also been used to determine the upper limit on the front surface recombination in string ribbon mc-Si wafers passivated with various methods [152]. Recently, Bowden et al. developed an analytical model applicable to silicon blocks irradiated with IR light that describes the measured effective lifetime as a simple function of bulk lifetime [153]. Comparable to this, another model has been derived for wafers with perfectly
uniform photogeneration and infinite surface recombination velocity [93]. This approach served to determine the bulk lifetime of mc-Si wafers using IR light [154].

Cuevas et al. firstly brought into sharp focus the notion of the spectral response of the excess photoconductance [155]. They inaugurated the spectral response as the ratio of photoconductance versus incoming light intensity in direct analogy to the short-circuit current definition. Furthermore, they applied the two-wavelength method to emitter diffused samples in order to assess the emitter collection efficiency. The concept behind this method is quite similar to the one above: light in the UV range is mainly absorbed in the emitter and is a reflection of the recombination mechanism at the surface and in the emitter region. A second illumination in the IR serves as a reference point, since it is predominantly absorbed in the base region and thus fairly untouched by the recombination channels of the front region. The ratio of both measurements proves to be a good measure of the collection ability of the emitter region. In all applications of the two-wavelength method, the quasi-steady-state photoconductance technique devised by Sinton et al. stepped in as the measurement tool.

Recently, a novel diagnostic tool based on the microwave PCD has also exploited the spectral response of the photoconductance: the resonance-coupled photoconductance decay (RCPCD) [156]. This contactless technique uses lower frequencies than the standard MW-PCD with the advantage that the microwave reflectance is very linear in sample conductance. The light sources are laser-pumped optical parametric oscillators, where the wavelengths can be tuned to allow a broad range of monochromatic irradiations.

In this chapter, we extend the two-wavelength method to a full spectral analysis. Since the underlying technique to measure the photoconductance is QSSPC, the technique is dubbed QSSPC-\( \lambda \). Instead of the spectral response of the excess photoconductance, we prefer to foster the notion of the external and internal quantum efficiency of the excess photoconductance. In view of the definition of the quantum efficiency of the short-circuit current response, it makes sense to adopt a similar definition for the external and internal quantum efficiency of the excess photoconductance:

\[
\begin{align*}
EQE(\Delta \sigma) &= \frac{\Delta \sigma}{qN_{ph}}, \\
IQE(\Delta \sigma) &= \frac{\Delta \sigma}{qN_{ph}(1 - R)}. \\
\end{align*}
\]

These magnitudes, commensurate with the quantum efficiency of the voltage, certainly do not represent a 'quantum' efficiency as such. Here as well, it is difficult to sketch what represents 100% conversion of photons into photoconductance. In the SPC technique, the
spectral response of the photoconductance is usually measured at a constant photocurrent or photovoltage. It is then scaled down to a reference value, but it is here where the methods differ. Tiedje et al. scaled the photoconductance to its maximum response [147], while Campbell et al. deducted the front reflectance from the photoconductance before normalising it to the maximum [148]. There are two drawbacks of such scaling: First, the relationship between incident photon flux and photoconductance is not clearly defined in such an approach. Second, the excess photoconductance is closely related to the integrated carrier concentration and is, as such, very affected by recombination processes. For instance, its value can change by several orders of magnitudes as a consequence of low or high front surface recombination. This is a result of the injection-level dependence of the effective lifetime, which responds very sensitively to the various active recombination mechanisms.

The definition of $EQE(\Delta \sigma)$ eschews the first ambiguity, as it clearly brings the photoconductance into context with the photon flux. Next, it is important to evaluate the quantum efficiency of the photoconductance at a constant conductance and scale it to a reference point in the same way as has been initiated for the quantum efficiency of the voltage. Details of this procedure will be discussed in Section 4.4.2. Note that logging the ratio of the excess photoconductance to the same incident photon flux does not do the trick. This can be explained by the fact that the excess photoconductance does not change linearly with the photon flux.

In the next section, the measurement set-up of the quasi-steady-state photoconductance response will be described. The remainder of this chapter is divided into two categories: firstly, investigation of bare silicon wafers and secondly, diffused emitter devices. In both segments, a one-dimensional model is concocted that serves as the backbone for the subsequent analysis of the experimental results. The quantum efficiency of the photoconductance of bare silicon is the stepping stone to determine the surface recombination in un-passivated silicon wafers. The diagnosis of dopant diffusions, in turn, is the incentive to delve into the quantum efficiency of the photoconductance of diffused devices.

4.2 Comparison between the experimental set-up of SPC and QSSPC-λ

The contact scheme of the photoconductor and the detection circuit most commonly used in the SPC technique are shown in Figure 4.1. The photoconductor is located in a circuit containing a voltage source and a load resistance. The principles of the photo-
conductance detection are the same as in the contact photoconductance decay [14]. The photocurrent is measured across the load resistance $R$. The photovoltage is obtained by evaluating the difference between the voltage with and without radiation. The excess photoconductance is the reciprocal of the difference in resistance between the dark and illuminated case. From this, a relation between the steady-state photoconductance and photovoltage can be established.

![Figure 4.1: Schematic design of the experimental set-up of SPC. Indexspectral photoconductivity method](image)

In general, there exist two versions of the technique: the constant current and the constant voltage method. Apart from this configuration, the exact nature of the experimental set-up depends on the material investigated, notably on its resistivity and the response time of the photoconductance to the incident light [144]. If the material benefits from high resistivity and a good photoresponse, the photosignal will be much stronger than the dark component. The simple set-up presented in Figure 4.1 combined with a monochromatic light source is sufficient in this situation. In the case of a low resistivity photodetector and good photoresponse, the photosignal is usually buried within the dark signal and noise. As a consequence, the light source has to be modulated and the signals have to be measured by lock-in detection. The frequency of modulation is determined in such a way to match the response time of the photoconductor [144]. In some circumstances, the response of the photodetector is very slow, meaning the dark signal can be much higher than the photosignal. The chopping technique and lock-in amplification using the simple circuit shown in Figure 4.1 is then unsuccessful. Here, the photoconductor is part of a Wheatstone bridge. The dark current is balanced in one branch of the bridge. The potential difference arising from the variation in sample resistance due to the incident light is amplified by an operational amplifier. A similar principal is used in the contactless photoconductance technique described below. In some cases, an additional bias light is used in the SPC method that produces uniformly absorbed light [149].
4.2 Comparison between the experimental set-up of SPC and QSSPC-λ

The photoconductance measured by means of the SPC technique is not only subject to the amount of minority charge carriers generated in the material, but also by transport to the electrodes and contact effects [144]. The latter are a particular problem if the contacts are illuminated leading to heating or injection of minority carriers from the conductor to the metal [14]. QSSPC-λ, in turn, is a non-destructive, contactless technique offering the scope for process control of semiconductor devices.

The sketch of the novel measurement set-up is shown in Figure 4.2. The light source, filter compartment, housing and detection system are the same as in the other quasi-steady-state techniques. The QSSPC testing equipment has been devised by Sinton [157]. The samples are situated above a coil, which is connected to a resonant circuit. The coil and the oscillating circuit are coupled to a Wheatstone bridge that comprises a variable capacitor in one branch and a variable resistor in a second branch. While the wafer is in the dark, the bridge is balanced by changing the capacitor and the resistor, until a zero voltage output of the total bridge circuit is reached. Under illumination, an excess conductance is generated in the sample, which induces a voltage signal at the output of the circuit. This voltage signal is quasi-linear on the excess photoconductance of the wafer. In general, an exact calibration between wafers of known conductance and the

![Figure 4.2: Schematic design of the experimental set-up of QSSPC-λ.](image-url)
measured voltage signal is necessary to account for non-linear effects that come into play if a high excess photoconductance is generated in the wafer. Details of the circuit and the calibration can be found in References [78, 158, 159]. The bridge integrated in the photoconductance tester is highly sensitive; as a result, any metal contacts will boost the current flow through the first branch, which is often difficult to match in the second. Nonetheless, small fingers of a 2 × 2 cm cell are usually still acceptable.

The excess photoconductance depends on the total concentration of excess electrons and holes and the mobility of these charge carriers. In detail, \( \Delta \sigma \) can be written as:

\[
\Delta \sigma = \int_{0}^{W} q (\mu_n \Delta n + \mu_p \Delta p) \, dx. \tag{4.2}
\]

Here, \( \Delta n \) and \( \Delta p \) denote the excess carrier density of electron and holes, respectively. \( \mu_n \) and \( \mu_p \) stand for the mobilities of these charge carriers. Note that the term inside the integral is equivalent to the conductivity of the wafer.

Figure 4.3 pictures a typical measurement of the photoconductance signal in comparison with the incoming light pulse. The photoconductance signal drops generally less fast than the excitation signal. Under quasi-steady-state conditions, the balance of generation and recombination is nearly perfect. The decline of the generation rate is proportional to that of the photon flux; the recombination rate follows suit owing to this balance. The photoconductance decrease, in turn, is proportional to the change of the integrated excess

![Figure 4.3](image-url)

**Figure 4.3:** The photon flux and photoconductance signal responding to the photographic flash pulse at 400 nm of a 1 \( \Omega \)cm \( p \)-type FZ silicon wafer with SiO\(_2\) surface passivation.
4.3 Non-diffused wafers

4.3.1 One-dimensional analytical model of the spectral photoconductance of non-diffused wafers

The analytical model devised here is concerned with a non-diffused silicon wafer with arbitrary front and rear surface recombination that is illuminated with monochromatic light. It assumes low-injection conditions, which allows us to neglect any electric field inside the wafer. Furthermore, it assumes uniform behaviour throughout the lateral dimensions of the wafer. As is often the case, the one-dimensional continuity equation serves as the

Figure 4.4: The photoconductance versus photon flux for various wavelengths of a 1 Ωcm p-type FZ silicon wafer with SiO₂ surface passivation.

carrier concentration. However, the total excess carrier density does not follow faithfully the decreasing rate of the recombination in all cases, as it hinges as well on the minority carrier lifetime, which is itself dependent on the carrier density.

Figure 4.4 depicts an example showing the wavelength dependence of the photoconductance as a function of photon flux. The straight lines denoting the lower and upper limits of the photoconductance mark the window in which the photoconductance response is analysed. Between these limits, $EQE(\Delta\sigma)$ is extracted at several different $\sigma$, normalised to a reference point and averaged over all extracted curves exactly in the same fashion as in the QSSV$_{\sigma-\lambda}$ technique (Section 2.2.3 on page 63).
cornerstone of the evaluation. This equation was the foundation for the two-wavelength model of Bail et al. [19] as well as the other models that aim to measure the bulk lifetime of unpassivated silicon wafers and blocks [153, 154]. In this derivation, it is used to describe the external quantum efficiency of the excess photoconductance in terms of the bulk lifetime and the front recombination processes. This section also provides a framework for the analytical model of the spectral photoconductance that is applicable to wafers with a p-n junction.

The derivation starts with the wavelength dependent continuity equation in low-injection:

$$D_n \frac{\partial^2 \Delta n(x, \lambda)}{\partial x^2} + \frac{\Delta n(x, \lambda)}{\tau_{\text{bulk}}} - G(\lambda, x) = 0,$$

(4.3)

with $D_n$: diffusion coefficient, $\Delta n$: carrier density, $\tau_{\text{bulk}}$: bulk lifetime and $G(\lambda, x)$: generation rate. For the boundary conditions, the front and back surface recombination velocities $S_{\text{front}}$ and $S_{\text{back}}$ come into play:

$$D_n \frac{\partial \Delta n}{\partial x} \bigg|_{x=0} = S_{\text{front}} \Delta n(0)$$

(4.4)

and

$$- D_n \frac{\partial \Delta n}{\partial x} \bigg|_{x=W} = S_{\text{back}} \Delta n(W).$$

(4.5)

The excess photoconductance is obtained with the help of Equation 4.2. In a first approximation, $\mu_n$ and $\mu_p$ are considered independent of the injection level and the amount of excess electrons and holes is expected to be equal (charge neutrality conditions). This gives rise to the following approximation for $\Delta \sigma$:

$$\Delta \sigma \approx q (\mu_n + \mu_p) \int_0^W \Delta n \, dx.$$

(4.6)

Introducing the continuity equation into Equation 4.6 gives rise to the following:

$$\Delta \sigma(x, \lambda) \approx q (\mu_n + \mu_p) \int_0^W \tau_{\text{bulk}} G(x, \lambda) \, dx - q (\mu_n + \mu_p) \int_0^W \tau_{\text{bulk}} D_n \frac{\partial^2 \Delta n(x, \lambda)}{\partial x^2}.$$

(4.7)

The next approximation implies that the bulk lifetime is uniform in the direction of the illumination. This condition is of course not totally fulfilled, as the bulk lifetime is spatially dependent via its injection-level dependence. Nevertheless, comparison of this model with PC1D [41] confirmed that this approach leads to the right description of the photocon-
4.3 Non-diffused wafers

ductance response. This permits us to take $\tau_{\text{bulk}}$ out of both integrations in Equation 4.9. The first integral can be rewritten with the introduction of the absorption fraction $f_{\text{abs}}$ (see also Appendix C.2):

$$\int_{0}^{W} G(x, \lambda) \, dx = f_{\text{abs}}(\lambda) N_{\text{ph}}(\lambda).$$  (4.8)

Application of the boundary conditions to the second integral allows the external quantum efficiency of the photoconductance to be expressed as a function of $\tau_{\text{bulk}}$, $S_{\text{front}}$ and $S_{\text{back}}$:

$$EQE(\Delta\sigma, \lambda) \approx (\mu_n + \mu_p) \tau_{\text{bulk}} f_{\text{abs}}(\lambda) - (\mu_n + \mu_p) \tau_{\text{bulk}} \frac{S_{\text{front}} \Delta n(0) + S_{\text{back}} \Delta n(W)}{N_{\text{ph}}(\lambda)}.  \tag{4.9}$$

$\Delta n(0)$ and $\Delta n(W)$ can be determined by solving the continuity equation with the boundary conditions 4.4 and 4.5. The solutions can be found in Appendix E. A simplified form of this equation is in general employed in the SPC method [146, 160]:

$$\Delta \sigma = q (\mu_n + \mu_p) \tau_{\text{bulk}} N_{\text{ph}} (1 - R)(1 - e^{-\alpha W}).  \tag{4.10}$$

In this formulation, the absorption fraction is simply approximated by the reflectance and an exponential decline in the absorption rate (Appendix C.2). Naturally, Equation 4.10 does not account for any surface effects nor does it include any variation of the generation rate due to the internal rear and front reflectance. When studying the absorption in amorphous silicon with SPC, usually the regime $\alpha W \ll 1$ is investigated. This ensures a uniform absorption across the films, which served as a reason to discard any surface effects. However, it has been shown recently that surface recombination can significantly alter the reading in a SPC measurement [148]. Equation 4.9, by contrast, is a very general description of the spectral photoconductance or photoconductivity involving all these factors. It may thus serve to improve the analysis of SPC.

Equation 4.9 predicts that $EQE(\Delta\sigma)$ follows closely the shape of the absorption fraction for zero recombination at the surface. In this circumstance, the otherwise non-uniform terms $\tau_{\text{bulk}}$, $\mu_n$ and $\mu_p$ can be regarded as homogeneous throughout the wafer, since the excess carrier concentration will be essentially flat. A lower bulk lifetime therefore decreases the external quantum efficiency independently of the wavelength. With a rising surface recombination rate, the second term in Equation 4.9 will increasingly deform the original shape of $f_{\text{abs}}$. This is further elucidated in Figure 4.5 with the simulation of the external quantum efficiency of a non-passivated 1 $\Omega$ cm $p$-type silicon wafer with electron
Figure 4.5: The external quantum efficiency of the photoconductance and the absorption fraction as a function of wavelength of an unpassivated silicon wafer for different $S_{\text{eff}}$. The parameter used for the calculations are: thickness 300 µm, resistivity 1 Ω cm, fixed electron and hole carrier mobilities of 1520 and 500 cm$^{-2}$/Vs, respectively and a fixed bulk lifetime of 1000 µs. $S_{\text{eff}}=S_{\text{front}}=S_{\text{back}}$ has been varied from 0 to $10^6$ cm/s.

and hole carrier mobilities of 1520 and 500 cm$^{-2}$/Vs respectively, and a fixed bulk lifetime of 1000 µs. The surface recombination velocity, $S_{\text{eff}} = S_{\text{front}} = S_{\text{back}}$, has been varied from 0 to $10^6$ cm/s. Additionally, a typical absorption fraction of a bare silicon wafer is shown in Figure 4.5.

Commensurate with the above, the external quantum efficiency possesses the same shape as the absorption fraction for the case of neglecting surface recombination. $EQE(\Delta\sigma)$ is very sensitive to the surface recombination velocity, which causes the possible curves for $EQE(\Delta\sigma)$ to stretch over several orders of magnitude. As $S_{\text{eff}}$ increases above $10^4$ cm/s, a characteristic hump becomes visible. This is due to the fact that the finite diffusion coefficient $D_n$ limits the flow of carriers generated deep in the wafer towards the surfaces [161]. A similar effect can be seen in studies of the external quantum efficiency of the photoconductance of emitter samples (see Section 4.4.2). It should be mentioned that the analytical model agrees perfectly with PC1D simulations and that the shape of the external quantum efficiency is only slightly affected in the IR if $S_{\text{back}}$ is changed.

Figure 4.5 reveals that the UV range of the spectrum is the most sensitive to changes in (front) surface recombination. If one of the two recombination parameters is known, a single measurement in this range is in principle best suited to determine the other recombination parameter. To further investigate this, $\tau_{\text{bulk}}$ and $S_{\text{eff}}$ have been varied and
4.3 Non-diffused wafers

Figure 4.6: The external quantum efficiency of the photoconductance at 400 nm of a non-passivated silicon wafer for different bulk lifetimes and surface recombination velocities represented as a two dimensional surface in the \(E QE(\Delta \sigma)\)-\(\tau_{\text{bulk}}\)-\(S_{\text{eff}}\)-space. The same parameters have been used for the PC1D calculation as in Figure 4.5.

