Luminescence Imaging Techniques for Silicon Photovoltaics

Dissertation

zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.)

vorgelegt von David Kiliani
an der Universität Konstanz
Mathematisch-Naturwissenschaftliche Sektion
Fachbereich Physik

1. Referent Prof. Dr. Giso Hahn
2. Referent Prof. Dr. Thomas Dekorsy

Konstanzer Online-Publikations-System (KOPS)
URL: http://nbn-resolving.de/urn:nbn:de:bsz:352-258608
Cover Picture: Multicrystalline silicon wafer illuminated by the LED panel, with a schematic plot of the normalized time-resolved photoluminescence emission under periodic excitation. The minority carrier lifetime is color-coded on the curve surface.
# Contents

**Table of Contents**

1 

**List of Acronyms**

V

**List of Symbols**

VII

**List of Samples**

IX

**Introduction**

1

1 Semiconductor Basics and Luminescence

1.1 Charge Carriers in Silicon ............................... 7
  1.1.1 Absorption of Light ................................. 9
  1.1.2 Doping ........................................... 11
  1.1.3 p-n Junction in Thermal Equilibrium .................. 12
  1.1.4 p-n Junction under Illumination .................... 13
  1.1.5 Charge Carrier Lifetime and Recombination Mechanisms ... 15
  1.1.6 Effective Lifetime ................................ 17
  1.1.7 Minority Charge Carrier Diffusion .................. 19
1.2 Luminescence in Silicon ................................ 19
  1.2.1 Excess Charge Carrier Profiles for EL and PL .......... 20
  1.2.2 Luminescence Intensity ............................ 26

2 The Luminescence Imaging Setup

2.1 Camera ................................................. 31
  2.2 Camera Mounting ..................................... 33
  2.2.1 Filters ........................................... 34
  2.3 Sample Placement and Excitation ........................ 36
  2.3.1 Electroluminescence ............................... 37
A Source Code 127

A.1 Shutter Wheel Excitation Controller Firmware . . . . . . . . . . . . . 127
  A.1.1 controller.h . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 127
  A.1.2 controller.cpp . . . . . . . . . . . . . . . . . . . . . . . . . . . . 128

A.2 Image Intensifier Excitation Controller Firmware . . . . . . . . . . . . 137
  A.2.1 controller.h . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 137
  A.2.2 controller.cpp . . . . . . . . . . . . . . . . . . . . . . . . . . . . 138

A.3 TR-PLI Evaluation Algorithms: Python C Module . . . . . . . . . . . . 143
List of Acronyms

BSF     back surface field
CCD     charge coupled device
CDI     carrier density imaging
Cz-Si   Czochralski grown silicon
EL      electroluminescence
ELI     electroluminescence imaging
EQE     external quantum efficiency
FWHM    full width at half maximum
IIU     image intensifier unit
ILM     infrared lifetime mapping
LBIC    light beam induced current
LED     light emitting diode
MCP     micro channel plate
µPCD    microwave induced photoconductance decay
PCB     printed circuit board
PDE     partial differential equation
PL      photoluminescence
PLI     photoluminescence imaging
PLL     phase-locked loop
PWM     pulse width modulation
QE      quantum efficiency
QFL     quasi Fermi level
QSSPC   quasi steady state photoconductance
QSSPL   quasi steady state photoluminescence
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNR</td>
<td>signal to noise ratio</td>
</tr>
<tr>
<td>SRH</td>
<td>Shockley-Read-Hall (recombination)</td>
</tr>
<tr>
<td>TEC</td>
<td>thermo-electric cooler</td>
</tr>
<tr>
<td>TR-PLI</td>
<td>time-resolved photoluminescence imaging</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>a.u.</td>
<td>arbitrary units</td>
</tr>
<tr>
<td>eq.</td>
<td>equation</td>
</tr>
<tr>
<td>fig.</td>
<td>figure</td>
</tr>
<tr>
<td>mc-Si</td>
<td>multicrystalline silicon</td>
</tr>
</tbody>
</table>
List of Symbols

$A$ camera sensitivity factor
$A$ area fraction of circular aperture
$B$ coefficient of radiative recombination
$D$ shutter duty cycle
$E$ energy
$E_c$ energy of conduction band edge
$E_f$ Fermi energy
$E_g$ band gap energy
$E_v$ energy of valence band edge
$FF$ fill factor
$F$ excitation photon flux
$G$ carrier generation rate
$H$ shutter transmissivity
$I$ camera image intensity
$J$ current
$I_0$ diode saturation current
$L$ diffusion length
$N$ doping concentration
$N_A$ acceptor doping concentration
$N_D$ donator doping concentration
$Q$ QSSPC sensitivity
$R$ sample reflectivity
$R$ recombination rate
$R_{ser}$ series resistance
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{sh}$</td>
<td>shunt resistance</td>
</tr>
<tr>
<td>$S$</td>
<td>surface recombination velocity</td>
</tr>
<tr>
<td>$\mathcal{T}$</td>
<td>excitation cycle period</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$U$</td>
<td>voltage</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>$f$</td>
<td>excitation frequency</td>
</tr>
<tr>
<td>$j_{sc}$</td>
<td>short circuit current density</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$l$</td>
<td>absorption length</td>
</tr>
<tr>
<td>$n$</td>
<td>electron density</td>
</tr>
<tr>
<td>$n_0$</td>
<td>electron density in thermal equilibrium</td>
</tr>
<tr>
<td>$n_i$</td>
<td>intrinsic electron density</td>
</tr>
<tr>
<td>$p$</td>
<td>hole density</td>
</tr>
<tr>
<td>$p_0$</td>
<td>hole density in thermal equilibrium</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$w$</td>
<td>sample thickness</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>coefficient of absorption</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>photon</td>
</tr>
<tr>
<td>$\Delta n$</td>
<td>excess minority charge carrier density</td>
</tr>
<tr>
<td>$\Delta \eta$</td>
<td>quasi Fermi level splitting</td>
</tr>
<tr>
<td>$\mu$</td>
<td>chemical potential</td>
</tr>
<tr>
<td>$\tau$</td>
<td>minority charge carrier lifetime</td>
</tr>
<tr>
<td>$\tau_{eff}$</td>
<td>effective minority charge carrier lifetime</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>luminescence intensity</td>
</tr>
<tr>
<td>$\varphi_n$</td>
<td>phase shift of image $n$</td>
</tr>
</tbody>
</table>

VIII
List of Samples

The measurement techniques presented in this work have been tested on a wide variety of samples. However, to facilitate comparison, all measurements shown in this work have been performed on a small set of samples. They were chosen to be a representative subset of the whole spectrum of wafers and solar cells typically found in silicon photovoltaics.

A. multicrystalline Si wafer, p-type $2 \Omega \text{cm}$
   size*: $5 \times 5 \text{cm}^2$, $200 \mu\text{m}$ thick
   saw damage removed
   activated SiN$_x$:H passivation on both sides

B. multicrystalline Si wafer, p-type $1 \Omega \text{cm}$
   size: $5 \times 5 \text{cm}^2$, $150 \mu\text{m}$ thick
   saw damage removed and P-gettered
   activated Al$_2$O$_3$ passivation on both sides

C. floatzone Si wafer, p-type $2 \Omega \text{cm}$
   size: $5 \times 5 \text{cm}^2$, $525 \mu\text{m}$ thick
   activated Al$_2$O$_3$ passivation on both sides

D. multicrystalline Si wafer
   size*: $5 \times 5 \text{cm}^2$, $200 \mu\text{m}$ thick
   unprocessed as-cut wafer
   no surface passivation

*The central area of a larger wafer was measured.
monocrystalline Si solar cell
size: 12.5 × 12.5 cm², 200 μm thick

\( j_{sc} = 37.1 \text{ mA/cm}^2, \ V_{oc} = 630 \text{ mV}, \ FF = 78.3 \% \)
screen printed metallization, full Al-BSF
homogeneous 50 Ω/□ emitter

monocrystalline Si solar cell
size: 12.5 × 12.5 cm², 200 μm thick

\( j_{sc} = 38.0 \text{ mA/cm}^2, \ V_{oc} = 640 \text{ mV}, \ FF = 77.8 \% \)
screen printed metallization, full Al-BSF
selective emitter, 30 Ω/□ etched back to 65 Ω/□

multicrystalline Si solar cell
size: 12.5 × 12.5 cm², 200 μm thick

screen printed metallization, full Al-BSF, solder pads
homogeneous emitter
Introduction

In view of the increasing price and climate impact of fossil fuels, renewable energy sources have gained significant use in the last decade. A rapidly increasing part of this renewable energy is generated by direct photovoltaic energy conversion using solar cells [1]. Most of the currently produced and installed solar cells are made from crystalline silicon, due to the high efficiency and module lifetime obtainable with this technology at reasonable cost. For the ongoing reduction of solar cell price per watt of power generation capacity, in-depth characterization of silicon wafers and solar cells, both in production and in research and development is essential. Many characterization techniques exist in this area, however most of them do not offer spatially resolved information or require long measurement times. To evaluate inhomogeneous materials like multicrystalline silicon (mc-Si) wafers or the metallization structures on solar cells, an imaging technique has great advantages.

One such technique is the measurement of luminescence emission with a digital camera. As the whole sample is imaged simultaneously, the total acquisition time is usually ~1 s at a high spatial resolution. However, due to the low luminescence activity of silicon, very sensitive cameras are required, which is the reason this camera based approach was only made possible in recent years by the advances in digital camera technology. Compared to luminescence imaging, other spatially resolved characterization methods using sequential point-by-point mapping of the wafer surface like microwave induced photoconductance decay (µPCD) [2] or light beam induced current (LBIC) [3] require 2 to 3 orders of magnitude more time. The thermal imaging method known as infrared lifetime mapping (ILM) [4] or carrier density imaging (CDI) [5] is similarly fast as luminescence imaging, but it requires more expensive thermal camera equipment and lacks the high resolution of up-to-date near-infrared cameras used for luminescence imaging.
Introduction

The first spatially resolved measurements of luminescence on silicon wafers used for photovoltaics were published around 2000 by Koshka et al. [6] and Ostapenko et al. [7]. A scanning setup was used to map the photoluminescence (PL) emission under local illumination by an infrared laser. Due to the high illumination intensity of $>10^3$ suns, a sufficiently strong PL signal for spectrally resolved measurements was obtained and maps of both band-to-band PL and defect band PL were studied. However, the required high excitation intensity did not allow the measurement of device parameters under realistic solar cell operating conditions of $\sim 1$ sun.

In 2005, Fuyuki et al. published the first results of electroluminescence imaging (ELI) on solar cells, using a CCD camera and electric excitation [8]. Only one year later, camera based photoluminescence imaging (PLI) of a whole wafer using a homogenized laser beam was published by Trupke et al. [9]. While scanning PL was not widely adopted as a characterization method in silicon photovoltaics, the attractiveness of luminescence imaging as a fast, non-destructive, spatially resolved characterization method led to a boost of activity in the following years. Since 2006, numerous techniques based on luminescence imaging have been published that allow for a spatially resolved determination of many device parameters, both for silicon wafers and finished solar cells. To give an overview of the current state of research, a survey of published literature categorized by the obtained quantity is given in the following paragraphs.

For passivated and unpassivated wafers, PLI can be applied to characterize recombinative effects. The first PLI article by Trupke et al. already showed a map of the effective minority charge carrier lifetime $\tau_{\text{eff}}$ obtained by calibrating the PL intensity with an integral quasi-steady-state photoluminescence (QSSPL) measurement [9]. This was later refined by Herlufsen et al., integrating a quasi-steady-state photoconductance (QSSPC) sensor directly into the measurement setup [10] and by Giesecke et al., where averaging procedures for QSSPL calibration were introduced [11]. Time-resolved PLI measurements on silicon wafers were published in 2010 by our group [12] and Herlufsen et al. [13] and refined in the following years [14–16]. To determine quantitative images of the carrier lifetime in whole silicon bricks before wafer sawing, two different approaches have been published. The method by Mitchell et al. [17, 18] is based on PL reabsorption inside the sample, while Herlufsen et al. [19] used the same approach of dynamic PLI previously applied on wafer level to determine transient carrier lifetime maps.
Introduction

of bricks.

The fact that PL reabsorption in combination with carrier density profiles inside the sample leads to changes in the emitted PL spectrum has been used by Würfel et al. in 2007 to determine the diffusion length in solar cells from electroluminescence (EL) images [20]. Subsequent publications by Giesecke et al. [21, 22] improved on this to account for several experimental difficulties. A different approach of Hinken et al. [23] is based on the changing carrier profile of a cell for short circuit and open circuit conditions under PL excitation. The reabsorption based method was also successfully applied to silicon bricks by Mitchell et al. [17, 18].

As Giesecke et al. demonstrated, EL reabsorption can not only be used to characterize diffusion length, but also for a separation of bulk and surface recombination. Based on several measurements with different optical filters and sample orientations, separate maps of bulk and surface recombination activity can be calculated [24]. A method proposed by Haug et al. [25] for the characterization of dielectric surface passivation measures the PL emission as a function of an applied bias field.

On the basis of carrier lifetime maps from PLI, Macdonald et al. [26] used the variation in recombination activity of different states of interstitial iron to obtain density maps of iron in silicon wafers. The approach by Herlufsen et al. [27] for interstitial iron mapping does not require absolute lifetimes but instead evaluates the time constant of light induced FeB splitting, measured with PLI. Luminescence imaging can also be applied to measure the concentration of desired dopant atoms, if the effective carrier lifetime is known. This was demonstrated by Mitchell et al. [17] on silicon bricks, where \( \tau_{\text{eff}} \) was known from PL reabsorption measurements. The technique shown by Lim et al. [28] determines dopant concentration maps by bringing \( \tau_{\text{eff}} \) to a defined, small value due to increased surface recombination. An approach by Yang et al. [29] which also uses PLI on unpassivated wafers allows for the imaging of emitter saturation current. Crystallographic properties extracted from PL images include the crystal orientation in mc-Si wafers estimated from the orientation dependant surface energy [30] and the direction of crystal solidification [31].

On cell level, many publications have dealt with the spatially resolved measurement of series resistance \( R_{\text{ser}} \). This can either be done solely from EL images [32–35], or from a combination of illumination and electrical current extraction [36–42].
Introduction

A pure PL measurement without electrical connections to the cell is not suitable for this task, as a homogeneous illumination does not lead to currents and voltage gradients in the sample. An exception is the method of Wagner et al. [43], where the sample is only partially illuminated and serves as its own current sink.

In contrast to series resistance, parallel resistance in solar cells is not as easily accessible from EL images, as the current flow through a shunt can only be detected indirectly from the voltage drop in its vicinity. Several articles describe this process for localization [44, 45] and quantification [46, 47] of shunts.

A very important parameter of Si solar cells is the diode characteristic, i.e., the local saturation current density $J_0$, as it defines the obtainable voltage of the device. This is often obtained in combination with the series resistance measurement, either from EL images [35, 48-50] or more recently using PL with electrical current extraction [38, 39, 41, 42], which is generally more robust and yields better results. Notable in this category is the method published by Shen et al. [41], as it allows for a spatially resolved measurement of $R_{ser}$, saturation current densities $J_{01}$ and $J_{02}$ from a two diode model, as well as derived parameters like voltage, efficiency and fill factor.

Another way to characterize the diode behaviour of solar cells is the application of a reverse bias voltage. The luminescence emitted from hot carriers at diode breakdown sites is voltage dependent and can be used to characterize the defect [51-53]. Alternatively, the degree of polarization of emitted EL may be used to characterize recombination active areas [54].

The focus of this work lies on the development of new methods for the quantitative characterization of silicon wafers and solar cells, based on luminescence imaging. The PLI method by itself allows only a relative measurement of carrier density and carrier lifetime, as the absolute signal intensity depends on many other parameters and sample properties, which are hard to quantify [21]. This leads to the requirement of a separate measurement to calculate effective carrier lifetime from the PL intensities recorded by the camera. The development of a time-resolved PL imaging technique presented in this work circumvents this additional measurement and allows for a calibration-free measurement of minority carrier lifetime. Similarly, the commonly used series resistance imaging methods based on ELI return only an overall value, which motivated the development of a
technique to separately quantify the series resistance contributions of finger grid, finger contacts and emitter.

In chapter 1, the physical principles of silicon semiconductors and their luminescence emission are described. The following chapter covers the experimental details and design considerations of the measurement setup. It also describes a method for the lifetime-calibration of PL images using QSSPC measurements, followed by a comparison of InGaAs charge coupled device (CCD) cameras and their application for defect band luminescence measurements.

A method to quantitatively differentiate between several contributing factors of series resistance is presented in chapter 3. The local solar cell voltage is calculated from EL images and fitted with a suitable two-dimensional finite differences model of the solar cell. The series resistance of different parts of the solar cell can then be obtained from the resulting set of model parameters.

Chapter 4 covers the newly developed method of time-resolved photoluminescence imaging (TR-PLI) on silicon wafers. After an explanation of the physical principles and the algorithm used to calculate effective carrier lifetimes from the PL images, three different measurement setups are presented and compared with their respective advantages and disadvantages. A detailed section with measurement results illustrates the obtainable lifetime maps and shows beneficial measurement parameters. The chapter closes with a quantitative comparison of TR-PLI to established lifetime measurement techniques.
1 Semiconductor Basics and Luminescence

In this chapter, the relevant basics to understand and quantitatively explain luminescence measurements of crystalline silicon samples will be presented. In agreement with the general scope of this work, the focus is on silicon solar cells and photovoltaic applications, but most concepts are equally applicable to other uses of silicon. To keep this introduction short, only topics which are relevant to more than one of the following chapters are covered here. For a more comprehensive description of the basics of silicon photovoltaics, a variety of books are available [55–57].

1.1 Charge Carriers in Silicon

The quantum mechanical states of electrons in a crystalline solid state body like silicon can be described by the band model. It is based on solutions $\Psi_k$ of the Schrödinger equation for the periodic potential of the crystal atoms and the associated energy values $E_k$ [58]. Other than a single atom, the weak periodic potential in a crystal does not produce discrete energy states but a continuum of possible energy values $E_k$, each belonging to a certain crystal momentum $k$. As the solutions $\Psi_k$ according to the Bloch theorem are a product of the solution for free electrons and a periodic part [59], they form a smooth “band” when plotted over $k$. A plot of all possible $E_k$ over $k$ is called the band structure of a solid state material. For crystalline silicon, it is shown in fig. 1.1.

The occupation probability in thermal equilibrium of these possible states is determined by the Fermi distribution

$$f_e(E) = \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1},$$

(1.1)
where $k_B$ is the Boltzmann constant and $T$ the temperature of the solid. The chemical potential $\mu$ is mainly defined by the amount of electrons in the solid. At room temperature or below, states with $E \gg \mu$ have a very low probability of being occupied, while nearly all states $E < \mu$ are occupied. The Fermi energy $E_f$, which is defined as the energy where $f_e(E) = \frac{1}{2}$, in this case equals the chemical potential $\mu$.

The band structure in combination with $E_f$ determines the electronic behaviour of a solid. If $E_f$ intersects with a band, electrons at $E_f$ can reach free states with very little additional energy. Therefore, a small external electric field is sufficient to favor states of corresponding momentum and cause a net current.

If, however, $E_f$ lies inside a band gap where no electronic states exist, a net current flow can not be easily effected. The electrons with the highest energy state, which are closest to a free electronic state, are at the top of the so called valence band, which is the band below the band gap. Virtually all states in this band are occupied. The nearest free states lie in the conduction band, which is the band directly above the band gap and is almost unoccupied. The energy difference between those two levels $E_v$ and $E_c$ is called the band gap energy $E_g = E_c - E_v$.

For crystalline silicon at room temperature, it has a value of $E_g = 1.12 \text{eV}$ and can be seen in fig. 1.1. Due to this separation of occupied and free states, current transport by electrons near $E_f$ as described above cannot occur in this case.

A non-vanishing intrinsic occupation of the conduction band with electrons stems from thermal broadening of the Fermi distribution according to eq. (1.1). Each electron which is excited to the conduction band also leaves a free electronic state
in the valence band. These free states are commonly called holes. They may also contribute to the current transport, as other electrons in the valence band occupy the free state, forming a new hole at a slightly different energy and crystal momentum. Effectively, the hole behaves like a charge carrier with the positive elementary charge. The densities of these free charge carriers are denoted by \( n \) for negatively charged electrons and \( p \) for positively charged holes.

For \( E_g \) of the order 1 V and the thermal energy \( k_B T = 25 \text{ meV} \) at room temperature, the concentration of these free charge carriers is very small. Only this small number of electrons and holes can gain energy in an external field, switch states within the band and so contribute to net current flow. For this reason, such materials are called semi-conductors. At \( E_g > 4 \text{ V} \), the exponentially decreasing amount of free charge carriers becomes negligible and the material is an insulator.

The intrinsic carrier concentration \( n_0 = p_0 = n_i \) depends on the band gap energy \( E_g \), the temperature \( T \), as well as the density of states in the valence band \( D_v(E) \) and conduction band \( D_c(E) \). It is given by the convolution of the Fermi distribution and the density of states:

\[
    n_i = \int_{E_c}^{\infty} \frac{D_c(E)}{\exp\left(\frac{E-E_f}{k_BT}\right) + 1} \, dE = \int_{-\infty}^{E_c} \frac{D_v(E)}{\exp\left(\frac{E-E_f}{k_BT}\right) + 1} \, dE. \tag{1.2}
\]

For pure crystalline silicon at room temperature, it has a value of \( n_i \approx 10^{10}/\text{cm}^3 \) [55].

### 1.1.1 Absorption of Light

There are different ways to excite electrons in a semiconductor across the band gap. One process, which is always present, is thermal excitation. It leads to the intrinsic carrier density from eq. (1.2). Another possibility is the photo effect—the absorption of photons by electrons—which was first described by Einstein in 1905 [61] and later applied to semiconductors [62]. The basic process is the absorption of a single photon by a single electron, where the electron absorbs the whole energy \( E_\gamma \) and momentum \( k_\gamma \) of the photon. This is only possible if an occupied electronic state at \( (E,k) \) and a free state at \( (E + E_\gamma, k + k_\gamma) \) exist. So except for the usually rare case of free carrier absorption, where an electron in the conduction band absorbs the photon, only light with \( E_\gamma > E_g \) can be absorbed by a
Semiconductor Basics and Luminescence

However, for silicon the situation is more complicated. As can be seen from the band structure diagram in fig. 1.1, the maximum of the valence band and the minimum of the conduction band are not at the same crystal momentum. The momentum of a photon is not sufficient for the difference, so an additional transfer of momentum is required to absorb photons with $E_\gamma$ near $E_g$. This momentum is carried by a phonon, which may be either generated or absorbed in the process. The small amount of energy transferred by the phonon leads to a broadening of the light absorption edge, as the concurrent absorption of a phonon may enable a photon with less energy than $E_g$ to excite an electron across the band gap.

Semiconductors with this kind of band structure, where light absorption near $E_g$ is a three particle process, are called indirect semiconductors. They have a significantly lower probability of absorption than direct semiconductors, where the maximum of the valence band and the minimum of the conduction band are at the same crystal momentum and the photo effect can occur without phonon interaction.

As the photo effect is a stochastic process, the absorption is proportional to the intensity of light. This leads to an exponential decrease of the light intensity $P$ inside the semiconductor as described by the Beer-Lambert law

$$P(x) = P(0) \exp \left( -\frac{x}{l(E_\gamma)} \right),$$

where $x$ is the distance from the illuminated surface and $l$ is the energy-dependent absorption length. A measurement of $l(E_\gamma)$ for crystalline silicon can be seen in fig. 1.2.

![Figure 1.2: Absorption length of photons in crystalline silicon (data from [63]).](image-url)
1.1 Charge Carriers in Silicon

1.1.2 Doping

As stated above, the intrinsic concentration of free charge carriers is very low in pure silicon, giving it a high specific resistance of $3.2 \times 10^5 \, \Omega \cdot \text{cm}$. For the application in electronic devices like solar cells, where resistive losses have to be minimized, the conductivity has to be enhanced. This is done by adding low quantities of foreign elements into the semiconductor crystal, a process called doping. Typical doping atom concentrations $N$ are between $10^{15}/\text{cm}^3$ and $10^{20}/\text{cm}^3$.

To dope crystalline silicon, elements of the 3rd main group like boron (B) and aluminum (Al) and the 5th main group like phosphorous (P) can be used, which replace Si atoms in the crystal lattice. As Si is an element of the 4th main group with four valence electrons, replacing it with a 3rd main group atom removes one valence electron from the crystal, while a 5th main group atom increases the number of valence atoms by one. Consequently, 5th main group atoms are called donors, leading to n-type doping and 3rd main group atoms are called acceptors, leading to p-type doping due to an abundance of holes. The respective concentrations of donor and acceptor atoms are $N_D$ and $N_A$.

The additional electrons or holes introduced by doping are weakly bound to their dopant atom and delocalized over a large area of the crystal lattice. The dopant atoms are therefore easily ionized, with an ionization energy of only 45 – 75 mV.\(^1\) The corresponding electronic states $E_D$ and $E_A$ introduced by donors and acceptors lie slightly below the conduction band and slightly above the valence band, respectively (see fig. 1.3a). For very low temperatures, these additional electronic states lead to a Fermi energy between the respective band edge and the dopant level. At room temperature, thermal energy is sufficiently high to cause almost complete ionization of the doping atoms, so $E_f$ lies below $E_D$ for n-type and above $E_A$ for p-type doping, respectively.

This defect exhaustion at room temperature leads to an asymmetrical equilibrium density of free charge carriers with $n \approx N_D$ for n-type material and $p \approx N_A$ for p-type material. The additionally introduced electrons or holes are called majority carriers, as their density is much higher than $n_i$. On the other hand, a change in $E_f$ due to the majority carriers leads to a correspondingly reduced density of the

\(^1\)Ioffe Institute, http://www.ioffe.ru/SVA/NSM/Semicond/Si/bandstr.html, 2013-08-11
oppositely charged species, which can be described by the mass action law

\[ n \cdot p = n_i^2. \]  

Consequently, the depleted type of charge carriers is called minority charge carriers.

\[ \text{(a) Isolated n- and p-doped semiconductors} \quad \text{(b) p-n junction in thermal equilibrium} \]

**Figure 1.3:** Energy of donator and acceptor levels \( E_D \) and \( E_A \), as well as Fermi level \( E_f \) for two isolated n- and p-doped semiconductors (a) and a p-n junction (b) in thermal equilibrium at room temperature. The n-doped section is on the left and the p-doped section on the right side in both figures.

### 1.1.3 p-n Junction in Thermal Equilibrium

In semiconductor devices like silicon solar cells, differently doped parts of semiconductors are combined. The boundary layer between a p-doped and an n-doped section is called a p-n junction. At the junction, majority charge carriers from one region may diffuse into the oppositely doped region driven by a concentration gradient. This in turn leads to a charge separation, as the ionized dopant atoms can not diffuse, causing an electric field to build up which counters the concentration gradient driven diffusion until equilibrium is reached. The resulting zone of charge carrier inter-diffusion is called space charge region.

At the p-n junction, the diffusion of charge carriers leads to a common Fermi level for both areas and a corresponding shift of \( E_c \) and \( E_v \) (see fig. 1.3b). This makes the device usable for photovoltaic energy conversion: If a photo-generated minority charge carrier is generated in one area and reaches the space charge region by
1.1 Charge Carriers in Silicon

diffusion, it will instantly move across the p-n junction due to the electrical field and can be collected in the other area as a majority charge carrier.

1.1.4 p-n Junction under Illumination

The mass action law in eq. (1.4) is only valid for semiconductors without external excitation. For a semiconductor under illumination, both carrier concentrations $p$ and $n$ are elevated above their respective base values $p_0$ and $n_0$ by the same amount $\Delta n = n - n_0$, which is called the excess charge carrier density. Therefore, eq. (1.4) can not hold true in this case, as $n \cdot p > n_1^2$.

\[ n \cdot p > n_1^2 \]

\[ \Delta n = n - n_0 \]

\[ \Delta p = p - p_0 \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ E_c \]

\[ E_v \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \cdot 10^2 \]

\[ n(E) \cdot 10^2 \]

\[ p(E) \cdot 10^2 \]

\[ n(E) \cdot 10^2 \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]

\[ E_i \]

\[ E_c \]

\[ E_f \]

\[ \eta_e \]

\[ \eta_h \]

\[ D(E) \]

\[ F(E) \]

\[ p(E) \]

\[ n(E) \]

\[ E_v \]
and $\eta_h$ for holes:

$$n = \int_{E_c}^{E_F} \frac{D_n(E)}{\exp\left(\frac{E-E_c}{k_B T}\right) + 1} \, dE,$$

$$p = \int_{-\infty}^{E_F} \frac{D_p(E)}{\exp\left(\frac{E-E_v}{k_B T}\right) + 1} \, dE.$$  

(1.5)  

(1.6)

The difference between $\eta_n$ and $\eta_h$ is called the quasi Fermi level splitting $\Delta \eta = \eta_n - \eta_h$, which is obviously zero for the earlier case of a non-illuminated semiconductor in equilibrium. A plot of both the intrinsic and the illuminated case can be seen in fig.1.4.