\(E QE(\Delta \sigma)\) has been deducted at \(\lambda = 400\) nm for each combination with PC1D. The other simulation parameters were the same as in Figure 4.5. Figure 4.6 shows the external quantum efficiency of the photoconductance as a surface map over the lifetime-SRV space. It can be seen that there are several regions in which a single measurement at 400 nm can be one-to-one mapped to a single pair of recombination parameters. Table 4.1 summarises

Table 4.1: Rules for the one-to-one determination of one recombination parameter if the other one is known. For example: if \(S_{\text{eff}}\) is known to be \(< 100\) cm/s, the bulk lifetime can be predicted by measuring \(E QE(\Delta \sigma)\) at \(\lambda = 400\) nm, provided \(\tau_{\text{bulk}}\) is lower than 1000 \(\mu\)s.

<table>
<thead>
<tr>
<th>If (\tau_{\text{bulk}}) known as [(\mu)s] is</th>
<th>If (S_{\text{eff}}) [cm/s] is known in the range</th>
<th>(\tau_{\text{bulk}}) [(\mu)s] can be determined in the range</th>
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<td>10000</td>
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</tbody>
</table>
the different cases. For example: if $S_{\text{eff}}$ is known to be $< 100 \text{ cm/s}$, the bulk lifetime can be predicted by measuring $EQE(\Delta \sigma)$ at $\lambda = 400 \text{ nm}$, provided $\tau_{\text{bulk}}$ is lower than $1000 \text{ ps}$. In practice, a higher wavelength in the range 500–600 nm will give higher signal to noise ratios, due to a low photon flux of the flash light in the UV.

The pronounced hump that occurs for very high surface recombination and the fact that the $EQE(\Delta \sigma)$ curve shifts quasi-linearly with the bulk lifetime offers scope to match the measurement of bare silicon wafers with an exact fit, provided the bulk lifetime and the mobilities are known. This is the basic idea in the next investigation that is aimed to unveil the surface recombination velocity of wafers ‘out of the box’; that is, unprocessed wafers that are as-cut, lapped or polished.

### 4.3.2 Surface recombination velocity of unpassivated silicon

The surface recombination velocity $S_{\text{eff}}$ has a substantial impact on the performance of solar cells. The knowledge of $S_{\text{eff}}$ is particularly important to classify measurements of the effective lifetime. In industrial silicon solar cell fabrication, effective lifetime measurements are used prior to processing to evaluate the quality of the bulk material. In multicrystalline silicon the bulk lifetime can vary with the location inside the ingot from where the wafer has been cut out. The knowledge of $S_{\text{eff}}$ of unpassivated silicon may permit a more accurate determination of the bulk lifetime. It can also be used to estimate the amount of residual surface damage and optimise its elimination.

In bare silicon, a very high $S_{\text{eff}}$ of $10^6$–$10^7 \text{ cm/s}$ has usually been assumed to calculate the bulk lifetime, independently of the wafer resistivity. In this section, spectral measurements of the photoconductance of bare silicon are studied in order to calculate accurate values for the surface recombination velocity. The measurements indicate that the actual $S_{\text{eff}}$ is lower than $1.5 \times 10^5 \text{ cm/s}$ and depends strongly on the doping density of the wafer.

A range of polished, as-cut and lapped $p$-type and $n$-type FZ silicon wafers with resistivities between 0.3 and 1000 $\Omega \text{ cm}$ have been used for the investigation. Table 4.2 specifies the characteristics of the wafers.

The external quantum efficiency of the excess photoconductance has been fitted with the one-dimensional model devised in the last chapter. In all cases, $S_{\text{eff}} = S_{\text{front}} = S_{\text{back}}$ has been assumed, so that $S_{\text{eff}}$ remains the only fitting parameter. The bulk lifetime is calculated using a fit of Kerr et al., which accounts for the dependance of $\tau_{\text{bulk}}$ with injection level and doping concentration [162]. The optical parameters of the wafers are modelled by the ray-tracing software SUNRAWS [163]. A least-square procedure has been used to
4.3 Non-diffused wafers

<table>
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</tbody>
</table>

Table 4.2: Characteristics of the non-passivated wafers used in this investigation. The orientation was <100> apart from the 7 Ω cm wafer, where the orientation is not known.

model the measurement with Equation 4.9. More details about the models for the optical parameters, the bulk lifetime and the solution of the one-dimensional continuity equation necessary for the model of \( EQE(\Delta \sigma) \) can be found in the appendix in the sections C.2, D.1 and E.

Figure 4.7 shows the comparison of measured and simulated \( EQE(\Delta \sigma) \). The simulated \( EQE(\Delta \sigma) \) of the 100 Ω cm n-type wafer is characterised by a flat response. In contrast, the measurement shows a hump in the IR. In this case, the measurement is not well described by the simple analytical formula developed in section 2. Fortunately, this problem only occurs for high resistivity wafers (> 50 Ω cm) with low spectral response. As can be seen in the second example in Figure 4.7, the \( EQE(\Delta \sigma) \) of the 2 Ω cm n-type wafer can be fitted excellently. This confirms that the mobilities assumed in the analytical model are correct for low resistivity wafers (< 50 Ω cm). At present, neither the analytical model nor PC1D can explain the phenomenon in high resistivity wafers; it is possible that the assumption of a constant mobility or low injection are inappropriate in this case. Note that neither the analytical model or PC1D include injection dependent mobilities. In the following, \( S_{eff} \) values where the simulation matched the measurement only inaccurately, are shown in brackets.

The external quantum efficiency of the photoconductance of polished bare silicon is very sensitive to surface treatment. This is illustrated in Figure 4.8 with the evolution of \( EQE(\Delta \sigma) \) of a 100 Ω cm n-type wafer before and after a HF dip and with storage
4. Spectral response of the photoconductance

Figure 4.7: Measurement and simulation of $EQE(\Delta \sigma)$ as a function of wavelength for two cases: a 100 $\Omega$ cm $n$-type and a 2 $\Omega$ cm $n$-type wafer. In the first case, $EQE(\Delta \sigma)$ can not be fitted accurately, while the second fit is in excellent agreement with the measurement.

Figure 4.8: Evolution of the $EQE(\Delta \sigma)$ of a polished 100 $\Omega$ cm $n$-type wafer after HF dip and with time. The sample was: 1) taken ‘out of the box’ and measured, 2) cleaned in a 5% HF solution, rinsed in DI water and measured 1 h after the dip, 3) measured 1 day, 1 week and 5 1/2 months after the rinse. After the HF dip, the external quantum efficiency increased strongly, but decreased again with time until it regained the same magnitude after 1 week. Unexpectedly, the external quantum efficiency decreased further after 5 1/2 months. The
changes of the fitted $S_{\text{eff}}$ due to the HF dip and the subsequent storage for several polished $n$ and $p$-type wafers are shown in Figure 4.9. It illustrates that this phenomenon is common for all wafer resistivities, but slightly stronger for low resistivities. The range of $S_{\text{eff}}$ between the HF treatment and several months after the treatment spans 1–2 orders of magnitudes. An excellent $S_{\text{eff}}$ of 5.8 cm/s for the 1000 Ω cm $n$-type wafer is observed after HF dip. The highest $S_{\text{eff}}$ in the graph is $1.3 \times 10^5$ cm/s for the 1 Ω cm $p$-type wafer after 5 1/2 months.

![Graph showing evolution of $S_{\text{eff}}$ with time and doping density.](image)

**Figure 4.9:** Evolution of $S_{\text{eff}}$ of polished Si wafers of different resistivities after an HF dip and with time. Values in brackets indicate that these measurements can not be modelled accurately.

It is well known that an immersion in hydrofluoric acid serves as an excellent passivation of silicon, comparable to that of SiO$_2$/Si interfaces [164]. In general, best results have been produced if the surface has been oxidised prior to the HF dip. The HF treatment leads to a positive surface charge causing a strong inversion in $p$-type Si and an accumulation in $n$-type Si independent of the time of the HF dip [165]. After the HF treatment, the electronic properties are stable for up to 300 min [165]. The growth of the first monolayer coverage of native oxide takes between 2 hours [166] and 7 days [167]. In this period the electronic properties change strongly, particularly the positive surface charge and the density of extrinsic states reduces. The oxidation stabilises after 70–700 days [166, 167] and the electric properties become similar to the thermally oxidised Si/SiO$_2$ interface but generally with a higher density of states [165].

These observations help to explain the changes in $EQE(\Delta \sigma)$ in this work. The surface conditions of the polished wafers taken 'out of the box' are not clear. Most likely, they have
a thin oxide on the surface, probably created by chemical cleaning after wafer polishing. The flat curve of $EQE(\Delta \sigma)$ (Figure 4.8) for the 'out of the box' condition indicates a relatively well passivated surface. The dissolution of the oxide layer in hydrofluoric acid initially produces an even better passivation due to an almost ideal hydrogen termination of Si dangling bonds [164, 168] and a higher fixed positive charge. After exposure to air, the wafers traverse a phase of rapidly changing electronic properties at the surface, which is manifested by the decrease of the spectral response. After 5 1/2 months the native oxide stabilised, yet to a different state than the wafers 'out of the box'. The last measurement of $EQE(\Delta \sigma)$ in (Figure 4.8) represents therefore the stable state of a polished Si wafer covered with a native oxide.

Finally, the focus is turned to the determination of $S_{eff}$ of as-cut and lapped wafers taken 'out of the box' (Figure 4.10). Also included in Figure 4.10 are the measurements of polished wafers in the 'out of the box' condition. $S_{eff}$ shows a tendency to increase with increasing doping concentration. In general, the as cut and lapped wafers show a higher $S_{eff}$ than the polished wafers. For the latter, n-type wafers seem to exhibit better surface recombination than their p-type counterparts. The values of $S_{eff}$ range from 70 cm/s for 1000 $\Omega$ cm Si to $1.2 \times 10^5$ cm/s for 0.5 $\Omega$ cm Si and are much lower than the previously assumed surface recombination velocity of $10^6$–$10^7$ cm/s for bare silicon.

![Figure 4.10: $S_{eff}$ of bare silicon wafers of different material and surface conditions taken 'out of the box'.](image)

The error bars are calculated from an assumed measurement error of $EQE(\Delta \sigma)$ of 10% and from a variation of $S_{eff}$ due to the injection dependence of $EQE(\Delta \sigma)$. Only for the 100 and 1000 $\Omega$ cm n-type wafer was this variation in $S_{eff}$ bigger than the measurement error. Values in brackets indicate that these measurements can not be modelled accurately.
In summary, the measured external quantum efficiency of the excess photoconductance can be accurately simulated by the analytical model proposed in this investigation for low resistivity wafers. For high resistivities and a low spectral response, a hump in the IR, which is not predicted by the theory, impedes the accurate extraction of $S_{\text{eff}}$. Neither the analytical model nor PC1D calculations are able to clarify this problem. It is suggested that the assumption of constant mobilities or low-injection is not valid anymore for high resistivity wafers.

$S_{\text{eff}}$ is found to be much lower than previously assumed and generally increases with increasing doping density. $S_{\text{eff}}$ is very dependent on surface treatment, as it is higher for as cut and lapped wafers than for polished wafers taken 'out of the box'. Furthermore, polished n-type wafer show a higher surface quality than p-type wafers for a given doping density. It is nevertheless very likely that $S_{\text{eff}}$ reaches higher values for deliberately abraded surfaces.

The external quantum efficiency of the excess photoconductance of polished wafers is subject to dramatic changes after a HF treatment. Changes in the fixed positive oxide charges and in the density of states of the SiO$_2$/Si interface are likely to be the reason for this effect. Due to this change, $S_{\text{eff}}$ can vary by 1–2 orders of magnitude depending on the surface treatment. Thus, the surface conditions have to be taken into account before assuming $S_{\text{eff}}$ values of bare silicon in experiments or simulations.

If the surface recombination velocity is known without ambiguity, on the other hand, the spectral photoconductance of bare silicon wafers could possibly be used to to determine the mobilities. Similar studies have been done in the past using white light measurements of bare silicon wafers of different thickness [169, 170]. The difficulty herein lies clearly in the fact that $S_{\text{eff}}$ depends not only on the doping density and the surface treatment, but also varies with time, if an HF dip has been performed. A proper approach would have to treat both $S_{\text{eff}}$ and the mobility as unknown parameters and as dependent on carrier injection, which certainly complicates the analysis.

### 4.3.3 Determination of surface and bulk damage of implanted silicon

A practical application of the external quantum efficiency of the photoconductance is the examination of surface and bulk damage due to the implantation of foreign atoms into the silicon lattice of the wafer [171]. Ion implantation is the key technique used in the microelectronic industry to infiltrate dopants into semiconductor devices. There are two categories of damage that occur as a result of the implants: near-surface and deeply
penetrating defects. A high-temperature step is employed to heal any lattice damage; nevertheless, this is unable to counteract all of the residual defects near the surface. This study unveils furthermore that a fraction of the defects spreads deeply into the lattice and remains there even after annealing at 1000 °C.

The implantation leaves behind vacancies and interstitials that annihilate each other upon annealing, each implanted atom finally introducing one extra interstitial into the lattice. The excess interstitials may agglomerate into rod-like clusters [172] or dislocation loops [173], the latter occurring mainly at the interface between the amorphous zone caused by the implantation and the surrounding silicon. The excess interstitials dissolve upon further annealing if the implant dose stays below a critical value. Above this critical value, these defects are known to form dislocation loops [174, 175]. The critical value has been found to lie between $5 \times 10^{13}$ and $2 \times 10^{14}$ cm$^{-2}$ for implant energies in the kV range [174, 175].

A recent study of lifetime measurements of silicon implanted silicon wafers showed that the recombination activity is dependent on the implant dose [176]. The samples received Si implantations of different doses between $10^{11}$ and $3 \times 10^{16}$ cm$^{-2}$ and were annealed in N$_2$ at 900 °C. No increase in recombination was detectable for doses below $10^{13}$ cm$^{-2}$, but for higher doses, the effective lifetime decreased linearly with increasing Si dose. The silicon samples in this study had been etched prior to the lifetime measurements. This excludes dislocation loops at the surface as the cause for the increased recombination processes. Excess interstitials, by contrast, may penetrate deeper into the silicon volume as a consequence of trapping and de-trapping by native defects [171, 177]. The spectral response of the photoconductance opens the path to a very sensitive detection of these deep-lying defects, as it is can be employed to create a depth resolution of the implanted wafers.

In the following investigation, silicon wafers have been implanted with silicon ions and investigated with measurements of the (white-light) lifetime and the spectral response of the photoconductance. 500 micron thick 1 Ω cm boron-doped p-type FZ silicon have been implanted with 36 keV Si$^{28}$ ions of two different doses: $1 \times 10^{14}$ and $3 \times 10^{15}$ cm$^{-2}$. The wafers have been kept at 100 °C during implantation, resulting in buried amorphous pockets and ion damage whose peak was situated around 50 nm below the surface [171]. Subsequently, the wafers were annealed at either 900 or 1000 °C for 60 min in nitrogen and received a surface passivation with PECVD silicon nitride [105]. Such implant and annealing conditions are prone to form large concentrations of end-of-range dislocation loops [173]. Alongside the implanted samples, a control wafer was subjected to the same
4.3 Non-diffused wafers

Cleaning, annealing and passivation procedures. This permits the assessment of the influence of the surface and bulk recombination of the original material as well as any contamination from the furnaces. Some samples were etched to a depth of 5 µm prior to annealing to investigate any damage occurring during implantation.

Lifetime measurement with QSSPC confirmed that pre-etched wafers did not suffer from defects that may have been inflicted below 5 µm due to the implantation [171]. The control wafers and the pre-etched samples exhibited high lifetimes around 100–200 µs. The annealing step at 900 °C causes the lifetime of the low-dose samples to decrease to 10–20 µs; the impact on the high-dose implants is even more pronounced by low lifetimes in the range 3–7 µs. For the lighter dose, the annealing at 1000 °C causes the lifetime to reach the same level as in the control wafers indicating a full recovery of the defected areas. The higher temperature step improves the situation for the highly implanted samples considerably, but not to an extent where all damage is removed [171].

These findings are corroborated by the spectral analysis of the photoconductance. Figure 4.11 presents the external quantum efficiency of the photoconductance, normalised to 1000 nm for better comparison, for the control samples and the implanted wafers that have been annealed at either 900 or 1000 °C. Included in this plot is the optical absorption fraction \( f_{\text{abs}} \) of the silicon wafer coated with silicon nitride passivation layers on both sides (normalised to 100 nm). The control samples express only little wavelength depen-

![Figure 4.11: External quantum efficiency of the excess photoconductance, normalised to 1000 nm, of the control sample and the wafers that received a low or high Si dose and were annealed at either 900 or 1000 °C.](image-url)
Spectral response of the photoconductance

dence. Their high-quality surface passivation ensures that $E_{\text{QE}}(\Delta \sigma)$ is essentially shaped by the absorption fraction (Equation 4.9). A higher annealing temperature decreases the photoconductance output of the control samples only slightly. A low dose of silicon implantation already leads to a stronger wavelength dependence. The sample annealed at 900 °C exhibits the characteristic hump indicating an increased surface recombination rate. The annealing at 1000 °C improves the response in the front region, but contrary to the lifetime measurements, it does not recover entirely. The high silicon dose results in an even stronger decrease in photoconductance sensitivity. Here again, the higher annealing temperature alleviates the recombination activity. The strong degradation in the UV response with increasing implantation dose is a clear sign that the front recombination is influenced by the presence of near-surface dislocation loops.

The depth of the residual defects after annealing can be disclosed by etching and re-passivating the samples. The etching of the control sample, which came as no surprise, did not show any change in carrier lifetime [171]. However, the etching of the first 15 µm of the contaminated samples lifted the carrier lifetime enormously. This indicates that the first 15 µm contained strong recombination channels in the form of end-of-range dislocation loops. A subsequent etching did not, admittedly, increase the life expectancy of charge carriers any further, even after removing 100 µm of silicon. This points to a homogenous distribution of deeply propagated defects up to a depth of 100 µm and maybe even throughout the whole wafer [171].

The spectral analysis of the photoconductance sheds more light on this enigma. Figure 4.12 shows the external quantum efficiency of the photoconductance of the samples annealed at 900 °C. The control sample and the silicon implanted samples annealed at 900 °C are the same as in Figure 4.11. In addition to this, the graph shows the high dose wafer illuminated from the rear and illuminated from the front after etching of 15 µm of the front surface.

The sample that has been etched and re-passivated after annealing shows explicit signs of improvement compared to the wafers with high and low dose after annealing. The characteristic hump in the IR disappeared hinting that the front surface recombination rate has again reached similar levels to the control sample. The rear illumination of the sample irradiated with a high ion dose also unveils no distinct spectral dependence. The shape of $E_{\text{QE}}(\Delta \sigma)$ mimics the absorption fraction, since the rear surface recombination scarcely impacts on the photoconductance response. Importantly, the spectral response of the post-etched and rear-illuminated samples are quite similar. This underlines the conjecture of a uniform profile of defects throughout the wafer thickness in the implanted
4.3 Non-diffused wafers

A likely candidate for the defects are silicon interstitials that possess the necessary properties to create a uniform distribution: they easily migrate back and forth through the wafer during annealing. Higher implant doses will leave more interstitials behind resulting in a higher concentration after annealing. This is supported by the lifetime measurements. Note that, even though most interstitials will be bound in dislocation loops, a mere density of $10^{14}$ cm$^{-2}$ will be enough to substantially curtail the lifetime [176]. The healing effect at higher annealing temperatures gives rise to the assumption that more interstitials are getting annihilated as a result of an elevated recombination. Another conjecture regards the dislocation loops as the source for interstitial injection. The raised temperatures may then speed the annihilation of these loops and thus prevent the diffusion of interstitial into the silicon volume [171]. These reflections are supported by recent DLTS measurements of Si implanted silicon wafers [176]. The DLTS analysis disclosed that highly-implanted wafers experience a decrease in the vacancy-related defect concentration, which can be construed as an increase of excess interstitials.

In brief, the spectrally resolved photoconductance measurements provide valid inside information as to the location of defects, regardless if they are fixed at the surface or propagate deeply into the bulk. The spectral response therefore acts as a depth resolution
tool. The highly distinct hump in $EQE(\Delta \sigma)$ unveils a high front recombination, while the absolute magnitude serves as a marker if a uniform defect distribution is hampering the volume lifetime.

4.4 p-n structures

Diffused regions, that is, emitters, are omnipresent in solar cells, frequently dominating or strongly influencing their performance. The emitter diffusion creates a p-n junction that is essential for the separation and collection of charge carriers. When illuminated, the resulting separation of the fermi level produces a voltage difference on both sides of the junction, which enables a current to be drawn from the device. Apart from this fundamental importance of the emitter, it has multiple functions that help to improve device performance. A heavily doped emitter provides a low work function difference between metal contact and the silicon enhancing the tunnelling of charge carriers. A heavy diffusion moreover minimises the surface recombination under the metal contacts [11] and helps to repel minority carriers from recombination channels at the surface.

The emitter region may be negligible in size compared to the rest of the cell dimension, but this does not justify neglecting its contribution to the generation of charge carriers. A 1 $\mu$m thick emitter absorbs nearly 30% of the standard AM1.5G spectrum. Consequently, there is reason enough not to underestimate the amount of charge carriers that add to the overall photoconductance. Or viewing it from the opposite side, recombination in the emitter and at its surface may contribute a considerable part to the electrical losses. As an example, a 1 $\mu$m thick emitter can cause a high emitter recombination equivalent to a 15% photocurrent loss. Emitter recombination limits the open-circuit voltage of the solar cell and hence the overall efficiency attainable. To accurately measure the photoconductance of emitter samples with the QSSPC technique, it is wise to block off the low-wavelength range ($< 600$ nm) that is not impervious to the emitter losses. Heavily-doped, non-passivated emitters with deep diffusions are the most likely to produce this sort of recombination loss.

This kind of error source can be turned into an advantage by exacerbating the emitter losses using short-wavelength light that is entirely consumed within the emitter. The quantum efficiency of the photoconductance of the emitter region is then very susceptible to the recombination channels surrounding it, rendering the quantum yield highly spectrally dependent. The quantum efficiency of the photoconductance of long-wavelength illumination, by contrast, is undisturbed by the emitter losses, making it suitable for
a reference point. This is the basic concept of the two-wavelength method devised by Cuevas et al. to deduce the emitter collection efficiency [161]. They used two different wavelengths, one in the UV range (410 nm), the other one in the IR (1000 nm) to discern between emitter and base efficiency. They convincingly demonstrated this technique with a range of emitter diffusions with or without surface passivation. The quantum efficiency of the photoconductance introduced in this chapter is none other than an extension from a two-wavelength method to a full spectral analysis.

The emitter saturation current $J_{oe}$ is the key parameter for characterising the quality of the emitter diffusion. The technique of choice to access $J_{oe}$ is the measurement of the photoconductance via QSSPC [20]. The photoconductance of a diffused wafer reflects an average carrier density $\Delta n_{av}$ that is sensitive to all recombination mechanisms in the bulk and in the emitter region. The picture of the effective lifetime $\tau_{\text{eff}} = \Delta n_{av} W / G$ is a concise way of portraying the global effect of these recombination processes. Expressing $\tau_{\text{eff}}$ for an identical diffusion on the front and rear side delivers the following:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + 2J_{oe} \frac{N_A + \Delta n_{av}}{q n_i^2 W}.$$  \hspace{1cm} (4.11)

This expression implies uniform carrier generation throughout the bulk, or more specifically: $\Delta n(W_e) \approx \Delta n(W) \approx \Delta n_{av}$. $W_e$ and $W$ denote the width of the emitter region and the total sample, respectively. Necessarily, the emitter saturation current can only be extracted if the emitter is the dominant recombination channel. Nevertheless, the distinct injection level dependence of $J_{oe}$ and $\tau_{\text{bulk}}$ provides an additional opportunity to explore the effective lifetime. The recombination rate in the emitter follows the square of the carrier density if the later is sufficiently high. The main process characterising the bulk recombination at high injection level, the Auger recombination, is proportional to $\Delta n^3$. If this term is subtracted from $\tau_{\text{bulk}}$, Equation 4.11 dictates that a plot of $1/\tau_{\text{eff}}$ versus $\Delta n_{av}$ yields a linear regime, whose slope is attributable to $J_{oe}$. This is exactly the method proposed by Kane et al. [20]. The use of a lowly-doped base material facilitates reaching high-injection conditions in the device.

The following study combines aspects of the emitter collection efficiency and the emitter saturation current. The next section is reserved to extend the analytical model contrived earlier for non-diffused wafers to p-n structures. This enables extraction of the emitter saturation current via a spectrally resolved measurement. PC1D calculations elucidate the behaviour of the external quantum efficiency. Following that, emitter samples with different diffusion schemes are analysed with photoconductance measurements using white and monochromatic light.
4. Spectral response of the photoconductance

4.4.1 One-dimensional analytical model of the spectral photoconductance of diffused wafers

The conversion of the analytical model described earlier to diffused wafers is straightforward if the concept of the emitter saturation current is introduced. Instead of locating the boundaries at the front surface itself, it is useful to combine the front region containing the surface and the emitter into one ‘virtual’ surface located at the edge of the junction. The recombination of the front region can be embodied in an effective surface recombination velocity $S_{\text{eff}}$ or directly within the emitter saturation current. The boundary condition at the junction edge $W_e$ can then be written as:

$$D_n \frac{\partial \Delta n}{\partial x} \bigg|_{x=W_e} = J_{\text{oc}} \frac{\Delta n(W_e)(\Delta n(W_e) + N_A)}{q n_t^2}.$$  \hspace{1cm} (4.12)

Keeping the rear boundaries as before, the external quantum efficiency of the photoconductance can be obtained in the same fashion as done earlier in this chapter:

$$EQE(\Delta \sigma, \lambda) \approx (\mu_n + \mu_p) \tau_{\text{bulk}} f_{\text{abs}}(\lambda) - (\mu_n + \mu_p) \tau_{\text{bulk}} \frac{1}{N_{\text{ph}}(\lambda)} \left( J_{\text{oc}} \frac{\Delta n(W_e)(\Delta n(W_e) + N_A)}{q n_t^2} + S_{\text{back}} \Delta n(W_b) \right).$$  \hspace{1cm} (4.13)

The emitter characteristics enter the quantum yield thus only via the front boundary. The non-linearity in $\Delta n(W_e)$ in this boundary condition makes an analytical solution impossible, except in low injection or very high injection. Despite this, the experimental set-up always allows us to examine $EQE(\Delta \sigma)$ at very low photon fluxes, ensuring that $\Delta n(W_e)$ is much smaller than the doping density. In this case, the non-linearity vanishes in a first approximation. If an effective SRV $S_{\text{eff}} = J_{\text{oc}} N_A/q n_t^2$ is introduced into Equation 4.13, the latter becomes effectively the same as Equation 4.9. Note, however, that $S_{\text{eff}}$ refers to a surface that includes the emitter region, it is therefore different from the surface recombination velocity $S_{\text{front}}$ that appears in Equation 4.9. Since the analytical model for the spectral response of the voltage and the photoconductance are different in a mathematical sense, a combined analysis should in principle offers scope to discern between bulk and rear surface recombination.

Equation 4.13 indicates that the shape of $EQE(\Delta \sigma)$ is given by the optical properties of the wafer if $J_{\text{oc}}$ and $S_{\text{back}}$ can be neglected. A high current flow via the recombination channels in the front region is likely to diminish $EQE(\Delta \sigma)$, especially for absorption within or nearby this region. This foreshadows that $EQE(\Delta \sigma)$ exhibits the same hump in the IR as its counterpart of non-diffused wafers for high losses in the front region.
4.4 p-n structures

4.4.2 Computer simulations

To provide a context for the experimental technique described in the following, the computer program PC1D is used to compare the traditional internal quantum efficiency to the quantum efficiency of the photoconductance. The ensuing discussion bears a close connection to the PC1D calculation of the spectral response of the voltage. In particular, the same model cells 1-5 have been used. The device parameters can be found accordingly in Section 2.2 on page 63.

The deduction of the external and internal quantum efficiency of the photoconductance proceeds exactly in the same way as for the voltage case. First, illumination-photoconductance curves are calculated with PC1D for a range of different wavelengths. Second, these curves are interpolated at several constant photoconductance values. The external quantum efficiency is determined and scaled to a suitable reference point, in general at the wavelength at which $EQE(\Delta\sigma)$ takes its maximum. The following simulations will show that the spectral response of the photoconductance is not independent of the constant photoconductance at which it is evaluated. The dependency is related to the sensitivity of the photoconductance to surface recombination.

The difference between the relative external and internal quantum efficiency is the same as for the voltage definition: $EQE(\Delta\sigma)|_{rel}$ reflects perfectly the shape of its short-circuit counterpart, but is offset by the amount of reflectance and recombination that prevails at the reference wavelength (see also the discussion on page 56). $IQE(\Delta\sigma)|_{rel}$ manifests the same quantum yield as the traditional internal quantum efficiency if no electrical losses degrade the yield at the reference point. Consequently, the PC1D calculations concentrate on the comparison of the internal quantum efficiencies.

The first device, cell 1, represents a typical well-passivated high-efficiency cell. The short-circuit and photoconductance response are shown in Figure 4.13 on the left. The latter has been contemplated at two different $\Delta\sigma = 0.02$ and 0.23 mS, which correspond to excess carrier densities of $2.7 \times 10^{12}$ and $3.1 \times 10^{13}$ cm$^{-3}$. The total photoconductance at standard conditions is 11.3 mS, which is representative of a high performance device. It can be inferred from the plot of $IQE$ that the relative internal quantum efficiency of the photoconductance perfectly mimics the short-circuit current $IQE$ apart from minor discrepancies in the IR. The magnitude of the photoconductance does not influence the outcome of $IQE(\Delta\sigma)|_{rel}$.

This point is changed if the front surface recombination is increased from 100 to $10^6$ cm/s (cell 2 on the right of Figure 4.13). Both the current and photoconductance yield
suffer tremendously in the UV from the strong recombination rate at the front surface. The de-passivation causes the total photoconductance to drop considerably to $\Delta \sigma (\text{AM1.5G}) = 1.1 \, \text{mS}$. The decrease in photoconductance arises from the strong correlation between voltage and photoconductance [127]. Surprisingly, the front surface recombination extends its impact on the photoconductance response to the high wavelength range. This influence is, as a second surprise, not equally sensed at each photoconductance level. At very low

$\Delta \sigma = 0.01 \, \text{mS} \quad (\Delta n = 1.4 \times 10^{12} \, \text{cm}^{-3})$, the photoconductance response still follows the short-circuit one. However, a slight increase in photoconductance causes it to diverge in the IR. The maximum difference is reached at $\Delta \sigma = 0.14 \, \text{mS} \quad (\Delta n = 1.9 \times 10^{13} \, \text{cm}^{-3})$. Above that, the discrepancy does not increase any further.

Due to the high surface recombination at the front side, more photons are needed to obtain a constant photoconductance when the wafer is illuminated with UV light instead of IR light. This trend is increased when a higher photoconductance and thus a higher carrier density has to be gained. In other words: The $N_{ph} - \Delta \sigma$ curve depends differently on the photoconductance for each wavelength. Thus, relative to the short wavelength measurement of $IQE(\Delta \sigma)_{rel}$ at a given $\Delta \sigma$, there is a surplus of photoconductance response in the IR, which is not seen in the short-circuit measurement. This surplus increases with increasing carrier density until it saturates at a certain excess carrier level. The reason why this surplus is not detected with the short-circuit response lies in the fact that in the latter, charge carriers generated at IR light still have to travel to the junction in order to be collected. However, the diffusion of these surplus charge carriers is limited by

Figure 4.13: PC1D calculations of $IQE(J_{sc})$ and $IQE(\Delta \sigma)_{rel}$ for a high efficiency device with low surface recombination (cell 1, left graph) and high front surface recombination (cell 2, right graph).
the finite diffusion constant $D_n$ [161]. Note that the relative photoconductance response of non-diffused silicon wafers is independent of the charge carrier density at which it is evaluated.

The next case, cell 3, is representative of a high-efficiency cell produced on low quality silicon material. It has the same structure as cell 1, the only difference being a low bulk lifetime of 10 $\mu$s. This substantially lowers the total excess photoconductance at standard conditions to 0.55 mS. It affects the short-circuit current response in the IR as a result of the high likelihood that carriers generated at these wavelengths recombine before being collected (Figure 4.14 on the left). The photoconductance yield, in turn, follows the latter closely if a very low excess photoconductance is established at each wavelength. For higher $\Delta\sigma$, the response in the IR increases until it saturates at the level shown in Figure 4.14. The saturated response predicts a near-perfect quantum efficiency. Relative to the short-circuit response, the improvement in yield is up to 50%. Comparably to the surplus of charge carriers seen in cell 2, $IQE(\Delta\sigma)|_{rel}$ thus detects an excess of charge carriers in the IR. However, the high amount of recombination channels in the bulk inhibits the collection of these carriers at the junction under short-circuit conditions.

![Figure 4.14: PC1D calculations of $IQE(J_{sc})$ and $IQE(\Delta\sigma)|_{rel}$ for a device with low quality bulk material (cell 3, left graph) and a device with high rear surface recombination (cell 4, right graph).](image)

The graph on the right of Figure 4.14 shows a device whose rear surface passivation is deteriorated from 100 to $10^6$ cm/s compared to cell 1. $\Delta\sigma(AM1.5G)$ is consequently diminished to 0.87 mS. The high losses at the rear surface impact on the short-circuit current and photoconductance response in equal measure, but less so on the latter. $IQE(\Delta\sigma)|_{rel}$ proves to be fairly independent of the exact injection level. This represents the first case
where the photoconductance yield at a certain small excess carrier concentration is not able to reproduce exactly the same shape as $IQE(J_{sc})$.

Cell 5 represents the industrial-type cell structure with deep and heavily doped emitter, no surface passivation and low bulk quality. The total excess photoconductance dwindles to 0.23 mS owing to the detrimental recombination mechanisms. Not surprisingly, the internal quantum efficiency incorporates both losses that afflict cell 2 and 3 (Figure 4.15). The photoconductance response mimics the short-circuit response only for a very low constant photoconductance. At higher constant $\Delta \sigma$, the typical hump in the IR becomes visible. Note that in all examples, the upper limit of the constant photoconductance at which $IQE(\Delta \sigma)_{rel}$ still expresses the same behaviour as its short-circuit current analogy, is around 0.01 mS ($\Delta n = 1.4 \times 10^{12}$ cm$^{-3}$).

The dependence of $IQE(\Delta \sigma)_{rel}$ on the constant photoconductance at which it is extracted only occurs if the device received an emitter diffusion. This indicates that the hump in the IR is influenced by the emitter saturation current. To consolidate this, the same scenario as in cell 2 has been simulated with two different bulk doping densities $N_{dop}$. From Equation 4.12, it is expected that a higher doping density leads to a higher sensitivity of $IQE(\Delta \sigma)_{rel}$ to the constant photoconductance, while a lower $N_{dop}$ will deliver a response independent of the constant photoconductance.

As anticipated, a highly-doped cell with $N_{dop} = 5.9 \times 10^{16}$ (0.3 $\Omega$ cm) is much less sensitive to the fixed photoconductance chosen to calculate $IQE(\Delta \sigma)_{rel}$ (Figure 4.16 on
Figure 4.16: PC1D calculations of $IQE(J_{sc})$ and $IQE(\Delta \sigma)|_{rel}$ for a high efficiency device akin to cell 1, but with doping density $N_{dop} = 5.9 \times 10^{16}$ cm$^{-3}$ (0.3 $\Omega$ cm, left graph) and $N_{dop} = 2.7 \times 10^{14}$ cm$^{-3}$ (50 $\Omega$ cm, right graph).

If we change to a lowly-doped wafer with $N_{dop} = 2.7 \times 10^{14}$ cm$^{-3}$ (50 $\Omega$ cm), the discrepancy between $IQE(\Delta \sigma)|_{rel}$ and $IQE(J_{sc})$ is even more remarkable and makes a comparison valuable only for wavelengths < 600 nm (Figure 4.16 on the right). It is salutary to note that the computer modelling reveals the same result for cell 4 if the doping density is increased or decreased. For cell 3 however, the divergence in the IR does not disappear for highly-doped base material.

Still this does not explain why the surplus in $IQE(\Delta \sigma)|_{rel}$ in the IR saturates at a certain carrier density. Moreover, the injection levels at which the transformation of the IR response occurs are too small compared to the doping densities to change the emitter saturation current sufficiently. It has to be added that an increase of $S_{\text{front}}$ or $S_{\text{back}}$ up to 1000 cm/s does not cause any divergence of $IQE(\Delta \sigma)|_{rel}$ in the IR. This is an important result, since the new method will therefore always be applicable for passivated high-efficiency devices.