Using the product of eqs. (1.5) and (1.6) together with eq. (1.2), a generalized form of the mass action law can be formulated:

$$n \cdot p = n_i^2 \exp\left(\frac{\Delta \eta}{k_B T}\right).$$

(1.7)

As the QFL splitting $\Delta \eta$ is maximal at the space charge region and vanishes at the terminals, its maximum value is equivalent to the potential difference of $E_f$ at the terminals. Except for voltage losses at the terminals, this potential difference corresponds to the voltage $U$ across the device. For this reason, it is a more directly accessible quantity than for example the carrier densities. In chapter 3, this equality will be the basis to determine local p-n junction voltages from EL images and subsequently calculate resistive losses in the solar cell.

![Figure 1.5](image_url)

**Figure 1.5:**
Spatial course of the QFLs $\eta_h$ and $\eta_e$ for a p-n junction under forward bias. The band bending (see fig.1.3b) is reduced due to the different Fermi levels at the left and right terminals. In the middle of the device, a region with non-zero $\Delta \eta$ can be seen, where luminescence is emitted.
1.1 Charge Carriers in Silicon

1.1.5 Charge Carrier Lifetime and Recombination Mechanisms

As described before, excess charge carriers may be generated within the semiconductor, driving the system away from thermal equilibrium. However, just as an electron-hole pair can be generated it can recombine, leading to a stable non-thermal equilibrium under continuous excitation and a relaxation to thermal equilibrium after an excitation.

There are four relevant recombination mechanisms in crystalline silicon which can cause a free electron in the conduction band to recombine with a hole in the valence band. All of these are detrimental to the performance of a solar cell, as the energy of the excited electron is released during the recombination process and cannot be used as electrical power outside the device. The key to an efficient solar cell is to suppress these recombination mechanisms as far as possible, so the probability of a photo-excited charge carrier being collected at the terminals is high, making it contribute to the current produced by the cell. To understand their contribution to the net recombination rate $R$, each of these mechanisms will be described briefly.

Defect Recombination

If the perfect regularity of the silicon crystal lattice is disturbed, e.g. by impurity atoms or crystallographic defects, electronic states outside the normal band structure may occur and can be populated by electrons. When the energy of this new state lies inside the band gap of silicon, the quantum mechanical probability of transitions from the conduction band to the valence band via this “trap” level may be significantly larger than a direct transition from conduction band to valence band, making this an efficient recombination channel. This mechanism was first described by Shockley, Read and Hall [64, 65] and is generally known as SRH recombination.

Using the density of trap states $n_{tr}$, as well as their respective capture cross sections $\sigma_e$ and $\sigma_h$ for electrons and holes with the thermal velocity $v_e$, $v_h$, a quantitative expression can be derived [55] for the recombination rate

$$R_{SRH} = \frac{n \cdot p - n_i^2}{n + N_c \exp(-(E_c - E_{tr})/kT)} + \frac{p + N_v \exp(-(E_v - E_{tr})/kT)}{n + N_v \exp(-(E_v - E_{tr})/kT)}.$$  (1.8)
Looking at the denominator of eq. (1.8), it can be shown that trap levels $E_{tr}$ in the middle of the band gap—also called deep traps—are especially recombination active. The energy from the two transitions may be dissipated radiatively, producing defect luminescence light.

In silicon solar cells, SRH recombination occurs mostly inside the space charge region of the p-n junction, where electron and hole densities are similar and existing trap levels can be easily occupied by an electron and a hole for recombination.

**Surface Recombination**

Surface recombination in principle is a special case of SRH recombination. It is, however, usually treated separately, as it is a surface effect and has other dimensions than the recombination mechanisms occurring in the bulk. The physical principle is the existence of unsaturated (“dangling”) bonds of silicon atoms at the crystal surface, which generate additional electronic states in the band gap. Also, impurities and foreign atoms tend to accumulate on surfaces and may lead to additional states inside the band gap, as mentioned above. These intermediate states allow for efficient SRH recombination and have to be removed by surface passivation steps during solar cell processing.

Quantitatively, the surface recombination is described by similar parameters as the SRH recombination in the bulk:

$$\mathcal{R}_{\text{surf}} = n_{tr} \sigma_e \nu_e n = S n. \quad (1.9)$$

The product of the surface density of trap states $n_{tr}$, electron capture cross section $\sigma_e$ and electron velocity $\nu_e$ has the unit of a velocity and is known as the surface recombination velocity $S$. In general, both holes and electrons can occupy trap states. However, one carrier type is usually predominant, so the formulation was only done for electrons here.

**Auger Recombination**

The Auger recombination process involves three charge carriers. This can be either one hole and two electrons or one electron and two holes. As one electron and one hole recombine, the released energy is transferred to the third charge carrier.
1.1 Charge Carriers in Silicon

this is an electron, it is lifted to an energetically higher state in the conduction band, from which it rapidly relaxes back to the band edge, usually dissipating its energy in many small steps to phonons or thermal radiation. Similarly, a hole can receive the recombination energy and be transferred to a “hot” state in the valence band, which likewise relaxes quickly back to the edge of the valence band.

As the mechanism is a three particle process, it is only relevant at high carrier concentrations, e.g. in the highly doped emitter of a silicon solar cell or under strong illumination. It can be quantified using empiric proportionality constants and the respective carrier concentrations:

\[
R_{\text{Auger},n} = C_{A,n} n^2 \cdot p \\
R_{\text{Auger},p} = C_{A,p} n \cdot p^2,
\]

(1.10) (1.11)

where \( C_{A,n} \approx C_{A,p} \) are both in the range of \( 10^{-30} \text{cm}^6/\text{s} \) [55].

Radiative Recombination

Radiative recombination is the direct transition of an electron from the conduction band into the valence band, where the released energy is emitted as a photon. It is the inverse process of the photo effect described in section 1.1.1, so it has the same properties regarding momentum and energy transfer. In an indirect semiconductor like Si, the emission of photons due to radiative recombination also requires interaction with a phonon.

The rate of recombination \( R_{\text{rad}} \) is proportional to the density of free electrons and holes \( R_{\text{rad}} \propto n_e n_h \). A quantitative derivation follows in section 1.2.2, as radiative recombination is the fundamental process for luminescence measurements. Compared to other recombination mechanisms, radiative recombination is usually negligible in silicon solar cells with respect to total recombination activity.

1.1.6 Effective Lifetime

The recombination rates of all bulk recombination effects are proportional to the excess charge carrier density \( \Delta n \), so a proportionality constant \( \tau_x = \frac{\Delta n}{R_x} \) can be defined for each mechanism. It equates to the average time an excited charge carrier remains in its excited state before it recombines via the respective process
and is therefore called lifetime. Most of the previously mentioned recombination processes happen in the bulk volume of the sample and are therefore independent of the shape or thickness. Only the surface recombination process has to be described in terms of sample dimensions and will be treated separately.

The overall recombination rate in the bulk $R_b$ is the sum of all contributions

$$R_b = R_{\text{SRH}} + R_{\text{Auger}} + R_{\text{rad}}. \quad (1.12)$$

The corresponding bulk lifetime $\tau_b = \frac{\Delta n}{R_b}$ is a property of the silicon material, and in first order independent of the illumination intensity or carrier density. It is therefore more suitable for characterization than the raw recombination rate and is experimentally better accessible.

For thin silicon wafers as used in photovoltaics, the surface recombination has to be taken into account. It further reduces $\tau_b$ to an effective minority charge carrier lifetime $\tau_{\text{eff}}$, which includes a surface recombination lifetime $\tau_{\text{surf}}$:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \frac{1}{\tau_{\text{surf}}}. \quad (1.13)$$

For the simple case of identical recombination velocity $S$ on both wafer surfaces and a surface recombination which is not limited by carrier diffusion (see below), $\tau_{\text{surf}}$ can be estimated as $\tau_{\text{surf}} = \frac{w}{S}$, where $w$ is the sample thickness. A more general formulation by Sproul [66] covers both asymmetric wafer surfaces and diffusion effects.

As SRH recombination in the bulk and on the surface is the dominant recombination process for silicon solar cells, a lot of effort in silicon photovoltaics goes into the elimination of trapping centers. In the bulk material, this can be done by removal or precipitation of impurity atoms, called gettering. Surface passivation processes can reduce recombination by saturating surface Si atoms with hydrogen or electrostatic shielding of surface defects. To quantify the improvements gained by these steps, $\tau_{\text{eff}}$ is a good parameter. A main focus of this work (see chapter 4) is therefore the development of fast measurement techniques for a reliable, quantitative measurement of $\tau_{\text{eff}}$. Differences between steady-state and dynamic measurement approaches for $\tau_{\text{eff}}$ may result in substantial deviations under certain conditions [67] and should be kept in mind when dealing with this quantity.
1.1.7 Minority Charge Carrier Diffusion

The movement of minority charge carriers in a doped semiconductor is—unlike that of majority carriers—limited to diffusion. If an external electric field is applied to the material, the field inside the semiconductor is virtually instantaneously neutralized by the movement of majority charge carriers [55]. Therefore, the minority carriers do not experience any electric field and only move in a random pattern due to thermal diffusion. Similarly to other dispersive processes, gradients in $\Delta n$ are reduced by a net flow of carriers. The diffusion current density $j$ can be described by Fick’s first law as

$$j(r) = -D \nabla [\Delta n(r)].$$

(1.14)

The diffusion coefficient $D$ depends on a number of parameters like doping and is slightly different for holes and electrons. For crystalline Si, it is usually between 25 and 40 cm$^2$/s for electrons and $\sim \frac{1}{3}$ of that for holes [68].

During an average minority charge carrier lifetime $\tau$, the mean distance a charge carrier moves is given by $L = \sqrt{D\tau}$ and is called the diffusion length. As with the carrier lifetime, the diffusion length can be used either without the influence of surface recombination as $L_b = \sqrt{D\tau_b}$, or as an effective diffusion length $L_{\text{eff}} = \sqrt{D\tau_{\text{eff}}}$ if surface recombination is taken into account. With the aforementioned values, $\tau_{\text{eff}} = 10 \mu s$ yields a value of $L_{\text{eff}} \approx 170 \mu m$, while a high $\tau_{\text{eff}} = 1 \text{ ms}$ results in $L_{\text{eff}} \approx 1.7 \text{ mm}$. From this estimation, the limiting effect of $L_{\text{eff}}$ on the resolution of luminescence images can be seen: The luminescence image is determined by the concentration of excess minority charge carriers $\Delta n$. Features significantly smaller than $L_{\text{eff}}$ can not be resolved, as the diffusion process leads to a uniform $\Delta n$ on those length scales.

1.2 Luminescence in Silicon

Luminescence is the process of charge carrier excitation and subsequent light emission by radiative recombination in a sample. There are many different types of luminescence, categorized by the way of excitation. However, only the two experimentally most accessible of them are commonly used for the characterization of crystalline silicon wafers and solar cells: For electroluminescence (EL), excess
charge carriers are generated by an external current, which is sent through the sample via electrical contacts. It therefore requires a finished solar cell with metallic contacts on both base and emitter regions. The applied forward current leads to a flow of charge carriers across the p-n junction. As stated above, current flowing through the two doped regions of the cell is carried only by majority charge carriers, which can move in the small electric field generated by the applied voltage. Charge carriers flowing across the p-n junction then become excess minority carriers, which recombine via the described processes. The small fraction of radiative recombination can be measured as EL radiation.

When the excess charge carriers are generated by illuminating the sample with a light source, the process is called photoluminescence (PL). The excess minority carriers in this case are generated throughout the sample by the photo effect, identical to normal operating conditions of the solar cell. This way, not only finished solar cells can be characterized, but also wafers at every intermediate step of solar cell manufacture. Even raw wafers and silicon bricks can be analyzed to measure the material quality. On the other hand, PL is experimentally more challenging, as the excitation light and the emitted luminescence have to be separated by means of optical filters.

In practice, the distinction between EL and PL is not always that clear. With the setup presented in chapter 2, simultaneous control of electric current and illumination is possible and allows for a variety of solar cell operating conditions, e.g., a measurement at maximum electric power generation under illumination.

### 1.2.1 Excess Charge Carrier Profiles for EL and PL

For a quantitative look at the luminescence emission of a sample, the spatial distribution of excess charge carriers has to be known. It may be quite different for EL and PL, depending on the relationship between generation, bulk recombination and surface recombination. For a more concise formulation, only the in silicon photovoltaics predominant case of minority electrons in a p-doped wafer will be described here. However, the argumentation can be done equivalently for holes in an n-type wafer.

Following the argumentation of Giesecke [22], the first step in describing the
local excess charge carrier density $\Delta n(r)$ is the continuity equation
\[
\frac{\partial \Delta n(r)}{\partial t} + \nabla j(r) = 0,
\] (1.15)
where $j(r)$ is the minority carrier flux inside the sample. Obviously this equation is only valid when excess charge carriers are not generated or recombine. For the semiconductor under excitation, generation and recombination rates $G$ and $R$ have to be included, they form an inhomogeneity to this partial differential equation (PDE).

For a laterally homogeneous sample with $(x, y)$ dimensions far larger than the diffusion length $L$, lateral components of the divergence term in eq. (1.15) are negligible and only a change in depth $z$ is present. This is a good assumption for wafers or single crystallites extending several mm or more but featuring typically $L < 1 \text{ mm}$. In addition, illumination of the sample is often laterally homogeneous but strongly depth dependent due to the exponential damping of light absorption (see eq. (1.3)). This leads to
\[
\frac{\partial \Delta n(z)}{\partial t} + \frac{\partial j(z)}{\partial z} = G(z) - R(z).
\] (1.16)
Looking at the steady-state case, the first term vanishes and the recombination term—which is generally proportional to $\Delta n$—may be described in terms of a carrier lifetime. Using the diffusion equation eq. (1.14) and $L = \sqrt{D\tau_b}$, we obtain
\[
\frac{\partial^2 \Delta n(z)}{\partial z^2} - \frac{\Delta n(z)}{L^2} = -\frac{G(z)}{D}.
\] (1.17)
Note the use of $\tau_b$ for $L = L_b$ throughout this section, as surface recombination will be handled separately in the boundary conditions of the PDE. Under the assumption of a constant $\tau_b$ which is independent of $\Delta n$, this second order PDE can be solved analytically for a given generation profile and boundary conditions.

**Electroluminescence in Solar Cells**

For EL measurements, the sample is typically not illuminated, so $G(z) = 0$. Instead, the excess electrons are injected into the base at the p-n junction. As the emitter region above the p-n junction is only $\sim 500 \text{ nm}$ thick in a typical solar cell, it is not
relevant for luminescence emission in comparison to the much thicker base. Only the base region, from the p-n junction at \( z = 0 \) to the rear side of the solar cell at \( z = w \) will be examined here.

The boundary condition at the front side is determined by the excess minority carrier density corresponding to the p-n junction voltage \( U \). Using eq. (1.7) with the approximations \( \Delta n \gg n_0 \) and \( p \approx N_A \), we obtain

\[
\Delta n|_{z=0} = \frac{n_i^2}{N_A} \exp \left( \frac{eU}{k_B T} \right). \tag{1.18}
\]

For the rear side, the carrier density is defined by the back surface recombination velocity \( S_b \) and the corresponding excess electron diffusion current

\[
-D \frac{\partial \Delta n}{\partial z} \bigg|_{z=w} = S_b \Delta n|_{z=w}. \tag{1.19}
\]

The general solution to the homogeneous case of eq. (1.17) is of the form

\[
\Delta n(z) = A \exp \left( \frac{z}{L} \right) + B \exp \left( -\frac{z}{L} \right), \tag{1.20}
\]

with the coefficients \( A \) and \( B \) being determined by the boundary conditions in eqs. (1.18) and (1.19). The solutions for \( A \) and \( B \) published by Giesecke [22] and Würfel et al. [20] differ slightly in notation but are mathematically equivalent, so only the result by Giesecke is shown here:

\[
A = \frac{n_i^2}{N_A} \exp \left( \frac{eU}{k_B T} \right) \frac{1 - \frac{D}{S_L}}{1 - \frac{D}{S_L} - \left( 1 + \frac{D}{S_b} \right) \exp \left( \frac{2w}{L} \right)} \tag{1.21}
\]

\[
B = \frac{n_i^2}{N_A} \exp \left( \frac{eU}{k_B T} \right) \frac{1}{1 + \frac{D}{S_L} - \left( 1 - \frac{D}{S_b} \right) \exp \left( -\frac{2w}{L} \right)} \tag{1.22}
\]

Fig. 1.6 shows a plot of \( \Delta n(z) \) for different diffusion lengths and rear surface recombination velocities. It can be seen that both parameters have a significant impact on the integral carrier density \( \int \Delta n(z) \, dz \) and consequently the intensity of EL emission. A separation of local surface and bulk recombination based on EL images is possible due to the different shapes of the resulting carrier density profiles [24].

22
1.2 Luminescence in Silicon

![Graphs showing carrier density variation with depth and diffusion length](image)

**Figure 1.6:** Calculated excess electron density $\Delta n$ inside the p-doped base of a solar cell under electric excitation of $U = 600 \text{ mV}$, with $w = 200 \mu\text{m}$ and $D = 30 \text{ cm}^2/\text{s}$. (a) shows the effect of different diffusion lengths at a constant rear surface recombination velocity $S_b = 10^2 \text{ cm/s}$, while (b) shows carrier profiles for different values of $S_b$ at constant $L = 200 \mu\text{m}$.

**Photoluminescence in Wafers**

PL measurements are mostly performed on wafers which do not have the electrical contacts of finished solar cells. The carrier density at the front surface ($z = 0$) is therefore not defined by a p-n junction voltage, but rather a recombination velocity $S_f$ like on the rear surface:

$$
\frac{D}{d^2} \frac{\partial \Delta n}{\partial z} \bigg|_{z=0} = S_f \Delta n \bigg|_{z=0}, \quad (1.23)
$$

$$
- \frac{D}{d^2} \frac{\partial \Delta n}{\partial z} \bigg|_{z=w} = S_b \Delta n \bigg|_{z=w}. \quad (1.24)
$$

Another difference to EL is the additional illumination, which leads to an inhomogeneous generation rate across the sample thickness. As described in section 1.1.1, light absorption inside the semiconductor creates an exponential intensity profile, with the slope depending on the photon energy. Integrating over all incident photon energies, we obtain

$$
G(z) = \int_0^\infty \alpha(E_\gamma) \frac{dF}{dE_\gamma} \exp \left(-\alpha(E_\gamma) z\right) dE_\gamma \quad (1.25)
$$
Semiconductor Basics and Luminescence

for illumination from the top and

\[ G(z) = \int_0^\infty a(E_\gamma) \frac{d\mathcal{F}}{dE_\gamma} \exp \left( -a(E_\gamma)(w - z) \right) dE_\gamma \]  

(1.26)

for illumination from the bottom side of the wafer. \( \frac{d\mathcal{F}}{dE_\gamma} \) is the spectral density of the incident photon flux and \( a(E_\gamma) = 1/l(E_\gamma) \) the absorption coefficient, which is the reciprocal of the absorption length introduced in section 1.1.1.

In most cases, this universal generation term can be simplified due to the use of an illumination source with a nearly monochromatic spectrum. For both laser and LED panel—as described later in more detail—the bulk of the emitted light is in a narrow range around the nominal photon energy \( E_{\gamma,0} \), so the absorption coefficient can be treated as a constant \( a_0 = a(E_{\gamma,0}) \). Eqs. (1.25) and (1.26) then simplify to

\[ G(z) = a_0\mathcal{F} \exp \left( -a_0z \right), \]  

(1.27)

\[ G(z) = a_0\mathcal{F} \exp \left( -a_0(w - z) \right). \]  

(1.28)

Due to the double differentiation in the PDE, the particular solution to eq. (1.17) with the above boundary conditions does not depend on the sign in the exponential term of \( G(z) \). For both illumination directions, it is

\[ \Delta n(z) = A' \exp \left( \frac{z}{L} \right) + B' \exp \left( -\frac{z}{L} \right) - \frac{G(z)}{D(a_0^2 - \frac{1}{L^2})}. \]  

(1.29)

However, the coefficients \( A' \) and \( B' \) required to satisfy the boundary conditions are different for front and back side illumination. In both cases, they are acquired by solving the linear equation system

\[
\begin{pmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{pmatrix}
\begin{pmatrix}
A' \\
B'
\end{pmatrix}
= 
\begin{pmatrix}
b_1 \\
b_2
\end{pmatrix},
\]

(1.30)

resulting in

\[ A' = \frac{b_1a_{22} - b_2a_{12}}{a_{11}a_{22} - a_{21}a_{12}}, \]  

(1.31)

\[ B' = \frac{b_1a_{21} - b_2a_{11}}{a_{21}a_{12} - a_{11}a_{22}}. \]  

(1.32)
Figure 1.7: Calculated excess electron density $\Delta n$ inside a p-doped wafer under optical excitation of $F = 2.5 \times 10^{17}/\text{cm}^2\text{s}$, with $w = 200 \mu\text{m}$ and $D = 30 \text{cm}^2/\text{s}$. (a) shows the effect of different bulk lifetimes at a constant surface recombination velocity $S_f = S_b = 10^2 \text{ cm/s}$, (b) shows carrier profiles for different values of $S$ at constant $\tau_b = 15 \mu\text{s}$. The solid lines are for front side illumination with $\lambda = 808 \text{ nm}$, the dashed lines for rear side illumination with $\lambda = 630 \text{ nm}$.

For front side illumination,

$$b_1 = \frac{a_0 F}{D (a_0^2 - \frac{1}{\tau^2})} \left( \frac{a_0 D}{S_f} + 1 \right) \quad \text{and}$$

$$b_2 = \frac{a_0 F}{D (a_0^2 - \frac{1}{\tau^2})} \exp(-a_0 w) \left( 1 - \frac{a_0 D}{S_b} \right),$$

while for illumination from the back side

$$b_1 = \frac{a_0 F}{D (a_0^2 - \frac{1}{\tau^2})} \exp(-a_0 w) \left( 1 - \frac{a_0 D}{S_f} \right) \quad \text{and}$$

$$b_2 = \frac{a_0 F}{D (a_0^2 - \frac{1}{\tau^2})} \left( \frac{a_0 D}{S_b} + 1 \right).$$

The entries

$$a_{11} = 1 - \frac{D}{S_f L'}, \quad a_{12} = 1 + \frac{D}{S_f L'}$$

$$a_{21} = \exp \left( \frac{w}{L} \right) \left( 1 + \frac{D}{S_b L} \right) \quad \text{and} \quad a_{22} = \exp \left( -\frac{w}{L} \right) \left( 1 - \frac{D}{S_b L} \right)$$

are identical for both illumination cases.
As shown above, the excess charge carrier profiles for both EL and PL can be solved analytically. However, in practice there is a limitation, making an analytical solution infeasible: the assumption of a constant $\tau_{\text{eff}}$ which does not depend on $\Delta n$ may be invalid. Especially the SRH recombination is nonlinear in $\Delta n$ due to the saturation of trap levels, leading to higher lifetime for increasing $\Delta n$. However, the differential equations can still be solved numerically if the relation $\tau_{\text{eff}}(\Delta n)$ is known [22].

1.2.2 Luminescence Intensity

Now that the effects of the excitation conditions on $\Delta n$ are known, the second step of the luminescence process, namely radiative recombination and its dependence on $\Delta n$, remains to be analyzed in detail. A quantitative formulation of the amount of radiation emitted by a semiconductor can be obtained by a generalization of Planck’s law of radiation [69] to include a photon gas with a non-vanishing chemical potential, as described by Würfel [70]. This potential can be identified with the QFL splitting $\Delta \eta$ derived in section 1.1.4. Additionally, a connection between $\Delta \eta$ and the excess charge carrier density $\Delta n$ can be drawn, leading to a formulation of the emitted PL intensity as a function of $\Delta n$.

The density $N_e, N_h$ of electrons and holes at a certain energy $E$ can be obtained from the integrands in the Fermi-model (see eq. (1.1)) at the respective QFLs $\eta_e$ and $\eta_h$:

$$
N_e(E) = D(E)f_e(E) = \frac{D(E)}{\exp\left(\frac{E-\eta_e}{k_B T}\right) + 1},
$$

$$
N_h(E) = D(E)(1 - f_h(E)) = \frac{D(E)}{\exp\left(\frac{\eta_h - E}{k_B T}\right) + 1},
$$

(1.36)

where $f_e(E)$ and $f_h(E)$ are the Fermi distributions of electrons and holes and $D(E)$ is the electronic density of states. Using these densities, we can describe the rate of spontaneous photo emission of energy $E_\gamma$ by integrating over the transition probabilities from energy $E + E_\gamma$ to the energy $E$:

$$
r_{sp} = D_\gamma(E_\gamma) \int_0^{\infty} \mathcal{M}(E, E_\gamma) N_e(E + E_\gamma) N_h(E) \, dE,
$$

(1.37)
where $D_\gamma(E_\gamma) = \frac{E_\gamma^2}{\pi^2\hbar^3c^3}$ is the photon density of states and $\mathcal{M}(E, E_\gamma)$ is the transition matrix element. Note that this formulation is per se only valid for direct semiconductors. However, it has been shown that only a change in the chemical potential is required to describe indirect semiconductors like silicon [71].

Without further knowledge of $\mathcal{M}$, we can use the equilibrium condition

$$r_{sp} + r_{st} - r_a = 0$$  \hspace{1cm} (1.38)

between spontaneous emission $r_{sp}$, stimulated emission $r_{st}$ and photon absorption $r_a$ to calculate the density of photons. The required terms

$$r_a = n_\gamma(E_\gamma) \int_0^\infty \mathcal{M}(E, E_\gamma) N_e(E) N_h(E + E_\gamma) \, dE$$
$$r_{st} = n_\gamma(E_\gamma) \int_0^\infty \mathcal{M}(E, E_\gamma) N_e(E + E_\gamma) N_h(E) \, dE$$  \hspace{1cm} (1.39)

are described in [70] and lead to the density of photons

$$n_\gamma(E_\gamma) = \frac{E_\gamma^2}{\pi^2\hbar^3c^3} \int_0^\infty \mathcal{M}(E, E_\gamma) N_e(E) N_h(E + E_\gamma) N_{\gamma}(E + E_\gamma) N_h(E) \left( \frac{N_e(E) N_h(E + E_\gamma)}{N_e(E + E_\gamma) N_h(E)} - 1 \right) \, dE.$$

(1.40)

With eq. (1.36), the term

$$\frac{N_e(E) N_h(E + E_\gamma)}{N_e(E + E_\gamma) N_h(E)} = \exp \left( \frac{E_\gamma - \Delta \eta}{k_B T} \right)$$  \hspace{1cm} (1.41)

is independent of the integration over $E$, leading to the result

$$n_\gamma(E_\gamma) = \frac{E_\gamma^2}{\pi^2\hbar^3c^3} \frac{1}{\exp \left( \frac{E_\gamma - \Delta \eta}{k_B T} \right) - 1}.$$

(1.42)

As mentioned above, it is a product of the photonic density of states and a Bose distribution with the chemical potential $\Delta \eta$. For the case of indirect semiconductors which involve phonon emissions and absorptions, this chemical potential would have to be modified. However, calculations by Würfel et al. [71] have shown that additional terms due to the phonon energy cancel out and the phonon chemical potential is negligible compared to $\Delta \eta$. Consequently, eq. (1.42) is also applicable.
Semiconductor Basics and Luminescence

Figure 1.8: Si luminescence emission spectrum for $T = 20 \degree C$. The blue curve shows data measured by Ostapenko et al. [7], for the green curve eq. (1.45) was evaluated with the absorption coefficient data from fig. 1.2 and $\Delta \eta = 0.5$ eV.

to the indirect semiconductor silicon.