In any event, the main application of the new method focuses on the investigation of the emitter region. As could be seen in the simulations of the internal quantum efficiency of the short-circuit current in Chapter 1 (page 16), $IQE(J_{sc})$ is very sensitive to the characteristics of the emitter. The peak surface concentration of the dopant, the sheet resistance, the junction depth and the diffusion profile all have an influence on the UV response of $IQE(J_{sc})$. The next simulations endeavour to expose a similar influence on $IQE(\Delta \sigma)|_{rel}$. 
In Chapter 2, a range of different emitter configurations have been used for the analysis of the spectral response of the voltage with PC1D calculations. The emitters 3–6 of these emitter structures are studied here for the comparison of $IQE(J_{sc})$ and $IQE(\Delta \sigma)|_{rel}$. The exact nature of the emitter diffusion can be found accordingly in Table 2.3 on page 96. Figure 4.17 pictures the short wavelength range of the two internal quantum efficiencies. The response in the UV decreases with increasing emitter saturation current for both approaches in equal measure. A high recombination in the emitter ($J_{0e}$ above 100 fA/cm$^2$) draws such a high amount of charge carriers from the base region that $IQE(J_{sc})$ in the base falls below 100%. Because $IQE(\Delta \sigma)|_{rel}$ is a relative measure, it cannot detect this decrease. As a consequence, the whole $IQE(\Delta \sigma)|_{rel}$ curve for the emitter structures with $J_{0e} = 130$ and 640 fA/cm$^2$ is shifted to slightly higher values.

![Figure 4.17: PC1D calculations of $IQE(J_{sc})$ and $IQE(\Delta \sigma)|_{rel}$ for several emitter configurations.](image)

Overall, the simulations show that the spectral response of the photoconductance accomplishes the task of disclosing recombination mechanisms in the emitter and bulk region, akin to the conventional spectral response of the short-circuit current. It is imperative that $IQE(\Delta \sigma)|_{rel}$ is measured at a very low constant photoconductance to ensure that no surplus of charge carriers is established at long wavelengths. The flash illumination always allows the study of devices at such low injection levels. Apart from that, $IQE(\Delta \sigma)|_{rel}$ is especially suited to study the emitter quantum efficiency of non-metallized wafers, where the traditional spectral response fails. The next section corroborates this with a study of phosphorus and boron doped emitters of different sheet resistances.
4.4 p-n structures

4.4.3 Comparison of emitter quantum efficiency and saturation current

Solar cells are produced in general on p-type silicon using n-type phosphorus emitters, the reason being partly historical and partly in light of the wealth of experience, which facilitates the diffusion of high quality emitters. The higher minority carrier mobility of p-type silicon also argues in favour of this material. The emitter saturation current $J_{0e}$ and the front surface recombination rate $S_p$ of $n^+$ emitters show a strong increase with increasing surface phosphorus concentration [102, 103, 178, 179]. A high temperature step with forming gas anneal (FGA) is the cornerstone for reducing $S_p$ for a given surface phosphorus concentration. $J_{0e}$ exhibits a better performance when the sheet resistance $R_{sheet}$ increases, and takes on values between 4 and 150 fA/cm$^2$. The emitter saturation current is not independent of the exact nature of the emitter surface passivation. A silicon oxide passivation performs better than a silicon nitride layer; the best results can be achieved on annealed thin oxides and oxide/SiN stacks [103].

Despite the historical head start of n-type emitters, there is a huge incentive to investigate its $p^+$ counterpart. For a start, higher effective lifetimes can be obtained in n-type silicon. Moreover, it can be inferred from the lower capture cross section for holes than for electrons of silicon oxide layers that it is easier to passivate than p-type Si. But the biggest advantage stems from the possibility of using n-type CZ silicon in view of its lower cost, its indifference to light-induced degradation and its electrical quality comparable to n-type FZ Si. Silicon oxide passivated boron emitters show the same tendency for $J_{0e}$ as a function of the sheet resistance as their n-type analogy. Values for $J_{0e}$ extend from 20 to 300 fA/cm$^2$ and best outcomes have been gained with a 100 nm thick silicon oxide passivation layer that formed during the TCA process or after the emitter diffusion in an additional oxidation step [159].

The following study elucidates the ability of the spectral response of the photoconductance to assess and optimise emitter structures. For this purpose, a series of phosphorus and boron doped emitters of different sheet resistances were fabricated and studied with QSSPC and QSSPC-λ. The phosphorus diffusions were carried out in a quartz tube using liquid POCl$_3$ as dopant source. The test structures, 2.5 $\Omega$ cm FZ silicon wafers of thickness $\sim$ 250 $\mu$m, received the diffusion on both sides after shiny etching their surfaces. The temperature during the phosphorus diffusion ranged from 850 to 900 $^\circ$C. The samples were annealed in forming gas at 400 $^\circ$C for 40 minutes. Thereafter, the wafers were stripped off the phosphorus glass and the sheet resistance $R_{sheet}$ was measured. The wafers were then oxidised at 900 $^\circ$C for 20 minutes resulting in a thin oxide layer of $\sim$ 10 nm. Finally, the test structures were annealed in forming gas at 400 $^\circ$C.
For the boron diffusions, shiny etched high resistivity n-type wafers with <100> orientation and resistivity of 20 and 90 Ω cm were used. The emitter formation were performed in a quartz tube at temperatures between 895 and 1015 °C using liquid BBr3 as dopant source. Following that, the boron glass was stripped off and the samples were oxidised at 1050 °C for 38 min with TCA. This yielded a thick oxide layer of 100 nm that serves as an antireflection layer and supports the drive in of the dopants. Next, an anneal in Ar had the aim to enhance a further drive in and re-distribute some of the boron concentration at the silicon surface. In a last step, the test structures were treated with FGA at 400 °C for 40 min.

The samples were measured with QSSPC to deduce the emitter saturation current following Kane’s method [20] and with QSSPC-λ to obtain the quantum efficiency of the excess photoconductance. The reflectance measurements of the samples were carried out with a spectrophotometer. Figure 4.18 illustrates the external and internal quantum efficiencies of the excess photoconductance, $EQE(\Delta\sigma)|_{rel}$ and $IQE(\Delta\sigma)|_{rel}$, respectively, of the phosphorus doped emitter structures. Note that the peak at 850 nm is related to a systematic error at this wavelength, presumably caused by stray light.

![Figure 4.18: Relative external and internal quantum efficiency of the excess photoconductance of the phosphorus emitter samples.](image)

Of particular interest is the visible part of the spectral measurements, since it concerns directly the emitter diffusions. Both $EQE(\Delta\sigma)|_{rel}$ and $IQE(\Delta\sigma)|_{rel}$ are clearly related to the sheet resistance. The quantum yield at short and mid wavelengths increases with increasing sheet resistance. As expected, the shortest wavelengths are affected the most, with the heaviest diffusion showing a drop in relative quantum efficiency of ~ 40% compared to the lightest diffusion. It can be noted as well that there exists a relative increase...
of the IR response compared to the mid-wavelength range with decreasing sheet resistance. That is, as the recombination at the diffused surfaces increases, IR generated carriers diffuse towards those surfaces to recombine, but they can only do so at the diffusion velocity, which is limited. This limitation is particularly acute for high carrier fluxes, when the surface recombination is high. As a result, carriers pile up in the base region, resulting in an increased photoconductance.

Figure 4.19: Relative external and internal quantum efficiency of the excess photoconductance of the boron emitter samples.

The measurements corresponding to the boron emitters are displayed in Figure 4.19. Here, a wider range of sheet resistances have been produced, stretching from 31 to 213 $\Omega/\square$. Despite of this, there exists less variation in relative quantum yield in the visible range of the spectrum, compared to the phosphorus emitters in Figure 4.18. Again, the short-wavelength response decreases with decreasing sheet resistance, although less markedly. The relative drop in quantum efficiency between the heaviest and lightest dopant diffusion is now only $\sim 20\%$.

The drop in relative quantum efficiency with decreasing sheet resistance observed for both the phosphorus and boron diffusions agrees with the classic view that heavy emitter diffusions degrade cell performance. A similar decrease in quantum yield is generally experienced by the traditional spectral response of the short-circuit current (see also the discussion of the characteristics of $IQE(J_{sc})$ in Chapter 1 on page 16).

In terms of the emitter saturation current, traditional wisdom says that $J_{0e}$ increases with decreasing sheet resistance (for surface passivated emitters). This is confirmed by our measurements of $J_{0e}$, which are shown in Figure 4.20. We have also plotted the emitter saturation current versus $IQE(\Delta\sigma)|_{rel}$ at 400 nm in Figure 4.21. As expected, there
Figure 4.20: Emitter saturation current as a function of sheet resistance $R_{\text{sheet}}$ for the phosphorus and boron emitter samples. The lines are guides to the eye.

Figure 4.21: Emitter saturation current as a function of $IQE(\Delta \sigma)|_{\text{rel}}$ at 400 nm for the phosphorus and boron emitter samples. The lines are guides to the eye.

There is a clear relationship between $IQE(\Delta \sigma)|_{\text{rel}}$ at 400 nm and the emitter recombination current: a higher quantum yield coincides with lower recombination loss in the emitter region. Although in general phosphorus emitters perform better than boron emitters [159], the results in Figure 4.21 show the opposite. This can be explained by the fact that the phosphorus diffusions are much shallower and have a higher surface dopant density than the boron diffusions used in this experiment.
In summary, the measurements of phosphorus and boron diffused emitters presented here demonstrate that the spectral photoconductance technique has the potential to study the physical mechanisms of surface and volume recombination within emitter regions. Even though a relative measure, the value of $IQE(\Delta \sigma)|_{rel}$ still indicates if a high or low emitter recombination is prevalent. Combined with measurements of the emitter dopant profile, the spectral response of the photoconductance should enable the extraction of the surface recombination velocity and other physical parameters of highly doped silicon from a contactless measurement.

### 4.4.4 Comparison of current and photoconductance response

In this section, the measurement of the spectral response of the photoconductance is compared to the spectral response of the short-circuit current. The test structure was cut out from the same original wafer as the solar cell FB99.8d studied in Chapter 1 and 2. FB99.8c is thus also a high-efficiency PERC cell with 120 Ω/□ emitter on 1.25 Ω cm p-type FZ silicon. Its output parameters are $J_{sc} = 39.0$ mA/cm$^2$, $V_{oc} = 661$ mV, $FF = 80.9\%$ and $\eta = 20.9\%$. First the $I-V$ characteristics and the traditional quantum efficiency were measured. Then the rear metallisation was removed and the measurement of the quantum efficiency of the photoconductance was performed. The reflectance was only measured after the removal of the rear metallisation. Hence, it is expected to be slightly less in the IR than the reflectance with the rear metallisation, owing to the mirror-like effect of the metal.

Figure 4.22 depicts $EQE(J_{sc})$ and $EQE(\Delta \sigma)|_{rel}$ as a function of wavelength. The comparison shows that $EQE(\Delta \sigma)|_{rel}$ mimics the shape of its short-circuit counterpart for $\lambda < 850$ nm. Naturally, $EQE(\Delta \sigma)|_{rel}$ cannot detect that the absolute $EQE$ lies slightly below 100% due to reflection losses. $EQE(\Delta \sigma)|_{rel}$ records a smaller yield in the IR compared to the mid-wavelength range than $EQE(J_{sc})$. This can be explained by the poorer quality of the rear silicon oxide layer as a back reflector than a combination of silicon oxide and aluminium.

Figure 4.23 presents the internal quantum efficiencies that correspond to Figure 4.22. Here, $IQE(J_{sc})$ and $IQE(\Delta \sigma)|_{rel}$ overlap perfectly for $\lambda < 850$ nm in view of the maximum internal yield manifested by the high-efficiency device in the mid-wavelength range. The perfect overlap accentuates the divergence in the IR resulting from internal reflection losses to a greater extent.
This example highlights convincingly that $IQE(\Delta \sigma)_{rel}$ is indeed a valuable measure of the spectral losses of solar cells. If the internal quantum conversion is perfect at (at least) a small range of the solar spectrum, the relative parameter $IQE(\Delta \sigma)_{rel}$ is able to reflect the absolute internal quantum losses of emitter structures and solar cells.
4.5 Conclusions

The spectral response of the excess photoconductance has been presented in this chapter as a generalisation of the two-wavelength method. The two-wavelength method compares the photoconductance response of the front region and the volume of the silicon wafer. From this, it draws valuable conclusions about the corresponding recombination activities. The spectral response brings this contemplation to the next level, since it allows us to visualise a complete picture of the spectral behaviour of the sample. The parameters that describe this response most impressively are the external and internal quantum efficiency of the photoconductance.

To bring the external quantum efficiency of the photoconductance into context with fundamental recombination parameters like the bulk lifetime and the surface recombination velocity, a one-dimensional model has been conceptualised. This model describes the external quantum efficiency of the photoconductance of non-diffused wafers as a function that is proportional to the mobility of charge carriers, the bulk lifetime and a wavelength dependent part. This latter function comprises a purely optical term, the absorption fraction, from which a second term is subtracted, which is governed by the front and rear recombination processes. The - at the same time surprising and characteristic - mark of the external quantum efficiency of the photoconductance is the emergence of a hump in the IR in the case of high front surface recombination. This is explained by the high sensitivity of the photoconductance towards charge carriers generated away from the front region. The diffusion of these charge carriers towards the front region is obstructed by the finite diffusion constant. This contribution is not detected by the spectral response of the current or voltage, since only charge carriers that reach the front region are registered. The model permits assessment of the surface recombination velocity via a spectral response measurement, provided the bulk lifetime is known.

The first application of the external quantum efficiency of the photoconductance and its simplified description in particular was the surface recombination velocity of undiffused bare silicon. In the past, the latter has been roughly estimated as being equal to its thermal limit: $10^7$ cm/s. The investigation of polished, lapped and as-cut wafers showed that it does not exceed $1.5 \times 10^5$ cm/s and is strongly dependent on the doping density. The surface recombination rate even decreases to very low levels of 70 cm/s for polished n-type FZ Si of resistivity 1000 $\Omega$ cm. The surface passivation is improved dramatically shortly after a HF treatment, but deteriorates gradually with time. This is attributed to changes in the fixed positive oxide charges and in the density of states at the silicon
The external quantum efficiency of the photoconductance has been shown to be very successful in providing a depth resolution for surface and bulk damage due to ion implantation. A thorough study of Si implantation in silicon has revealed that it leaves behind strong recombination channels in silicon material. The defects emerge in two different forms: first, as end-of-range dislocation loops within the first 15 $\mu$m and second, as a homogenous distribution of deeply propagated defects up to a depth of at least 100 $\mu$m. The latter are most likely composed of silicon interstitials. The wavelength dependence of the excess photoconductance acted as a marker to identify the migration depth and the amount of these defects.

The one-dimensional model of the photoresponse of the conductance has then been extended to emitter structures. If the excess carrier density is negligible compared to the doping density of the base material, similar boundary conditions can be applied than in single doped wafers. Instead of the surface recombination velocity, the emitter saturation current comes into play. If the bulk lifetime of a sample under test is known, this model allows the determination of the emitter saturation current from a spectral response measurement.

PC1D calculations underlined the potential of the photoconductance response to analyse p-n junction devices. If the photoresponse is studied at a photoconductance equal or lower to 0.01 mS, the internal quantum efficiency of the photoconductance follows perfectly the shape of its short-circuit current analogy. At higher constant photoconductance, a characteristic hump appears if the device suffers from high front recombination or bulk recombination. This hump has the same origin as in non-diffused wafers, but is here mainly triggered by the emitter saturation current. If present, it restricts the analysis of the spectral response to wavelength below 600 nm. Fortunately, the nature of the light source always allows study of the sample at a very low constant photoconductance, where this effect disappears. The most important outcome of the PC1D calculations is that the photoconductance response exhibits the same sensitivity to changes in the emitter configuration as the short-circuit current response.

This has been confirmed by the measurement of the photoconductance response of phosphorus and boron doped emitter structures. For both types of emitter, the quantum efficiency of the photoconductance showed a decrease in the UV response with decreasing sheet resistance of the emitter diffusion. This trend coincides with the classical view that the performance of the emitter deteriorates with decreasing sheet resistance. This has been further emphasised by the observation that the quantum yield at 400 nm decreases
with increasing emitter saturation current. However, the ultimate validation of the spectral response of the photoconductance has been established in this work by the direct comparison of a short-circuit current and photoconductance measurement on the same solar cell, which yielded a perfect agreement.

In summary, the spectral response of the photoconductance offers the prospect of a very valuable diagnostic tool to analyse the recombination parameters in un-diffused silicon, particularly as a depth resolution of recombination channels in ion-damaged samples. In the same light, it proves to be a very successful technique to monitor the quality of emitters from their early formation until the completion of the front metallisation.
Summary and outlook

Summary - Applicability of the novel diagnostic tools

In broad terms, this thesis has inaugurated novel measurement techniques that offer the prospect of a deeper insight into the interior processes of silicon solar cell precursors and devices. The new diagnostic tools are: the spectral response of the quasi-steady-state short-circuit current (QSS\(J_{sc}\)-\(\lambda\)), the spectral response of the quasi-steady-state open-circuit voltage (QSS\(V_{oc}\)-\(\lambda\)), the temperature dependent quantum efficiency of the voltage (TQEV\(V_{oc}\)), the temperature and injection dependent voltage spectroscopy (TIVS) and the spectral response of the quasi-steady-state excess photoconductance (QSSPC-\(\lambda\)). The work combined the design of the measurement set-up and the software for the automation, data acquisition and analysis with the experimental validation of the methods on appropriate test structures.

The concepts behind the techniques are not totally new; as their name suggests, they are based on existing methods like the quasi-steady-state open-circuit voltage and the quasi-steady-state photoconductance. The term quasi-steady-state alludes to the special feature that is common to all techniques: the light source. Instead of a constant light, with a signal small in intensity and spot size, a large, smoothly changing irradiation source is employed, all typical characteristics encompassed by photographic flashes. Naturally, spectral responsivity measurement of the current, the voltage and the photoconductance existed before. So what improvement do these new techniques offer? In short, we can state the following: Compared to the traditional current response, QSS\(J_{sc}\)-\(\lambda\) provides spectral response curves that constitute an integral measure and can be screened for intensity dependent effects in one single measurement. QSS\(V_{oc}\)-\(\lambda\) has the advantage over SPV that it examines the solar cell at actual device conditions rather than at very low voltages. TQEV\(V_{oc}\) can be applied already after junction formation, whereas TQEQ\(J_{sc}\) has to resort to finished solar cells. QSSPC-\(\lambda\), finally, presents itself as a contactless method, which enriches its applicability to bare, passivated or diffused silicon wafers in comparison to SPC.