Using Kirchhoff’s law of black body radiation [72] and generalizations thereof [70, 73, 74], the rate of spontaneous emission $r_{sp}$ can be related to a photon flux density $j_\gamma$ by the absorption coefficient $\alpha(E_\gamma)$

$$r_{sp}(E_\gamma) = \alpha(E_\gamma)j_\gamma(E_\gamma).$$  (1.43)

For isotropic emission, the photon flux density is

$$j_\gamma(E_\gamma) = \frac{c}{4\pi} n_\gamma(E_\gamma).$$  (1.44)

Combining eqs. (1.42) to (1.44), the rate of spontaneous emission is

$$r_{sp}(E_\gamma) = \frac{\alpha(E_\gamma)E_\gamma^2}{4\pi^2\hbar^2c^2} \frac{1}{\exp\left(\frac{E_\gamma-\Delta \eta}{k_B T}\right) - 1}.$$  (1.45)

For luminescence measurements with $E_\gamma \approx E_g$, the value $E_\gamma - \Delta \eta$ is typically $\gg k_B T$, so the expression can be simplified to

$$r_{sp}(E_\gamma) = \frac{\alpha(E_\gamma)E_\gamma^2}{4\pi^2\hbar^2c^2} \frac{1}{\exp\left(\frac{E_\gamma}{k_B T}\right)} \exp\left(\frac{\Delta \eta}{k_B T}\right).$$  (1.46)

The connection between $\Delta \eta$ and $\Delta n$ can easily be obtained from eq. (1.7), the product of charge carriers in non-thermal equilibrium:

$$n \cdot p = n_i^2 \exp\left(\frac{\Delta \eta}{k_B T}\right).$$  (1.47)
Assuming without loss of generality a p-doped material, we can identify the density of holes \( p \) as the sum of the equilibrium density \( p_0 \) and the density of excess charge carrier pairs \( \Delta n \). At room temperature, all dopant atoms are typically ionized, so

\[
p = p_0 + \Delta n = N_A + \Delta n
\]

(1.48)

Applying the mass action law from eq.(1.4) to the equilibrium density of electrons \( n_0 \), we get

\[
n = n_0 + \Delta n = \frac{n_t^2}{N_A} + \Delta n.
\]

(1.49)

These two expressions can be used to substitute \( n \cdot p \) in eq.(1.47), so we obtain

\[
n_t^2 \exp \left( \frac{\Delta \eta}{k_B T} \right) = \left( \frac{n_t^2}{N_A} + \Delta n \right) (N_A + \Delta n).
\]

(1.50)

A comparison of eqs.(1.46) and (1.50) shows the same exponential dependency on \( \Delta \eta \), so the two equations can be combined to

\[
r_{sp}(E_\gamma) = \frac{\alpha(E_\gamma) E_\gamma^2}{4\pi^2 \hbar^2 c^2 n_t^2} \frac{1}{\exp \left( \frac{E_\gamma}{k_B T} \right)} \left( \frac{n_t^2}{N_A} + \Delta n \right) (N_A + \Delta n)
\]

(1.51)

For the net luminescence emission \( \Phi \), \( r_{sp}(E_\gamma) \) has to be integrated over \( E_\gamma \). As the integration can be separated from the carrier concentration terms, we can define constant \( B \) as

\[
B = \int_0^{\infty} \frac{\alpha(E_\gamma) E_\gamma^2}{4\pi^2 \hbar^2 c^2 n_t^2} \frac{1}{\exp \left( \frac{E_\gamma}{k_B T} \right)} \, dE_\gamma,
\]

(1.52)

which was already introduced in section 1.1.5 as the coefficient of radiative recombination. The resulting luminescence intensity

\[
\Phi = B \left( \frac{n_t^2}{N_A} + \Delta n \right) (N_A + \Delta n)
\]

(1.53)

can be further simplified due to the fact that for all relevant measurements in silicon photovoltaics, \( \frac{n_t^2}{N_A} \ll \Delta n \):

\[
\Phi = B \Delta n (N_A + \Delta n).
\]

(1.54)
As mentioned before, the above derivation can be done equally for n-doped material using $N_D$. With the general doping concentration $N$, this leads to the commonly used term for luminescence intensity

$$\Phi = B\Delta n(N + \Delta n).$$  \hspace{1cm} (1.55)
2 The Luminescence Imaging Setup

Recording the weak luminescence emission of silicon samples requires a closed measurement setup to keep out stray light. The setup constructed for this purpose and described in this chapter is housed in an aluminum framework covered with PVC sheeting and light-tight closing doors. The housing serves a double purpose of keeping out ambient light and containing the intense illumination used for PLI (see section 2.3.3). A schematic layout of the components used for PLI can be seen in fig. 2.1.

![Figure 2.1: Schematic layout of the measurement setup used for photo-luminescence imaging. The sample (a) is homogeneously illuminated either with an LED panel (b) or a widened laser beam (c). The emitted PL image is focused onto the camera sensor (d) by an objective lens (e).](image)

2.1 Camera

The setup is based on an iKon-M DU934 BR-DD camera from Andor Technology to record the luminescence signal. Due to the low intensity and spectral range of the band to band luminescence of silicon, not every camera is equally suited for this purpose. Based on a comparison of several camera models [75], this camera
The Luminescence Imaging Setup

was selected as the main camera for the setup. It contains a back-thinned silicon CCD chip from e2v technologies (CCD47-10) with a resolution of 1024 × 1024 pixels and a pixel size of 13 × 13 µm [76]. Due to its deep depletion region and the back sided illumination, a high quantum efficiency (QE) of up to 45% at 1000 nm can be reached (see fig. 2.2b).

![Silicon CCD Camera](image1.png)

(a) The silicon CCD camera iKon-M DU934N-BRD from Andor Technology (from [76])

(b) Quantum efficiency of the CCD sensor at 20 °C (data from [76])

Figure 2.2: Picture and quantum efficiency curve of the iKon-M DU934 BR-DD silicon CCD camera. Unless otherwise stated, all shown luminescence images were recorded with this device.

To reduce thermal noise, the sensor is located in a sealed vacuum chamber and can be thermo-electrically cooled to −100 K below ambient temperature. Lower sensor temperatures exponentially decrease the dark current, for this camera at a rate of one order of magnitude every 13 K. However, this advantage is countered by an increase of the sensor material’s bandgap, shifting the quantum efficiency curve to shorter wavelengths and decreasing the sensitivity in the infrared range. With a temperature-dependant estimation of dark current noise, shot noise and measurement time, an optimal sensor temperature of −60 °C was found. This temperature can be reached reliably using only air cooling and is stabilized by the camera within minutes from startup. As the sensitivity of the sensor strongly depends on its temperature, a stabilization phase of 5 to 10 min should be maintained after startup. Otherwise, the measured PL intensities of different images might not be comparable.

The camera has a software controlled mechanical iris shutter in front of the CCD sensor, which can be used to set the exposure time. However, this shutter takes
~/50 ms for opening and closing, so exposure times below 1 s may be inaccurate and times below 100 ms are not feasible using this shutter. As the PL intensity of typical samples may vary by more than 3 orders of magnitude, an exposure time range of 10 ms to 100 s was desirable. This was accomplished by taking advantage of the lightproof setup housing. The camera shutter is opened just before the actual measurement, while the setup is completely dark. The sample is then excited for the desired amount of time and the shutter closed again after the excitation process. This way, the shutter transition time does not affect the exposure time and values down to 10 ms can be used reliably.

2.2 Camera Mounting

The camera is suspended above the sample on a metal beam, which is mounted on a linear unit made by ISEL Germany AG.\(^1\) It can therefore be positioned vertically from a position very close to the sample up to about 70 cm away at high accuracy and repeatability. The resulting camera field of view ranges from \(15 \times 15 \text{mm}^2\) to \(210 \times 210 \text{mm}^2\). To relieve the linear unit of static loads, a counterweight with the approximate camera suspension assembly mass of 10 kg was added.

![Figure 2.3: CAD drawing of the camera suspension frame, seen from below. The lever (a) and guide rails (b) used for lens focusing can be seen below the mounting beam (c). They are driven by a step motor and spindle drive (d). Not shown in the drawing is a bellows between frame and objective lens to keep out stray light.](image)

For high light sensitivity and good image quality in the near-infrared range, a Zeiss PLANAR T 1.4/50 ZF-IR objective lens from Carl Zeiss AG was used. It

\(^1\)A linear unit with spindle drive and 4 shaft slides was chosen to bear the weight and torque of the whole camera suspension assembly.
The Luminescence Imaging Setup features a focal length of 50 mm and an aperture range from $f/1.4$ to $f/16$. The optical elements are anti-reflection coated for wavelengths up to 1100 nm. Although the optical quality of this lens is very satisfying, the integrated focusing range of the objective lens ($45 \text{ cm} - \infty$) was not sufficient to cover the aforementioned wide range of possible focal distances. The lens was therefore mounted on an external focusing device, consisting of a parallel movement stage motorized with a computer controlled step motor (see fig. 2.3). Custom made bellows\(^2\) connect the two plates of the movement stage and prevent stray light from entering between lens and camera.

The aperture setting of the objective lens was intentionally not motorized, as most actuators have presumably worse repeatability compared to the vendor-supplied mechanical stop positions of the aperture selector. However, an electronic sensor was added to the lens to allow for a measurement software readout of the current lens aperture.

The camera mount on the suspension beam is designed as a dovetail guide. The counterpart of this dovetail guide is a flange plate screwed to the camera. This allows for a quick and precise removal and reinsertion of the camera, as required for the use of other cameras (see section 2.6) or the shutter module for time-resolved measurements (see section 4.2.2). The flange plate also holds the long-pass filter described in the following section directly in front of the camera, so no unfiltered stray light can enter. Note that this layout is only possible due to the use of F-mount lenses, which require a larger distance to the camera sensor than the standard C-mount lenses and leave room for the filter. On the other hand, when using C-mount lenses directly connected to the camera, stray light is not a problem and the filters could be simply affixed directly in front of the lens.

### 2.2.1 Filters

In order to record only the luminescence emission from the sample and not the excitation light, optical filters are required for photoluminescence measurements. In the case of silicon wafers, the incident excitation light is typically five to more than eight orders of magnitude stronger than the emitted PL signal, which is challenging for optical filters [77]. In the case of photoluminescence imaging,\(^2\) Folded from a sheet of aluminum coated plastic.
the filters not only have to be good in terms of blocking unwanted parts of the spectrum, but also need a high optical quality for the transmitted image.

The initial filter choice was a combined long-pass filter with a dielectric coating on top of a 4 mm thick absorption glass substrate\(^3\). The chosen edge wavelength of 850 nm ensures good transmission for \( \lambda > 900 \text{ nm} \). It could be shown, however, that this filter clearly has insufficient blocking of excitation light to be usable for PL imaging of silicon wafers [78]. This result was not entirely unexpected, as the specified optical density from UV to 760 nm is only \( \geq \text{OD} \) 2.

The PL image quality could therefore be substantially improved by substituting this filter with a semiconductor wafer used as an optical long-pass filter. The semiconductor material has to fulfill several requirements to be usable as an optical filter for luminescence imaging of silicon samples:

- Strong blocking of the LED (630 nm) and laser (808 nm) illumination.
- High transmission for the luminescence light above 900 nm.
- Good optical quality for the transmitted luminescence images.
- Low fluorescence/luminescence emission from the filter material itself.

All of these could be addressed by using an undoped gallium-arsenide (GaAs) wafer with polished (100) surfaces. GaAs is a direct semiconductor with a bandgap of \( E_g = 1.42 \text{ eV} \), corresponding to a cutoff wavelength of \( \lambda_{co} = \frac{hc}{E_g} = 875 \text{ nm} \). As can be seen in fig. 2.4, the transmitted intensity below 850 nm is very low. Using literature values for the absorption coefficient \( a(\lambda < 850 \text{ nm}) \geq 8000/\text{cm} \) [79] and a wafer thickness of \( d = 350 \mu\text{m} \), we can estimate the transmissivity as

\[
T = \frac{I(d)}{I(0)} = e^{-ad} < 10^{-120}.
\]

We can therefore safely assume that there is quite literally no single transmitted photon below 850 nm.

Another notable information from fig. 2.4 is the transmission of \( > 90 \% \) for \( \lambda > 950 \text{ nm} \), which was achieved with sputter deposition of a 150 nm thick \( \text{Al}_2\text{O}_3 \) anti-reflection coating on both wafer surfaces. Without this coating, the high refractive index of 3.5 would lead to reflection losses of \( > 30 \% \) at each GaAs-air

\(^3\)850FH90-50S from Andover Corporation
interface. Another very relevant factor for good transmission proved to be the choice of undoped GaAs, as any doping leads to strong free-carrier absorption above the bandgap.\textsuperscript{4}

To suppress undesired luminescence emission of the GaAs filter, a second dielectric long-pass filter\textsuperscript{5} was placed in front of the objective lens, while the GaAs filter is located between the lens and the camera sensor. This dielectric filter keeps most of the excitation light away from the GaAs wafer and the objective lens, thereby also suppressing inevitable fluorescence activity of the optical elements in the objective lens. Light emission from the filter or lens would otherwise lead to concentric measurement artifacts in the images and reduce the contrast of the sample’s PL signal.

### 2.3 Sample Placement and Excitation

Depending on the measurement, the solar cell or silicon wafer can be placed on two different fixtures. These are installed on top of a temperature-controlled base plate connected to a water recirculator to dissipate generated heat and keep the sample at a stable temperature.

\textsuperscript{4}Experiments with a doped GaAs wafer were reported by Sandra Herlufsen from ISFH (personal communication, Oct 2012).

\textsuperscript{5}LC-900ALP-50 from Laser Components GmbH
2.3 Sample Placement and Excitation

2.3.1 Electroluminescence

For electroluminescence measurements, a brass chuck is available to electrically contact solar cells with a standard busbar and front finger grid design. This chuck is described in detail in [75] so a complete description will be omitted here. Notable features include selectable vacuum areas to fixate samples of different sizes and swiveling front contact bars, which can be tilted to reduce the visible outline from the camera point of view. The applied voltage at the solar cell is measured independently of the current lines with a separate, current-free set of sense lines.

The usual approach to connect solar cells with more than one busbar is using several contact bars with spring-loaded pins connected to the same potential. However, it was found that this often leads to quite inhomogeneous EL images, as the different contact bars may introduce different amounts of series resistance due to cables, plugs and pins. Small variations of some mΩ can lead to large differences in the current supplied by the different contact bars due to the exponential character of the solar cell characteristic curve. This inhomogeneity was successfully removed by connecting additional resistors in series to each contact bar. The resistor values were chosen significantly higher than the aforementioned series resistance differences between the contact bars, leading to a symmetrical current flow across all contact bars.

Note that this solution is only valid for solar cells featuring equal current contribution for each busbar. With some solar cell designs, e.g., some interdigitated finger layouts, it leads to undesired results, increasing the potential differences between busbars instead of reducing them. Here, the series resistors have to be shunted out for a correct EL measurement.

For photoluminescence measurements, the sample can be illuminated either from the front side with a homogenized diode laser or from the rear side by placing it on a light emitting diode (LED) panel.

2.3.2 Photoluminescence with LEDs

The LED panel is made of a brass enclosure, which can be placed on top of a water-cooled base plate instead of the EL chuck described above. Inside of the enclosure, 1764 LEDs are arranged on a printed circuit board (PCB) with a pitch of
The Luminescence Imaging Setup

Figure 2.5:
CAD drawing of the LED panel. Above the LEDs, a large optical filter blocks long wavelength emissions. The bottom side of the LED board is placed on the brass housing for heat dissipation.

5 mm, covering an area of $21 \times 21 \text{ cm}^2$. The LEDs of type TOPLED LS E63F-DBFA-1 from Osram Semiconductors emit at 630 nm under an angle of 30° FWHM due to the included lens in front of each LED emitter. With a distance of $\sim 25 \text{ mm}$ between LEDs and the sample, a homogeneity of $\pm 5\%$ can be achieved at high illumination levels of $> 1$ sun equivalent. For good homogeneity and to prevent chain reactions in case of an LED failure, the diodes are connected in 84 independent strings of 21 series-connected LEDs. Each string is supplied by a separate current controller to make sure all LEDs equally receive the specified current. The LED control electronics also feature a global enable/disable input for pulsed operation of the panel, which is necessary for TR-PLI measurements (see chapter 4).

The full photon flux of the LED array at 100 mA LED current and a distance of 25 mm is about $5 \times 10^{17} \text{ cm}^2 \text{s}$, which is equivalent to $\sim 2$ suns$^6$ for typical silicon solar cells. Unfortunately, the LEDs emit a—for this application—relatively broad spectrum with a FWHM of 16 nm and significant contributions above 900 nm. The light from the LEDs therefore has to be filtered with a short-pass filter before exiting the panel, with an optical filter as large as the illuminated area.

A dielectric reflection filter “SIR” from Präzisions Glas & Optik GmbH with a cutoff wavelength of 750 nm was the only dielectric filter obtainable in this size. It offered transmission of 95% for $\lambda = 630 \text{ nm}$ but reduced the infrared emissions of the panel only less than 2 orders of magnitude.

$^6$1 sun illumination is defined in IEC 60904-3 as a power density of 1 kW/m$^2$ with an AM1.5 spectrum.
2.3 Sample Placement and Excitation

The LED panel was therefore outfitted with a Schott KG5 absorption filter made from ionically colored glass. A thickness of 4 mm was chosen, which is twice the reference thickness of 2 mm. As can be seen in fig. 2.6, this reduces the transmissivity at \( \lambda = 630 \text{ nm} \) to only \( \sim 50 \% \) but on the other hand leads to an optical density \( > 4 \) for \( \lambda > 850 \text{ nm} \). The biggest available size of the KG5 filter is \( 165 \times 165 \text{ mm}^2 \), which is not enough to cover the entire LED panel. For the currently available silicon wafers up to \( 156 \text{ mm} \) it is however sufficient.

An uncoated fused silica plate was added on top of the filter to protect it against scratches and other damage by the comparatively hard silicon wafers. Fused silica was chosen not only because of its durability, but mainly because of the low fluorescence emission of the material compared to other glasses (see section 2.3.3).

With this stack in place, the maximum photon flux of the LED panel is limited to \( 2.5 \times 10^{17} \text{ cm}^{-2} \text{s}^{-1} \), about 1 sun equivalent for silicon. For absolute intensity calibration, a reference cell is used similarly to the laser calibration procedure described below.

### 2.3.3 Photoluminescence with Laser

The alternative to the LED panel for optical excitation is an 808 nm diode-laser system, which illuminates the sample from the top using a beam homogenizer. As shown in fig. 2.1, the illumination in this case is not directly from the top, but tilted about 35° to the side to make room for the camera.

The laser system is decoupled from the homogenizer optics and emits a con-
The Luminescence Imaging Setup

Continuous laser beam of up to 100 W into a 600 µm fiber. In addition to the main 808 nm laser, it contains a 630 nm pilot laser with 10 mW output power that can be used for optical alignment. The system is water-cooled and features an internal thermo-electric cooler (TEC) to keep the laser diodes at a fixed temperature. The main power of the laser system was connected to a flow switch to make sure the laser and TEC only operate with a steady supply of external cooling water.

The laser head is made of several laser diode bars, which are connected in series and supplied with the desired current by a computer controlled driver circuit. At full power, the diodes receive up to 14 A of current. Unfortunately, this high current makes fast switching of the laser difficult. The laser driver therefore had to be refurbished and modified by the manufacturer to achieve the required switching speeds for TR-PLI (see section 4.2.2).

To avoid accidental exposition of an operator to the laser light, two safety features are present. The first one is the hardware interlock-circuit of the laser system, which instantly stops the laser as soon as the circuit is interrupted. It was connected to four pins on the doors of the measuring cabin so the interlock circuit is only closed when all doors of the setup are shut. The second security measure is an active door lock, which is engaged by the measurement software before the laser is activated. This prevents users from accidentally opening the doors while the laser is on.

The laser light is transmitted to the homogenizer optics in an optical fiber. The layout of this beam homogenizer can be seen in fig. 2.7. The beam exiting the fiber (a) is collimated in lens (b) to a parallel beam with a Gaussian profile. This collimated beam then hits an assembly of micro-lens arrays. The two arrays (d) and (e) have a distance of about twice the focal length. Together with the spherical exit lens (f), each microlens pair essentially projects a small part of the primary Gaussian beam onto a square area (g). The superposition of all these projected squares results in a homogeneous exiting beam profile at (g). However, the laser light is coherent and interference effects between the superpositioned microlens projections can occur. The resulting speckle pattern significantly reduces the illumination homogeneity. It can be removed by inserting a rotating diffusion disk (c) between the collimator lens and the microlens array. The diffusion disk is made of fused silica and has a surface roughness of a few µm (greatly exaggerated in fig. 2.7). It introduces a slight variable phase shift into the incoming beam, leading
2.3 Sample Placement and Excitation

![Figure 2.7: Schematic layout of the laser beam homogenizer, which generates a flat-top profile out of the Gaussian beam profile exiting the laser fiber (a). As indicated by the line widths, the different intensities from the incoming beam profile are mixed by microlens arrays (d and e) and superposed to form a homogeneous output profile at (g). The diffusion disk (c) reduces laser interference patterns.](image)

Figure 2.7: Schematic layout of the laser beam homogenizer, which generates a flat-top profile out of the Gaussian beam profile exiting the laser fiber (a). As indicated by the line widths, the different intensities from the incoming beam profile are mixed by microlens arrays (d and e) and superposed to form a homogeneous output profile at (g). The diffusion disk (c) reduces laser interference patterns.

to quasi random fluctuations of the speckle pattern. By rotating the disk, the pattern shifts so fast that on all relevant time scales only the averaged intensity can be observed, which equals the intensity profile without interference effects.

As mentioned before, the beam homogenizer is tilted about 35° to the side so it does not interfere with the camera. If the homogenizer were used as shown in fig. 2.7, this would lead to a trapezoidal illumination shape at the sample position, with higher intensity at the near side and lower intensity at the far side of the homogenizer. To avoid this, the exit lens (f) has to be tilted until it is approximately parallel to the sample. The resulting illuminated area is less trapezoidal and—apart from the edges—has a very good homogeneity. Using a small photodiode, relative standard deviations of 3.3 % were measured on a 16 × 16 cm² area and 2.5 % on a 12 × 12 cm² area.

The laser diodes, similar to LEDs, also generate some long wavelength background emission. Together with fluorescence from the optical fiber and other components in the beam homogenizer, it may lead to measurement artifacts in the PL images due to reflection of the long wavelength components at the sample’s surface. To suppress these parasitic wavelengths, a dielectric short-pass filter was placed between homogenizer (e) and exit lens (f). However, the original exit lens made from BK7 glass still contributed enough fluorescence light to have a significant negative impact on measurements. It was replaced with a lens made out of fused silica with good results. Images of the fluorescence emission of both lenses illuminated by the LED panel are shown in fig. 2.8 for comparison.
Despite the anti-reflection coating of all optical elements, diffraction, refraction and absorption in the beam homogenizer lead to an intensity loss of $\sim 20\%$. To dissipate the generated heat of up to 30W under full load, the homogenizer had to be retrofitted with a heat sink and a fan. Illumination periods of several minutes at full intensity are now possible without significant temperature rise of the homogenizer.

All functions of the laser system are remotely controlled by the measurement software. This includes turning the laser emission on and off, as well as setting the emitted light intensity via the laser diode current $I_{LD}$. In order to precisely control the incident photon flux $F$ on the sample, a calibration procedure for the correlation between laser diode current and photon flux was included in the measurement software: The laser current is gradually increased, while the incident photon flux at the sample position is measured with a calibrated solar cell. This calibration cell has an area of $A = 4.0\,\text{cm}^2$ and is connected to a Keithley 2400 digital source-meter. The photo-current $I_{ph}$ is measured at 100mV reverse bias by subtracting the current at dark conditions from the current under laser illumination. As the external quantum efficiency (EQE) of the calibration cell is known, this
2.4 Lifetime Calibration of Steady-State PL Images

photo-current can be converted to a photon flux via

\[ F = \frac{I_{ph}}{A \cdot e \cdot EQE}, \]  

(2.2)

where \( e \) is the elementary charge. The calibration curve \( F(I_{LD}) \) is saved and subsequently used to obtain the required laser diode current by interpolating \( I_{LD}(F) \) at the nominal photon flux.

All excitation sources (LEDs, laser and EL power supply) feature an external modulation input to switch the output on and off. This is used for exact exposure timing, as mentioned in section 2.1 and for the time-resolved PL method discussed in chapter 4.

2.4 Lifetime Calibration of Steady-State PL Images

As derived in section 1.2.2, the PL emission \( \Phi \) of a sample as a function of excess charge carrier density \( \Delta n \) can be written as

\[ \Phi(\Delta n) = B \Delta n(N + \Delta n), \]  

(2.3)

where \( N \) is the base doping of the silicon wafer and \( B \) the constant of radiative recombination. The intensity \( I \) recorded by the camera is directly proportional to this, \( I = A \Phi \). However, the proportionality constant \( A \) is determined by various factors, including sample emissivity, surface roughness, lens aperture and absorption, long-pass filter absorption, CCD quantum efficiency, as well as CCD and sample temperatures. Some of these are hard to determine accurately, so an estimation of \( \Delta n \) solely on the basis of recorded PL intensity is difficult to accomplish [21]. A calibration procedure to determine \( A \) is therefore required to obtain quantitative measurements of \( \Delta n \) or \( \tau_{eff} = \Delta n/G \) from a steady-stage PL image. Essentially two similar approaches have been proposed for this steady-state calibration: The inclusion of a QSSPC measurement unit into the setup [10], or the use of a QSSPL measurement [9, 11]. In light of the recent advances of QSSPL measurements [80, 81], this method may be preferable to QSSPC calibration. However, in a first step a calibration procedure using already available measurement equipment was implemented.
The Luminescence Imaging Setup

This was based on a Sinton Instruments WCT-120 photoconductance lifetime tester [82], which was in contrast to the approach of Herlufsen et al. [10] not integrated into the PL setup but used as a standalone unit. This has the benefit of keeping the device available for measurements independent of the PL setup, but the disadvantage of using different light sources for the PL measurement and the photoconductance calibration measurement. Due to the much larger absorption length of the infrared light used in the QSSPC setup, a more homogeneous excitation of the sample volume can be achieved. The excitation caused by the PL light sources is much more confined to the surface area of the wafer. For this reason, the effective lifetime $\tau_{\text{eff}}$ measured by PL is much more affected by the surface recombination velocity $S$ than the one obtained via QSSPC. For samples with good surface passivation where $\tau_{\text{eff}} \sim \tau_{\text{bulk}}$, this has virtually no effect. But for samples where $\tau_{\text{eff}}$ strongly depends on $S$, the results from both measurement setups cannot be reliably compared. A lifetime calibration of PL images using this approach is therefore limited to the first category of samples.

The calibration procedure is based on the relation between charge carrier density $\Delta n$ and PL emission (see eq.(1.55)). To account for all multiplicative factors between this emission rate $\Phi$ and the camera count rate $I$, a constant factor $A$ was introduced and combined with $B$ from eq.(1.55) to a constant $B'$:

$$I(\Delta n) = AB \Delta n(N + \Delta n) = B' \Delta n(N + \Delta n).$$  \hspace{1cm} (2.4)

The calibration constant $B'$ has to be chosen in a way to satisfy

$$\tau_{\text{QSSPC}} = \overline{\tau_{\text{PL}}}$$  \hspace{1cm} (2.5)

where $\tau_{\text{QSSPC}}$ is the lifetime value obtained from the QSSPC setup and $\overline{\tau_{\text{PL}}}$ is the averaged lifetime from the PL image at identical $\Delta n$. Solving eq.(2.4) for $\Delta n$, we get

$$\Delta n = \sqrt{\frac{N^2}{4} + \frac{I}{B'} - \frac{N}{2}},$$  \hspace{1cm} (2.6)

which can be divided by $G$ to obtain a lifetime image.

To compare this lifetime image to the integral value $\tau_{\text{QSSPC}}$ and satisfy eq.(2.5), an average value $\overline{\tau_{\text{PL}}}$ has to be calculated, where each pixel is weighted by the sensitivity $Q(x, y)$ of the QSSPC setup at the corresponding position. This information
can be acquired with the following experiment [14]:

The QSSPC measures the photoconductivity of the sample in response to illumination. The conductivity is measured indirectly by coupling an LC oscillator circuit in the MHz range to the sample with a pickup coil. Based on the fact that the pickup coil, which is located below the sample, has a circular shape, $Q$ depends only on the radius $\sqrt{x^2 + y^2}$, where $x = 0, y = 0$ is the center of the coil. This position of course has to be correctly identified in the PL image, ideally being the center of the image. To quantify the radial dependency of $Q$, two circular monocrystalline Czochralski-grown silicon (Cz-Si) wafers were passivated by amorphous hydrogenated SiN$_x$:H on both sides, resulting in a homogeneous lifetime $\tau_{\text{eff,h}} \sim 60\,\mu$s. Steady-state PL images of the wafers were used to ensure good lifetime homogeneity. The lifetime was then gradually reduced to $\tau_{\text{eff,l}} \sim 2\,\mu$s by removing concentric rings of the top passivation layer via laser ablation. After each ablation step, the sample was centered on the QSSPC device and the apparent lifetime $\tau_{\text{QSSPC}}$ was recorded. Both wafers were processed this way, one starting the ablation in the center and one starting at the edge.

The resulting lifetime as a function of the ablation radius can be seen in fig. 2.9. Assuming $\tau_{\text{eff}}(r)$ is a step function changing from $\tau_1$ to $\tau_2$ at $r = r'$ and $Q(r)$ is a sensitivity function which depends only on the radius $r$, the integral quantity
\( \tau_{\text{QSSPC}}(r') \) can be expressed as an integral over the local effective lifetime \( \tau_{\text{eff}} \):

\[
\tau_{\text{QSSPC}}(r') = \int_{0}^{r'} 2\pi r Q(r) \tau_{\text{eff}}(r) \, dr \\
= \int_{0}^{r'} 2\pi r Q(r) \tau_1 \, dr + \int_{r'}^{r} 2\pi r Q(r) \tau_2 \, dr.
\]  

(2.7)

(2.8)

\( Q(r) \) may then be determined from the derivative of the measured lifetime \( \tau_{\text{QSSPC}}(r) \) by the distance \( r \) to the sensor center:

\[
Q(r) = \frac{1}{2\pi r(\tau_1 - \tau_2)} \frac{d\tau_{\text{QSSPC}}}{dr}.
\]  

(2.9)

Depending on the direction of ablation, the values \( \tau_1 \) and \( \tau_2 \) equal \( \tau_1 = \tau_{\text{eff},h} \) and \( \tau_2 = \tau_{\text{eff},l} \) or vice versa. With the resulting sign change of \( \tau_1 - \tau_2 \), both curves from fig. 2.9 yield positive derivatives, as can be seen in fig. 2.10.