But the most important message conveyed by this thesis is that spectral response
measurement are not anymore confined to fully processed solar cells. A unique aspect of the novel diagnostic tools is the possibility to complement one another in the process monitoring of silicon wafers from its early stage to the final creation of the solar cell. Figure 3 elucidates the most important steps a silicon wafer traverses during the fabrication process, accompanied by the appropriate measurement technique. By passing through the different process steps, we review the realm of possibilities offered by the novel techniques.

![Diagram](image.png)

**Figure 3:** Schematic presentation of the different steps a silicon wafer traverses until its completion as a solar cell and the corresponding methods that can be applied at each step.

In the semiconductor industry, it is crucial for the manufacturer to assess the quality of the raw material before it enters the production process. Low quality material can be discarded beforehand, which helps to lower wasteful processing and thus production costs. The spectral response of the photoconductance is one technique, which can assist in this quality control. The effective lifetime of bare silicon wafers is influenced by the surface and the bulk losses. Even though in most cases the spectral response can not pin down the minority bulk lifetime and the surface recombination velocity at the same time, it is able to extract one of these parameters accurately if the other one is known. In this work, a theoretical value for the bulk lifetime of mono-crystalline wafers has been assumed and the surface recombination velocity of bare silicon wafers of different surface conditions has
been deduced. The resulting surface recombination velocities can serve as an input value to more accurately determine the bulk lifetime of silicon, an application that is not only restricted to mono-crystalline wafers.

Ion implants are highly relevant in the semiconductor industry for the formation of very defined doped regions. Ion implantation is currently the technique of choice to form junctions in microelectronics and one day it might even supplant the traditional junction formation in a solar cell production. It is already conceivable as a technique to implant impurities in silicon to produce 'impurity photovoltaic devices', which - though until now only theoretically - benefit from an increased electron-hole generation due to the presence of impurities. Ion implantations are not without risk - the detailed investigation in this thesis unearthed that it leaves behind deeply penetrating defects. The spectral response of the photoconductance was a major driving force in disclosing the nature and especially the migration depths of the defects. This is just an example of many possible applications. For passivated silicon, QSSPC-λ is thus a very valuable technique for studying the various impacts on the bulk lifetime of silicon wafers.

The formation of a p-n junction introduces a new degree of electrical activity in the silicon. The spectral response of the photoconductance of diffused devices mimics in most cases the typical shape of the spectral response of the current. Consequently, its measurement provides an early glimpse at the internal loss mechanisms that emerge as a result of the mingling of the recombination processes on both sides of the junction. One parameter that stands for the recombination activity of the emitter region, the emitter saturation current, is of particular interest. The sensitivity of the UV response of the spectral photoconductance is matched by the electrical losses of the emitter region. Not surprisingly, the analysis of the spectral response allows extraction of the emitter saturation current, and the results are, as shown in this work, in good agreement with traditional methods used to measure it.

Most notably, the presence of differently doped areas enables a voltage to be established in the device and thus the possibility to study the sensitivity of the voltage to light of different wavelengths. Unlike the spectral photoconductance, no hump that overestimates the contribution in the IR appears in the spectrum of the voltage response. Moreover, this thesis showed that the spectral photovoltage holds the same explanatory power as its short-circuit counterpart. Its analysis permits the determination of the bulk diffusion length, the rear surface recombination rate and the emitter saturation current; and all of this directly after junction formation. The models developed in this work to this aim can be easily extended to Schottky contacts or chemically induced junctions. Most noteworthy
is the adaptation of the theoretical expressions of Isenberg, which improve the accuracy of the diffusion length compared to the models traditionally used in the SPV method. However, the main attraction of the spectral photovoltage is its ability to extract the injection-level dependence of the bulk and surface recombination rates.

The measurement of the quantum efficiency of the voltage at different temperatures constitutes a logical next step. Akin to its short-circuit analogue, $TQE_{J_{sc}}$, $TQE_{V_{oc}}$ helps to unravel valuable information about contaminants in the silicon bulk, like their energy level within the band-gap or their capture characteristics. The white light measurement of the voltage at several temperatures, $TIVS$, is an interesting concept that is unfortunately impeded by the uncertainty to correctly predict the bulk lifetime from the open-circuit voltage. However, combined with $TQE_{V_{oc}}$, it offers the possibility to study the temperature and injection dependence of samples, where the conventional lifetime tools fail. Even though cumbersome, it might be employed in the characterisation of thin film cells that lack the high-quality passivation necessary for lifetime experiments.

The presence of front contacts usually does not present an obstacle to perform photoconductance measurements. Both, $QSSPC\cdot\Lambda$ and $QSSV_{oc}\cdot\Lambda$, are applicable before and after contact formation and are sensitive to changes in the emitter saturation current. This paves the way for a sophisticated study of the impact of the front metallisation on the emitter quality and to optimise the emitter-contact combination. Finally, the rear metallisation brings the quasi-steady-state approach to the spectral response of the current into the foreground. This method promises to be a low-cost alternative to the conventional spectral response. Furthermore, it’s employment offers the possibility of studying non-linear effects that make their presence felt on the current response. The subsequent measurement of $QSSJ_{sc}\cdot\Lambda$ and $QSSV_{oc}\cdot\Lambda$ can be easily achieved, and this clears the way to accurately discern between emitter, bulk and rear surface recombination.

Further work

The completion of a PhD thesis rarely signals the end of the work that can be done in its field of inquiry. The core of this investigation was based on three pillars: the design and construction of the measurement set-up, the experimental validation of the diagnostic tools and finally its application to solar cell precursors and finished devices. Hence, improvements, ideas and proposals for future work are suggested in these three directions.
Improvement of the measurement set-up

The current measurement set-up is only the first prototype, thus there is always the potential to upgrade its components to improve the accuracy of the measurement. Most errors arise from the optics and the calibration and can be mitigated by simple adjustments. It emerged that the Broncolor flash is best suited for spectral measurement. However, its spectrum was unfortunately not available. The knowledge of this spectrum would help to abate the errors from the calibration factors that have been used to calculate the photon flux, the intensity and the generation from the monitor cell current (see also Appendix B for further details of these correction factors).

Instead of measuring the monitor cell and the test structure in subsequent steps, a simultaneous recording would avoid fluctuations of the flash from pulse to pulse. This would impose the largest change to the existing set-up, since a set of optical fibres would have to be installed that guide the light to both the monitor cell and sample. If additionally a calibrated reference cell is measured before the test cell, and the photocurrent is simultaneously detected by the monitor cell during the reference and test measurement, the reading of $EQE(J_{sc})$ can be further improved. This sort of monitoring is standard in the conventional spectral response. A similar approach could also be applied to spectral measurements of the voltage and the photoconductance.

Finally, the optics of the set-up can be ameliorated by improving the collimation of the light source. This would further perfect the homogeneity of the light spot and suppress stray-light occurring from the reflection of white light inside the filter compartment and the housing. Scattered light can be further suppressed following the design of Budde et al. [72]. They shielded the measurement stage from the flash lamp by enclosing it and using diaphragm plates inside the enclosure. Additionally, a diffuser between the bandpass filter and the test sample will improve the uniformity of the light at the test plane.

Data analysis

The analysis of the spectral response of the voltage is complicated by the constant that links it to the current response according to the one-dimensional analytical model. This does not present a drawback to the application of the linear model to the internal quantum efficiency, since the constant as well as the diffusion length are determined by the slope and intercept of the linear fit. However, the more sophisticated models of Lagowski-Spiegel and Isenberg require a non-linear fit with three unknowns. In this work, the non-linear fit has been simplified by the assumption that the constant determined by the linear model...
is accurate enough to be used in the other models. The reasoning for this approximation was the observation that a non-linear least-square fit always retained the initial value for the constant, which was the one deduced by the linear model. This might be eschewed by changing to a mathematical fitting procedure that can handle this kind of equation better.

The model of Isenberg proved to be the most successful one in correctly predicting the diffusion length and the rear surface recombination velocity. The accuracy of the model hinges partly on the optical model, which is based on the model of Basore (Appendix C.2). This model includes the effect of multiple reflectance at large wavelengths and thus an enhanced light absorption. This enables the model to be extended beyond the limit of an absorption depth that is smaller than the device thickness. In principal, this model is designed to include the whole spectrum. Nonetheless, this has to be handled with care. Basore specified constant values for the internal front and rear reflectance. Using these values, most of the fitted $IQE$ curves diverged from the measurement for the wavelengths where multiple reflections gain importance. Instead of the values proposed by Basore, the measured reflectance has been fitted with standard formulas that emerged from his optical model. This led to a much better agreement between theory and experiment up to a wavelength of 1050 nm.

The discrepancy for higher wavelength can be explained by the fact that Basore’s model assumes a flat rear surface. In reality, this is rarely the case and the internal rear reflectance is more accurately described by a partial Lambertian reflectance. Firstly, this renders the rear reflectance wavelength dependent. Secondly, this has a profound impact on each subsequent light path. Brendel et al. concocted a model that represents an improvement to Basore’s model by accounting for these effects (Appendix C.2). Their research resulted in the creation of a one-dimensional software tool IQE1D [53, 62, 63], which convincingly models the measured internal quantum efficiency of the current. Future work in this direction could be the implementation of their optical model into the existing framework and the conceptualisation of a software program IQE$\omega$1D that analyses the spectral photovoltage.

Experimental

The main attraction of the quasi-steady state short-circuit current response is its ability to measure over a broad range of intensities. An illumination dependence should be expected in the $EQE$ of the short-circuit current, if the bulk lifetime is highly dependent on the carrier concentration or a silicon oxide passivation is present at the rear side of the device. Even though light intensities up to $\sim$ 10 suns can be achieved, the resulting
carrier density under short-circuit conditions is still much lower compared to open-circuit. More devices with a likely non-linear current response will be measured in future work to test the potential of the QSS$J_{sc}$-$\lambda$ method.

This thesis has demonstrated that the spectral response of the voltage and the photoconductance reveal vital information about the emitter region, in particular about the emitter saturation current. As alluded to above, both methods can be in principle applied regardless of a front contact being present or not. This provides the incentive to direct future work into a thorough study of emitter structures. However, the application of the spectral photovoltage without metal contacts is not without concern. Practically, the presence of a surface passivation layer or antireflection coating exacerbates the difficulty of making a good contact to the silicon due to its insulating nature. The front passivation is necessary in order to avoid high surface saturation currents that screen the emitter losses, especially in lightly doped emitters. Despite this, a reasonable contact should be possible by increasing the impedance of the contact probes. This has been successfully proven by other groups [180]. Future work will assess the potential and limits for the application of the voltage response to such devices.

Recently, an exciting material entered the arena of photovoltaics: n-type multicrystalline silicon. Several important findings have been reported: it responds effectively to phosphorous gettering, achieves high lifetime above one millisecond and does not falter under illumination [181]. Furthermore, a more compelling motivation to investigate n-type silicon comes from the prediction that it should be much more tolerant to metal contaminants than p-type Si [182]. The formation of the p-n junction in this material still represents a major challenge, as boron-diffused emitters, the first choice traditionally, contain many flaws [183]. The investigation of viable alternatives to boron ranks high in future projects. Two likely contestants promise to be a viable alternative: gallium and aluminium. The use of QSSPC-$\lambda$ and QSSV$_{sc}$-$\lambda$ will help to optimise these novel emitter structures.

The resemblance of the spectral response of the photoconductance and the short-circuit current suggest that the long-wavelength range of the first might be fitted in a similar way to deduce the diffusion length. Further investigation will shed light on this possibility by studying the internal quantum efficiency of the photoconductance as a function of penetration depth.

The hump that has been observed in the spectral response of the photoconductance for samples with high front surface recombination could only be explained qualitatively as a result of the finite diffusion constant of charge carriers. Future work will elucidate if this
phenomenon can be disclosed quantitatively and if new information can be derived from this hump. Possibly, the analysis of the spectral photoconductance of bare silicon wafers will permit the determination of the diffusivity constants $D_n$ and $D_p$.

Finally, the proposal for a new, powerful and versatile technique emerges from this work and is presented in the following: the voltage mapping of silicon materials and solar cells. This method represents the logical extension of QSSV$_{oc}$ to spatially resolved measurements. A contact probe would scan the device in a non-destructive manner. The slowly varying intensity of the flash lamps would then enable the direct measurement of the local intensity-voltage curve in a single measurement. This curve is sensitive to shunt resistance, thus allowing a topographical map of leakage currents. QSSV$_{oc}$$-\lambda$, TQE$V_{oc}$ and TIVS can be directly transferred to the new tool, hence providing the means to extract a local diffusion length or a spatial distribution of defect centres.

A promising application of the voltage mapping is the measurement of multicrystalline and polycrystalline silicon. This material is prone to lifetime degradation during cell fabrication processes such as oxidation [106]. Thus, accurate correlations between substrate quality and final cell parameters have to be performed near the end of the fabrication process. The presence of metal contacts makes lifetime imaging impossible - this is the moment where voltage mapping makes its entrance. After the formation of the p-n junction, the technique can pursue every consecutive processing step until the finalisation of the solar device and note any minor change on its way.

Another application is the voltage mapping of emitter devices, mainly in view of novel dopants like aluminium and gallium. Phosphorus is known to segregate to disordered regions such as grain boundaries. Aluminium as well has been proven to be a gettering agent. The voltage mapping would assist in elucidating whether gallium and aluminium segregate to grain boundaries and to what extent they are beneficial for the spatial uniformity of recombination and cell efficiency.
The automated measurement, data acquisition and analysis of the new techniques has been incorporated in a software package QssFlash® developed as part of this work. The software is built on two pillars apart from the automation program: the data acquisition models and the models used for the data analysis. The data acquisition models comprise standard mathematical models applicable to data sets and the models that correct the optical mismatch between the monitor and sample cell. The models of the data analysis consist of the following: First, several optical models are used for the determination of the generation, absorption and internal reflection. Second, the evaluation of the bulk lifetime requires the knowledge of all recombination processes coming into play in silicon. Third, defect spectroscopy makes use of models that govern the temperature dependence of silicon parameters like the intrinsic carrier density and the band gap. Finally, the solution of the continuity equation is important for the one-dimensional models of the external quantum efficiency of the current, voltage or photoconductance. This appendix gives an overview of all models involved in the spectral response measurements and the voltage spectroscopy necessary to understand the 'theory behind the scenes'.

A  Mathematical procedures used in the data acquisition

Due to the quasi-steady-state light source, the balance between generation and recombination is not always perfect, especially if a high lifetime in the sample compared to the characteristic flash decay time gives rise to a slow decrease in carrier density. The general analysis that links the effective lifetime, the carrier density and the generation accounts for this effect by implementing the derivative of the excess carrier injection level as a function of time [143]. In the same sense, when the quasi-steady state open-circuit voltage is converted into effective lifetime, the imperfectness of the carrier balance is compensated for with a term that uses the derivative of the voltage [136]. In both cases, a numerical differentiation of observational data has to be performed. Depending on the algorithm used, the results can be quite erroneous or noisy.
For instance, the spreadsheet devised by Sinton for QSSPC and QSSV\textsubscript{oc} resorts to a linear regression (LR) around the data point at which the derivative is calculated [158]. If a data set \((x_i, f_i(x_i))\) is measured (for example the carrier density as a function of time), the linear regression calculates the slope in a grid with element size \(s\) located around the value \(f_i(x_i)\). This gives rise to the following approximation of the derivative \(f_i'(x_i)\):

\[
f'_i(x_i) = \frac{2(s + 1) \sum_{k=-s}^{s} x_{i+k} f_{i+k} - (\sum_{k=-s}^{s} x_{i+k})(\sum_{k=-s}^{s} f_{i+k})}{2(s + 1) \sum_{k=-s}^{s} x_{i+k}^2 - (\sum_{k=-s}^{s} x_{i+k})^2}.
\]

Another standard approximation of the derivative of the grid-points uses the mid-point rule, which compares the next neighbours of the data point \(f_i\) [184]:

\[
f'_i(x_i) = \frac{f_{i+1} - f_{i-1}}{2\Delta x},
\]

where \(\Delta x\) is the step size of the data points. The pair \([i + 1, i - 1]\) is called a ‘grid’ with grid size 1. Unfortunately, if the step size tends to zero, the mid-point rule fails to yield a convergent approximation to the derivative \(f'_i(x_i)\). More stability can be achieved by applying the mid-point rule to a variety of different sized grids and averaging over all grids [184]. Thus, by defining the maximum grid size \(r\), the mid-point rule is applied to the grids \([i + s, i - s]\) with \(k = 1, 2, \ldots, r\):

\[
f'_i(x_i) = \frac{1}{r} \sum_{s=1}^{r} \frac{f_{i+s} - f_{i-s}}{2s\Delta x}.
\]

The number of averaging is then equal to \(r\). Another method based on the mid-point formula uses a fixed grid size \(s\). The mid-point rule is then evaluated on spatially adjacent grids and averaged. In order to ensure that the average converges, the boundary of the grid can not move away from the grid point \(i\) more than \(s + r\) with \(r = s - 1\). The combination of different grids fulfilling this condition is then given by \([i + k + s, i + k - s]\) with \(s = -r, \ldots, r\) [185]:

\[
f'_i(x_i) = \frac{1}{2(r + 1)} \sum_{k=-r}^{r} \frac{f_{i+k+s} - f_{i+k-s}}{2s\Delta x}.
\]

Figure A.1 delineates the averaged mid-point rule (MPR) and the spatial neighbourhood averaging (SNA) in more detail. In this example, the maximum grid size for the averaged mid-point rule is \(r = 3\). This means that the derivative is obtained as the average over
Averaged mid-point rule

Maximum grid size \( r = 3 \),
\( s = 1, 2, 3 \)

Spatial neighbourhood averaging

Fixed grid size \( s = 2 \),
\( r = 1, k = -1, 0, 1 \)

Figure A.1: Averaged mid-point rule and spatial neighbourhood averaging for a given grid size.