The obtained sensitivity values for both directions of ablation can be well fitted by Gaussian functions with similar values of \( \sigma \). A notable difference is the radial position of the maxima, which are about 1.5 mm apart. As there is no reason why the measurement itself should depend on the direction of ablation, we can conclude that the area of reduced \( \tau_{\text{eff}} \) is larger than the ablated area. This can be explained by two effects. First of all, the ablation process may damage the crystal structure and surface passivation even outside the ablation area. Secondly, excited charge carriers from passivated areas near the ablation edge may diffuse to the unpassivated surface and recombine, leading to a reduced \( \tau_{\text{eff}} \) on a diffusion length.
2.4 Lifetime Calibration of Steady-State PL Images

Scale\textsuperscript{7} This effect can also be seen in fig. 2.9, where the two curves do not reach \( \frac{\tau_{\text{Diff}}}{} \) at the same radius and in fig. 2.11, which shows a PL image of a partially ablated wafer.

Apart from the direction, the ablation procedure was done in the same way for both wafers, so an equal amount of radial shift can be expected. The average of both curves was therefore used to obtain the final sensitivity distribution:

\[
Q(x, y) = C \exp \left( - \left( \frac{\sqrt{x^2 + y^2}}{\sigma} - r_0 \right)^2 \right),
\]

(2.10)

with \( r_0 = 9.3 \text{ mm} \) and \( \sigma = 3.6 \text{ mm} \). The normalization factor \( C \) derives from the integration in eq. (2.7) with \( \tau_{\text{eff}} = \tau_{\text{QSSPC}} \) and is easily acquired for numerical calculation.

\textbf{Figure 2.11:}
PL image of the partially ablated wafer #2. The inner region is still passivated and accordingly shows a high amount of PL emission. Near the edge of the ablated region, an intensity gradient due to carrier diffusion can be seen.

\textbf{Figure 2.12:}
Spatial distribution of the QSSPC sensitivity \( Q(x, y) \) from eq. (2.10) on a 5 \( \times \) 5 cm\( ^2 \) area.

Using this weight function \( Q(x, y) \) on the lifetime images from eq. (2.6), a numer-
The Luminescence Imaging Setup

ical solution for $B'$ can be found which satisfies eq. (2.5). The resulting lifetime image is valid for low- and high-injection, provided that $G$ and $N$ are sufficiently well known.

A similar approach to measure the sensitivity function of a WCT-120 device was independently published by Giesecke et al. [11]. The reported sensitivity curve is slightly broader than the one shown here, which may be explained by the several times larger diffusion lengths in the floatzone Si wafer used by Giesecke et al.

Due to the averaging procedure this approach is only compatible with the quasi-steady-state mode of photoconductance measurements. When using the QSSPC setup for transient photoconductance measurements, the resulting lifetime value is not a sensitivity-weighted average of the local $\tau_{\text{eff}}$. Due to the superposition of exponential decay signals, high lifetime areas in the sample dominate the measurement in transient mode. This is much more difficult to reproduce quantitatively from a PL image, so a lifetime calibration with transient photoconductance measurements was out of the scope of this work.

2.5 Comparison of InGaAs Cameras

The predominantly used camera in the setup (see section 2.1) has a silicon CCD sensor. This is a good choice in terms of resolution and noise levels, but due to the bandgap of silicon, the spectral sensitivity range of the camera is limited to $\sim 1150\,\text{nm}$. A silicon based CCD can therefore only measure the PL resulting from band-to-band recombination in a silicon sample. To directly measure the radiation emitted by sub-bandgap transitions in the sample, a camera with sensitivity at higher wavelengths has to be used. Camera sensors with sensitivity up to 1700 nm can be made from the direct semiconductor material $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, which has a bandgap of $\sim 0.8\,\text{eV}$. As the manufacturing and handling of InGaAs is more challenging than the use of silicon, CCD arrays from this material typically feature much higher levels of image noise and a lower sensor resolution than commonly available silicon CCDs. Also, a vertical stripe pattern caused by varying sensitivity of the InGaAs CCD columns is often present in the raw image data, which has to be corrected by the camera firmware or by subsequent software calibration. For this comparison, only the corrections applied by the camera or recording software as supplied by the vendor were used.
2.5 Comparison of InGaAs Cameras

To compare currently available InGaAs cameras for their suitability for luminescence measurements on silicon wafers and solar cells, test images with four different cameras under similar conditions were recorded. The four tested cameras are

- ARTCAM-031TNIR from Artray Co., Ltd., Japan
- Goldeye P-032 SWIR Cool from Allied Vision Technologies GmbH, Germany
- IK1523 from EHD imaging GmbH, Germany
- SWIR-HR InGaAs from Photonic Science Ltd., UK

A comparison of technical specifications can be seen in the following table:

<table>
<thead>
<tr>
<th></th>
<th>ARTCAM</th>
<th>Goldeye</th>
<th>IK1523</th>
<th>SWIR-HR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution [pixel]</td>
<td>640 × 512</td>
<td>636 × 508</td>
<td>640 × 512</td>
<td>640 × 512</td>
</tr>
<tr>
<td>A/D Resolution [bit]</td>
<td>12</td>
<td>14</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>Exposure Time [µs]</td>
<td>55 – 3.6 s</td>
<td>5 – 1 s</td>
<td>10 – 3 s</td>
<td>1 – 1 s</td>
</tr>
<tr>
<td>Frame rate [fps]</td>
<td>33.6</td>
<td>30</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>Cooling [°C]</td>
<td>—</td>
<td>−5 °C</td>
<td>−20 °C</td>
<td>−20 °C</td>
</tr>
<tr>
<td>Connection</td>
<td>USB 2.0</td>
<td>GigE Vision</td>
<td>USB 2.0</td>
<td>GigE Vision</td>
</tr>
</tbody>
</table>

To test the suitability of each camera for typical PL measurements, a multicrystalline Si wafer with SiNx:H passivation on both surfaces (sample $\text{A}$) was illuminated with an intensity of $2.5 \times 10^{17} \text{cm}^2\text{s}^{-1}$ using the LED panel. Each camera was then tested with the same lens at $f/2.0$ and the same filters to obtain comparable results. Examples of the recorded images for an exposure time of 10 ms can be seen in fig. 2.13. For each image, a signal to noise ratio (SNR) was calculated by dividing the difference of maximum and minimum values in the image by the standard deviation in a homogeneous area, e.g., the dark area near the edge in fig. 2.13.

From these images, along with the SNR values, a first conclusion about sensitivity can be drawn. The ARTCAM could not obtain a reasonably clear image at 10 ms

---

8In practice, values > 100 ms could not be set.
exposure time, while the two most sensitive cameras Goldeye and SWIR-HR were already overexposed at this PL intensity. The IK1523 shows a good image but can not keep up with the Goldeye and SWIR-HR in terms of SNR.

To further differentiate the sensitivity of the cameras, a second test at much lower PL intensity was performed. For this test, an unprocessed and not passivated as-cut mc-Si wafer (sample D) was examined under laser excitation of $5.9 \times 10^{17}$ cm$^{-2}$s. For comparison again all cameras were exposed for the same amount of time, in this case 100 ms. The ARTCAM did not detect any signal above the detector noise and was therefore not included in the evaluation of this test. Images from the remaining three cameras can be seen in fig. 2.14.

A further set of images of the same wafer under identical conditions was recorded
2.5 Comparison of InGaAs Cameras

![Graphs showing intensity counts for Goldeye, IK1523, and SWIR-HR with their respective SNR values.](image)

**Figure 2.14:**
PL measurements of the unpassivated as-cut mc-Si wafer at $5.9 \times 10^{17}$/cm$^2$ illumination and 100 ms exposure time. The SNR was calculated using the standard deviation in the homogeneous bottom right area.

with the silicon CCD camera from Andor Technology (see section 2.1). These reference images (shown in fig. 2.15) were taken at exposure times of 100 ms (a) and 10 s (b). It is obvious that the silicon sensor has a much lower sensitivity for the PL radiation, leading to a SNR of only 7.1 for the exposure time of 100 ms. For a fast measurement as required by inline characterization in a solar cell production facility, the InGaAs cameras produce much better image quality as shown in fig. 2.14. On the other hand, the better sensor homogeneity and significantly lower dark current of the silicon CCD allow for much better image quality if exposure time is not a limiting factor, as can be seen in fig. 2.15b. For this reason, the predominantly used camera for this PL setup is the silicon CCD camera. Only for applications where this camera cannot be used, e.g., defect band luminescence measurements, the InGaAs camera is the better choice.

The sensitivity to defect band luminescence was tested for the more sensitive
The Luminescence Imaging Setup

![Image](image_url)

**Figure 2.15:** Reference PL measurements of sample D at identical illumination as fig. 2.14, recorded with the Andor iKon-M silicon CCD camera. The SNR was similarly calculated using the standard deviation in the marked area.

Cameras Goldeye, IK1523 and SWIR-HR with the SiN$_x$:H passivated wafer A. A LC-1300ALP long pass filter from Laser Components GmbH with an edge wavelength of 1300 nm was installed in front of the camera to block all radiation from band-to-band recombinations. The sample was illuminated with a laser intensity of $5.9 \times 10^{17}$ cm$^{-2}$s$^{-1}$ and all cameras were set to 100 ms exposure time. The resulting measurements are shown in fig. 2.16.

As a conclusion of the test, the following results can be established:

- The ARTCAM-031TNIR is significantly less sensitive for this application than the other three cameras. The IK1523 provides serviceable images in most situations but is still noticeably less sensitive than the Goldeye P-032 SWIR Cool and SWIR-HR InGaAs, which perform nearly identical in terms of sensitivity.
- The IK1523 seems to have decent sensitivity, but has obvious problems with image non-uniformity corrections.
- Although the Goldeye P-032 SWIR Cool has a slightly lower SNR than the SWIR-HR InGaAs, it seems to perform better for defect band PL, showing a higher level of detail.

Consequently, the Goldeye P-032 SWIR Cool from Allied Vision Technologies ranked highest, as the main application of the InGaAs camera in this setup will be defect band PLI. Another strong argument in favour of this camera is the
Figure 2.16: Defect band PL of sample $A$ at $5.9 \times 10^{17} / \text{cm}^2 \text{s}$ illumination and 100 ms exposure time. The band-to-band PL was blocked by a 1300 nm long pass filter.

considerably better documentation and software availability at the time of these tests, compared to the similarly sensitive SWIR-HR InGaAs from Photonic Science Ltd.

Note that these results are only valid for the cameras available at the time of this test (Nov 2012). Subsequent camera or software improvements or fluctuations of image sensor quality may change the ranking on a comparatively short time scale.

2.6 Defect Band PL Measurements

Based on the above comparison, the Goldeye InGaAs camera was selected as the most suitable camera and acquired. As a first application the PL emission of a screen-printed multicrystalline silicon solar cell (sample $G$) was examined. By
The Luminescence Imaging Setup

inserting or removing a suitable optical long-pass filter,⁹ both the defect band and
the band-to-band PL could be recorded. Fig. 2.17 shows the respective PL images
> 1300 nm (a and b), and band-to-band PL as seen by the silicon CCD camera (c). To
study the influence of sample temperature, images (a) and (c) were taken with the
sample at room temperature of $T = 300 \text{ K}$. For image (b), the solar cell was placed
onto a metallic base and cooled below 100 K using liquid $\text{N}_2$. The exact sample
temperature could not be measured during this experiment due to electrical and
mechanical problems of the available temperature sensors.

![Image](image_url)

Figure 2.17: Defect band PL (a, b) and band-to-band PL (c) of
sample $\{\text{G}\}$ at $2.5 \times 10^{17}/\text{cm}^2\text{s}$ illumination and 1 s
exposure time. The band-to-band PL was blocked
by a 1300 nm long pass filter for (a) and (b).

As reported by other groups [83, 84], a clear anticorrelation between defect
band luminescence and band-to-band PL can be observed. Areas of high defect
band PL intensity are a sign of strong SRH recombination activity and consequently
emit less band-to-band PL due to the reduced $\Delta n$ under steady-state illumination.

⁹ALP1300 from Laser Components GmbH
The advantage of using defect band PLI to characterize recombination activity can also be seen in fig. 2.17: identifying the bright areas in an image like (a) is an easy task for automation in an industrial environment like solar cell fabrication. In contrast, separating the darker areas in (c) caused by high recombination from other dark structures like the metallization grid requires a significant amount of effort and computational power. For inline solar cell characterization, an InGaAs camera therefore might be beneficial [83].

Another possible application of defect band PLI is the localized classification of SRH recombination centers. As suggested by Johnston et al. [85], the temperature dependence of the defect band PL intensity might allow for the identification of different types of recombinative structures or foreign atoms. Although the intensity increase for lower temperatures reported by Johnston et al. is clearly visible in (b), a quantitative evaluation is not yet possible with the current setup.

With an improved version of the sample holder that enables temperature control and reduces condensation and ice buildup, a spatially resolved measurement of SRH trap potentials might be feasible. Sample temperatures below 100 K, in combination with suitable optical filters would also allow for the spatially resolved measurement of the dislocation lines $D_{1-4}$ reported by Sauer et al. [86] and Koshka et al. [6]. These correspond to various types of dislocations in crystalline silicon, and might enable the contact-free characterization of dislocation density and distribution in silicon wafers.
3 Series Resistance Parametrization

Series resistance in solar cells has a very obvious effect on EL images due to the exponential dependency of intensity on voltage according to eq. (1.46). At current densities similar to those obtained under solar irradiation, these lateral resistances in fingers and emitter lead to a noticeable reduction of the local diode voltage. The voltage drop increases along the current path through finger and emitter. This leads to the reduced luminescence intensity that can be seen in the center between fingers and between busbars, e.g. in the EL measurement displayed in fig. 3.1.

![EL Image at 30 mA/cm²](image1)
![Voltage image calculated from (a)](image2)

**Figure 3.1:** Electroluminescence image (a) of a 12.5 × 12.5 cm² mono-crystalline silicon solar cell (sample F) under an average excitation current density of 30 mA/cm². A 950 nm short-pass filter was placed in front of the camera to reduce blurring. (b) shows the same EL image converted to p-n junction voltages according to eq. (3.2). The dashed rectangle marks the area subsequently used in the averaging process (see section 3.2).

Several approaches to obtain images of series resistance from EL measurements have been published [32, 35–39, 41]. Most of these methods, however, only evaluate the cumulative series resistance from the terminals to the respective point of the solar cell. The series resistance may stem from different parts of the solar cell like front side metal grid, contact between front side metallization and emitter,
emitter sheet resistance, silicon bulk and contact between base and rear side metallization. Being able to quantitatively attribute the global series resistance to these contributing factors would significantly help to determine manufacturing and design problems of silicon solar cells.

The approach presented here is to combine the spatially resolved data from EL images with the cell geometry. The voltages and flow of (majority) charge carriers in the solar cell are simulated with a multilayered, 2-dimensional finite differences model. The different contributions to series resistance listed above are part of the model’s set of parameters. Comparing the resulting voltage map with the one obtained from EL images, the model parameters are adjusted until the best agreement is observed, leading to a final set of series resistance parameters.

3.1 Mathematical Model

To separate the various parameters which have an effect on the local p-n junction voltage, a multilayered analytical model of the solar cell was developed in cooperation with the numerical mathematics group of Prof. Dr. Michael Junk at the University of Konstanz [87]. It includes lateral resistances in the metallization and the emitter layer. Based on a first finite differences solver written in Matlab by Dr. Vita Rutka, a Python implementation of this solver was created to include into the luminescence measurement software. It yields a voltage distribution of the p-n junction surface, which can be fitted to a voltage map obtained from EL measurements. From eq. (1.46) we can derive that the difference in $\Delta \eta$ and therefore p-n junction voltage $U$ between two points with luminescence intensities $\Phi_1$ and $\Phi_2$ is given by

$$
\Delta U = \frac{k_B T}{e} \ln \left( \frac{\Phi_1}{\Phi_2} \right).
$$

We can assume that the maximum EL intensity $\Phi_{\text{max}}$ is generated at a point close to the solar cell busbars and corresponds to the externally measured voltage $U_{\text{ext}}$. This allows for a map of absolute junction voltages

$$
U_{x,y} = U_{\text{ext}} + k_B T \ln \left( \frac{\Phi_{x,y}}{\Phi_{\text{max}}} \right).
$$
3.1 Mathematical Model

3.1.1 Solar Cell Model Layout

In fig. 3.3 the schematic layout of a solar cell with screen printed front metallization is shown. The figure shows the series resistances (blue, green, yellow) that were included in the mathematical model of the solar cell. The local diode characteristics (red) were simulated by the two-diode model [55, 88]:

\[
J(U) = -J_{ph} + J_{01} \left( \exp \left( \frac{eU}{k_B T} \right) - 1 \right) + J_{02} \left( \exp \left( \frac{eU}{2k_B T} \right) - 1 \right) + \frac{U}{R_{sh}}. \tag{3.3}
\]

It accounts for the photo-generated current \( J_{ph} \), diode saturation currents \( J_{01} \) and \( J_{02} \) and the recombination due to shunt resistance \( R_{sh} \). The equivalent circuit of this model is shown in fig. 3.2. The reason to use a parallel circuit of two diodes stems from the different voltage characteristics of the recombination mechanisms introduced in section 1.1.5. Auger and radiative recombination require band-to-band transitions and are described by \( J_{01} \) with an exponent proportional to \( U \). The SRH recombination \( J_{02} \) is dominated by transitions via intermediate states in the middle of the band gap, leading to an exponent proportional to \( U/2 \) [55].

![Figure 3.2: Equivalent circuit of the two-diode model, which was used in the solar cell model to calculate the local current-voltage characteristics between the emitter and rear contact layers.](image)

The modeled area shown in fig. 3.3 is determined by the symmetry constraints in a solar cell. The whole area of a screen printed silicon solar cell is a periodic repetition of the area between the fingers, provided the voltage along the busbars is constant. In a homogeneous solar cell the voltage profile along each finger can therefore be assumed to be the same, which leads to two kinds of symmetry axes parallel to the fingers: One in the middle of each finger (\( \Gamma_F \)) and one in the middle between two fingers (\( \Gamma_S \)). Correspondingly, the symmetry axes parallel to the busbars lie in the middle of a busbar and in the middle between busbars (\( \Gamma_B \) and \( \Gamma_S \)). The whole area of a homogeneous solar cell can therefore be modeled by regarding the area between two symmetry axes, resulting in a symmetry reduced
area with a width of half the finger distance and a height of half the busbar distance.

**Figure 3.3:**
Schematic layout of the solar cell model. The resistances are depicted in a discrete grid only for this illustration, the mathematical model uses continuous conductance values. Blue resistors represent resistance in the metallization, green the contact resistance and yellow the emitter sheet resistance. The local p-n junction including shunt resistance (see eq. (3.3)) is shown as red diodes.

### 3.1.2 Formulation of the Model

In contrast to the simplified depiction in fig. 3.3, the mathematical model is continuous along the two lateral dimensions. A detailed description of the model, along with a proof of the existence of a unique solution can be found in [89]. The modeled two-dimensional areas are the metallization $\Omega_C$ and the emitter $\Omega_E$, with the respective voltage distributions $U_C$ and $U_E$. Both voltage distributions are relative to the equipotential line $\Gamma_B$ on the busbar, while an external voltage $U_{\text{ext}}$ is applied between the busbar and the equipotential rear contact.

The lateral currents $I_C$ and $I_E$ in $\Omega_C$ and $\Omega_E$ are given by Ohm’s law

\[
I_C = -\Sigma_C \nabla U_C \quad \text{(3.4a)} \\
I_E = -\Sigma_E \nabla U_E \quad \text{(3.4b)}
\]

with the metallization conductance $\Sigma_C$ and the emitter conductance $\Sigma_E$. The current densities in $z$-direction follow the continuity equations

\[
\text{div} \ I_C = \frac{1}{R_c} (U_E - U_C) \quad \text{in } \Omega_C, \quad \text{(3.5a)}
\]

\[
\text{div} \ I_E = j(U_{\text{ext}} - U_E) - \frac{1}{R_c} (U_E - U_C) \quad \text{in } \Omega_E, \quad \text{(3.5b)}
\]

where $R_c$ is the specific contact resistance between metallization and emitter areas.
3.2 Fitting Procedure

To compare the mathematical solar cell model with the measured image data, the EL images have to be reduced to the same symmetry region the model describes. The voltage image (see eq. (3.2)) is first segmented along the symmetry lines and the resulting patches are averaged to form a single voltage map of the symmetry region. This requires the exact positions of the busbars and fingers in the EL
An algorithm to automatically detect busbars and fingers was developed, based on autocorrelation of the EL image:

- For further processing, the image usually has to be rotated a little bit so the fingers are perfectly vertical. This is done by averaging the rotated image along the vertical axis until the contrast generated by the fingers is maximal.
- Then, a Fourier transformation of this vertically averaged image is used to obtain the distance and rough position of the periodic finger grid.
- The finger positions are further refined in real space by searching for the minimum EL signal at the finger position.

To rule out edge effects, only the center area of the solar cell is used (see dashed rectangle in fig. 3.1). The intensity data of each symmetry region in this area is averaged and yields a distribution like the one shown in fig. 3.5. Analogous to the model solution in fig. 3.4, the symmetry region is not shown in true geometric scale for clarity.

The mathematical model is then fitted to the solar cell using a least squares approximation, comparing of the voltage distributions from the model and from the EL measurement. The finger line resistance, emitter sheet resistance and $J_{01}$ diode parameter were fitted, while $J_{02}$ and the parallel resistance were kept fixed at values previously determined from a current-voltage (IV) characteristic measurement. As the mathematical model does not account for the missing EL emission from areas covered by the metallization, the left and upper borders of the symmetry region, where the fingers and busbars are located, are excluded from the fit error calculation.
3.3 Fit Results

The presented fitting procedure was applied to multiple screen printed solar cells. The results for the samples $E$ and $F$—which feature homogeneous and selective emitters respectively—are discussed here. For comparison, the resistance values were determined with traditional methods. The emitter sheet resistance of cell $E$ is $\sim 50 \, \Omega/\square$, the line resistance of the fingers was determined to $0.71 \, \Omega/cm$ with a 4-point measurement of the resistance between the two busbars. The contact resistance between metallization and emitter could not be measured non-destructively, it typically lies in the range of $1-10 \, m\Omega \, cm^2$. For cell $F$, a $30 \, \Omega/\square$ emitter was etched back selectively to $65 \, \Omega/\square$ and a finger resistance of $0.63 \, \Omega/cm$ was measured electrically.

Most of the EL images were recorded using the Si CCD camera due to its high spatial resolution. As long wavelength parts of the luminescence spectrum have a long absorption length inside the sensor (see fig. 1.2) and lead to a loss of resolution, a dielectric $950 \, nm$ short-pass filter was placed in front of the camera.

Applying the fitting algorithm to the EL image of sample $E$ shown in fig. 3.1 results in an emitter sheet resistance of $27 \, \Omega/\square$ and a finger line resistance of $0.33 \, \Omega/cm$. Both values are substantially lower than the real values mentioned above. The most probable cause for resistivities being systematically estimated too low is an effect reducing the contrast in the EL image, which the fitting algorithm interprets as a sample with high lateral conductivity. To rule out insufficient camera resolution as a source of low contrast, the same solar cell $E$ was measured again under identical excitation, but with a lower camera position to only acquire the area between the two busbars instead of the whole cell. Even with the increased resolution, virtually the same resistivities were fitted, which can be seen in the second row of table 3.1. So the discrepancy to the real values is most likely not an effect of optical blurring in the camera CCD sensor or objective lens.

A diffusive process inside the solar cell would lead to reduced carrier density gradients and correspondingly lower EL contrast. Likewise, a diffuse refraction of EL light leaving solar cell surface reduces contrast. To simulate this effect, the calculated voltage distributions were subjected to a Gaussian filter function before comparison with the measured voltage map. The standard deviation $\sigma$ of the Gauss distribution was set to $0.5 \, mm$. This did indeed lead to significantly
Table 3.1: Comparison of resistivity values obtained by 4-point probe measurements and the EL image fitting procedure. As can be seen, the fitted values are consistently smaller than the directly measured resistivities, indicating a systematic problem in the EL fit technique.

higher values for the fitted emitter sheet resistance, as shown in row 3 of table 3.1. However, the finger resistance increased only marginally. This is to be expected for a geometrically isotropic blur function, as contrast along the short horizontal dimension of the symmetry region is reduced much more than contrast along the fingers.

The effect of different camera sensors on the measurement and fit result was examined on solar cell $\text{F}^{-}$, which has a selective emitter. As most of the area between contact fingers has an emitter resistivity of $65 \, \Omega/\square$, this is the expected value to obtain from the EL fit. The second to last row of table 3.1 shows the actual results for an EL image recorded by the silicon CCD camera and without the previously applied Gaussian filter. Again, the fitted resistance values are much lower than the reference values for both finger and emitter resistance.

For comparison, an EL image of the same solar cell $\text{F}^{-}$ was recorded using the InGaAs camera detailed in section 2.5 and without the optical 950 nm short-pass filter. It was also fitted with the same model and identical fixed parameters, yielding the results shown in the last row of table 3.1. Interestingly, the resulting emitter sheet resistance is again underestimated and even lower than with the silicon CCD camera. This suggests a systematic error which reduces EL contrast and is more pronounced for the InGaAs camera than for the Si based one.

One process often responsible for reduced contrast in luminescence imaging is the light absorption length inside the camera sensor. If the incident photons are not absorbed close to the CCD sensor surface but rather scattered and absorbed away from the point of incidence, they may contribute to the signal of adjacent pixels. The net effect of this is a blurring of the camera image, which is largely caused by
3.4 Conclusions and Outlook

the long wavelength fraction of the luminescence spectrum [90]. As the absorption length for luminescence light is much shorter for the direct semiconductor InGaAs than for silicon, InGaAs based cameras do not face this problem. If the reduced EL contrast and corresponding low resistance fit values were caused by this effect, the fit values from the InGaAs EL image should be closer to the real values. However, the opposite is the case, making blurring in the camera sensor a rather improbable explanation of the deviations.

Another possible effect leading to contrast reduction is the scattering of luminescence light exiting the solar cell at the front surface. This surface is usually textured to improve light trapping during operation, which on the other hand enables EL from a wide array of angles to exit the solar cell surface towards the camera. Due to the possibility of lateral travel, the EL light exiting from one spot on the solar cell surface also contains photons from adjacent regions. As the InGaAs camera sensor is much more sensitive to the long wavelength part of the luminescence spectrum, it records photons which have travelled longer lateral distances inside the solar cell. This may lead to a higher amount of blurring and explain the reduced contrast observed by this camera.

However, the explanation above may only account for the discrepancy of the emitter resistance and can not satisfactorily explain the deviating finger resistance values, which are consistently off by a factor of \( \sim 2 \). Another possible explanation which may not be completely ruled out are errors in the formulation or implementation of the solar cell model. However, Glatthaar et al. reported a similar factor of 2 for a completely different approach to estimate lateral resistance from EL images [39], so a physical cause seems more likely. Also, solar cell geometry optimizations with the same model and implementation used here resulted in parameters very close to those reported by other simulations.

3.4 Conclusions and Outlook

The presented method allows for a fast, quantitative and nondestructive measurement of series resistances in crystalline silicon solar cells. Although quantitative agreement to the actual resistivity values could not yet be reached, it could be shown that a combination of luminescence imaging and geometrical properties extracted from these images allows for a separation of different contributions to
the series resistance of a screen printed solar cell. To further improve on this technique and make it applicable for quantitative measurements, several approaches may be considered:

- An improved solar cell model including diffusive effects of the minority charge carriers inside the solar cell base has been developed by Kümpflein and published recently [91]. Integrating this model with the fitting algorithm may account for some of the observed contrast reduction and lead to better fit values. It is certainly a much more sophisticated approach than the previously applied Gaussian filter on the end result, with physically well defined parameters.

- The use of deconvolution on luminescence images to mitigate blurring effects of the camera has recently been demonstrated by Walter et al. [90]. With proper algorithms and characterization of the camera setup, a significant increase in image sharpness is possible. However, for subsequent quantitative evaluations like the one presented here, it may be difficult to precisely quantify blurring processes in the camera and the wafer. Due to the evaluation of gradients in the image, the series resistance fitting might be very susceptible to slight variations of the deconvolution parameters.

- Several other approaches for luminescence based series resistance characterization are based on combining luminescence images with varying electrical and optical excitation [35, 38, 41]. This may also be applied here to improve the fit convergence and robustness, as well as reducing the number of fixed parameters to be supplied to the algorithm.

Some of these improvements have already been applied with good results in a recent publication by Padilla et al. [92], where a similar approach for another type of solar cells was evaluated. With this in mind, suitable improvements of the technique proposed in this work are a promising path to a fast, quantitative characterization of series resistance contributions in screen printed silicon solar cells.
4 Time-Resolved Photoluminescence Imaging

During the course of this work, a new characterization method for silicon wafers called time-resolved photoluminescence imaging (TR-PLI) was developed and filed for patent [93]. Three different measurement setups were created, with the aim to increase the time-resolution for minority charge carrier lifetime maps. While the experimental realization is slightly different for each setup, they are all based on the same measurement process and evaluation procedure. The general steps of evaluation to obtain minority charge carrier lifetime maps will therefore be covered in the first section of this chapter, followed by sections describing each measurement setup and the associated adaptions of the evaluation theory. Each of the three setups has its advantages and disadvantages. In the order presented here, the general trend is an increase in experimental complexity and equipment cost on the one hand, which leads to a simplified evaluation and a wider measurement range on the other hand. Therefore, all three approaches are presented here to provide a broad basis for further development. The first generation shutter setup will be discussed in section 4.2.1, followed by section 4.2.2 for the more advanced second generation setup using a shutter in an intermediate image plane. Section 4.2.3 will finally cover the use of an image intensifier unit as an alternative to the rotating shutter wheel.