Figure A.2: Excess carrier density \( \Delta n \) and its derivative \( -d\Delta n/dt \) as a function of time. The latter has been calculated with several different methods.

three different grid sizes, as indicated in Figure A.1. However, the SNA method fixes the grid size first (i.e. \( s = 2 \)) and moves this grid across the adjacent data points as seen in Figure A.1. Hence, in the first formula, one averages over different estimates of the same derivative, whereas in the second, one averages over the same estimate of spatially-adjacent derivatives.

The quality of the three models, linear regression, averaged mid-point rule and spatial neighbourhood averaging, is examined with an example of the excess carrier density. Fig-
Figure A.2 shows an overview of $\Delta n$ and its derivative $-d\Delta n/dt$ as a function of time, the latter calculated with several methods. Two sections of the derivative have been enlarged in order to better judge the quality of its deduction. The left part of Figure A.3 depicts the steep peak of the derivative. The linear regression and the models based on the mid-point rule with small numbers of averaging ($r = 3$ for AMP, $s = 1$ for SNA) overlap well. If the number of averages and thus the grid size increases, the differentiation smooths more and more. This suggests that a too large grid size will produce errors in the derivation at data points, where the original function changes rapidly.

![Figure A.3: Two enlarged section of the derivative $-d\Delta n/dt$ as a function of time. On the left, the peak section is shown, while on the right, a part with small changes in the derivative is amplified.](image)

The right side of Figure A.3 depicts a strongly magnified section of the derivative, where the original function and the derivative change only slowly. Here, it becomes obvious that the linear regression is the noisiest followed by the average mid-point rule with the smallest grid size. The smallest fluctuations are seen for the spatial neighbourhood averaging with the biggest grid size. Note that the errors of the differentiation are much smaller than at the peak. From this evaluation it can be concluded that the best trade off between small errors at strong slopes and small fluctuation is given by the spatial neighbourhood averaging with grid size $s = 2$. If a slower decaying flash signal is used, a higher grid number is recommended.

## B Calibration and correction factors

The quasi-steady-state techniques used in this work all resort to the same measure of obtaining the photon flux, intensity and generation of the sample under test. A moni-
tor cell is measured either simultaneously or subsequently to the test structure and its photocurrent is employed to determine the parameters of interest. Adequate calibration factors are required to transfer from photocurrent to either of these parameters. These factors have to account for the different optical properties of the monitor cell and test device. In particular, the quasi-steady-state photoconductance is a very widespread technique, but the calibration factors used in the past rarely incorporated the external quantum efficiency of the monitor cell or the spectrum of the flash. This section explains in detail the calibration factors that correct for this spectral mismatch.

B.1 Calculation of the photon flux and intensity from the monitor cell current

Since the spectrum of photographic flashes can be quite different from the solar spectrum and often change to warmer colours with elapsing time, it is important to assess the impact of such a spectrum on the cell performance. The spectrum of the flash comes into play when the photon flux is needed, as in spectral response measurements, or when the intensity is the subject of interest, as is the case for illumination-voltage curves.

The photon flux of the standard AM1.5G spectrum and the Quantum flash spectrum are compared in Figure B.4, the latter at the peak pulse and 5 ms after the beginning of the pulse. The striking difference between the sun and the flash spectra are the large spikes that appear in the IR of the flash spectra. These spikes originate from the Xenon

![Figure B.4](image-url)

**Figure B.4:** Relative photon flux of the standard AM1.5G spectrum and the flash spectrum of the Quantum flash at the peak of the pulse and after 5 ms.
emission lines and increase relative to the UV part with time. The UV spectrum, on the other hand, behaves quite similarly to the standard spectrum.

In order to obtain the correct photon flux and intensity from the monitor current, the latter is spectrally decomposed into the external quantum efficiency and the absolute number of photons:

$$ J_{ph} = q \int E Q E(\lambda) N_{ph,abs}(\lambda) T(\lambda) d\lambda. \quad (B.5) $$

To make this evaluation valid for white and monochromatic light, the factor $T$ has been introduced that stands either for the transmission of the bandpass filters used in the spectral measurement or is equal to one for white light. The absolute photon flux is rarely known, since it changes strongly with distance between light source and sample. Nonetheless, we can make use of a characteristic of the photon flux, that is, that it alters linearly with distance. Consequently, it is sufficient if only a relative spectrum is known:

$$ N_{ph,abs} = c \cdot N_{ph,rel}. \quad (B.6) $$

The proportionality constant $c$ can then be deduced combining Equation B.5 and B.6:

$$ c = \frac{J_{ph}}{q \int E Q E(\lambda) N_{ph,rel}(\lambda) T(\lambda) d\lambda}. \quad (B.7) $$

The total photon flux incident on the measurement plane can be obtained by integrating the absolute photon flux per wavelength over the total spectrum involved:

$$ N_{ph} = \int N_{ph,abs}(\lambda) T(\lambda) d\lambda $$

$$ = \frac{\int N_{ph,rel}(\lambda) T(\lambda) d\lambda}{\int E Q E(\lambda) N_{ph,rel}(\lambda) T(\lambda) d\lambda} \cdot \frac{J_{ph}}{q} $$

$$ = \frac{1}{E Q E_{eff}} \cdot \frac{J_{ph}}{q}. \quad (B.8) $$

Here, the integral external quantum efficiency $E Q E_{eff}$ has been introduced as the correction factor to calculate the photon flux from the photocurrent of the monitor cell. In a white light measurement, $E Q E_{eff}$ is about 0.9 for a monitor cell from SunPower. In a spectral measurement, the transmission of the bandpass filters is narrowed down to a wavelength range of 20–40 nm. In a good approximation, $E Q E_{eff} \approx E Q E$.

As can be seen in Figure B.4, the spectrum of the flash changes with time, which is especially noticeable by a shift to longer wavelength. In principle, this requires a determination of the flash spectrum at very short time intervals to account for the spectral mismatch with
time. This is a difficult task, given the short flash times involved. Bail et al. conceived a time correction factor that compares the measured photocurrent at visible and infrared light as a function of time with the theoretical photocurrent at these spectral ranges [186]. We refrain from this correction, since it will have only a minor effect for white light, and even less if monochromatic light is used.

The intensity is defined as the integral over the energy flux $E_{\text{ph}} = \frac{hc}{\lambda} N_{\text{ph}}$, where $E_{\text{ph}}$ is in suns/$\lambda$. Using this relation, an intensity correction factor $ICF$ can be defined by:

$$ I = \int E_{\text{ph,abs}}(\lambda) T(\lambda) \, d\lambda = \int \frac{hc}{\lambda} N_{\text{ph,rel}}(\lambda) T(\lambda) \, d\lambda \cdot \frac{J_{\text{ph}}}{q} = ICF \cdot J_{\text{ph}}. \tag{B.9} $$

If white light is used, $ICF$ amounts to $\sim 16 \text{ suns cm}^2/\text{A}$ using the Quantum flash. Under monochromatic light, $ICF \approx \frac{hc}{\lambda qEQE}$, if the bandwidth of the filter is sufficiently small. To obtain a fuller picture, Figure B.5 compares $EQE_{\text{eff}}$ and $ICF$ for the bandpass filters of the spectral response set-up between 400 and 1050 nm with its respective approximation. The photon flux is only known up to 1070 nm, so that no statement can be made for the bandpass filters at 1100 and 1150 nm. It is safe to conclude from both graphs that the approximations represent the integral values excellently. $EQE_{\text{eff}}$ and $EQE$ show slight differences at 400, 1000 and 1050 nm. The divergence lies between 0.3 and 0.8%.

![Figure B.5: Left graph: comparison of the effective external quantum efficiency, $EQE_{\text{eff}}$ and its approximation, $EQE$ of the monitor cell, as a function of wavelength. Right graph: Intensity correction factor $ICF$ and its approximation $hc/(\lambda qEQE)$ as a function of wavelength.](image)
Only minor discrepancies appear between ICF and its approximation. Most spectral response measurements have been carried out with the Broncolor flash, where no spectrum could be measured. Despite of this, Figure B.5 underlines that the approximations are a valid alternative.

B.2 Calculation of the generation from the monitor cell current

The correction factors for the photon flux and the intensity only involve the characteristics of the flash spectrum and the monitor cell, hence they can be implemented into the data acquisition process beforehand. However, the generation also has to account for the optical properties of the test device, like the absorption in the antireflection layer or multiple reflection inside the electrically active layer. The probability that a photon is converted into an electron-hole pair is embodied in the absorption fraction \( f_{\text{abs}} \). The generation rate can then be written as the product of \( f_{\text{abs}} \) and the photon flux integrated over the wavelength range of interest (see also Section C.2):

\[
G = \int f_{\text{abs}}(\lambda) \, N_{\text{ph,abs}}(\lambda) \, T(\lambda) \, d\lambda = \frac{\int f_{\text{abs}}(\lambda) \, N_{\text{ph,rel}}(\lambda) \, T(\lambda) \, d\lambda \cdot J_{\text{ph}}}{q \cdot \int \text{EQE}(\lambda) \, N_{\text{ph,rel}}(\lambda) \, T(\lambda) \, d\lambda} = A_{\text{eff}} \cdot \frac{J_{\text{ph}}}{q}.
\]

The correction factor \( A_{\text{eff}} \) introduced here consequently stands for the effective absorption that corrects for the optical losses of the monitor cell. For white light, \( A_{\text{eff}} \) depends strongly on the antireflection layer and the thickness of the silicon wafer. As an example, \( A_{\text{eff}} \) has been calculated for a \( \text{SiO}_2 \) antireflection layer and silicon wafer of different thickness (Figure B.6).

It can be inferred from this depiction that the effective absorption indeed changes strongly with the thickness of the antireflection coating (ARC). For a wafer thickness of 500 \( \mu \text{m} \), \( A_{\text{eff}} \) takes on values between 0.75 and 1. An incorrect effective absorption can thus entail errors of up to 25% in the determination of the lifetime, for example. The thickness of the sample plays another decisive role, since it shifts the magnitude of the effective absorption.

Note that for monochromatic light, \( A_{\text{eff}} \approx f_{\text{abs}}/\text{EQE} \). In Figure B.7 this approximation is evaluated. Apart from errors at 400 and 1050 nm, the approximation proves to be very accurate. At these two \( \lambda \), the divergences amount to \( \sim 1\% \). This validates the use of the approximation for the correction factors \( \text{EQE}_{\text{eff}} \), ICF and \( A_{\text{eff}} \) in view of the fact
that the spectrum of the Broncolor flash is not available.

C Optical models

C.1 Absorption coefficient and band-gap of silicon

The exact knowledge of the wavelength dependence of the absorption coefficient \( \alpha \) of silicon is crucial for the determination of the internal reflectance and particularly of the generation rate. Measurements of \( \alpha \) over the whole sun spectrum at \( \sim 300 \) K are available in the literature [187-189]. For the proper interpretation of the quantum efficiency in a TQE\( J_{sc} \) or TQE\( V_{oc} \) experiment, by contrast, the temperature dependence of \( \alpha \) is an important prerequisite. This section revises empirical formulas for the absorption coefficient and the band-gap used in the spectral analysis.

The absorption coefficient consists approximately of three components: two indirect and one direct transition. Since silicon is an indirect semiconductor, the absorption of photons can occur with the assistance of the absorption or emission of phonons. This contribution is proportional to the density of states in the conduction and valence band and to the distribution function of the phonons (Bose-distribution). Band structure calculations predict the existence of two fundamental indirect band-gaps \( E_{g,\text{i}} \) of silicon [190]. A third, direct transition takes place, if the photon energy \( h\nu \) is larger than the band-gap.
In total, the absorption coefficients of crystalline silicon can be described by:

\[
\alpha(T) = \sum_{i=\text{phonon}, j=\text{bandgap}} A_i C_i \left[ \frac{(\hbar \nu - E_{g,j}(T) + E_{ph,i})^2}{\exp \left( E_{ph,i}/kT \right) - 1} + \frac{(\hbar \nu - E_{g,j}(T) - E_{ph,i})^2}{\exp \left( -E_{ph,i}/kT \right) - 1} \right] + A_d \frac{(\hbar \nu - E_{g,d})^{3/2}}{\hbar \nu}.
\]

(C.11)

The first two terms denote the indirect transitions that are assisted by the absorption and emission of phonons, respectively. The third term stems from the direct transition of absorbed light. The constants \(C_i\) are a measure of the interaction strength between electrons and phonons. The phonons in the temperature range 20–500 K and with photon energies higher than 1.1 eV (\(\lambda < 1130 \text{ nm}\)) consist only of TA and TO phonons [190, 191]. \(A_j\) and \(A_d\) are fit parameters to experimental data using the following temperature dependence for the band-gap [191]:

\[
E_g(T) = E_g(0) - \frac{\beta T^2}{T + \gamma}.
\]

(C.12)

Note that the exponent in the direct transition term in Equation C.11 is in some references noted as \(3/2\), in others \(1/2\). The fit parameters have been adjusted by Bücher et al. to match experimental data available at \(T = 298\) and 363 K [190]. The corresponding parameters are displayed in Table C.1:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{g,1})</td>
<td>1.1557 eV</td>
</tr>
<tr>
<td>(E_{g,2})</td>
<td>2.25 eV</td>
</tr>
<tr>
<td>(E_{g,d})</td>
<td>3.2 eV</td>
</tr>
<tr>
<td>(E_{ph,1})</td>
<td>0.01827 eV</td>
</tr>
<tr>
<td>(E_{ph,2})</td>
<td>0.05773 eV</td>
</tr>
<tr>
<td>(C_1)</td>
<td>5.5</td>
</tr>
<tr>
<td>(C_2)</td>
<td>4.0</td>
</tr>
<tr>
<td>(A_1)</td>
<td>253 cm(^{-1}) eV(^{-2})</td>
</tr>
<tr>
<td>(A_2)</td>
<td>3312 cm(^{-1}) eV(^{-2})</td>
</tr>
<tr>
<td>(A_d)</td>
<td>(2.3 \times 10^7) cm(^{-1}) eV(^{-1/2})</td>
</tr>
<tr>
<td>(\beta)</td>
<td>7.021 \times 10^{-4}) eV/K</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>1108 K</td>
</tr>
</tbody>
</table>

Table C.1: Values of the energy levels of the indirect and direct band-gaps (\(E_{g,1}\) and \(E_{g,d}\)), the phonon energies (\(E_{ph,i}\)), the interaction strength between electrons and phonons (\(C_i\)) and the fit parameters \(A_i, A_d, \beta\) and \(\gamma\) determined by Bücher et al. as part of an empirical fit to experimental data of the absorption coefficient [190].

The data of the absorption coefficient most often used in solar cell calculations were tabulated by Green et al. [192] from measurements of various authors ([187–189]). The empirical formula C.11 agrees well with this data in the range 430–1070 nm, but above \(\lambda = 1070\) nm the theoretical model underestimates the measurement data (see also Figure C.8). Wagner et al. proposed a correction for the temperature dependence of \(\alpha\) by comparing
the measurement data with the theoretical data:

\[ \alpha_{\text{corr}}(T) = \alpha_{\text{meas}}(300\text{K}) \frac{\alpha(T)}{\alpha(300\text{K})}. \]  \hspace{1cm} (C.13)

Figure C.8 compares the empirical formula C.11 with the corrected and the measured absorption coefficient. Next to the measured and empirical data at 300 K, the empirical and corrected data for \( \alpha \) are presented at \( T = 400 \text{ K} \). For this temperature, the corrected data is smaller than the theoretical one in the range 400–550 nm. Naturally, it convenes well between 550 and 1070 nm. But the spectrum of concern is beyond that point, since the corrected data diverges more and more from the theoretical calculation with increasing \( \lambda \) and follows a different trend to the measurement. It is hard to judge whether the theoretical or corrected data predict the true behaviour of \( \alpha \) better. Nevertheless, we chose the corrected form together with Equations C.11 and C.12 for the spectral analysis.

![Figure C.8: Absorption coefficient \( \alpha \) from measurement data, empirical data and corrected data for 300 and 400 K.](image)

The exact nature of the indirect band-gap also comes into play when analysing the temperature dependence of the SRH lifetime. Pässler et al. presented a novel analytical description of the band-gap that fits experimental data better than the empirical evaluation given by Equation C.12 [193]:

\[ E_g(T) = E_g(0) - \frac{\kappa \Theta}{2} \left[ \sqrt{1 + \left( \frac{2T}{\Theta} \right)^p} - 1 \right]. \]  \hspace{1cm} (C.14)

Here, \( \kappa \) is the limiting shrinkage coefficient, \( \Theta = \hbar \omega / k \) denotes the effective phonon tem-
Figure C.9: Left: Absorption depth 1/α taken from the measured absorption coefficient. The circles highlight 1/α for the wavelengths used in the spectral response measurements. Right: Values for 1/α at these wavelengths.

Table C.1: Values for 1/α at filter wavelengths.

<table>
<thead>
<tr>
<th>λ</th>
<th>1/α</th>
<th>λ</th>
<th>1/α</th>
</tr>
</thead>
<tbody>
<tr>
<td>nm</td>
<td>μm</td>
<td>nm</td>
<td>μm</td>
</tr>
<tr>
<td>400</td>
<td>0.1</td>
<td>800</td>
<td>11.8</td>
</tr>
<tr>
<td>450</td>
<td>0.4</td>
<td>850</td>
<td>18.7</td>
</tr>
<tr>
<td>500</td>
<td>0.9</td>
<td>900</td>
<td>32.7</td>
</tr>
<tr>
<td>550</td>
<td>1.6</td>
<td>950</td>
<td>63.7</td>
</tr>
<tr>
<td>600</td>
<td>2.4</td>
<td>1000</td>
<td>156.3</td>
</tr>
<tr>
<td>650</td>
<td>3.6</td>
<td>1050</td>
<td>613.5</td>
</tr>
<tr>
<td>700</td>
<td>5.3</td>
<td>1100</td>
<td>2857.1</td>
</tr>
<tr>
<td>750</td>
<td>7.7</td>
<td>1150</td>
<td>14705.9</td>
</tr>
</tbody>
</table>

The inverse of the absorption coefficient, 1/α, indicates the depth at which the absorption takes place. It is beneficial to assess this absorption depth for the wavelengths used in the experimental set-up, especially in relation to the sample thickness and the diffusion depth of emitters. Figure C.9 on the left illustrates the absorption depth as a function of wavelength, while the table on the right displays the values for the wavelengths used in the quasi-steady-state techniques.