Some of the methods and results shown in this chapter have already been presented at scientific conferences [12, 15] or published in peer-reviewed journals [14, 16] at the time of their development. The scope of this work is to give a comprehensive comparison of the required experimental equipment and evaluation steps, as well as the obtainable results of each method.
4.1 Basics and Evaluation Theory

In contrast to the calibration procedure for steady-state PL images presented in section 2.4, the evaluation of time-resolved (sometimes also called transient) PL imaging does not rely on the absolute intensity of the recorded luminescence light. Instead, information about the dynamic behaviour of excited charge carries in the sample is extracted from a sequence of PL images.

While the relative intensities of these images are certainly important and the basis for the analysis, a key feature of time-resolved measurements is that they are calibration-free, i.e., the proportionality constant $A$ from section 2.4 may remain unknown. In particular—and in contrast to the calibrations in section 2.4—$A$ and $N$ do not have to be laterally constant across the sample area for the methods presented here. The case of a non-constant calibration factor $A_{x,y}$ is for example possible for multicrystalline silicon wafers, where different grain orientations can lead to significant differences in light absorption and emission [11]. An overview of factors influencing the relationship between PL generation and camera signal may be found in [21].

The development of this time-resolved photoluminescence imaging technique was inspired by a publication of Ramspeck et al. [94] using time-resolved thermal imaging on silicon wafers. While this method called dynamic ILM offers many of the above mentioned advantages, it has a lower spatial resolution than PLI and requires the use of expensive thermography cameras. This led to the development of time-resolved PLI as described here, as well as an independent realization by Herlufsen et al. [13] using a high-speed InGaAs camera.

In the following section, the theoretical considerations leading to the current setup and measurement procedure will be described. They are also basis for the evaluation procedure required to calculate effective lifetime images from the recorded data. For an implementation of the described algorithm in the C programming language, see appendix A.3. It should be noted that other evaluation approaches for similar measurement methods have been published [13, 95], which might prove advantageous if properly adapted to this technique. This adaption could, however, not be realized in the course of this work and remains a promising field for further study.
To determine the dynamic properties of minority charge carriers in a silicon wafer, the wafer has to be subjected to a time-dependent, non-constant generation rate $G(t)$. In the case of TR-PLI this is accomplished by a periodic illumination of the sample with an excitation frequency $f_{\text{exc}}$ and a corresponding excitation period $T = 1/f_{\text{exc}}$.

The experimentally easiest and most reliable way of non-continuous illumination is the rectangular on/off modulation of the light source. To obtain a high average illumination intensity and therefore strong PL signals, a high illumination duty cycle is advantageous. For the similar method of fluorescence lifetime imaging microscopy (FLIM), rectangular pulses of different duty cycles were compared and an optimal duty cycle of 20% was reported [96]. However, the loss of SNR at 50% duty cycle is moderate, so in the following a fixed duty cycle of 50% was chosen to take advantage of symmetry effects in the convolution integral (see below).

The thickness-averaged generation rate in the sample

$$G(t) = \begin{cases} \mathcal{F}(1 - R)/w & \text{for } t < T/2, \\ 0 & \text{for } t > T/2 \end{cases}$$

depends on the incident photon flux $\mathcal{F}$, the thickness of the sample $w$ and the reflectivity $R$ at the illumination wavelength. Transmission of excitation light was neglected in this model because both light sources (see section 2.3) have short absorption lengths below 15 µm in silicon. However, it could be accounted for straightforwardly by including it into the term $(1 - R)$.

Thickness-averaged values for $G$ and $\Delta n$ were used rather than depth-dependent quantities, which is a significant simplification. However, numerical simulations showed that the transient of $\Delta n$ is mainly unaffected by this depth-dependency for realistic values of surface recombination velocity and bulk lifetime. As the absolute value of $\Delta n$ is not particularly relevant for the evaluation of $\tau_{\text{eff}}$, the simplification may be considered acceptable in this case. Note that for samples with high surface recombination and steep carrier density profiles (see section 1.2.1), the approximation may lead to larger errors [67]. However, such samples—e.g., as-cut silicon wafers—are not the main focus of the TR-PLI technique, as an absolute effective carrier lifetime for samples with strongly dominant surface recombination is usually not a good measure for bulk material quality or final solar
The basic differential equation for the excess carrier density $\Delta n$ is

$$\frac{d\Delta n}{dt} = G(t) - \frac{\Delta n}{\tau_{\text{eff}}}.$$  \hspace{1cm} (4.2)

In general, $\tau_{\text{eff}}$ depends on the density of excess charge carriers $\Delta n$, so the solution to eq. (4.2) may become complicated. For most wafers and the available illumination intensities of the measurement setup, this dependence of $\tau_{\text{eff}}$ on $\Delta n$ is small, so a constant $\tau_{\text{eff}}$ may be assumed. This leads to a simple mono-exponential solution for $\Delta n(t)$ but may be inaccurate if the assumption does not hold. However, this limitation is common to all methods extracting a single lifetime value from a transient curve and should be kept in mind when interpreting the results. Solving for $\Delta n(t)$, we obtain

$$\Delta n(t) = \begin{cases} 
\Delta n_0 \left(1 - s \exp\left(-\frac{t}{\tau_{\text{eff}}}\right)\right) & \text{for } t < T/2, \\
\Delta n_0 \left(s \exp\left(-\frac{t-T/2}{\tau_{\text{eff}}}\right)\right) & \text{for } t > T/2
\end{cases} \hspace{1cm} (4.3)$$

where $\Delta n_0 = G(0)\tau_{\text{eff}}$ is the excess carrier density under steady-state illumination and $s$ is a factor corresponding to the “charge carrier saturation” $\max(\Delta n(t))/\Delta n_0$ of the sample during the excitation phase. It can be determined by solving eq. (4.3) for periodic boundary conditions:

$$s = \frac{1}{1 + \exp\left(-\frac{T}{2\tau_{\text{eff}}}\right)}.$$

The assumption of periodic boundary conditions $\Delta n(0) = \Delta n(T)$ is valid for the long-term steady-state after several excitation cycles, when the amount of generated charge carriers during an excitation cycle is equal to the number of recombination processes in the same time.

The injection-dependent PL intensity $\Phi$ at room temperature is given by

$$\Phi(\Delta n) = B\Delta n(N + \Delta n), \hspace{1cm} (4.4)$$

where $N$ is the doping concentration and $B$ is the coefficient of radiative recombination. $B$ is constant except for high values of $\Delta n$ [98], which do not occur in
4.1 Basics and Evaluation Theory

the wafers currently investigated with this method. For samples with high \( \tau_{\text{eff}} \) and high illumination intensities, the effect may become relevant and would have to be included, at the cost of making the subsequent equations more complex. Using the time-dependent excess carrier density from eq. (4.3), we obtain a PL intensity \( \Phi(t) \).

If we integrate \( \Phi(t) \) over the entire excitation period \( T \), we obtain

\[
\int_0^T \Phi(t) \, dt = B \Delta n_0 (N + \Delta n_0) \frac{T}{2} + B \Delta n_0^2 \int_0^{T/2} 2s^2 \exp \left( -\frac{2t}{\tau_{\text{eff}}} \right) - 2s \exp \left( -\frac{t}{\tau_{\text{eff}}} \right) \, dt.
\]

\[
= \Phi_0 \frac{T}{2} + B \Delta n_0^2 \tau_{\text{eff}} \left( 2s \exp \left( -\frac{T}{2\tau_{\text{eff}}} \right) - s^2 \exp \left( -\frac{T}{\tau_{\text{eff}}} \right) - 2s + s^2 \right)
\]

(4.5)

The first summand \( \Phi_0 \frac{T}{2} = B \Delta n_0 (N + \Delta n_0) \frac{T}{2} \) is the expected result for a steady-state PL measurement of the exposure time \( T/2 \). Comparing the second summand to the first, it can be seen that its contribution is not significant if either \( \Delta n_0 \ll N \) or \( \tau_{\text{eff}} \ll T \) (see fig. 4.1). For many silicon wafers, the condition \( \Delta n_0 \ll N \) (also called low injection) cannot be overcome with the light intensity available in the measurement setup. It is therefore not feasible to measure time-dependent effects of the charge carrier concentration by integrating the PL intensity over one or many excitation periods. On the other hand, the evaluation of \( \Phi(t) \) at a single specific point \( t \) is not possible with PL imaging, as the camera always requires a finite exposure time during which the incoming signal is integrated. Making this integration time very short leads to a small signal and a bad signal to noise ratio.

**Figure 4.1:**
Normalized PL signal \( \frac{\int_0^T \Phi(t) \, dt}{\Phi_0 T} \) as a function of \( T/\tau_{\text{eff}} \). At typical values of \( \Delta n_0 / N \ll 0.1 \), the time-integrated PL signal under pulsed excitation is close to the constant value 0.5 under continuous illumination and depends only weakly on \( \tau_{\text{eff}} \). Solely for samples where \( \Delta n_0 \approx N \) can be reached, an evaluation of \( \tau_{\text{eff}} \) based on the comparison of time-integrated PL under steady-state and pulsed illumination might be feasible.
especially in the case of the comparatively weak PL emission of silicon.

This shows that a measurement of the transient carrier lifetime is only possible with a synchronized non-steady-state excitation and a non-steady-state recording of the PL emission on a time-scale comparable to $\tau_{\text{eff}}$. Typical values of $\tau_{\text{eff}}$ in crystalline Si range from $<1$ µs to 5 ms, depending on material and surface passivation quality. To reliably resolve lifetime values in the low µs range, modulation periods $<100$ µs have to be used.

The shutters and image readout times of CCD cameras commonly used for PL imaging are two to three orders of magnitude slower than this, so a time-resolved measurement with a stock silicon CCD camera is not viable. However, with the addition of an external shutter device between sample and camera, the slow internal camera shutter can be permanently kept open and does not limit the obtainable time-resolution. Two very different high speed shutters were evaluated in this work and will be compared in the following sections. Despite their differences, the effect of each shutter can be described by a respective transfer function $H(t)$, which describes the transmissivity as a function of time. When the excitation and the shutter are synchronized, a camera integration over many excitation periods yields the same average signal as integrating over just one cycle. The accumulation of many periods on the camera sensor creates a clear image even at low light levels and leads to much lower noise levels than multiple short exposures and readouts used in similar approaches [13]. The resulting image intensity $I$ for a pixel at position $(x,y)$ can be written as the convolution

\[ I_{x,y}(\varphi) = A_{x,y} \int_0^T \Phi_{x,y}(t) H \left( \frac{(\varphi + \theta_{x,y})T}{2\pi} - t \right) dt, \]  

where $\varphi$ is the phase offset between excitation and shutter. The constant $\theta_{x,y}$ is an offset to accommodate for a laterally varying shutter phase and depends on the pixel position. This is relevant for the mechanical shutter used in sections 4.2.1 and 4.2.2.

In practice, $I_{x,y}(\varphi)$ is only observed at a finite set of $N$ phase values $\varphi_n$, which are usually equally spaced like

\[ \varphi_n = \frac{2\pi n}{N}. \]  

Typical values of $N$ are in the range of 4–16 for a reasonably fast measurement.
4.1 Basics and Evaluation Theory

without excessive amounts of raw data. The actual TR-PLI measurement therefore consists of \( N \) PL images, each taken with the respective value of \( \varphi_n \) and otherwise identical conditions. An example for such a set of images can be seen in fig. 4.10.

To reduce systematic errors from changes in PL intensity during the measurement due to sample degradation [99, 100], the images are not recorded sequentially. The recording order \( n = P_N(1 \ldots N) \) is determined by permutation sequences \( P_N \) computed by Munster and Gadella [101], which minimize systematic error for an assumed slow exponential degradation.

To extract \( \tau_{\text{eff}} \) from the measured intensities \( I_{x,y}(\varphi_n) = I_{x,y,n} \), several approaches may be considered:

- To directly determine the time-dependent luminescence \( \Phi_{x,y}(t) \) from the measured intensities, the convolution integral in eq. (4.6) has to be deconvoluted. Effective lifetime values can then be calculated from the slope of this transient PL curve. However, due to the limited number of measurement points and the noise of the PL images this approach is difficult to realize. Efforts in this direction were prone to oscillatory artifacts and did not produce useful results.

- An alternative approach is the comparison and fitting of \( I_{x,y,n} \) with a model of the expected intensities depending on \( \tau_{\text{eff}} \) and other parameters. The model of \( \Phi(t) \) as introduced above was used for this purpose. After convolution according to eq. (4.6) with the respective transfer function \( H(t) \), \( \tau_{\text{eff}} \) and other parameters can be obtained by a least squares fit using the Levenberg-Marquardt algorithm [102].

- A third approach, which was only recently brought to our attention, is the use of discrete Fourier transformations (DFT) to obtain the phase shift between \( G(t) \) and \( \Phi_{x,y}(t) \), which may be used to determine \( \tau_{\text{eff}} \) [103]. This method is commonly used for FLIM of biological samples [95]. However, for a straightforward evaluation it requires a sinusoidal modulation of excitation light and shutter transmission, or even stronger assumptions on the PL signal shape than the evaluation theory presented above. This could not yet be accomplished in this PL setup, but may be a promising approach for further development.
In conclusion, the most stable approach proved to be the least squares fit of the convoluted signal $I_{x,y}(\varphi)$ with a suitable model. In the following sections, each of the shutter setups will be described along with its transfer function and implications for the evaluation procedure.

### 4.2 Setups and Measurement Procedures

#### 4.2.1 Single Lens Setup

A layout of the first generation measurement setup for time-resolved photoluminescence imaging (TR-PLI) is shown in fig. 4.2. Based on the standard PLI setup as described in chapter 2, a rotating shutter wheel was placed in front of the objective lens. The shutter wheel in this design has a diameter of 14 cm. Four sectoral slits with an opening angle of $9^\circ$ each yield a mark to space ratio of 9 : 1, or $D = 10\%$ duty cycle.

As in standard (steady-state) photoluminescence measurements, the sample (a) is placed beneath the camera on an LED panel (b) and illuminated homogeneously from below. The LED panel can be switched on and off by an excitation controller with very little delay. A detailed analysis of the LED time characteristics will follow in section 4.2.2.

The shutter wheel (f) is driven by a brushless DC motor at speeds between
3000 rpm and 15000 rpm, which is a slit frequency range from 200 Hz to 1 kHz with 4 slits. An additional small laser and a photodiode form a light barrier to detect the shutter wheel slits. This reference signal from the photodiode is the input for a software phase-locked-loop (PLL) implemented on an ATmega328 micro controller. The PLL generates a rectangular output signal for the LED panel with exactly the shutter frequency $f$ and a phase offset $\phi$ which can be programmed by the measurement PC.

The exposure process of the CCD chip during one excitation cycle is determined by the transfer function $H(t)$ of the shutter wheel (fig. 4.3). To understand this transfer function $H(t)$, we have to take a look at the light propagation from a point $X$ on the sample surface to the corresponding pixel $Y$ on the CCD sensor as shown in fig.4.4.

In a standard PL setup without shutter wheel, a cone of light from $X$ to the circular aperture area of the objective lens is focused by the lens to point $Y$. The intersection of this cone with the rotational plane of the shutter wheel forms a slightly smaller circle $C$, through which all light going to $Y$ must pass. For reasonable aperture sizes, we can assume a homogeneous contribution of the whole lens aperture area to the light intensity reaching $Y$. This is equally true for the light passing through $C$, which is depicted in fig.4.3 below the resulting transfer function $H$. For full occlusion of $C$, the resulting $H = 0$ is obvious. Likewise, no occlusion, i.e., a slit in front of the lens, leads to $H = 1$. For partial occlusion, $H$
corresponds to the area $\mathcal{A}$ of the resulting circular segment:

$$
\mathcal{A}(\alpha) = \frac{2}{\pi} \int_{0}^{\alpha} \sqrt{1-x^2} \, dx + \frac{1}{2} = \frac{\alpha \sqrt{1-\alpha^2} + \arcsin(\alpha)}{\pi} + \frac{1}{2},
$$

(4.8)

where $\alpha \in [-1, 1]$ is the amount of occlusion. It depends on the previously introduced shutter duty cycle $D$ and period $\mathcal{T}$, as well as the ratio between diameter $c$ of $C$ and the arc length $d$ of the slit (at the initial point of contact between $C$ and the slit):

$$
\alpha(t) = \begin{cases} 
1 & \text{for } |t| < \frac{DT}{2} - \frac{D\mathcal{T}}{2} \xi \frac{1}{3} \\
-(|t| - \frac{DT}{2})/(\frac{D\mathcal{T}}{2} \xi) & \text{for } \frac{DT}{2} - \frac{D\mathcal{T}}{2} \xi < |t| < \frac{DT}{2} + \frac{D\mathcal{T}}{2} \xi \\
-1 & \text{for } |t| > \frac{DT}{2} + \frac{D\mathcal{T}}{2} \xi
\end{cases},
$$

(4.9)

Consequently, for slits larger than $c$, the transmit function $H(t)$ of the shutter wheel consists of three regions: the rising slope, given by $\mathcal{A}(-1\ldots1)$, a plateau with 100% transmission and the falling slope, given by $\mathcal{A}(1\ldots-1)$. If the shutter wheel slits are smaller than $c$, only a fraction of the circular area contributes to the transmitted signal at any time and the integration boundaries in eq.(4.8) have to be modified to integrate over this stripe.

For a shutter wheel with sectorial slits, the transition time of a slit is equal for
4.2 Setups and Measurement Procedures

all points of the intermediate image, so $H(t)$ does not depend on the pixel position $(x,y)$.

Due to the arcsin in eq. (4.8), the exact solution of $A(\alpha)$ is not well suited to calculate the convolution integral in eq. (4.6). However, a polynomial approximation accurate to $\sim 10^{-3}$ could be found, which is given by

$$A_{pol}(\alpha) = \begin{cases} 
\frac{4\sqrt{2}\alpha+1)^{3/2}}{3\pi} - \frac{\sqrt{2}(\alpha+1)^{3/2}}{5\pi} & \text{for } \alpha < -\frac{1}{2} \\
\frac{1}{2} + \frac{2\alpha}{\pi} - \frac{\alpha^3}{3\pi} & \text{for } -\frac{1}{2} < \alpha < \frac{1}{2} \\
1 - \frac{4\sqrt{2}\alpha+1)^{3/2}}{3\pi} + \frac{\sqrt{2}(\alpha+1)^{3/2}}{5\pi} & \text{for } \alpha > \frac{1}{2}
\end{cases}$$

(4.10)

and shown in fig. 4.5, along with $A(\alpha)$ and the residual difference $A_{pol}(\alpha) - A(\alpha)$.

Using this approximation in combination with eq. (4.9), we obtain a piecewise transmit function

$$H(t) = A_{pol}(\alpha(t)),$$

(4.11)

which can be used to convolve the modeled PL signal $\Phi(t)$ as shown in fig. 4.6. This convolution integral consists only of polynomial and exponential expressions and should have an analytical solution. However, the analytical solution proved to be too unwieldy for practical application, so a numerical solution with 500 points/2$\pi$ node density was used for fitting the camera signal.

In addition to the transmit function $H(t)$, the local phase shift $\theta_{x,y}$ introduced in eq. (4.6) has to be determined. This can also be derived from fig. 4.4 by looking at the previously introduced circle $C$ in the shutter plane. Its center is offset from the
Figure 4.6: PL signal $\Phi(t)$ (magenta) of a sample with $\tau_{\text{eff}} = 530\,\mu$s and convolved intensity $I(\varphi)$ as seen by the camera (blue). The dashed red line shows $G(t)$ from illumination, the inset shows $H(t)$ in the correct horizontal scale as parametrized for the described setup. For better comparison, all curves are shown in one plot. However, note that $I$ is a function of phase, while $G$, $\Phi$ and $H$ are functions of time.

symmetry axis by an amount proportional to the distance of $(x, y)$ from the middle of the image and the distance between shutter wheel and lens aperture.

The resulting phase shift may be written as

$$\theta_{x,y} = N_{\text{slits}} \arctan \left( \frac{x + \delta x}{y + \delta y} \right) + O. \quad (4.12)$$

The constants $\delta x$ and $\delta y$ correspond to the lateral offset between image origin and rotational axis of the shutter wheel, scaled with the vertical distance between shutter wheel and lens aperture. The constant $O$ is a position-independent offset, which may result from small position errors and delay times of the feedback light barrier.

As all parameters in eq. (4.12) have a strong influence on the lifetime evaluation results, they can and must be obtained experimentally from a calibration measurement. For the single lens setup, this was done by removing the short-pass filter from the LED panel and directly recording the long wavelength part of the excitation light through the shutter wheel. A full sequence of phase images $I_{x,y,n}$ was then recorded and used to calculate $\theta_{x,y}$ by interpolating $I$ for minimum intensity. Subsequently, the parameters of eq. (4.12) were obtained from a least squares fit of this map of $\theta_{x,y}$.

For later setups, the procedure was simplified by the use of a suitable calibration sample (see section 4.2.2) to avoid the risky and time consuming procedure of filter removal and installation.
4.2 Setups and Measurement Procedures

4.2.2 Double Lens Setup

![Diagram of double lens setup]

Figure 4.7: Layout of the improved shutter wheel setup with two objective lenses. As before, the sample (a) is periodically illuminated by the LED panel (b) or laser (c). The emitted PL image is focused by the first objective lens (e) to an intermediate image plane, where the shutter wheel (f) rotates. The shuttered image is then projected onto the camera sensor (d) by a second objective lens (g).

The TR-PLI setup described in the previous section is limited to carrier lifetimes above ~300 µs. This is mainly due to the limited shutter frequency, which stems from the maximum angular velocity of a rotating shutter disk and the requirement of a slit size larger than the lens aperture due to the wide slopes of $H(t)$. Another shortcoming is the fact that the complex shape of eq. (4.11) makes the solution of the convolution integral in eq. (4.6) difficult. Although an analytical solution of eq. (4.6) might be possible when using the polynomial approximation in eq. (4.10), no such solution was found in practice. The evaluation therefore had to be done using a highly interpolated numerical convolution, making it computationally expensive and slow.

To avoid these limitations, the previous setup shown in section 4.2.1 was modified by adding a second objective lens. The resulting double lens setup is schematically shown in fig. 4.7.

The first objective lens (e) creates an intermediate image of the luminescence radiation of the sample. The shutter wheel (f) rotates in the image plane of this intermediate image and periodically interrupts the focused luminescence radiation with a 1:1 mark to space ratio. The shuttered intermediate image is then projected
onto the CCD sensor of the camera (d) with a second objective lens (g). Both lenses are Zeiss PLANAR T 1,4/50 ZF-IR with custom made mounting to allow for the unusual reproduction scale. The lens (e) is in the same position as with steady-state PL imaging, creating an intermediate image with the camera sensor size of $13 \times 13 \text{mm}^2$. The second lens (g) does a nearly 1:1 reproduction. Only a small margin of the camera sensor area has to remain unused due to vignetting effects of the double lens system. To keep these vignetting effects small, both lenses must have a large aperture diameter. The Zeiss $f = 50 \text{mm}$ lenses with aperture $a = f/1.4 \approx 35 \text{mm}$ proved to be the best available solution to this requirement.\footnote{Obviously, the lenses also have to satisfy the basic requirements for PL imaging described in section 2.2.}

Although most of the components remain unchanged, this setup significantly differs from the earlier one. All luminescence light emitted at a point $X$ of the sample is focused to a point $X'$ on the intermediate image plane. By placing the shutter wheel at this intermediate image plane, the whole signal from $X$ is blocked instantaneously as soon as the shutter wheel edge passes through $X'$. In section 4.2.1, all PL light had to pass through a circular area $C$. The equivalent of $C$ in the double lens setup is the point $X'$. As the circle diameter $c$ becomes zero, eq. (4.9) simplifies to

$$a(t) = \begin{cases} 1 & \text{for } |t| < \frac{D}{T} \\ -1 & \text{for } |t| > \frac{D}{T} \end{cases}. \quad (4.13)$$

The knowledge of $A(a)$ (eq. (4.8)) is not required anymore and $H(t)$ becomes a simple rectangular function

$$H(t) = \begin{cases} 1 & \text{for } |t| < \frac{D}{T} \\ 0 & \text{for } |t| > \frac{D}{T} \end{cases}. \quad (4.14)$$

As can be seen from this, the double lens setup allows for a true rectangular shuttering of a whole image, albeit not with a global phase for the whole image. It is to our knowledge the first use of focal plane shuttering in an imaging setup and was therefore filed for patent [93].

With this simple form of $H(t)$, the convolution integral from eq. (4.6) can be
written as

\[ I_{x,y}(\varphi_n) = I_{x,y} \left( A_{x,y} \int_{0}^{T} \Phi_{x,y}(t) H \left( \frac{(\varphi_n + \theta_{x,y}) t}{2\pi} - t \right) dt \right) = A_{x,y} \int_{t_1}^{t_2} \Phi_{x,y}(t) dt, \]

where \( t_1 = \left( \frac{n + \theta_{x,y}}{N} \right) T \) and \( t_2 = t_1 + DT \). To make the numerical evaluation more robust and avoid rounding errors, the solution for this integral was calculated after some normalization steps, namely setting \( A = 1 \) and replacing \( t_1, \tau_{\text{eff}} \) and \( N \) with \( \hat{t} = \frac{2\pi}{\tau_1} t_1, \hat{\tau} = \frac{2\pi}{\tau_\text{eff}} \) and \( \hat{N} = \frac{N}{\Delta n_0} + 1 \), respectively. The resulting normalized intensity function after some simplifications is

\[
I_{x,y,n} = \begin{cases} 
\left(4(\pi + \hat{\tau} - \hat{t}) - 6\hat{\tau}e^{-\hat{t}/\hat{\tau}} - \hat{t}/\hat{N}\right)e^{\hat{t}/\hat{\tau}} + (4(\pi + \hat{\tau} - \hat{t}) - 2\hat{\tau}e^{-\hat{t}/\hat{\tau}} + \hat{t}/\hat{N})/e^{\hat{t}/\hat{\tau}} \\
+((\pi + \hat{\tau} - \hat{t}) - 2\hat{\tau}e^{-\hat{t}/\hat{\tau}} - \hat{t}/2\hat{N})e^{\frac{2\pi}{\hat{\tau}}} + ((\pi + \hat{\tau} - \hat{t}) + \hat{t}/2\hat{N})/e^{\frac{2\pi}{\hat{\tau}}} \\
+6(\pi + \hat{\tau} - \hat{t}) - 6\hat{\tau}e^{-\hat{t}/\hat{\tau}} \right)/\left((1 + 2e^{\frac{2\pi}{\hat{\tau}}} + e^{\frac{2\pi}{\hat{\tau}}})\right) & \text{for } \hat{t} < \pi, \\
-\left(4(\pi + \hat{\tau} - \hat{t}) - 6\hat{\tau}e^{-\hat{t}/\hat{\tau}} + \hat{t}/\hat{N}\right)e^{\hat{t}/\hat{\tau}} + (4(\pi + \hat{\tau} - \hat{t}) - \hat{t}/\hat{N})/e^{\hat{t}/\hat{\tau}} \\
+((\pi + \hat{\tau} - \hat{t}) - 6\hat{\tau}e^{-\hat{t}/\hat{\tau}} - 2\hat{\tau}e^{-\hat{t}/\hat{\tau}} + \hat{t}/2\hat{N})e^{\frac{2\pi}{\hat{\tau}}} + ((\pi + \hat{\tau} - \hat{t}) - \hat{t}/2\hat{N})/e^{\frac{2\pi}{\hat{\tau}}} \\
+6(\pi + \hat{\tau} - \hat{t}) - 2\hat{\tau}e^{-\hat{t}/\hat{\tau}} \right)/\left((1 + 2e^{\frac{2\pi}{\hat{\tau}}} + e^{\frac{2\pi}{\hat{\tau}}})\right)^2 & \text{for } \hat{t} > \pi 
\end{cases}
\]

The C implementation of this solution, which was used to evaluate the measurements shown in this work, can be seen in appendix A.3. An exemplary lifetime fit for a single pixel can be seen in fig. 4.8.

It is important to note that in eq. (4.14) \( H(t) \) is now independent of the ratio \( c/d \), so the slit width is not constrained by the aperture diameter. This allows for a much higher number of slits in the shutter wheel and corresponding higher shutter frequencies, significantly improving the obtainable time resolution. Shutter wheels with 2, 10 and 60 slits were manufactured out of 0.5 mm thick aluminum. In combination with a precisely controllable brushless DC motor\(^2\) stable frequencies from 40 Hz with a 2 slit wheel up to 10 kHz with the 60 slit wheel can be obtained. For a smooth rotation at low frequency, it proved to be essential that the shutter wheel is directly mounted to the motor shaft and no additional transmission elements are

\(^2\)Faulhaber GmbH, model 4490H024B K1155

81
used. Mechanical transmissions like gears or belt drives introduce additional drag and vibrational modes, reducing the motors ability of smooth low-speed rotation.

As in the single lens setup, the excitation controller synchronizes to the shutter wheel using a phase-locked-loop and switches the LED panel with an adjustable phase delay and duty cycle. Due to the higher frequencies supported by this shutter, the previous controller based on an ATmega328 micro controller was not fast enough for a precise software-defined PLL. It was replaced by a new design based on an STM32F103 chip, which is a 32 bit processor running at 72 MHz. The final PLL design on this controller (see appendix A.1) was tested using a frequency generator and showed good locking speed and jitter < 1 % in the 20 Hz to 20 kHz range.

As the excitation signal is phase locked to the shutter wheel frequency, the primary control of the excitation frequency is done by setting the appropriate rotational speed of the shutter motor. This is also a task of the excitation controller, which uses a feedback loop to generate the control signal sent to the motor driver. For the previously mentioned frequency range, the excitation frequency is typically stabilized to about ±0.2 Hz.

During the measurement, the light source (LED panel or laser) is switched on at $t = 0$ for half the period $T$. As the model introduced in section 4.1 assumes instantaneous switches between full illumination and no illumination, the slopes of the light sources have to be significantly shorter than the measured effective

---

3 Olimex Ltd., STM32-H103 board
4 Faulhaber GmbH, model SC5008S 4289
minority charge carrier lifetime $\tau_{\text{eff}}$ of the silicon sample. A fast Si photodiode with ns rise-time and a digital storage oscilloscope were used to measure the slopes shown in fig. 4.9. Due to the smaller current of a diode string in the LED panel ($\leq 100\,\text{mA}$) compared to the laser diode current (up to $14\,\text{A}$), the slopes of the LED illumination are shorter than the laser slopes.

![Graph showing rising and falling slopes of the two light sources at full power.](image)

**Figure 4.9:** Rising and falling slopes of the two light sources at full power. Note the different time axis scaling. In order to quantify the switching times, the measured data were fitted with an exponential decay.

From the fitted exponential curves in fig. 4.9, we can obtain switching time constants of $\sim 0.3\,\mu\text{s}$ for the LED panel and $\sim 2\,\mu\text{s}$ for the laser. This constitutes a lower limit of reasonably measurable carrier lifetimes of about 10 times the switching times of the respective light source. For lower $\tau_{\text{eff}}$, the influence of the slopes would have to be included into the evaluation model. Some of the systematic error introduced by this illumination delay may also be avoided by the following calibration procedure.

As in section 4.2.1, the rotation of the shutter wheel through the intermediate image leads to a pixel-dependent phase offset $\theta_{x,y}$ (see eq. (4.15)). It is of the same form as in eq. (4.12), with the difference that $\delta x$ and $\delta y$ now only depend on the relative size and position of intermediate image and shutter wheel.

For this setup, the calibration of $\theta_{x,y}$ was done by minimizing the difference between apparent and true lifetime of a known calibration sample. The most suitable sample for this purpose proved to be a piece of FR-4 circuit board base material, which is made of fiber glass layers embedded in epoxy. It emits a comparatively strong fluorescence signal at about 1000 nm with a lifetime below
Figure 4.10: TR-PLI data set of $N = 8$ PL images of sample $A$, recorded with the double lens setup. Each image is recorded with a different phase shift $\varphi_n = \frac{2\pi n}{N}$, causing the apparent left to right progression of the shutter wheel occlusion pattern described by $\theta_{x,y}$.

10 ns.\textsuperscript{5} In comparison to the much larger photoluminescence lifetimes of Si in the $\mu$s to ms range, this can be used in good approximation as a zero lifetime sample. A TR-PLI recording of this FR-4 board is iteratively evaluated while varying $\delta x$, $\delta y$ and $O$ to minimize any gradients in the lifetime map and obtain a homogeneous value of 0 $\mu$s.

Although the double lens setup described above performs significantly better than the single lens version in terms of lifetime detection limits, it is still limited by the speed of the rotating shutter wheel. At 10 kHz—which is 10000 revolutions per minute (RPM) with 60 slits—values down to $\tau_{\text{eff}} = 5 \mu$s could be resolved with a fitting uncertainty of $\sigma \approx 20 \%$. Above 12 000 RPM, the metal shutter wheel begins to warp and oscillate in the turbulent air stream it drags along. The PL light is then partially shuttered out of the intermediate image plane, reintroducing the blurring effect from the single lens setup in a weaker but undefined manner. Similarly, the number of slits cannot be arbitrarily increased. This is on the one hand due to manufacturing reasons: the slits have to be made consistently with width variations $\lessapprox 1 \%$. Otherwise, the higher amount of jitter negates the resolution gained by higher frequency. On the other hand, the intermediate image has to be focused exactly at the shutter wheel position, with all light from one point concentrated to an area much smaller than the slit width. This conflicts with the aforementioned

\textsuperscript{5}Measurements courtesy of Lambert Instruments BV, The Netherlands
mechanical stability at high speeds, so more than 60 slits did not prove to be beneficial in this setup.

### 4.2.3 Image Intensifier Setup

Due to the aforementioned disadvantages of mechanical shutters, other possibilities of fast optical shutters—preferably without moving parts—were evaluated.

Electronic shutters based on the Faraday-effect have been used since the 1940s for high speed photography, e.g., to record early stages of nuclear explosions. Exposure times down to a few µs can be reached with these systems [104]. Unfortunately, these systems are not well suited for the high aperture diameters required by low light intensity of PL imaging [105]. For this application also high repetition rates are needed for a sufficient integral exposure time, which are difficult to accomplish with the high currents and voltages required by this shutter.

Shutters based on liquid crystals were also considered, but the obtainable switching times of twisted nematic (TN) cells or in plane switching (IPS) cells are in the range of several ms. Even recent developments as the blue phase mode LCD [106], which are not yet commercially available, do not allow for speeds > 10 kHz. It is very doubtful if µs lifetimes could be resolved at 100 or 200 Hz shutter rate, so this approach was not pursued.

Another applicable technology, which was only recently made possible by the availability of suitable cathode materials, is the use of an image intensifier unit (IIU). Modern IIUs are capable of sub-microsecond gating time and are ideally suited for low light applications like PLI. A shutter setup featuring such an IIU was successfully built (see fig. 4.11) and will be described in this section.

The image intensifier unit\(^6\) consists of a photo-cathode, a micro channel plate (MCP) photo-multiplier and a phosphorous screen (see fig. 4.12). An InGaAs photocathode was used to make the device sensitive to the spectral range of the silicon PL emission between 950 and 1250 nm. However, the quantum efficiency of the InGaAs photo-cathode is in the range of 1% and not comparable to the > 70% QE of the InGaAs CCD cameras tested in section 2.5. For similar amounts of shot noise, the required cumulative exposure time with the IIU is therefore significantly longer.

\(^6\)Model C9546-01InGaAs from Hamamatsu Photonics
Electrons emitted from the photo-cathode by the photo effect are drawn to the MCP by a gate voltage and enter a channel corresponding to the place they were generated. A further acceleration voltage across the several mm thick MCP accelerates the electron and leads to a cascade of secondary electrons generated by collisions with the channel walls. The amplified bunch of electrons then hits a phosphorous layer and generates photons at $545\text{ nm}$. As the amplification factor is homogeneous across the device and interactions between two photo-electrons are negligible, the resulting green image at the phosphorous screen is a linear amplification of the infrared image entering the photo-cathode, hence the name image intensifier. This amplified image is recorded by the CCD camera using a standard lens for visible light imaging and some spacer rings to allow for the 1:1 scale projection. At this point, an uncooled CCD camera may be used, as the contributions of dark current and readout noise are usually negligible for an IIU setup [107]. The dominant source of image noise in this setup is shot noise at the IIU photo-cathode, which is amplified and outweighs any noise contributions of the camera.

The gate voltage between the photo-cathode and the entrance of the MCP can
be modulated on the order of nanoseconds, which is the key property of the device for this application as it allows the image intensifier to be switched between no transmission (gate voltage off or reversed) and full transmission (gate voltage on). This electronic shuttering has several advantages:

- The excitation frequency $f_{\text{exc}}$ can be much higher than with a mechanical shutter wheel. With the currently used IIU, repetition rates up to 30 kHz are possible.

- The delay between control signal input and IIU gate switching is in the low ns range and very stable. No additional feedback component or synchronization PLL is required, a simple controller with two timers and adjustable phase offset for $\phi_n$ is sufficient (see appendix A.2).

- There is no lateral variation of the shutter phase, $\theta_{x,y} = 0$. This eliminates the need for the offset calibration procedures described in section 4.2.1 and 4.2.2.

All three factors lead to an increase in time-resolution. Especially the last two points significantly reduce phase jitter and offset errors, so even at the same $f_{\text{exc}}$, lower values of $\tau_{\text{eff}}$ can be reliably resolved. This can be seen in fig. 4.16, where sample [B] was measured with the double lens shutter wheel setup and the IIU setup at the same $f_{\text{exc}}$.

Combined with the higher available $f_{\text{exc}}$, effective carrier lifetimes down to 2.5 µs can be measured at a relative uncertainty of $< 10\%$. While for the previous setups the measurement range was limited by the shutter, IIU units similar to this one are used for biological samples to measure fluorescent lifetime images in the ns range.
range. Although the IIU used here is comparably fast, such lifetimes cannot be resolved for silicon samples due to other limitations. The first one is the speed of the excitation light source, which was characterized in fig. 4.9. There is probably still significant room for improvement by the use of faster control electronics or a high energy pulsed laser source.

The second, more problematic limit is the sensitivity of the photo-cathode in combination with the decreasing emission of PL at low \( \tau_{\text{eff}} \). Currently available IIUs have a QE of only \( \approx 1\% \) at 1000 nm, which leads to low count rates and correspondingly high amounts of shot noise. It is not clear if future generations of IIUs based on InGaAs or other materials will be able to provide infrared quantum efficiency values \( \approx 50\% \), as are currently available in the visible spectrum. If so, TR-PLI measurement times and noise rates can be expected to drop substantially, allowing even shorter values of \( \tau_{\text{eff}} \) to be determined reliably.

A more general aspect which might limit the adoption of IIU based TR-PLI is the manufacturing complexity of suitable image intensifiers with InGaAs photo-cathode, resulting in a unit price between 40 and 60 k€. In contrast to the moderate costs of 2–5 k€ for a mechanical shutter wheel setup, the use of an IIU may easily double the overall equipment price of a PLI setup.

### 4.3 Results and Comparison

#### 4.3.1 Lifetime Measurement Limits

To determine the lower limit of reliably resolvable values for \( \tau_{\text{eff}} \), a lifetime measurement of sample [A] was carried out with the double lens setup and the image intensifier setup. For the single lens setup, previous experiments showed a lower measurement limit of \( \approx 300 \mu\text{s} \), mainly due to the low number of slits in the shutter wheel and associated large excitation period \( \tau \). It therefore cannot be used to measure lifetimes \(< 30 \mu\text{s} \) of sample [A].

Both setups were operated close to their maximum excitation frequencies and with long exposure times to obtain optimal time-resolution. Mechanically, the double lens setup can safely operate up to \( f_{\text{exc}} = 12 \text{ kHz} \), which is 12000 RPM with a 60 slot shutter wheel. However, above \( \approx 10 \text{ kHz} \) the measurement quality diminishes due to oscillations of the shutter wheel, so \( f_{\text{exc}} = 10 \text{ kHz} \) was chosen for
4.3 Results and Comparison

The switching frequency of the image intensifier unit is limited by the power required to recharge the gate electrode. The data sheet of the C9546-01 specifies a limit of 30 kHz. For the measurements presented here, the image intensifier setup was operated at frequencies between $f_{\text{exc}} = 100\, \text{Hz}$ and $f_{\text{exc}} = 20\, \text{kHz}$.

The resulting lifetime images from both setups can be seen in fig. 4.13, along with a scatter plot of the relative fit uncertainty $\sigma(\tau_{\text{eff}})$—calculated from the fit covariance matrix—over the lifetime. Comparing images (a) and (b), a very good quantitative agreement can be seen for areas of high $\tau_{\text{eff}}$. However, in several

\begin{figure}[h]
\centering
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{image1}
\caption{TR-PLI lifetime with double lens setup}
\end{subfigure}\hfill
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{image2}
\caption{TR-PLI lifetime with IIU setup}
\end{subfigure}
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{image3}
\caption{Uncertainty with double lens setup}
\end{subfigure}\hfill
\begin{subfigure}{0.45\textwidth}
\centering
\includegraphics[width=\textwidth]{image4}
\caption{Uncertainty with IIU setup}
\end{subfigure}
\caption{TR-PLI measurements of sample $A$ at $F = 2.5 \times 10^{17}/\text{cm}^2\text{s}$ illumination. Image (a) was recorded using the double lens setup at $f_{\text{exc}} = 10\, \text{kHz}$, image (b) is from the image intensifier setup at $f_{\text{exc}} = 20\, \text{kHz}$. In (c) and (d), a scatter plot of the relative fit uncertainty $\sigma(\tau_{\text{eff}})$ over $\tau_{\text{eff}}$ for the respective lifetime image is shown. Several incorrectly measured areas in (a) are marked by white ellipses.}
\end{figure}
areas with $\tau_{\text{eff}} < 5\,\mu\text{s}$ the double lens setup measurement (a) erroneously reports high lifetime with a high fit uncertainty, marked by white ellipses in (a). This effect can also be seen in the fit uncertainty plot (c), where the incorrect pixels with $\tau_{\text{eff}} > 10\,\mu\text{s}$ lead to an apparent increase of $\sigma$.

This systematic error can be explained by scattered light from other parts of the sample or fluorescence within the setup, which becomes more relevant at positions where the PL emission from the sample itself is low due to a low $\tau_{\text{eff}}$. The time-characteristics of this parasitic signal may then predominate the original PL signal and lead to an erroneous lifetime fit value.

The double lens setup is especially prone to this kind of artifact due to the lateral component $\theta_{x,y}$ of the shutter phase. Stray light from adjacent regions, which is phase-shifted with respect to the PL emission from the examined spot, may easily introduce a significantly larger phase shift into the measured signal than the local excitation and recombination of charge carriers.

Regardless of this measurement artifact, the smallest value of $\tau_{\text{eff}}$ that is still resolvable with adequate certainty can be seen in fig. 4.13 (c) and (d). A median curve of $\sigma(\tau_{\text{eff}})$ was calculated and is shown in red. With an uncertainty threshold of $\sigma < 10\%$ (i.e., $95\%$ of the pixels have $< 20\%$ error), a lower measurement limit of $\tau_{\text{eff}} = 5\,\mu\text{s}$ for the double lens setup and $\tau_{\text{eff}} = 2.5\,\mu\text{s}$ for the IIU setup can be established.

As stated in section 4.2.2, these lifetime limits are also close to the limit where the assumption of an instantaneous LED panel switching still holds. Measurements of shorter $\tau_{\text{eff}}$ would have to take the time characteristics of the light source into account. Alternatively, the TR-PLI measurement can be used to calibrate a steady-state PL image. On the one hand, this makes use of the much lower detection limit of the CCD camera, allowing carrier lifetimes in the sub-microsecond range to be quantitatively characterized. On the other hand, it reintroduces some sources of systematic error mentioned at the beginning of this chapter.

An example of such a calibrated steady-state PL image of sample $\overline{A}$ is shown in fig. 4.14a, which uses the lifetime map from fig. 4.13a for calibration. The calibration constant $A$ between the emitted PL intensity $\Phi_{x,y}$ according to eq. (1.55) and the camera signal $I_{x,y}$ was calculated by dividing the steady-state image by
4.3 Results and Comparison

Figure 4.14: (a) Steady-state PL image of sample A at $F = 2.5 \times 10^{17} \text{cm}^{-2}\text{s}$ illumination, calibrated to absolute lifetimes using the shutter wheel TR-PLI measurement shown in fig. 4.13a. Only the high lifetime areas of the sample were used for calibration to reduce systematic errors. (b) shows the IIU TR-PLI lifetime map from fig. 4.13b for comparison.

\[ A = \frac{I_{x,y}}{\Phi(\tau_{\text{eff}}(x, y))} = \frac{I_{x,y}}{BG\tau_{\text{eff}}(x, y)(G\tau_{\text{eff}}(x, y) + N)}. \]  

(4.16)

The averaging was weighted by the steady-state PL intensity to increase the influence of the more reliably measured high lifetime areas. Also, only pixels where $I_{x,y} > \frac{1}{2} \max(I_{x,y})$ were included in the average to avoid contributions of the aforementioned erroneous areas in the lifetime image. The calibrated steady-state PL image agrees very well to the TR-PLI measurement in fig. 4.13b using the IIU setup, which is also shown as fig. 4.14b for direct comparison. Only for $\tau_{\text{eff}} < 2.5 \mu\text{s}$, the histogram of fig. 4.14b shows a depletion of lifetimes outside the IIU setup’s measurement range, which are still well accessible by steady-state PLI in (a).

The upper measurement limit of the two setups is no constraint for all practical purposes. For optimal SNR, the excitation period $T$ should not be significantly smaller than $\tau_{\text{eff}}$. Using a 2 slit shutter wheel, the double lens setup can achieve stable operation up to $T = 25 \text{ms}$. Only when using shutter wheels with more slits, care has to be taken to use $f_{\text{exc}} \geq 20 \text{Hz} \cdot N_{\text{slits}}$, which is the lower limit for smooth motor rotation.

The image intensifier setup, being electronically shuttered, can operate on
arbitrarily long values of $\tau$. So even for $\tau_{\text{eff}} = 130\, \text{ms}$, the highest value ever measured on a Si wafer [108], the TR-PLI method would be applicable.

### 4.3.2 Comparison of TR-PLI setups

As shown above, a good quantitative agreement between the double lens setup and the image intensifier setup can be observed for low lifetime samples, as long as $\tau_{\text{eff}}$ is within the measurement range of both setups.

For a direct comparison of all three described setups sample $C$ was used, as its effective carrier lifetime is within the measurement range of all setups. The resulting lifetime maps can be seen in fig. 4.15, which generally also show very good agreement. However, the measurement in (a) was recorded earlier than the other two images. Frequent measurement and handling of the sample lead to a slight overall reduction of $\tau_{\text{eff}}$ and several spots where the thin $\text{Al}_2\text{O}_3$ surface

![Figure 4.15](image)

*Figure 4.15:* Comparison of lifetime images of sample $C$ as measured by the three described setups. Especially in the low lifetime regions near the right and bottom edges, the greater measurement range of the later setups can be seen. All measurements were done at $\mathcal{F} = 5 \times 10^{17}/\text{cm}^2\text{s}$ illumination and 100 Hz excitation frequency. Image (a) was recorded earlier than images (b) and (c). Some damage to the surface passivation occurred due to handling and is visible in (b) and (c).
passivation layer was damaged. In the low lifetime areas near the right and bottom edges of the sample, the greater measurement range of the IIU setup—compared to the shutter wheel—can be seen, which will be discussed later.

A comparison between the double lens setup and the image intensifier setup in the medium lifetime range was done with sample B and is shown in fig. 4.16. In this case, identical conditions of $\mathcal{F} = 2.5 \times 10^{17}/\text{cm}^2\text{s}$ illumination and an excitation frequency $f_{\text{exc}} = 2 \text{kHz}$ were chosen for both setups, to quantitatively compare the different shutter designs. The IIU setup was used to record both with LED and with laser illumination of the same intensity, testing the effect of different light sources.

Figs. 4.16a and 4.16b were both recorded with the LED panel at the same $f_{\text{exc}}$. Due to the higher amount of jitter of the rotating shutter wheel and the stray light effect described in section 4.3.1, the double lens setup overestimates low

![Figure 4.16](image)

**Figure 4.16:**
Double lens setup (a) and image intensifier (b and c) TR-PLI measurements of sample B at $\mathcal{F} = 2.5 \times 10^{17}/\text{cm}^2\text{s}$ illumination and 2 kHz excitation frequency. Comparing (a) and (b), the higher lifetime resolution of the IIU setup can be seen. Due to the faster switching of the LED panel and less stray light, the data for image (b) is fitted much more reliably than (c), especially in areas of low $\tau_{\text{eff}}$. 
lifetime values. This is especially visible in the lower right corner of fig. 4.16a. However, the effect is much less noticeable than in fig. 4.13, as the 10-slit shutter wheel was used instead of 60 slits. On one hand, the larger slits lead to less phase jitter caused by mechanical imperfections of the shutter wheel. On the other hand, broadening of the theoretically sharp shutter transfer function edges due to the intermediate image not being perfectly focused in the shutter wheel plane is also inversely proportional to the slit width. Both of these effects lead to smoothing of the convoluted measurement signal, which is interpreted by the evaluation algorithm as higher $\tau_{\text{eff}}$.

Comparing the IIU lifetime images of LED illumination (fig. 4.16b) and laser illumination (c) at the same intensity of $F = 2.5 \times 10^{17}$/cm$^2$s, a significant difference in measurement range can be seen. The fitted values in the low lifetime regions are 20 to 30 µs higher for the laser illumination than for the LED panel. For high lifetime regions, the offset is also present but not as significant in relative terms. However, no definite explanation for this discrepancy between LED and laser excitation could be found. One possible cause could be the different rise times of the light sources. As fig. 4.9 shows, the laser is indeed slower than the LED panel, but with a time constant of ~2 µs still much faster than the observed lifetime difference of 20 to 30 µs. Nevertheless, the assumption of instantaneous excitation switching in eq. (4.1) of the evaluation theory might be sufficiently broken in this case to result in the large observed deviation. Another possible explanation for the higher lifetime values would be a delay between the signal input and the light output of the laser system. Setting a delay of $\theta = 15$ µs in the TR-PLI evaluation procedure does indeed lead to lifetime values very similar to fig. 4.16b. However, a direct measurement of the laser signal delay using an oscilloscope and a photo diode revealed values < 2 µs, so this explanation is implausible.

In conclusion, it can be noted that the image intensifier setup is more accurate than the double lens setup at equal $f_{\text{exc}}$, due to the fast, global shuttering. The laser illumination—at least in the current state—is not an ideal light source for this application because of slow transients and a large amount of stray light.
4.3.3 Excitation Frequency

As stated before, the excitation frequency $f_{\text{exc}}$ is an important parameter with regard to lifetime resolution and measurement uncertainty. To determine $\tau_{\text{eff}}$, the most relevant feature of the convoluted PL signal—when fitting the evaluation model—is the curvature radius at the turning points. It is in good approximation proportional to $\tau_{\text{eff}}$ (see fig. 4.8 for an exemplary curve). For a reliable fit of $\tau_{\text{eff}}$, this curvature radius should not be too small, so a short $\tau$ is preferable. This can be seen in fig. 4.17, where TR-PLI lifetime images of sample $A$ were measured using the IIU setup at $f_{\text{exc}} = 2\, \text{kHz}$ and $f_{\text{exc}} = 20\, \text{kHz}$. From the uncertainty scatter

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.17.png}
\caption{Image intensifier TR-PLI measurements of sample $A$ at $F = 2.5 \times 10^{17}/\text{cm}^2\text{s}$ illumination and different excitation frequencies, showing the effect of insufficient $f_{\text{exc}}$. In good regions ($\tau_{\text{eff}} > 15\, \mu\text{s}$), both measurements show very similar values. Nevertheless, the increased excitation frequency leads to a significantly lower fit uncertainty, the $\sigma(\tau_{\text{eff}}) = 10\%$ point shifts from 15\,$\mu\text{s}$ in (c) to 2.5\,$\mu\text{s}$ in (d).}
\end{figure}
plots (c) and (d), the respective measurement limits of 15 µs and 2.5 µs demonstrate a significant improvement of time-resolution at higher $f_{\text{exc}}$.

An interesting aspect of a high $f_{\text{exc}}$ is its effect on the lateral resolution of a TR-PLI lifetime image, especially for samples with high $\tau_{\text{eff}}$. Here, the resolution of the image for steady-state PLI tends to be limited by the lateral diffusion of excited charge carriers. During their average lifetime $\tau_{\text{eff}}$, minority charge carriers can cover an average distance $L_{\text{eff}} = \sqrt{D\tau_{\text{eff}}}$, where $D$ is the diffusion coefficient of charge carriers in silicon with a value between 10 and 40 cm$^2$/s. If the sample is subjected to a high frequency excitation, the lateral diffusion is not limited by $\tau_{\text{eff}}$ any more, but rather by $T$. This may explain the increased lateral resolution at higher $f_{\text{exc}}$ visible in fig. 4.18.

On the other hand, $T$ has to be sufficiently long for the sample to respond. For $T \ll \tau_{\text{eff}}$, the PL signal approaches the PL signal under steady-state excitation with $1/2 G$ (see eq. (4.5)) and the amplitude vanishes. Taking into account the signal noise of the PL measurement, the fit uncertainty significantly rises for lower signal amplitude. This can be seen in fig. 4.18, where the homogeneous $\tau_{\text{eff}}$ in the good areas is measured much more reliably at $f_{\text{exc}} = 200$ Hz (a) than at $f_{\text{exc}} = 2$ kHz (c).

In combination, a compromise for the value of $T$ has to be found, also taking into account the often very different lifetimes on one sample. Empirically, choosing $T$ approximately to the highest expected $\tau_{\text{eff}}$ on the sample has proven to give the best overall results. Obviously this is not possible for all samples due to the hardware limitations detailed in section 4.3.1. If required by the sample, a combination of several TR-PLI measurements at different $f_{\text{exc}}$ might prove helpful to increase the dynamic range from about one order of magnitude to $10^2$ or $10^3$.

### 4.3.4 Comparison to Other Methods

Although the above measurements have shown consistent results for the different TR-PLI setups, an important test for any new measurement technique is the comparison to established methods. To determine the effective minority charge carrier lifetime of silicon wafers, two methods are commonly used in photovoltaic research: the quasi steady-state and transient photoconductance (QSSPC) [82] measurement, which is an integral (not spatially resolved) technique, and the microwave induced photoconductance decay (μPCD) [2] for point by point mapping.
4.3 Results and Comparison

of local $\tau_{\text{eff}}$.

The QSSPC technique has already been introduced in section 2.4 as a tool for the lifetime calibration of steady-state PL images. It is very fast and inherently allows to determine $\tau_{\text{eff}}$ on a wide range of excess carrier densities, usually about 2 orders of magnitude. On the other hand, only a single lifetime value is obtained for the whole measurement area, so lateral variations can not be resolved. In quasi steady-state (QSS) operation, the illumination is changed much slower than $\tau_{\text{eff}}$ and the photoconductance amplitude is measured, so the resulting lifetime signal is a spatially averaged value as detailed in section 2.4.

When the photoconductance setup is operated in transient mode, a $\mu$s light pulse is emitted from the illuminating flash. Then, the time dependent photoconductance decay (PCD) is used to obtain $\tau_{\text{eff}}$. In the case of inhomogeneous $\tau_{\text{eff}}$, the measured signal is a superposition of decay curves with different time constants and different

![Image](a) TR-PLI lifetime at $f_{\text{exc}} = 200\,\text{Hz}$

![Image](b) TR-PLI lifetime at $f_{\text{exc}} = 500\,\text{Hz}$

![Image](c) TR-PLI lifetime at $f_{\text{exc}} = 2\,\text{kHz}$

**Figure 4.18:** Image intensifier TR-PLI measurements of sample $\mathcal{C}$ at $f = 2.5 \times 10^{17}/\text{cm}^2$ illumination and increasing $f_{\text{exc}}$. Some of the blurred surface defects visible in (a) become more sharp at higher $f_{\text{exc}}$ due to the reduced time for lateral carrier diffusion. However, the measurement noise increases as $T$ becomes significantly shorter than $\tau_{\text{eff}}$. A lifetime fit for the position marked in (a) can be seen in fig.4.8.
amplitudes. Consequently, the calculated lifetime from this composite curve does not represent the spatially averaged lifetime, but rather favors the regions of highest $\tau_{\text{eff}}$ inside the sensitive area of the pickup coil [109]. The transient mode was therefore only used for sample $[\overline{C}]$, which is the most homogeneous.

A comparison of photoconductance measurements and averaged TR-PLI lifetimes at different excess carrier densities for the wafers $[\overline{A}, \overline{B}]$ and $[\overline{C}]$ can be seen in fig. 4.19. The multicrystalline samples $[\overline{A}]$ and $[\overline{B}]$ were measured in QSS mode, so the obtained $\tau_{\text{eff}}$ equals the spatially averaged local lifetime, weighted with the QSSPC sensitivity function determined in section 2.4. These average values from two TR-PLI measurements at $F = 7.5 \times 10^{16} / \text{cm}^2\text{s}$ and $F = 2.5 \times 10^{17} / \text{cm}^2\text{s}$ are shown in (b), together with the $\tau_{\text{eff}}$ vs. $\Delta n$ data from QSSPC. Both methods agree very well within their common measurement range. Lower values of $\Delta n$ are not available to the QSSPC method, as it suffers from systematic errors like trapping of excited charge carriers [110] and depletion-region modulation (DRM) [111]. On the other hand, the LED light source used for TR-PLI can not supply more than $2.5 \times 10^{17} / \text{cm}^2\text{s}$, which results in $\Delta n \approx 5 \times 10^{14} / \text{cm}^3$ at the respective lifetime and 50% duty cycle. In contrast to QSSPC, PL measurements are not affected by trapping, as they depend on the product of carrier densities instead of the sum [112, 113].