The first two wavelength, 400 and 450 nm, are absorbed entirely within the emitter, even for a small junction depth of 0.5 μm. A huge proportion of the sunlight is absorbed within the first 10 μm, including the total visible spectrum. For wavelength larger than 1000 nm, the fraction of transmitted light increases, placing more importance on the internal reflection at the back side of the silicon.

C.2 Generation rate - optical model of Basore

The generation rate in silicon is the parameter that determines the photocurrent in the device. It comes into play each time the balance between recombination and generation is contemplated, for example in the evaluation of the one-dimensional continuity equation. This section reviews the different optical models used in the thesis. In the following, we will distinguish between parameters that are spatially and wavelength dependent and parameters that constitute the integral over the wafer thickness of the latter with the
prefix ‘int’ (for example $G(x, \lambda)$ and $G^{\text{int}}(\lambda)$).

The generation rate $G$ at the distance $x$ and the wavelength $\lambda$ is proportional to the fraction of absorbed photons $f_{\text{abs}}$ and the amount of photons incident to the wafer surface, $N_{\text{ph}}$:

$$G(x, \lambda) = f_{\text{abs}}(x, \lambda) N_{\text{ph}}(\lambda).$$  \hfill (C.15)

The total generation rate integrated over wafer thickness at the wavelength $\lambda$ is then accordingly:

$$G^{\text{int}}(\lambda) = f_{\text{abs}}^{\text{int}}(\lambda) N_{\text{ph}}(\lambda).$$  \hfill (C.16)

For the continuity equation, it is thus necessary to determine the spatially dependent absorption fraction. For photoconductance measurements, where the integral generation rate in the sample is needed to access the effective lifetime, $f_{\text{abs}}^{\text{int}}$ is the figure of interest (see also the determination of the effective absorption discussed in Section B.2). The probability of absorption of a photon and the generation of an electron-hole pair is governed by the absorption coefficient $\alpha$. When a ray of photons passes through the wafer, the photon flux decays exponentially with $\alpha \exp(-\alpha x)$. This decaying law represents the basic building block of the absorption fraction.

The simplest model considers the case where all light is absorbed in the wafer, i.e. no internal reflection occurs. In this model, $f_{\text{abs}}$ is simply proportional to the decay of the absorption rate and the amount of light that is not reflected by the wafer:

$$f_{\text{abs}}(x, \lambda) = (1 - R(\lambda)) \alpha(\lambda) e^{-\alpha(\lambda)x}. $$  \hfill (C.17)

The linear model and the model of Lagowski-Spiegel, for example, utilises this simplified approach.

A more sophisticated model incorporates internal reflection at the front and rear side of the device. Figure C.10 illustrates the model schematically. From the perpendicularly incoming light, a fraction $R_f$ is reflected at the external front surface, the rest is transmitted through the device. If the energy of the photons is near the band-gap of silicon, a proportion of this light reaches the back of the cell ($T$), is partially reflected at the internal rear side by a factor $R_b$ and transmitted back into the cell. A fraction of the reflected light reaches the internal front surface of the cell. Some of the photons escape out the front with the probability $R_{\text{esc}}$, while the rest bounces back inside for the next pass with $R_f$. Any successive pass is transmitted and internally reflected with the same probabilities $T$, $R_b$ and $R_f$ until every photon is either absorbed or has escaped the device. The proportion
of light that will be transmitted to the back surface of the cell is given by:

\[ T(\lambda) = e^{-\alpha(\lambda)W}. \quad (C.18) \]

The analysis of such light absorption reveals that the absorption fraction is composed out of two exponentials, one for the light passing through the cell from the front to the back and one for the way back [19]:

\[ f_{abs}(x, \lambda) = a_1(\lambda) e^{-\alpha(\lambda)x} + a_2(\lambda) e^{\alpha(\lambda)x}. \quad (C.19) \]

The constants \( a_1 \) and \( a_2 \) are consequently a function of the transmission and reflectance parameters \( R_{fe}, T, R_b \) and \( R_f \):

\[
a_1 = \frac{(1 - R_{fe}) \alpha}{1 - R_b T^2 R_f},
\]
\[
a_2 = \frac{(1 - R_{fe}) \alpha R_b T^2}{1 - R_b T^2 R_f}.
\quad (C.20)

The total reflection and the integrated proportion of photons of wavelength \( \lambda \) absorbed within the sample can be approximately described by these factors:

\[
R(\lambda) = R_{fe} + (1 - R_{fe}) (1 - R_f) \frac{R_b T^2}{1 - R_b T^2 R_f}, \quad (C.21)
\]
\[
f_{abs}^{int}(\lambda) = (1 - R_{fe}) \frac{(1 - T) + R_b T^2 (e^{\alpha W} - 1)}{1 - R_b T^2 R_f}. \quad (C.22)
\]

This model is employed in the analytical description of the external quantum efficiency of the photoconductance (Section 4.3.1). \( R_{fe}, R_b \) and \( R_f \) form part of the unknown pa-
rameters. For the extraction of the front surface recombination of bare silicon wafers, these parameters have been accessed with the help of the ray-tracing program SUNRAYS [163, 194] (see Section 4.3.2). In principle, all of these factors are wavelength dependent, but $R_b$ and $R_f$ can be considered to be nearly constant. The external reflectance $R_{fe}$ can be obtained by extrapolating the measured reflectance from its values between 700–900 nm towards the infrared [19]. By fitting the measured reflectance with Equation C.21, the remaining two constants can be deducted. This path has been taken for the determination of the emitter saturation current from the external quantum efficiency of the photovoltaic (Section 4.4.1). The accuracy of the factors $R_b$ and $R_f$ can be increased if the absorption is also measured [19]. Then the wavelength dependence of $R_b$ and $R_f$ can be extracted via Equations C.21 and C.22.

![Figure C.11: Sketch of a textured device to explain the optical model of Basore.](image)

Basore refined the model to accommodate for textured surfaces and internal reflectance to non-perpendicular directions [45]. The schematic view of a textured sample explains the model in more detail (Figure C.11). The textured surface has first and foremost the effect that light entering the cell is refracted to an angle $\theta_1$. For chemically textured (100)-oriented silicon, this angle is $41.8^\circ$ for $\lambda \approx 900$ nm [45]. The absorption of light is also attenuated by the respective angle: $\alpha \rightarrow \alpha / \cos \theta_1$. This give rise to the following attenuation when the light passes the first time through the cell:

$$T_1 = e^{-\frac{\alpha}{\cos \theta_1} W}.$$  \hspace{1cm} (C.23)

At the back of the device, the light is reflected with a reflectance $R_{b1}$ to an effective mean angle $\theta_2$. This changes the transmission of the second path to:

$$T_2 = e^{-\frac{\alpha}{\cos \theta_2} W}.$$  \hspace{1cm} (C.24)
After the light is reflected again at the internal front side with $R_{f1}$ to the angle $\theta_n$, it is in all likelihood completely randomised. It is assumed that each subsequent bounce occurs with the same transmittance $T_n$ and internal back and front reflectance $R_{bn}$ and $R_{fn}$. $T_n$ follows a similar logic to above:

$$T_n = e^{-\frac{\alpha}{\cos \theta_n} W}.$$  

This gives rise to an absorption fraction composed of four different exponentials [53]:

$$f_{abs}(x, \lambda) = \sum_{i}^{4} a_{i} e^{b_{i} x},$$

where the constants $a_i$ and $b_i$ are given by:

$$a_1 = (1 - R_{fe}) \frac{\alpha}{\cos \theta_1},$$
$$a_2 = (1 - R_{fe}) T_1 R_{b1} \frac{\alpha}{\cos \theta_2} e^{-\frac{\alpha}{\cos \theta_n} W},$$
$$a_3 = (1 - R_{fe}) T_1 R_{b1} T_2 R_{f1} \frac{1}{1 - R_{bn} T_n^2 R_{fn}},$$
$$a_4 = (1 - R_{fe}) T_1 R_{b1} T_2 R_{f1} \frac{T_n R_{fn}}{1 - R_{bn} T_n^2 R_{fn}} e^{-\frac{\alpha}{\cos \theta_n} W}$$

and

$$b_1 = -\frac{\alpha}{\cos \theta_1},$$
$$b_2 = \frac{\alpha}{\cos \theta_2},$$
$$b_3 = -\frac{\alpha}{\cos \theta_n},$$
$$b_4 = \frac{\alpha}{\cos \theta_n}$$

Similarly to above, this model permits the total reflectance and the integral absorption fractions to be written in terms of the optical parameters [45]:

$$R = 1 - (1 - R_{fe}) \left\{ 1 - T_1 R_{b1} T_2 (1 - R_{f1}) - \frac{T_1 R_{b1} T_2 R_{f1} R_{bn} T_n^2 (1 - R_{fn})}{1 - R_{bn} T_n^2 R_{fn}} \right\},$$

$$f_{abs}^{int} = (1 - R_{fe}) \left\{ (1 - T_1) + R_{b1} T_1 (1 - T_2) + \frac{T_1 R_{b1} T_2 R_{f1} (1 - T_n) (1 + R_{bn} T_n)}{1 - R_{bn} T_n^2 R_{fn}} \right\}.$$  

The optical model of Basore forms part of the model of Isenberg describing the internal quantum efficiency. There are eight unknown parameters that emerge in the optical model: the external front reflectance $R_{fe}$, the angles of light propagation of the first, second and
each successive passes, $\theta_1$, $\theta_2$ and $\theta_n$, the internal rear reflectance of the first and subsequent passes, $R_{b1}$ and $R_{bn}$ and the internal front reflectance of the second and subsequent passes, $R_f$ and $R_{fn}$. The angles of light propagation are considered as approximately constant and are taken from Reference [45] (Table C.2).

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Planar</th>
<th>Textured</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\cos \theta_1$</td>
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<td>0.75</td>
</tr>
<tr>
<td>$\cos \theta_2$</td>
<td>0.75</td>
<td>0.65</td>
</tr>
<tr>
<td>$\cos \theta_n$</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table C.2: Angles of light propagation for a planar and textured cell [45].

For the PC1D calculations of Section 2.5.2, the parameters $R_{b1}$, $R_{bn}$, $R_{f1}$ and $R_{fn}$ have been taken as constant and have been adjusted to the PC1D values. The external front reflection has then be calculated from the PC1D reflectance data and Equation C.29. For the analysis of experimental data with the model of Isenberg, a different tactic has been chosen, which improves the accuracy of the internal reflectance parameters proposed by Basore. The measured reflectance has first been extrapolated in the long wavelength range to obtain $R_{fe}$. A least-square fit was then used to model the remaining constants with Equation C.29. The same procedure was performed when the effective absorption $A_{eff}$ was necessary. Equation C.30 was then used to calculate the integral absorption fraction that is needed to evaluate $A_{eff}$.

The most sophisticated optical model has been devised by Brendel et al. [53, 194]. The model is not employed in the thesis, nevertheless we shortly outline the refinement to the model of Basore made in this approach: First, different angles of light propagation are assumed for the emitter and base region. This is reasonable, since the thin emitter structure follows in general the pattern of the surface structure (Figure C.11). It follows that the attenuation is different in both sections. Both angles are given by the diffraction at the front surface and the dispersion of the refractive index. This brings about a wavelength dependence for both angles. The back reflectance has been designed to account for partial Lambertian reflectance, since the surface is never ideally flat nor completely rough. The transmittance $T_n$ and the angle $\theta_n$ from the third and subsequent bounces accommodate for randomised light after the second internal reflectance in a more precise way than the model of Basore. As a consequence, both parameters depend on the wavelength. The angle of the first internal back reflectance, the transmittance of the second path and the first internal front reflectance are calculated considering that the light is partly specular and partly randomised during the second pass. All parameters are either adjusted to values calculated by SUNRAYS or fitted to the measured reflectance.
D Models describing recombination in silicon and temperature dependence of silicon parameters

The temperature and injection-level dependent lifetime spectroscopy techniques utilise a set of equations that describe the injection-level dependence of the fundamental recombination mechanisms in silicon and the changes in temperatures of elementary silicon parameters. Furthermore, the extraction of the surface recombination rate from the external quantum efficiency of the photoconductance assumes a maximum bulk lifetime attainable in single crystalline silicon. The ensuing section shortly describes all the models involved in these evaluations.

D.1 Recombination mechanisms in the silicon bulk

Radiative recombination

Radiative recombination is the opposite of optical absorption, hence it involves the emission of a photon with energy approximately equal to the band-gap. It depends jointly on both the electron and hole concentrations, since both types of carriers are required for the mechanism to occur. The radiation rate is given by:

\[ \tau_{rad} = \frac{1}{B(N_A + \Delta n)}, \]

where \( B \) has the value \( 1.0 \times 10^{-14} \text{ cm}^3\text{s}^{-1} \) [195]. The radiative recombination is in general out-weighed by other recombination activities at any injection level.

Auger recombination

Auger recombination is a three-particle interaction, where the recombination of an electron-hole pair releases energy that is carried off by a third carrier. The total recombination rate is than proportional to the probability that an electron-hole-electron or an electron-hole-hole interaction occurs. The relation between recombination rate on one side and the excess carrier density and the doping concentration on the other side is described by similar empirical factors as does the factor \( B \) for the radiative recombination [196, 197]. Unfortunately, the relationship can not be pinned down as easily as in the previous case.

At low injection, Coulombic interaction between mobile charge carriers leads to a strong correlation between electrons and holes, enhancing the Auger recombination rate [198].
Models describing recombination in silicon and temperature dependence of silicon parameters

This effect is diminished in highly-injected, lowly-doped silicon or highly-doped silicon as a result of screening of electron-hole interactions. The coulomb-enhancement and the possible influence of other Auger processes renders a simple description of the Auger lifetime as a function of doping density and injection level impossible. Several parameterisations have been developed that account for the Coulomb-enhancement and the concentration of minority and majority carriers [196, 197, 199–201], but they tend to diverge from experimental data. A totally empirical parametrisation has been proposed by Kerr et al [162] that provides a best fit to both low and high-injection lifetime data available in the literature. It is seen as a three-particle process, where the probability of an electron-hole pair interacting with a third particle depends on the equilibrium concentration of free electrons and holes and the excess carrier density. This allows the following parametrisation:

\[
\tau_{\text{Auger}} = \frac{\Delta n}{np\left(1.8 \times 10^{-24} n_0^{0.65} + 6 \times 10^{-25} p_0^{0.65} + 3 \times 10^{-27} \Delta n^{0.8}\right)}. \tag{D.32}
\]

**Emitter recombination**

The emitter region is heavily doped in general, so that the recombination current can be simplified by two assumptions: Firstly, the minority carrier concentration is low ensuring that the recombination lifetime is independent of the injection level. Secondly, the recombination is most likely dominated by Auger processes. The recombination current is thus often expressed in terms of the emitter saturation current and the ratio between the \(np\) product under light excitation and in equilibrium. This gives rise to the following expression for the effective emitter lifetime:

\[
\tau_{\text{Emitter}} = \frac{qWn_i^2}{J_{0e}(N_A + \Delta n)}. \tag{D.33}
\]

**SRH recombination**

In Chapter 4, the external quantum efficiency of the photoconductance has been used to determine the surface recombination velocity (Section 4.3.2) and the emitter saturation current (Section 4.4.3). In both cases, the bulk lifetime of crystalline silicon has been estimated. A lower bound to the intrinsic bulk lifetimes can be assessed by combining Equation D.31 and D.32. This still leaves the process, which is in general more dominant in low injection: SRH recombination. Kerr et al. fitted a simple expression of the SRH lifetime proposed by Kendall [202] to experimental data of the bulk lifetime of high quality silicon. The expression is given by:
\[
\tau_{SRH} = \frac{\tau_{max}}{1 + \frac{N_A}{C_{ref}}}, \quad \text{(D.34)}
\]

where \( \tau_{max} = 35 \text{ ms} \) denotes the low-injection SRH lifetime measured in lightly-doped silicon and \( C_{ref} = 10^{16} \text{ cm}^{-3} \) is a fitting parameter \([159]\). Combining this expression with the formulas of the radiative and Auger component gives thus a upper limit to the total bulk lifetime.

### D.2 Capacitive effects in quasi-static voltage measurements

When measuring the quasi-steady state voltage, it is important to consider the time dependence of the excess carrier density in the device. Capacitive effects in the bulk and the space charge region can have a significant effect on the intensity-voltage curve, which have to be taken into account to accurately reconstruct the static I-V characteristics \([136, 137]\). Even though quasi-steady-state experiments are usually performed with light sources that have a very long decay time, transient effects can still have an impact if the carrier lifetime is greater than the dimming constant of the light source.

The capacitive effect in the base region is attributed to the change of the carrier density profile in the base region and can considerably influence the intensity-voltage curve at medium and high voltages. The junction capacitive effect, in turn, is associated with a time-dependence of the excess charges in the space-charge region and becomes dominant at lower injection levels. Both effects greatly impact on the device characteristics in experiments, where abrupt changes in the light excitation are present, as is the case in the open-circuit voltage decay technique \([203]\). Following the work of Kerr et al. and Cuevas et al. \([136, 137]\), a general formulism for the intensity-voltage curve is established that accounts for these effects. It thus allows reconstruction of the static I-V characteristic for transient, quasi-transient and quasi-steady-state voltage measurements.

**Balance equation of excess carrier charge**

To fully understand the impact of the capacitive effects, it is useful to consider first the balance of the excess carrier charge in the device. The excess carrier charge is commonly defined as the integrated excess carrier density times the charge \( q \). For example, in the base region with thickness \( W_b \), it is given by:

\[
Q_b = q \int_0^{W_b} \Delta n_b \, dx = q \Delta n_{at} W_b, \quad \text{(D.35)}
\]
where $\Delta n_{eq}$ is the average excess carrier concentration in the bulk region. The generation of excess carriers is balanced by their recombination, their change with time and their outflow of the device. If we express the change of excess carriers in forms of their charge rates, we obtain the following for the balance equation:

$$qG_{tot} = qU_{tot} + \frac{dQ_b}{dt} + \frac{dQ_{scr}}{dt} + J. \quad (D.36)$$

Here, $G_{tot}$ denotes the total generation, $U_{tot}$ the total recombination, $dQ_b/dt$ and $Q_{scr}/dt$ the changes of charges in the bulk and junction region, respectively, and $J$ the outflow of charge carriers.