This problem is even more visible in fig. 4.19a, where the two methods do not have a common measurement range. The QSSPC curve starts to bend upwards below $3 \times 10^{14} / \text{cm}^3$ due to trapping, while the actual $\tau_{\text{eff}}$ should continue to decrease for lower carrier densities due to the increasing influence of SRH recombination and recombination active traps [113]. With the available LED panel intensity, only a $\Delta n \approx 3 \times 10^{13} / \text{cm}^3$ can be reached for this sample, so the two methods can not be quantitatively compared in this case. Nevertheless, the value measured by TR-PLI is close to a SRH model extrapolation (dashed curve in fig. 4.19a), fitted to the part of the QSSPC curve unaffected by trapping.

In fig. 4.19c, a measurement of sample $[\overline{C}]$ can be seen. The photoconductance setup was operated in transient mode due to the higher $\tau_{\text{eff}}$, which is outside the valid range for quasi steady-state operation [82]. This leads to a different method to compare photoconductance and PL lifetimes. Looking at a lifetime image of sample $[\overline{C}]$ (e.g., fig. 4.18), the central area is of largely homogeneous high quality. Consequently, average values from a small area in the center of the TR-PLI lifetime
4.3 Results and Comparison

Figure 4.19: Comparison of photoconductance lifetime measurements and TR-PLI lifetimes at different \( \Delta n \). The TR-PLI lifetime maps of samples [A] and [B] were averaged using the weight function from section 2.4 for the values shown in (a) and (b). For comparison with the transient PCD measurement in (c), the TR-PLI lifetime in the center of the wafer was used.

maps were used for fig. 4.19c. The agreement of both methods is also very good in this case, as well as for other samples not shown here. In conclusion, it could be shown that both the QSSPC and the transient PCD techniques yield the same lifetime values as TR-PLI.

The evaluation of \( \tau_{\text{eff}} \) vs. \( \Delta n \) from several TR-PLI measurements can also be done for each pixel individually. A number of TR-PLI measurements are recorded at different illumination intensities. Each lifetime map corresponds to a map of \( \Delta n \), so for each pixel, \( \tau_{\text{eff}} \) can be interpolated at the desired \( \Delta n \). This way, a map of \( \tau_{\text{eff}} \) at a fixed \( \Delta n \) across the whole image may be obtained. Note that this kind of map cannot easily be obtained from other spatially resolved lifetime measurements like \( \mu \)PCD because of poorly defined injection conditions. Exemplary lifetime maps for \( \Delta n = 10^{14}/\text{cm}^3 \) and \( \Delta n = 3 \times 10^{14}/\text{cm}^3 \) are shown in fig. 4.20. This might be interesting for example to determine interstitial Fe concentrations [26]. However,
as the exposure to light affects the measured $\tau_{\text{eff}}$ while FeB pairs are present in the sample, a full TR-PLI measurement might only be possible when the FeB pairs are in the dissociated state and further exposure to light is without effect. This TR-PLI measurement can subsequently be used for a calibration of steady-state PL images as shown in fig. 4.14, which may be acquired with short exposure times so as not to impair the carrier lifetime in the associated state.

Another established method for minority charge carrier lifetime measurement on silicon wafers is $\mu$PCD [2]. In contrast to QSSPC it is a spatially resolved technique, as a focused laser beam and a microwave beam are used for localized excitation and photoconductivity measurement. After sequential mapping of the sample surface, a lifetime image can be generated from the carrier decay rate at each pixel. The disadvantages of $\mu$PCD are the long acquisition time of up to several hours and the fact that it may be difficult to reliably estimate the $\Delta n$ generated by the localized light source. The latter problem is usually mitigated by the use of a constant, large area bias light which is stronger than the laser, so $\Delta n$ is dominated by the well defined bias light intensity. However, even under defined illumination, the $\mu$PCD setup used here selects the $\Delta n$ for lifetime evaluation individually at each pixel and does not output this data, so only an upper limit of $\Delta n$ can be given for these measurements.

$^7$A WT-2000 wafer tester by Semilab Co. Ltd.
4.3 Results and Comparison

![Lifetime maps](image)

**Figure 4.21**: Lifetime maps of the samples A and B, measured by µPCD (a and b) and TR-PLI using the IIU (c and d). Both methods were set to an effective illumination of 0.5 suns and show good agreement. At the low ∆n in sample A, trapping artifacts increase the apparent lifetime in (a) (note the different scale).

For a quantitative comparison, µPCD scans with 125 µm step width were done for the samples A and B. The floatzone wafer C could not be measured with the available setup due to its difficulties measuring lifetimes in the ms range. Both lifetime maps are shown in fig. 4.21. For better comparison, the respective TR-PLI measurements for both samples were included in the bottom row of fig. 4.21. As the illumination intensity for TR-PLI was set to \( F = 2.5 \times 10^{17} \text{cm}^2/\text{s} \)—which is equivalent to \( \sim 1 \text{ sun} \) illumination—with a 50% duty cycle, the bias light for µPCD was set to 0.5 suns.

A very good qualitative and quantitative agreement can be seen between the images (b) and (d). Even with the comparatively long exposure times for the IIU
setup, the overall measurement time for (d) was only 90 s. Compared to 2.5 h for the µPCD measurement, TR-PLI allows for a much faster acquisition of virtually the same lifetime image result.

The images (a) and (c) of fig. 4.21 also show very good qualitative agreement. However, they are differently scaled, as the µPCD measurement yields ~ 75% higher values than TR-PLI for this wafer. No definite explanation for these differences could be established, but a higher $\Delta n$ than anticipated during the µPCD measurement could result in the observed lifetime values. If the additional excitation due to the laser is not negligible compared to the bias light, the effective $\Delta n$ might be substantially higher. Unfortunately, the device offers no means to determine the actual amount of photons emitted by the laser into a defined volume, so this interpretation could not be verified.

Another possible explanation of the higher values, especially in view of the QSSPC measurement shown in fig. 4.19a, is the presence of minority charge carrier trapping. At a previously estimated carrier density of $\Delta n < 10^{14}/\text{cm}^3$ for 0.5 suns illumination, the QSSPC measurement suggests a high amount of trapping, which will also affect the µPCD measurement and lead to higher lifetime values. As this is an inherent property of photoconductance measurements, it can not be evaded except by measuring at a higher $\Delta n$.

### 4.4 Conclusions and Outlook

In this chapter, a new camera-based method for time-resolved imaging of photoluminescence in large crystalline silicon wafers has been presented. It can be used for a quantitative and calibration-free measurement of the effective minority charge carrier lifetime $\tau_{\text{eff}}$. The most reliable way to determine $\tau_{\text{eff}}$ from the measured PL data proved to be a direct fit of PL intensities with a suitable model for the expected PL emission.

Compared to established techniques like QSSPC and µPCD, a very good qualitative and quantitative agreement could be shown. While a TR-PLI measurement takes longer than a steady-state PL image, it is still orders of magnitude faster than a µPCD scan of comparable resolution. Typical TR-PLI measurement time for a lifetime image of a multicrystalline wafer at 1 megapixel resolution is 1–2 min, whereas a µPCD measurement with the same resolution takes several hours. The
new technique is also not affected by charge carrier trapping, making it a good alternative to µPCD and QSSPC for samples with a large amount of trapping centers, especially at low $\Delta n$. Due to the evaluation of the PL signal shape rather than its amplitude, the assumption of a laterally homogeneous relationship between lifetime and PL emission is not required, as opposed to other techniques using an integral measurement to calibrate PL images for absolute $\tau_{\text{eff}}$ [10, 11]. Lifetimes of multicrystalline Si wafers, where optical absorption and emission may vary between grains can be characterized more reliably this way. However, for samples where this effect can be neglected, the TR-PLI measurement can also be used to calibrate a steady-state PL image, which typically has better contrast than the TR-PLI lifetime map. As the TR-PLI method provides the possibility of measuring $\tau_{\text{eff}}(\Delta n)$ for each point of the sample, lifetime maps at a fixed $\Delta n$ can be determined from a set of TR-PLI measurements, or from a set of steady-state PL images and one TR-PLI measurement for calibration.

Three different shutter setups have been presented, which differ in their experimental complexity and equipment costs. It could be shown that an electronically modulated image intensifier unit allows for a reliable measurement of $\tau_{\text{eff}}$ down to 2.5 $\mu$s. However, it significantly increases the PLI setup cost by 40–60 k€ for an InGaAs based IIU. The more economical double lens setup using a rotating shutter wheel can resolve $\tau_{\text{eff}}$ down to ~5 $\mu$s. No special cameras or short exposure times are required with this setup, so the equipment costs are similar to those of a traditional PLI setup plus 2–5 k€ for the shutter wheel assembly and electronics. Placing the shutter wheel at the intermediate image plane of two lenses has been shown to dramatically improve the time-resolution, compared to an out-of-focus shutter. As the presented shutter wheel setup is to our knowledge the first concept of an imaging device with a mechanical shutter fast enough to measure electronic processes inside a semiconductor, it was filed for patent in 2010. Comparative measurements between different setups show a very good agreement within the measurement range, using the same evaluation algorithm (shown in appendix A.3) for both mechanical and electronic shutters.

Although a lot of progress has been made in terms of measurement performance and robustness during the course of this work, there are several promising areas for further improvement.
• The pixel wise least squares fit of the whole image is computationally expensive and may take up to a minute for a 1 megapixel image, using the implementation in appendix A.3. An alternative way of extracting lifetime from phase-shifted images by Fourier transformation has been successfully applied to fluorescence lifetime imaging microscopy (FLIM) [95], which is similar to the TR-PLI technique described here, albeit on other time and length scales. As the PL signal is not a purely linear function of \( \Delta \tau \) but follows eq.(1.55), the evaluation procedure used for FLIM would have to be appropriately modified. The use of discrete Fourier transformations allows for a quick computation\(^8\) and should be even more robust than the fitting procedure.

• An alternative way to speed up the computation of lifetime maps is the use of general purpose computing on graphics processing units (GPGPU), i.e., utilizing the high amount of processing power of current computer graphics cards. Programming interfaces like OpenCL allow for efficient use of these resources and as the task of independently fitting millions of data points is well suited for parallelization, a large speedup\(^9\) could be expected. However, this approach was not yet pursued to keep the evaluation software platform- and hardware-independent.

• As shown in section 4.3.2, the currently used laser system is not well suited to measure low lifetimes. This is mainly due to its control electronics, which are designed for CW operation or slow modulation. A laser diode driver better suited for pulsed operation in the kHz range would make the existing laser diodes and optics equally suitable as the LED panel for low lifetime TR-PLI measurements. Alternatively, a real pulsed laser might be used for ns illumination pulses. The resulting PL decay curve could then be recorded and the evaluation algorithm adapted to extract lifetime values at \( \leq 50\% \) illumination duty cycle. For this case the IIU setup would probably be advantageous, as it might enable a time-domain filtering of excitation instead of the commonly used wavelength discrimination using optical filters. This way, the homogeneous generation profile of a 1064 nm laser could be used, which cannot be separated from the PL signal in steady-state PLI.

\(^8\)Direct computation should yield an estimated speed improvement of two or three orders of magnitude over fitting.

\(^9\)Most comparisons of CPU vs. GPU computing speed report factors between 10 and 100.
Summary

In this work, new approaches for the characterization of crystalline silicon wafers and solar cells using electroluminescence imaging (ELI) and photoluminescence imaging (PLI) were presented.

Basis for the measurements was the construction of a sensitive, camera based luminescence imaging setup with a widely adjustable field of view. GaAs based optical filters were introduced for near optimal excitation light suppression. The illumination of samples for PLI is possible both with an LED panel and a homogenized solid-state laser. Both light sources have an adjustable and calibrated photon flux.

A lifetime calibration method for PL images based on QSSPC measurements was implemented. To correlate the spatially resolved PLI data with integral QSSPC values, the QSSPC sensitivity distribution was characterized.

In addition to the default Si CCD camera, several InGaAs cameras were evaluated and compared for the measurement of defect band luminescence. Corresponding measurements of a multicrystalline Si solar cell at different temperatures show both an anticorrelation of band-to-band PL with defect band PL and a PL increase for low temperatures.

To separate the contributing factors to solar cell series resistance, a technique based on EL images was developed. A multilayered 2-D model of the solar cell is solved and fitted to p-n junction voltage maps from ELI until both voltage distributions agree. The series resistances of front metallization grid, metallization contact, emitter and base are parameters in the solar cell model and reach their respective values during fitting. The obtained results for different solar cells qualitatively respond correctly to changes, e.g. of emitter sheet resistance. However, light scattering effects lead to a systematic underestimation of the solar cell resistivity. Further refinements taking care of this issue are required to make quantitatively correct measurements.
Summary

A newly developed technique for calibration-free imaging of the minority charge carrier lifetime $\tau_{\text{eff}}$ using time-resolved photoluminescence imaging (TR-PLI) was presented. The measurement is based on a modulated illumination of the sample, synchronized to a periodically shuttered recording of the PL emission. Three different shutter setups were described, with increasing experimental complexity and correspondingly higher time-resolution. The first setup uses a rotating shutter wheel in front of the camera lens and was able to resolve $\tau_{\text{eff}}$ down to $\sim 300 \mu s$. The second setup—which was filed for patent—uses a shutter wheel in the intermediate image plane between two objective lenses, extending the measurement range down to $\sim 5 \mu s$. The third setup is based on an electronically switched image intensifier unit, which allows reliable mapping of $\tau_{\text{eff}}$ from $\sim 2.5 \mu s$ to several ms. The electronic shuttering also simplifies evaluation and calibration, making this setup the preferred choice if the required image intensifier can be acquired.

A comparison of the three shutter setups shows very similar results within their respective measurement range. The choice of excitation frequency has significant impact on the uncertainty of the measurement, an empirical optimum was found at $f_{\text{exc}} \approx 1/\tau_{\text{eff, max}}$. Compared to the established lifetime measurement techniques QSSPC and µPCD, very good agreement was observed. At low excess carrier densities the measurements could not be compared as the results from QSSPC and µPCD were impaired by trapping and DRM artifacts, to which TR-PLI is less susceptible.

To increase the dynamic range of the measurement, the TR-PLI lifetime map can be used to calibrate steady-state PL images. Also, a map of $\tau_{\text{eff}}$ at a laterally homogeneous excess carrier density can be obtained by the combination of several measurements.

During the course of this work, several ideas to improve upon the presented techniques could not yet be realized. The series resistance characterization method would benefit from the implementation of a solar cell model including carrier diffusion, as well as the deconvolution of blurring effects in the luminescence images. The combined use of EL and PL might improve the robustness of the fitting procedure for this technique.

For TR-PLI, a change of the evaluation method to use discrete Fourier transformation instead of fitting a model function is a promising approach to speed
Summary

up the evaluation procedure, provided it does not degrade measurement quality. Alternatively, the procedure may be accelerated by the use of GPU computing for the evaluation algorithm. To extend the TR-PLI measurement range to even shorter lifetimes, a pulsed laser might be used for illumination. Extending the evaluation theory to account for rise and fall times of the illumination is another possible step to a greater measurement range.
Zusammenfassung

In dieser Arbeit wurden neue Ansätze für die Charakterisierung kristalliner Siliziumwafer und -solarzellen mittels Elektrolumineszenzbildgebung (ELI) und Photolumineszenzbildgebung (PLI) vorgestellt.


In einem weiteren Teil der Arbeit wurde zur Trennung unterschiedlicher Beiträge zum Serienwiderstand von Solarzellen ein auf EL-Bildern basierendes Verfahren entwickelt. Dabei wird ein mehrschichtiges 2-D Modell der Solarzelle gelöst und an eine aus ELI bestimmte Spannungsverteilung des p-n Übergangs angepasst, bis beide Spannungsverteilungen übereinstimmen. Die Serienwiderstände von Vorderseitenmetallisierung, Metallkontakt, Emitter und Basis sind Parameter des Solarzellenmodells, welche während des Anpassens an die Messdaten ihre jeweiligen Werte annehmen. Die Ergebnisse reagieren qualitativ korrekt auf Änderungen...
Zusammenfassung


Zuletzt wurde ein neu entwickeltes Verfahren zur kalibrationsfreien Abbildung der Minoritätsladungsträgerlebensdauer $\tau_{\text{eff}}$ mittels zeitaufgelöster Photolumineszenzbildgebung (TR-PLI) vorgestellt. Die Messung basiert auf einer modulierten Beleuchtung der Probe, welche mit einer periodisch unterbrochenen Aufnahme der PL-Emission synchronisiert ist. Drei verschiedene Kameraverschluss-Einrichtungen mit zunehmender experimenteller Komplexität und entsprechend höherer Zeitauflösung wurden beschrieben. Der erste Aufbau nutzt eine rotierende Unterbrecherscheibe vor der Kameralinse und konnte $\tau_{\text{eff}}$ bis minimal um 300 µs auflösen. Der zweite, zum Patent angemeldete Aufbau verwendet eine Unterbrecherscheibe in der Zwischenbildebene zweier Objektive und vergrößert den Messbereich bis hinunter zu 5 µs. Der dritte Aufbau basiert auf einer elektronisch schaltbaren Bildverstärkereinheit, welche zuverlässige $\tau_{\text{eff}}$ Messungen von 2,5 µs bis zu mehreren ms erlaubt. Der elektronische Bildverschluss vereinfacht zudem die Auswertung und Kalibrierung, was dieses Setup zur bevorzugten Wahl macht, falls der erforderliche Bildverstärker verfügbar ist.

Ein Vergleich der drei Aufbauten zeigt gute Übereinstimmung innerhalb der jeweiligen Messbereiche. Die Wahl der Anregungsfrequenz hat einen deutlichen Einfluss auf die Messunsicherheit; das empirisch gefundene Optimum liegt bei $f_{\text{exc}} \approx 1/\tau_{\text{eff,max}}$. Im Vergleich mit den etablierten Lebensdauermessmethoden QSSPC und µPCD wurde ebenfalls eine sehr gute Übereinstimmung beobachtet. Bei niedrigen Überschussladungsträgerdichten war kein Vergleich möglich, da die Ergebnisse von QSSPC und µPCD durch trapping und DRM beeinträchtigt sind, für welche die TR-PLI Methode weniger anfällig ist.

Zur Erhöhung des dynamischen Bereichs der Messung kann das mit TR-PLI gemessene Lebensdauerbild zur Kalibrierung stationärer PL-Bilder genutzt werden. Ebenso kann eine Abbildung von $\tau_{\text{eff}}$ bei lateral homogener Überschussladungsträgerdichte aus der Kombination mehrerer Messungen berechnet werden.

Einige Ansätze zur Verbesserung der vorgestellten Methoden konnten in dieser Arbeit noch nicht umgesetzt werden. Die Methode zur Charakterisierung von Seri-
Zusammenfassung


Bibliography


Bibliography


Bibliography


List of publications

Journal papers


List of publications

**Talks**


**Patents**

Dank


. . . Prof. Dr. Giso Hahn für das Angebot, diese Arbeit innerhalb seiner Arbeitsgruppe anzufertigen, seine stets gute Betreuung und Unterstützung bei auftretenden Problemen und Fragestellungen, sowie die Möglichkeit einer weitgehend freien Wahl der bearbeiteten Themengebiete.

. . . Prof. Dr. Thomas Dekorsy für die Erstellung des Zweitgutachtens für diese Arbeit.

. . . Prof. Dr. Guido Burkard und PD Dr. Christof Aegerter für die Bereitschaft, meine Doktorprüfung abzunehmen.

. . . Axel Herguth für das Korrekturlesen der Arbeit und viele praktische und wissenschaftliche Anregungen im Laboralltag.

. . . Benjamin Steuer, der unter meiner Betreuung seine Diplomarbeit verfasst hat, für die gute Zusammenarbeit, die tatkräftige Unterstützung und seine Bereitschaft, sich in neue Themengebiete wie die Softwareprogrammierung einzuarbeiten.

. . . Dr. Gabriel Micard für die Mitarbeit an den theoretischen Modellen und der Berechnung von Lösungen für die Auswertung der TR-PLI Messmethode.

. . . Prof. Dr. Michael Junk für die erfolgreiche Kooperation im Bereich des Serienwiderstandsmodells und viele interessante Gespräche über Halbleiterphysik und Numerik.

. . . Bernd Raabe für die Anregungen und Mithilfe zu TR-PLI, die zur Patentanmeldung geführt haben.
Dank

... Dr. Tilo Streibl und Dr. Wolfgang Prestel von GP Inspect für die erfolgreiche und angenehme Zusammenarbeit.

... den Mitarbeitern der wissenschaftlichen Werkstätten, ohne deren zuverlässige Arbeit viele der in dieser Arbeit vorgestellten Messmethoden nicht hätten umgesetzt werden können.

... Jan Ebser, Thomas Lüder, Amir Dastgheib-Shirazi und Felix Book, die mir Proben zur Untersuchung der neuen Messmethoden zur Verfügung gestellt haben und Vergleichsmessungen beigesteuert haben.

... meinen Bürokollegen Svenja Wilking und Nestor Ximello für die angenehme Atmosphäre und zahlreiche Gespräche.

... Johannes Giesecke und Sandra Herlufsen für viele anregende Veröffentlichungen und Diskussionen zum Thema Lumineszenzmessungen.

... Michiel Kregel von Lambert Instruments, der mich auf die Parallelen zwischen TR-PLI und FLIM aufmerksam gemacht hat und viele interessante Informationen zu dieser Methode geliefert hat.

... Bertram Lohmüller von Hamamatsu Photonics für die unkomplizierte Leihstellung eines InGaAs Bildverstärkers für Testmessungen.


... Sebastian Joos für die zuverlässige Unterstützung bei Computerarbeiten und der PC-Infrastruktur.

... Sabine Groß-Buitenwerf, Prof. Dr. Günther Schatz und Sascha Scholz für das gewissenhafte und unkomplizierte Abnehmen vieler organisatorischer Arbeiten, sowie die Hilfe bei administrativen Fragen.

... meiner Familie und ganz besonders meiner Frau, die mit Rat und Tat, Unterstützung und Motivation, Korrekturlesen der Arbeit sowie der Betreuung unserer Kinder einen großen Beitrag zum Gelingen dieser Arbeit geleistet hat.
A Source Code

A.1 Shutter Wheel Excitation Controller Firmware

This section contains the source code of the excitation controller used in the double lens TR-PLI setup (see section 4.2.2). It was implemented on a STM32-H103 board from Olimex Ltd., which is plugged onto a custom PCB to break out the relevant connections. The main functionality is the control of the shutter motor speed and the software-defined PLL generating the excitation signal to switch the light source on and off. The source code uses the libmaple library for STM32 microcontrollers by LeafLabs, LLC, available at http://github.com/leaflabs/libmaple.

A.1.1 controller.h

```c
/*
 * controller.h
 *
 * Firmware for a STM32-based chopper module controller for time-resolved
 * photoluminescence imaging of silicon wafers.
 *
 * Copyright (c) 2012, David Kiliani, University of Konstanz
 * All rights reserved.
 *
 * Redistribution and use of this file is subject to the license terms in the
 * corresponding controller.cpp source file.
 */

#ifndef CONTROLLER_H_
#define CONTROLLER_H_

#define F_CPU 72000000UL

#define BL_MIN_PWM 480 // 20us
```

127
Source Code

```c
#define BL_MAX_PWM (48000 - 1) // 2.0ms
#define BL_MAX_TEMP 80 // °C

#define JITTER_BUFFER_LEN 1024
#define TEMP_BUFFER_LEN 1024
#define APER_BUFFER_LEN 256

struct chopper_t {
    double period_ref;
    double period;
    double phase;
    double duty_cycle;
    double nominal_freq;
    int slots;
    int period_timeout;
};

#define clip(x, min, max) ((x) > (min) ? ((x) < (max) ? (x) : (max)) : (min))

#endif /* CONTROLLER_H_ */
```

A.1.2 controller.cpp

```c
/*
 * controller.cpp
 *
 * Firmware for a STM32-based chopper module controller for time-resolved
 * photoluminescence imaging of silicon wafers.
 *
 * Copyright (c) 2012, David Kiliani, University of Konstanz
 * All rights reserved.
 *
 * Redistribution and use in source and binary forms, with or without
 * modification, are permitted provided that the following conditions are met:
 *
 * Redistributions of source code must retain the above copyright notice,
 * this list of conditions and the following disclaimer.
 * Redistributions in binary form must reproduce the above copyright notice,
 * this list of conditions and the following disclaimer in the documentation
 * and/or other materials provided with the distribution.
 * Neither the name of the University of Konstanz nor the names of its
 * contributors may be used to endorse or promote products derived from this
```
* software without specific prior written permission.

* THIS SOFTWARE IS PROVIDED BY THE COPYRIGHT HOLDERS AND CONTRIBUTORS "AS IS"
* AND ANY EXPRESS OR IMPLIED WARRANTIES, INCLUDING, BUT NOT LIMITED TO, THE
* IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE
* ARE DISCLAIMED. IN NO EVENT SHALL THE COPYRIGHT HOLDER OR CONTRIBUTORS BE
* LIABLE FOR ANY DIRECT, INDIRECT, INCIDENTAL, SPECIAL, EXEMPLARY, OR
* CONSEQUENTIAL DAMAGES (INCLUDING, BUT NOT LIMITED TO, PROCUREMENT OF
* SUBSTITUTE GOODS OR SERVICES; LOSS OF USE, DATA, OR PROFITS; OR BUSINESS
* INTERRUPTION) HOWEVER CAUSED AND ON ANY THEORY OF LIABILITY, WHETHER IN
* CONTRACT, STRICT LIABILITY, OR TORT (INCLUDING NEGLIGENCE OR OTHERWISE)
* ARISING IN ANY WAY OUT OF THE USE OF THIS SOFTWARE, EVEN IF ADVISED OF THE
* POSSIBILITY OF SUCH DAMAGE.
*/

#include <stdlib.h>
#include <string.h>
#include <stddef.h>
#include <stdio.h>
#include <wirish/wirish.h>
#include <libmaple/timer.h>
#include <libmaple/systick.h>

#include "controller.h"

HardwareTimer exc_timer(1);
HardwareTimer motor_timer(3);
HardwareTimer servo_timer(4);
#define PIN_TEMP_SENSOR 22 // PC2
#define PIN_APER_SENSOR 26 // PC3
#define PIN_PD_SIGNAL 1 // PA8
#define PIN_EXCITATION 4 // PA10
#define PIN_SERVO_1 10 // PB6
#define PIN_SERVO_2 12 // PB7
#define PIN_SERVO_3 13 // PB8
#define PIN_MOTOR_PWM 11 // PA6
#define PIN_MOTOR_DIR 19 // PA7
#define PLL_KP 0.25 // PLL proportional constant
#define PLL_KI 0.01 // PLL integral constant
#define MOT_KP 0.0 // motor proportional constant
#define MOT_KI 0.02 // motor integral constant
```c
#define EOL '
'
struct chopper_t chopper;
static double motor_pwm;
static uint16 pll_prescaler;
static uint8 mscl_disable = 0; // motor speed control loop timeout
static float jitter_buffer[JITTER_BUFFER_LEN];
static uint16 temp_buffer[TEMP_BUFFER_LEN] = { 0 }; // all elements 0
static uint16 aper_buffer[APER_BUFFER_LEN] = { 0 }; // all elements 0
static int jb_idx = 0, tb_idx = 0, ab_idx = 0, temp_sum = 0, aper_sum = 0;

#define f_to_p(f) ((f) > 0 ? F_CPU / ((f) * pll_prescaler) : 0)
#define p_to_f f_to_p

double get_temperature() {
    double x = temp_sum; // use rolling average
    return x / TEMP_BUFFER_LEN / 4096 * 3.3 * 100; // LM35 sensor, 10mv / °C
}

int get_aperture() {
    double x = aper_sum; // use rolling average
    return lround(x / APER_BUFFER_LEN / 4096 + 16); // 16 positions
}

void motor_calib_ss(uint32 max_pwm) {
    for (motor_pwm = 0; motor_pwm <= max_pwm; motor_pwm += 25) {
        motor_timer.setCompare(TIMER_CH1, lround(motor_pwm - 1));
        delay(100);
        SerialUSB.print(motor_pwm);
        SerialUSB.print(" ");
        SerialUSB.print(p_to_f(chopper.period));
        SerialUSB.print(EOL);
    }
    motor_timer.setCompare(TIMER_CH1, BL_MIN_PWM);
}

void motor_speed_control_loop() {
    double e = chopper.nominal_freq - p_to_f(chopper.period);
    if (mscl_disable > 0) {
        mscl_disable--;
        e = 0;
    } else
        e = clip(e / chopper.slots = 182, -40000, 40000);
```

double p_set = motor_pwm + MOT_KP * e;
motor_timer.setCompare(TIMER_CH1, lround(p_set - 1));
motor_pwm += e * MOT_KI;
motor_pwm = clip(motor_pwm, BL_MIN_PWM, BL_MAX_PWM);
}

void chopper_set_nominal_freq(double freq) {
    if (chopper.slots == 0)
        freq = 0;
    chopper.nominal_freq = freq;
    if (chopper.nominal_freq == 0) {
        motor_timer.setCompare(TIMER_CH1, BL_MIN_PWM);
        motor_pwm = BL_MIN_PWM;
    } else {
        // set pwm according to fit values of calibration run
        motor_pwm = clip(182 * chopper.nominal_freq / chopper.slots + 1360,
                         BL_MIN_PWM, 10000);
        mscl_disable = 50; // wait 1s until frequency reading stable
    }
}

int chopper_detect_slots() {
    motor_timer.setCompare(TIMER_CH1, 10000);
    delay(2000);
    double f = p_to_f(chopper.period);
    motor_timer.setCompare(TIMER_CH1, BL_MIN_PWM);
    if (f < 50)
        chopper.slots = 0;
    else if (f < 200)
        chopper.slots = 2;
    else if (f < 1200)
        chopper.slots = 10;
    else
        chopper.slots = 60;
    return chopper.slots;
}

void reset() {
    // set default values
    chopper.phase = 0;
    chopper.duty_cycle = 0.5;
    chopper.slots = 0; // unknown
chopper_set_nominal_freq(0);
}

void usb_comm() {
    static char buf[64];
    char * buffer = buf;
    while (!strchr(buf, '\n')) { // read until terminated by LF
        if (SerialUSB.available()) {
            int len = SerialUSB.read(buffer, SerialUSB.available());
            buffer += len;
        }
    }