**Base region capacitance**

When the rate of change of photo-generated charges exceeds the rate of change of the recombination, an excess charge is stored in the bulk. As the illumination decreases, the excess charge in the bulk is reduced alongside the generation and recombination rate. This change in integrated excess charges can not be extracted directly from a voltage measurement, unlike in a photoconductance measurement. However, the excess carrier density at the edge of the junction can be derived from the voltage using the following relationship:

$$np \approx \Delta n(0)[N_A + \Delta n(0)] = n_i^2 \exp\left(\frac{qV}{kT}\right). \quad (D.37)$$

Here, $n_i^2$ is the $pn$ product in equilibrium. For a p-type base region, $n \approx \Delta n$ and $p \approx N_A + \Delta n$. If a homogeneous carrier density profile prevails in the base, the carrier concentration at the junction edge equals the average excess carrier density in the base region and we can use Equation D.35 and D.37 to relate the excess base charge to the voltage across the junction [136]:

$$Q_b \approx \Delta n(0) \cdot W = \sqrt{N_A^2 + 4n_i^2 \exp\left(\frac{qV}{kT}\right) - N_A} \cdot W. \quad (D.38)$$

Note that for highly asymmetric carrier density profiles in the base region, this simplification can be very erroneous (see also the discussion in Section 3.3.1). The rate of change in excess charge stored in the bulk can be computed as [136]:

$$\frac{dQ_b}{dt} \approx \frac{q n_i^2 \exp\left(\frac{qV}{kT}\right) \cdot W}{kT \sqrt{N_A^2 + 4n_i^2 \exp\left(\frac{qV}{kT}\right)}} \cdot \frac{dV}{dt} = C_b \cdot \frac{dV}{dt}. \quad (D.39)$$
The relationship between the change in base charge and voltage can also be described in terms of the base capacitance $C_b$. Equation D.39 indicates that the change in base carrier charges is inversely proportional to the square root of the doping density and directly proportional to the change in voltage. The capacitive effect of the base is therefore expected to be more pronounced in high resistivity devices and under transient measurement conditions. This has been experimentally proven by Kerr et al. with solar cells fabricated on 90 Ωcm comparing transient and steady-state data [136].

**Junction capacitance**

The capacitive effect comes into play whenever the number of charges within the SCR region changes with time. The decaying light of a flash lamp entails a decrease in the voltage across the junction. This, in turn, reduces the excess carrier profile within the SCR region and widens its width towards its equilibrium value. During this process, part of the quasi-neutral region is engulfed in the SCR region, for which charge carriers have to be extracted from the edge of the SCR region. To calculate the change in charges, it is acceptable to consider an asymmetric, abrupt junction with higher emitter than base doping. In such a junction, the number of ionised dopant atoms $Q_{dop}$ is given by [137]:

$$Q_{dop} \approx \sqrt{2q\varepsilon_s N_A (\phi_0 - V)},$$  \hspace{1cm} (D.40)

where $\varepsilon_s$ is the permittivity of silicon, $N_A$ the doping density of the base, $\phi_0$ the electrostatic potential at equilibrium ($\phi_0 = \phi_v - 1.1 \text{ V}$ for typical solar cells) and $V$ is the voltage across the junction. The change of carriers stored in the junction is opposite in sign to the change of ionised dopant atoms [137]:

$$\frac{dQ_{scr}}{dt} = - \frac{dQ_{dop}}{dt} \approx \sqrt{\frac{q\varepsilon_s N_A}{2(\phi_0 - V)}} \cdot \frac{dV}{dt} = C_{scr} \cdot \frac{dV}{dt}. $$  \hspace{1cm} (D.41)

The relationship between change in charge and voltage can alternatively be expressed in terms of the junction capacitance $C_{scr}$ similar to the formulation in the base region. The modulation of the charge in the SCR is proportional to the square root of the base doping and the change in voltage. The capacitive effect will therefore impact more on devices made on low resistivity material and will be more present in experiments with a rapid change in voltage. The capacitive effect has been observed by Cuevas et al. on a solar cell made on a 0.1 Ωcm silicon wafer [137].
Influence on the static intensity-voltage curve

By scanning the voltage of a device subjected to a dimming illumination, a relationship between light intensity and voltage is established that can be used to reconstruct the dark I-V characteristic. The intensity is commonly derived via Equation B.9 and thus represents a purely ‘optical’ parameter, i.e. the integrated energy flux of the incident photons. If a steady-state light source is used, this so-derived intensity certainly leads to intensity-voltage curves that represent the true behaviour of the device. However, if transient effects influence the balance between generation and recombination of charge carriers, the intensity does not account for the excess charges stored in the base and junction regions. In a static measurement, the intensity that represents the true I-V characteristic is proportional to the total generation rate. In transient or quasi-transient conditions, by contrast, the factor that should be used to reconstruct the I-V characteristics is proportional to the total generation rate. Thus, by using these proportionalities, a corrected intensity \( I_{\text{corr}} \) can be derived by:

\[
\frac{I_{\text{corr}}}{I} = \frac{U_{\text{tot}}}{G_{\text{tot}}} \tag{D.42}
\]

Using the balance equation D.36 in open-circuit \((J = 0)\) together with Equations D.39 and D.41, we obtain:

\[
I_{\text{corr}} = \frac{G_{\text{tot}} - (C_b + C_{\text{scr}}) \cdot \frac{dV}{dt}}{G_{\text{tot}}} \cdot I \tag{D.43}
\]

Note that the capacitive effect has a similar effect on transient and quasi-transient lifetime measurements. Hence, a general formulism to calculate the effective lifetime has to be used that includes the rate of charges stored in the base and junction region [137, 143].

D.3 Temperature dependence of silicon material parameters

Density of states of conduction and valence band

The SRH formulism requires the knowledge of the electron and hole densities \( n_1 \) and \( p_1 \) (Equation 3.3 on page 118). These densities are a function of the effective densities of states in the conduction and valence band, \( N_C \) and \( N_V \), respectively. The temperature dependence of these parameters originates from a direct dependence of the order \( T^{3/2} \) and the temperature dependence of the effective masses in the conduction and valence band [204]. At temperatures between 200–500 K, this dependence increases the expo-
nent slightly. In detail, the following expressions can be ascribed to $N_C$ and $N_V$ in this temperature range [204]:

$$N_c(T) = 2.86 \times 10^{19} \cdot \left( \frac{T}{300} \right)^{1.58} \text{cm}^{-3},$$

$$N_v(T) = 3.10 \times 10^{19} \cdot \left( \frac{T}{300} \right)^{1.85} \text{cm}^{-3}. \quad (D.44)$$

**Intrinsic carrier density**

The intrinsic carrier density combines the temperature dependence of the density of states, the band-gap and the Boltzmann factor $\exp\left(-\frac{E_g}{kT}\right)$. Accurate measurements have been made by Misiakos et al. in the temperature range 78–340 K [205]. The best fit to their data is given by:

$$n_i(T) = 5.29 \times 10^{19} \cdot \left( \frac{T}{300} \right)^{2.54} \exp\left(-\frac{6726}{T}\right). \quad (D.45)$$

This fit leads to a value of $9.7 \times 10^9$ cm$^{-3}$ at 300 K. This is lower than the value $1.00 \times 10^{10}$ cm$^{-3}$ determined by Sproul et al. [206]. As Altermatt et al. demonstrated, their measurements were influenced by band-gap narrowing [207]. If this effect is accounted for in the measurements of Sproul et al., the value of the intrinsic carrier density is lowered to $9.65 \times 10^9$ cm$^{-3}$, which is very consistent with the results of Misiakos et al.

**Mobility, resistivity, doping density and diffusion constant**

The main temperature dependence of the resistivity, the doping density and the diffusion constant arise from their dependence on the mobility of electrons and holes. In weak fields, the mobility depends on the doping concentration and on the temperature. Not only are the mobilities of electrons and holes different, they also diverge if the carriers are in the minority or majority. In silicon, the mobilities are generally expressed in the Caughey-Thomas form [208]:

$$\mu = \mu_{\text{min}} \left( \frac{T}{300} \right)^{\beta_1} + \frac{(\mu_{\text{max}} - \mu_{\text{min}}) \left( \frac{T}{300} \right)^{\beta_2}}{1 + \left( \frac{N_A}{N_{\text{ref}} \left( \frac{T}{300} \right)^{\beta_3}} \right)^{\xi \left( \frac{T}{300} \right)^{\beta_4}}}. \quad (D.46)$$

Here, the maximum mobility $\mu_{\text{max}}$ is the same regardless if the carriers move under minority or majority conditions. However, the minimum mobility $\mu_{\text{min}}$ changes from type...
D Models describing recombination in silicon and temperature dependence of silicon parameters

...to type and from minority to majority carriers. \(N_{\text{ref}}\) denotes the reference doping density, while \(\xi\) is a fit parameter. The \(\beta\)'s are part of the thermal model that relates the actual temperature to the standard condition. Table D.3 lists the values carriers taken from PCID [41] for all parameters and classifies them for electrons, holes, minority and majority.

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<thead>
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<th>Quantity</th>
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</tr>
<tr>
<td>(\mu_{\text{min}})</td>
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</tr>
<tr>
<td>(N_{\text{ref}})</td>
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<td>(2.82 \times 10^{17})</td>
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<tr>
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<tr>
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</tr>
</tbody>
</table>

Table D.3: Values used in the mobility model (taken from PCID [45]).

For the determination of the resistivity and the doping density, the mobility of the majority carriers are the most important. To obtain the resistivity \(\rho\), the doping density has to be known independently from the mobility:

\[
\rho = \frac{1}{(q\mu N_A)}.
\]  

(D.47)

The reverse of this formula can be used to obtain the doping density. As the latter also forms part of the mobility model, one has to resort to a iteration to obtain \(N_A\). The diffusion constant, in turn, is determined by the minority carrier flow and is related to the mobility by the Einstein equation:

\[
D_n = kT q \cdot \mu.
\]

(D.48)

Thermal velocity

The thermal velocities of electron and holes, \(v_{\text{th},e}\) and \(v_{\text{th},h}\), appear in the SRH model as part of the description of the fundamental electron and hole lifetimes, \(\tau_{\text{no}}\) and \(\tau_{\text{po}}\) (Equation 3.4 on page 119). They are necessary to calculate capture cross sections from these capture rates. The thermal velocity of electrons and holes is directly proportional...
to $T^{1/2}$ and indirectly temperature dependent via the thermal effective masses of the conduction and valence band, $m_{tc}^*$ and $m_{tv}^*$, respectively. The exact description of $v_{th,e}$ and $v_{th,h}$ is found to be [204, 209]:

$$v_{th,e} = \left( \frac{8kT}{\pi m_{tc}^*} \right)^{1/2},$$
$$v_{th,h} = \left( \frac{8kT}{\pi m_{tv}^*} \right)^{1/2},$$  \hspace{1cm} (D.49)

where $m_{tc}^*$ and $m_{tv}^*$ are determined by [129, 204]:

$$m_{tc}^* = \left( \frac{4m_i^*}{1 + \left( \frac{m_i^*}{m_t^*} \right)^{1/2} \frac{1}{\sin(\delta) \delta}} \right)^{1/2},$$
$$m_{tv}^* = (0.37 + 1.98 \times 10^{-5} T^2 - 2.59 \times 10^{-7} T^3 + 1.42 \times 10^{-9} T^4$$
$$- 3.92 \times 10^{-12} T^5 + 5.41 \times 10^{-15} T^6 - 2.96 \times 10^{-18} T^7) / m_0. \hspace{1cm} (D.50)

Here, $m_l^*$ and $m_t^*$ are the longitudinal and transverse effective masses associated with the conduction band minima and $m_0$ is the electron rest mass. Equation D.51 sheds more light on these parameters:

$$m_0 = 9.109 \times 10^{-31},$$
$$m_t^* = 0.9163 m_0,$$
$$m_l^* = 0.1905 m_0 E_g(0)/E_g(T),$$
$$\delta = \left( \frac{m_t^*-m_l^*}{m_t^*} \right)^{1/2}. \hspace{1cm} (D.51)$$

The model of Faessler et al. (Equation C.14) has been employed here for the band-gap $E_g(0)/E_g(T)$.

E Analysis of the spectral response with the one-dimensional continuity equation

The continuity equation is the backbone of all one-dimensional models involved in the description of the spectral response used in this work, be it the voltage or the photoconductance response. In this section, the solution for the continuity equation for a general generation rate is reviewed. The exact solution of the excess carrier density that enters the analytical model of the spectral photoconductance is given next. Finally, the extraction
of the surface recombination velocity from this model is explained in detail.

Solution of the continuity equation for a general generation rate

The continuity equation for a spatially and wavelength dependent excess carrier density for a p-type silicon wafer under low-injection is given by:

$$D_n \frac{\partial^2 \Delta n}{\partial x^2} (x, \lambda) - \frac{D_n}{L_n^2} \Delta n (x, \lambda) + f_{abs}(x, \lambda) N_{ph}(\lambda) = 0. \quad (E.52)$$

Here, $D_n$ denotes the diffusion constant of electrons and $L_n$ the minority carrier diffusion length. The generation rate is written in terms of the absorption fraction and the photon flux. If the absorption fraction can be expressed as a multi-exponential function, as it is done in Equations C.17, C.19 and C.26, the generation solution for the excess carrier density, regardless of the boundary conditions, can be written as:

$$\Delta n(x, \lambda) = A(\lambda) \cosh \frac{x}{L_n} + B(\lambda) \sinh \frac{x}{L_n} + f(x, \lambda), \quad (E.53)$$

where $f(x, \lambda)$ is a function that contains all optical information:

$$f(x, \lambda) = N_{ph}(\lambda) \sum_i \frac{L_n^2 / D_n a_i(\lambda)}{1 - L_n^2 b_i^2(\lambda)} e^{b_i(\lambda) x}. \quad (E.54)$$

The constant $i$ stands for the number of exponentials that determine the absorption fraction. In the simplest model that neglects any internal reflection, $i = 1$ and the parameters $a_1$ and $b_1$ are given by Equations C.17: $a_1 = (1 - R) \alpha$, $b_1 = -\alpha$. For the optical model of a planar cell and the optical model of Basore, the parameters $a_i$ and $b_i$ are listed in Section C.2. This general form for the optical parameters offers the possibility to describe the solution in a very compact form and to specify the exact optical model for each case separately. The parameters $A$ and $B$ depend on the boundary conditions as well. The special case of non-diffused wafers with front and rear surface recombination rate at the boundaries is discussed next.

Solution of the continuity equation for non-diffused wafers

In the case of a front and back surface recombination rate describing the balance of the carrier density at the boundaries of the region of interest, the following conditions apply:
The boundaries can be the surfaces of the wafer or a virtual surface that separates a diffused region from the bulk region. Using this boundary assumption, the parameters $A$ and $B$ can be deduced:

\[
A(\lambda) = -\left( \frac{S_f L_n}{D_n} f(0, \lambda) - L_n f'(0, \lambda) \right) \varphi_1 + \frac{S_b L_n}{D_n} f(W, \lambda) + L_n f'(W, \lambda) \frac{S_f L_n}{D_n} \varphi_2, \]
\[
B(\lambda) = \left( \frac{S_f L_n}{D_n} f(0, \lambda) - L_n f'(0, \lambda) \right) \varphi_2 - \left( \frac{S_b L_n}{D_n} f(W, \lambda) + L_n f'(W, \lambda) \right) \frac{S_f L_n}{D_n} \varphi_2, \tag{E.56}
\]

where $\varphi_1$ and $\varphi_2$ are given by:

\[
\varphi_1 = \sinh \frac{W}{L_n} + \frac{S_f L_n}{D_n} \cosh \frac{W}{L_n},
\]

\[
\varphi_2 = \frac{S_f L_n}{D_n} \sinh \frac{W}{L_n} + \cosh \frac{W}{L_n}. \tag{E.57}
\]

In the analytical model of the spectral photoconductance, the external quantum efficiency of the photoconductance is expressed in terms of the excess carrier density at the boundaries, $\Delta n(0, \lambda)$ and $\Delta n(W, \lambda)$. The previous evaluations allow us to specify these further as:

\[
\Delta n(0, \lambda) = A(\lambda) + f(0, \lambda),
\]

\[
\Delta n(W, \lambda) = A(\lambda) \sinh \frac{W}{L_n} + B(\lambda) \cosh \frac{W}{L_n} + f(W, \lambda). \tag{E.58}
\]

**Extraction of the surface recombination velocity**

With these formulas in hand, we are just one step away from extracting the surface recombination velocity $S = S_f = S_b$ from the external quantum efficiency of the photoconductance. In this work, the extraction is facilitated by assuming a theoretical bulk lifetime. An upper limit of the bulk lifetime in high-quality silicon can be estimated by using the equations for the radiative, Auger and SRH lifetime developed in Section D.1. The radiative and Auger lifetime depend here on the excess carrier density that prevails
in the wafer. This parameter is not available directly through the measurement, in view of its space dependence. But the average excess carrier density can be obtained from the constant photoconductance at which the external quantum efficiency is deduced.

First, it is assumed that the excess electrons and holes are equally balanced and that their mobilities depend not on the excess carrier density. This permits to calculate a first approximation of $\Delta n_{av} = \frac{1}{W} \int_0^W \Delta n \, dx$ via:

$$\Delta \sigma = \int_0^W q (\mu_n \Delta n + \mu_p \Delta p) \, dx \approx q (\mu_n + \mu_p) \int_0^W \Delta n \, dx.$$  \hspace{1cm} (E.59)

Next, the actual carrier density dependence of the mobility is accommodated for by an empirical fit [201]:

$$\mu_n + \mu_p = 1800 \frac{1 + \exp \left[ 0.8431 \cdot \ln \left( \frac{\Delta n + N_A}{1.2 \times 10^{18}} \right) \right]}{1 + 8.36 \exp \left[ 0.8431 \cdot \ln \left( \frac{\Delta n + N_A}{1.2 \times 10^{18}} \right) \right]}.$$ \hspace{1cm} (E.60)

By using an iteration, $\Delta n_{av}$ can be estimated in a self-consistent way. This injection level is taken to determine the bulk lifetime. Knowing the latter, $S$ is extracted from the analytical model of the spectral photoconductance by means of a least-square fit.
List of Publications

Publications arising from the work in this thesis

Refereed journal papers


Refereed papers presented at international conferences


Submitted publications


Other related publications

Refereed journal papers


Refereed papers presented at international conferences


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