    *buffer = 0; // terminate string
    buffer = strtok(buf, "\r\n"); // remove CR and LF characters
    strlwr(buffer); // convert to lower case
    char * cmd = strsep(&buffer, " ");
    if (!strncmp(cmd, "*idn?", 5)) {
        SerialUSB.print("University of Konstanz,TR-PLI-Controller-SH2,001, ");
        SerialUSB.print(__DATE__); // report compile date as version number
        SerialUSB.print(EOL);
    } else if (!strncmp(cmd, "*rst", 4)) {
        reset();
    } else if (!strncmp(cmd, "*tst?", 5)) {
        if ((chopper_detect_slots() > 0) && (get_temperature() > 0)
            && (get_temperature() < BL_MAX_TEMP))
            SerialUSB.print('1');
        else
            SerialUSB.print('0');
        SerialUSB.print(EOL);
    } else if (!strncmp(cmd, "motor", 3)) {
        strsep(&cmd, ":");
        if (!strncmp(cmd, "calibrate", 5)) {
            motor_calib_ss(strtol(buffer, NULL, 10));
        } else if (!strncmp(cmd, "pwm", 3)) {
            motor_timer.setCompare(TIMER_CH1, strtol(buffer, NULL, 10));
        } else if (!strncmp(cmd, "direction", 3) && chopper.nominal_freq == 0) {
            digitalWrite(PIN_MOTOR_DIR, (buffer[0] == 'r') ? 0 : 1);
        } else if (!strncmp(cmd, "slots", 4)) {
            SerialUSB.print(chopper_detect_slots());
            SerialUSB.print(EOL);
        }
    } else if (!strncmp(cmd, "phase", 5)) {
        // code continues here...
    }
}
chopper.phase = strtod(buffer, NULL);
} else if (!strcmp(cmd, "duty", 4)) {
    chopper.duty_cycle = strtod(buffer, NULL);
} else if (!strcmp(cmd, "temperature", 4)) {
    SerialUSB.print(get_temperature());
    SerialUSB.print(EOL);
} else if (!strcmp(cmd, "aperture", 4)) {
    SerialUSB.print(get_aperture());
    SerialUSB.print(EOL);
} else if (!strcmp(cmd, "frequency", 4)) {
    if (strchr(cmd, '?')) {
        SerialUSB.print(p_to_f(chopper.period));
        SerialUSB.print(EOL);
    } else {
        chopper_set_nominal_freq(strtod(buffer, NULL));
    }
} else if (!strcmp(cmd, "jitter", 3)) {
    char *cmd = strsep(cmd, ":");
    if (!strcmp(cmd, "data", 3)) {
        for (int i = 0; i < JITTER_BUFFER_LEN; i++) {
            SerialUSB.print(jitter_buffer[i]);
            SerialUSB.print(EOL);
        }
    } else if (!strcmp(cmd, "stddev", 3)) {
        double sum = 0, min = jitter_buffer[0], max = jitter_buffer[0];
        for (int i = 0; i < JITTER_BUFFER_LEN; i++) {
            sum += jitter_buffer[i] * jitter_buffer[i];
            if (jitter_buffer[i] < min)
                min = jitter_buffer[i];
            if (jitter_buffer[i] > max)
                max = jitter_buffer[i];
        }
        SerialUSB.print(sqrt(sum / JITTER_BUFFER_LEN));
        SerialUSB.print(" ");
        SerialUSB.print(min);
        SerialUSB.print(" ");
        SerialUSB.print(max);
        SerialUSB.print(EOL);
    }
}
void set_pll_prescaler(uint16 prescaler) {
    pll_prescaler = prescaler;
    timer_set_prescaler(TIMER1, pll_prescaler - 1);
}

void excitation_pll_control_loop() {
    struct chopper_t *c = &chopper;
    static int t0 = 0, t1 = 0;
    int t_osc = timer_get_compare(TIMER1, 1);
    t1 = systick_get_count();
    if (t0 > t1) {
        c->period_ref = (t0 - t1) / (4.0 * pll_prescaler);
    }
    if (abs(c->period_ref - c->period) > 0.05 * c->period_ref) {
        c->period = c->period_ref;
        if ((t0 - t1) / 4.0 > 50000)
            set_pll_prescaler(72);
        else
            set_pll_prescaler(8);
    }
    t0 = t1;

double e = t_osc + (2.5 - c->phase) * c->period;
while ((e > c->period) && (c->period > 0))
    e -= c->period;
    e -= 0.5 * c->period;
jitter_buffer[jb_idx++] = e / c->period * 100;
    jb_idx %= JITTER_BUFFER_LEN;
double t_set = c->period + PLL_KP * e;
timer_set_reload(TIMER1, lround(t_set - 1));
timer_set_compare(TIMER1, 3, lround(t_set * c->duty_cycle - 1));
c->period += e * PLL_KI;
    c->period_timeout = 100; // 2s at 50Hz GP timer frequency
}

void gp_isr() {
/*
 * This is a general purpose timer with 50Hz frequency.
 */
if (chopper.period_timeout-- == 0) {
    chopper.period = 0;
    chopper.period_ref = 0;
    timer_set_compare(TIMER1, 3, 0); // disable excitation output
}
if (chopper.nominal_freq != 0 && chopper.slots != 0) {
    motor_speed_control_loop();
    if (get_temperature() > BL_MAX_TEMP)
        chopper_set_nominal_freq(0);
}

int i;
for (i = 0; i < 10; i++) {
    temp_sum -= temp_buffer[tb_idx];
    temp.buffer[tb_idx] = analogRead(PIN_TEMP_SENSOR);
    temp_sum += temp_buffer[tb_idx++];
    tb_idx %= TEMP_BUFFER_LEN;
}

for (i = 0; i < 10; i++) {
    aper_sum -= aper_buffer[ab_idx];
    aper_buffer[ab_idx] = analogRead(PIN_APER_SENSOR);
    aper_sum += aper_buffer[ab_idx++];
    ab_idx %= APER_BUFFER_LEN;
}

void setup() {
    // analog sensor inputs
    pinMode(PIN_TEMP_SENSOR, INPUT_ANALOG);
    pinMode(PIN_APER_SENSOR, INPUT_ANALOG);

    // excitation control
    pinMode(PIN_PD_SIGNAL, INPUT);
    pinMode(PIN_EXCITATION, PWM);

    // input capture for photodiode on CH1
    set_pll_prescaler(72);
    TIMER1_BASE ->CCMR1 |= TIMER_CCMR1_CC1S_INPUT_T11;
    TIMER1_BASE ->CCMR1 |= 0b0011 << 4; // input capture filter
    timer_cc_set_pol(TIMER1, 1, 0);
    timer_cc_enable(TIMER1, 1);
    timer_attach_interrupt(TIMER1, TIMER_CC1_INTERRUPT,
                          &excitation_pll_control_loop);

    // output pwm for excitation signal on CH3
    timer_set_mode(TIMER1, 3, TIMER_PWM);
    timer_resume(TIMER1);

    // systick timer used for period measurement
    systick_init(1000000000UL);
// servo outputs
pinMode(PIN_SERVO_1, PWM);
pinMode(PIN_SERVO_2, PWM);
pinMode(PIN_SERVO_3, PWM);

// servo & general purpose timer
servo_timer.setPrescaleFactor(24);
servo_timer.setOverflow(60000); // 50 Hz
servo_timer.setCompare(TIMER_CH1, 0);
servo_timer.setCompare(TIMER_CH2, 0);
servo_timer.setCompare(TIMER_CH3, 0);
servo_timer.attachInterrupt(3, gp_isr);

// motor output
pinMode(PIN_MOTOR_PWM, PWM);
pinMode(PIN_MOTOR_DIR, OUTPUT);

// motor timer
motor_timer.setPrescaleFactor(3);
motor_timer.setOverflow(48000); // 500 Hz

// invert PWM polarity (additional inversion by MAX232)
timer_oc_set_mode(TIMER3, TIMER_CH1, TIMER_OC_MODE_PWM_2, 0);

// set interrupt priorities
nvic_irq_set_priority(NVIC_TIMER1_CC, 0); // PLL highest priority
nvic_irq_set_priority(NVIC_TIMER4, 10); // GP timer higher than USB

// Force init to be called *first*, i.e. before static object allocation.
// Otherwise, statically allocated objects that need libmaple may fail.
__attribute__((constructor)) void premain() {
  init();
}

int main(void) {
  setup();
  reset();
  while (1) {
    usb_comm();
  }
}
A.2 Image Intensifier Excitation Controller Firmware

This section contains the source code of the excitation controller used in the image intensifier TR-PLI setup (see section 4.2.3). It was also implemented on a STM32-H103 board from Olimex Ltd using the libmaple library. This firmware is less complex than the one above, as the controller only has to output two pulse width modulated (PWM) signals with a defined phase offset and does not need to synchronize to an external signal. One of the PWM outputs controls the gate voltage of the IIU, the other one is the excitation signal to the light source.

A.2.1 controller.h

```c
/*
 * controller.h
 *
 * Firmware for a STM32-based image intensifier unit controller for
 * time-resolved photoluminescence imaging of silicon wafers.
 * *
 * Copyright (c) 2013, David Kiliani, University of Konstanz
 * All rights reserved.
 * *
 * Redistribution and use of this file is subject to the license terms in the
 * corresponding controller.cpp source file.
 */

#ifndef CONTROLLER_H_
#define CONTROLLER_H_

#define F_CPU 72000000UL

#define APER_BUFFER_LEN 256

struct chopper_t {
    double phase;
    double exc_duty;
    double iiu_duty;
}
```
double frequency;

#endif /* CONTROLLER_H_ */

A.2.2 controller.cpp

/*
controller.cpp
*
Copyright (c) 2013, David Kiliani, University of Konstanz
* All rights reserved.
* Redistribution and use in source and binary forms, with or without
* modification, are permitted provided that the following conditions are met:
* Redistributions of source code must retain the above copyright notice,
* this list of conditions and the following disclaimer.
* Redistributions in binary form must reproduce the above copyright notice,
* this list of conditions and the following disclaimer in the documentation
* and/or other materials provided with the distribution.
* Neither the name of the University of Konstanz nor the names of its
* contributors may be used to endorse or promote products derived from this
* software without specific prior written permission.
* THIS SOFTWARE IS PROVIDED BY THE COPYRIGHT HOLDERS AND CONTRIBUTORS "AS IS"
* AND ANY EXPRESS OR IMPLIED WARRANTIES, INCLUDING, BUT NOT LIMITED TO, THE
* IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE
* ARE DISCLAIMED. IN NO EVENT SHALL THE COPYRIGHT HOLDER OR CONTRIBUTORS BE
* LIABLE FOR ANY DIRECT, INDIRECT, INCIDENTAL, SPECIAL, EXEMPLARY, OR
* CONSEQUENTIAL DAMAGES (INCLUDING, BUT NOT LIMITED TO, PROCUREMENT OF
* SUBSTITUTE GOODS OR SERVICES; LOSS OF USE, DATA, OR PROFITS; OR BUSINESS
* INTERRUPTION) HOWEVER CAUSED AND ON ANY THEORY OF LIABILITY, WHETHER IN
* CONTRACT, STRICT LIABILITY, OR TORT (INCLUDING NEGLIGENCE OR OTHERWISE)
* ARISING IN ANY WAY OUT OF THE USE OF THIS SOFTWARE, EVEN IF ADVISED OF THE
* POSSIBILITY OF SUCH DAMAGE.
*/

#include <stdlib.h>
#include <string.h>
#include <stddef.h>
#include <stdio.h>
#include <wirish/wirish.h>
#include <libmaple/timer.h>
#include <libmaple/systick.h>
#include "controller.h"

HardwareTimer exc_timer(1);
HardwareTimer iiu_timer(2);
HardwareTimer servo_timer(4);

#define PIN_APER_SENSOR 26 // PC3
#define PIN_IIU_GATE 25 // PA1
#define PIN_EXCITATION 4 // PA10
#define PIN_SERVO_1 10 // PB6
#define PIN_GATE_EN 19 // PA7
#define EOL '
'

struct chopper_t chopper;
static uint16 aper_buffer[APER_BUFFER_LEN] = { 0 }; // all elements 0
static int ab_idx = 0, aper_sum = 0;

int get_aperture() {
    double x = aper_sum; // use rolling average
    return lround(x / APER_BUFFER_LEN / 4096 * 16); // 16 positions
}

void update_timer_parameters() {
    exc_timer.pause();
    iiu_timer.pause();
    exc_timer.setPeriod(lround(1e6 / chopper.frequency));
    iiu_timer.setPeriod(lround(1e6 / chopper.frequency));
    int of = exc_timer.getOverflow();
    exc_timer.setCompare(TIMER_CH3, lround(of * chopper.exc_duty));
    iiu_timer.setCompare(TIMER_CH2, lround(of * chopper.iiu_duty));
    exc_timer.refresh();
    iiu_timer.refresh();
    // add phase offset and 43 clock cycles to compensate start delay
    exc_timer.setCount(lround(of * chopper.phase + 43 / exc_timer.getPrescaleFactor())
        % of);
iiu_timer.resume(); // this takes about 43 clock cycles
exc_timer.resume();
}

void chopper_set_frequency(double freq) {
    chopper.frequency = freq;
    if (chopper.frequency == 0) {
        digitalWrite(PIN_GATE_EN, 1); // disable output driver IC
        iiu_timer.setCompare(TIMER_CH2, 0); // disable IIU gate output
        exc_timer.setCompare(TIMER_CH3, 0); // disable excitation output
    } else {
        digitalWrite(PIN_GATE_EN, 0); // enable output driver IC
        update_timer_parameters();
    }
}

void reset() {
    // set default values
    chopper.phase = 0;
    chopper.exc_duty = 0.5;
    chopper.iiu_duty = 0.5;
    chopper_set_frequency(0);
}

void usb_comm() {
    static char buf[64];
    char * buffer = buf;
    while (!strchr(buf, '\n')) { // read until terminated by LF
        if (SerialUSB.available()) {
            int len = SerialUSB.read(buffer, SerialUSB.available());
            buffer += len;
        }
    }
    *buffer = 0; // terminate string
    buffer = strtok(buf, "\r\n"); // remove CR and LF characters
    strlwr(buffer); // convert to lower case
    char * cmd = strsep(&buffer, " ");
    if (!strncmp(cmd, "*idn?", 5)) {
        SerialUSB.print("University of Konstanz,TR-PLI-Controller-IIU1,001,");
        SerialUSB.print(__DATE__); // report compile date as version number
        SerialUSB.print(EOL);
    } else if (!strncmp(cmd, "*rst", 4)) {

```c
void gp_isr() {
  /*
   * This is a general purpose timer with 50Hz frequency.
   */
  int i;
  for (i = 0; i < 10; i++) {
    aper_sum -= aper_buffer[ab_idx];
    aper_buffer[ab_idx] = analogRead(PIN_APER_SENSOR);
    aper_sum += aper_buffer[ab_idx++];
    ab_idx %= APER_BUFFER_LEN;
  }
}

void setup() {
  // analog sensor inputs
  pinMode(PIN_APER_SENSOR, INPUT_ANALOG);
  // output pwm for excitation signal on CH3
  pinMode(PIN_EXCITATION, PWM);
}
```
exc_timer.setMode(TIMER_CH3, TIMER_PWM);
exc_timer.setCompare(TIMER_CH3, 0);

// output pwm for IIU gate signal on CH2
pinMode(PIN_IIU_GATE, PWM);
pinMode(PIN_GATE_EN, OUTPUT);
iiu_timer.setMode(TIMER_CH2, TIMER_PWM);
iiu_timer.setCompare(TIMER_CH2, 0);

// servo output
pinMode(PIN_SERVO_1, PWM);
// servo & general purpose timer
servo_timer.setPrescaleFactor(24);
servo_timer.setOverflow(60000); // 50 Hz
servo_timer.setCompare(TIMER_CH1, 0);
servo_timer.attachInterrupt(3, gp_isr);

// set interrupt priorities
nvic_irq_set_priority(NVIC_TIMER4, 10); // GP timer higher than USB

// Force init to be called *first*, i.e. before static object allocation.
// Otherwise, statically allocated objects that need libmaple may fail.
__attribute__((constructor)) void premain() {
    init();
}

int main(void) {
    setup();
    reset();
    while (1) {
        usb_comm();
    }
    return 0;
}
A.3 TR-PLI Evaluation Algorithms: Python C Module

The TR-PLI evaluation model and fit algorithm described in section 4.1 were implemented in the C programming language, to be used as an extension module from the measurement software written in Python. The initial pure Python implementation was replaced by the C module shown here for performance reasons. The code contains functions to fit single pixels, as well as whole lifetime images. It uses the open source library CMINPACK\(^1\) by Manolis Lourakis and Frédéric Devernay for fitting with the Levenberg-Marquardt algorithm.

\[^1\]Available at http://devernay.free.fr/hacks/cminpack/index.html
/* CONTRACT, STRICT LIABILITY, OR TORT (INCLUDING NEGLIGENCE OR OTHERWISE)
* ARISING IN ANY WAY OUT OF THE USE OF THIS SOFTWARE, EVEN IF ADVISED OF THE
* POSSIBILITY OF SUCH DAMAGE.
*/

#define _USE_MATH_DEFINES
#include <Python.h>
#include <numpy/arrayobject.h>
#include <math.h>
#include "cminpack/cminpack.h"

#define N_FIT_PAR 3 // number of fit parameters
#define FIT_PAR_AMP 1 // PL signal amplitude
#define FIT_PAR_TAU 2 // carrier lifetime
#define MAXFEV 50 // maximum no. of fit function evaluations

// data required to fit a pixel
struct fit_data_lifetime {
  double T;
  double t_shift;
  double N_factor;
  const double *data;
};

/* Implementation of the convoluted PL emission model.
 * x: phase value, 0 < x < 2*pi
 * tau: carrier lifetime
 * N_factor: doping divided by generation rate
 */
static double pl_model(double x, double tau, double N_factor) {
  if (tau == 0) {
    // special case to avoid division by 0
    if (x <= M_PI)
      return M_PI - x;
    else
      return x - M_PI;
  }
  // N is the doping concentration divided by (G * tau) for normalization
  double N = N_factor / tau;
  double ept = exp(M_PI / tau);
  double e2pt = ept * ept;

double emxt = exp(-x / tau);

double ptx = M_PI + tau - x;

if (x <= M_PI)
    return ((4 * ptx - 6 * tau * emxt - tau / (N + 1)) * ept
        + (4 * ptx - 2 * tau + emxt + tau / (N + 1)) / ept
        + (ptx - 2 * tau + emxt - 0.5 * tau / (N + 1)) * e2pt
        + (ptx + 0.5 * tau / (N + 1)) / e2pt + 6 * ptx - 6 * tau * emxt)
        / ((1 + 2 * ept + e2pt) * (1 / ept + 1) * (1 / ept + 1));

else
    return -(4 * ptx - 6 * tau * emxt + tau / (N + 1)) * ept
        + (4 * ptx - tau / (N + 1)) / ept
        + (ptx - 6 * tau + emxt - 2 * tau + ept + emxt
        + 0.5 * tau / (N + 1)) * e2pt
        + (ptx - 0.5 * tau / (N + 1)) / e2pt + 6 * ptx - 6 * tau * emxt)
        / ((1 + 2 * ept + e2pt) * (1 / ept + 1) * (1 / ept + 1));

}

/*
 * Fit function to be called by lmdif. This function calculates the difference
 * between the measured data and the model.
 *
 * *p: pointer to a fit_data_lifetime structure
 * m: number of data points
 * n: number of parameters
 * *par: array of the fit parameters
 * *fvec: fit error vector to be returned
 *
 */
static int fit_fcn_pl(void *p, int m, int n, const double *par, double *fvec,
    int iflag) {
    int i;

double fcn_val;

struct fit_data_lifetime *fd = static_cast<fit_data_lifetime *>(p);

for (i = 0; i < m; i++) {
    // calculate phase value from image number and offset
    double x = ((double) i / m - fd->t_shift);
    x = (x - floor(x)) * 2 * M_PI; // ensure 0 <= x < 2*pi

    // calculate the PL model values
    fcn_val = par[FIT_PAR_AMP] * pl_model(x, par[FIT_PAR_TAU],
        fd->N_factor);

    // calculate the fit error (weighted for correct sigma)
    fvec[i] = (fd->data[i] - fcn_val) / sqrt(par[FIT_PAR_AMP]);
}
Source Code

```
return 0;
}

/* Function to fit one pixel by calling lmdif */

static void fit_pixel(const double *img, int images, const double *phase, 
const double *T, const double *N_factor, double *rfnorm, double *n_fev, 
double *par) {
    int i, mode, nprint, nfev;
    int ipvt[N_FIT_PAR];
    double ftol, xtol, gtol, epsfcn, factor, fnorm;
    double diag[N_FIT_PAR], qtf[N_FIT_PAR], wa1[N_FIT_PAR], wa2[N_FIT_PAR], 
    wa3[N_FIT_PAR];
    double *fvec = new double[images];
    double *fjac = new double[images * N_FIT_PAR];
    double *wa4 = new double[images];
    struct fit_data_lifetime fd;

    // start value for the amplitude: maximum value / pi
    par[FIT_PAR_AMP] = img[0];
    for (i = 1; i < images; i++)
        if (par[FIT_PAR_AMP] < img[i]) {
            par[FIT_PAR_AMP] = img[i];
        }
    par[FIT_PAR_AMP] /= M_PI;
    par[FIT_PAR_TAU] = 1.0; // start value for tau: T / 2*pi
    fd.T = *T;
    fd.t_shift = *phase;
    // adapt N_factor for normalized tau
    fd.N_factor = *N_factor * (2 * M_PI) / *T;
    fd.data = img;

    /* Set ftol and xtol to the square root of the machine
```
and gtol to zero. Unless high solutions are
required, these are the recommended settings. */

ftol = sqrt(dpmpar(1));
xtol = sqrt(dpmpar(1));
gtol = 0.;

epsfcn = 0.;
mode = 1;
factor = 1.e2;
nprint = 0;

lmdif(fit_fcn_pl, &fd, images, N_FIT_PAR, par, fvec, ftol, xtol, gtol,
MAXFEV, epsfcn, diag, mode, factor, nprint, &nfev, fjac, images,
ipvt, qtf, wa1, wa2, wa3, wa4);
if (rfnorm != NULL) { // return R value (uncertainty) of tau
fnorm = enorm(images, fvec);
covar1(images, N_FIT_PAR, fnorm * fnorm, fjac, images, ipvt, ftol, wa1);
fnorm = fjac[FIT_PAR_TAU + images + FIT_PAR_TAU];
*rfnorm = (fnorm > 0) ? sqrt(fnorm) : 0;
}
if (n_fev != NULL) // return number of fit function evaluations
*n_fev = nfev;
delete[] fvec;
delete[] fjac;
delete[] wa4;

/*
 * The location dependent phase shift introduced by a rotating shutter wheel.
 * x, y: pixel position
 * dx, dy: position of the shutter wheel center relative to the image center
 * A: phase amplitude
 * O: phase offset
 */
static double phase_shift_model(int x, int y, double dx, double dy, double A,
    double O) {
    double f = A * atan2(x + dx, -(y - dy)) + O;
    return f - floor(f);
}
* Fit a lifetime image to a TR-PLI measurement. To allow for parallelization,
* this function only fits a single row of the image data using shared memory.
* It has to be called once for every row to obtain the whole image.

* img_stack: 3d data array of all PL images to fit
* result: 3d array for resulting parameters of each pixel
* i: index of the image row to fit
* (phase.xx): tuple of the 4 parameters of phase_shift.model
* T: excitation period in seconds
* N_factor: partially normalized doping concentration

static PyObject *
fit_lifetime_image(PyObject *self, PyObject *args) {
    PyArrayObject *img_stack, *result;
    int i, j, n, m, images;
    double *img, phase, T, N_factor, *rfnorm, *n_fev, *par, phase_dx, phase_dy,
             phase_A, phase_O;
    if (!PyArg_ParseTuple(args, "O!O!i(dddd)dd", &PyArray_Type, &img_stack,
                                 &PyArray_Type, &result, &i, &phase_dx, &phase_dy,
                     &phase_A, &phase_O, &T, &N_factor))
        return NULL;
    if (img_stack->nd != 3 || img_stack->descr->type_num != PyArray_DOUBLE) {
        PyErr_SetString(PyExc_ValueError, "img_stack must be 3-dimensional and of type float");
        return NULL;
    }
    n = img_stack->dimensions[0];
    m = img_stack->dimensions[1];
    images = img_stack->dimensions[2];
    if (images < 4) {
        PyErr_SetString(PyExc_ValueError, "at least 4 phase images are required");
        return NULL;
    }
    if (result->nd != 3 || result->dimensions[0] != n
        || result->dimensions[1] != m) {
        PyErr_SetString(PyExc_ValueError, "result array must be 3-dimensional"
            " and of same size as img_stack");
        return NULL;
    }
    if (result->descr->type_num != PyArray_DOUBLE) {
        PyErr_SetString(PyExc_ValueError, "result array must be of type float");
```c
        return NULL;
    }

    if (result->dimensions[2] != 2 + N_FIT_PAR) {
        PyErr_SetString(PyExc_ValueError,
                        "result array has wrong third dimension");
        return NULL;
    }

    /* Do the calculation without global interpreter lock
     * to enable parallelization. */
    Py_BEGIN_ALLOW_THREADS;
    for (j = 0; j < m; j++) {
        img = (double *) (img_stack->data + i * img_stack->strides[0]
                             + j * img_stack->strides[1]);
        phase = phase_shift_model(j - m / 2, i - n / 2, phase_dx, phase_dy,
                                  phase_A, phase_0);
        rfnorm = (double *) (result->data + i * result->strides[0]
                              + j * result->strides[1]);
        n_fev = (double *) (result->data + i * result->strides[0]
                            + j * result->strides[1] + 1 * result->strides[2]);
        par = (double *) (result->data + i * result->strides[0]
                         + j * result->strides[1] + 2 * result->strides[2]);
        fit_pixel(img, images, &phase, &T, &N_factor, rfnorm, n_fev, par);
        par[FIT_PAR_TAU] *= T / (2 * M_PI);  // calculate tau in seconds
        *rfnorm *= T / (2 * M_PI);
    }
    Py_END_ALLOW_THREADS;

    return Py_None;
}

/* Fit a single pixel of a TR-PLI measurement. The PL model data with the
* final parameters is returned for display in the 'result' array.
* The fitted lifetime value in seconds is returned as a float value.
*
* img_stack: 1d data array of the PL values to fit
* result: 1d array to return fitted PL model
* x, y: coordinates of the pixel to fit
* w, h: original size of the PL images
* (phase_xx): tuple of the 4 parameters of phase_shift_model
* T: excitation period in seconds
```
Source Code

```c
* N_factor:  partially normalized doping concentration
*/

static PyObject *
    fit_lifetime_pixel(PyObject *self, PyObject *args) {
    PyArrayObject *img_stack, *result;
    int x, y, w, h, images, r_len;
    double *img, phase, T, N_factor, par[N_FIT_PAR], phase_dx, phase_dy,
        phase_A, phase_O;
    if (!PyArg_ParseTuple(args, "O!O!iiii(dddd)dd", &PyArray_Type, &img_stack,
                      &PyArray_Type, &result, &x, &y, &w, &h, &phase_dx, &phase_dy,
                      &phase_A, &phase_O, &T, &N_factor))
        return NULL;
    if (img_stack->nd != 1 || img_stack->descr->type_num != PyArray_DOUBLE) {
        PyErr_SetString(PyExc_ValueError,
                        "img_stack must be 1-dimensional and of type float");
        return NULL;
    }
    if (result->nd != 1 || result->descr->type_num != PyArray_DOUBLE) {
        PyErr_SetString(PyExc_ValueError,
                        "result array must be 1-dimensional and of type float");
        return NULL;
    }
    images = img_stack->dimensions[0];
    r_len = result->dimensions[0];
    img = (double *) (img_stack->data);
    phase = phase_shift_model(x - w / 2, y - h / 2, phase_dx, phase_dy, phase_A,
        phase_O);
    fit_pixel(img, images, &phase, &T, &N_factor, NULL, NULL, par);
    // calculate resulting PL model curve
    int i;
    for (i = 0; i < r_len; i++) {
        double p = ((double) i / r_len - phase);
        p = (p - floor(p)) * 2 * M_PI;
        *(double *) (result->data + i * result->strides[0]) = par[FIT_PAR_AMP]
            * pl_model(p, par[FIT_PAR_TAU], N_factor * (2 * M_PI) / T);
    }
    // return the fitted lifetime in seconds
    return Py_BuildValue("f", par[FIT_PAR_TAU] * T / (2 * M_PI));
}
```

150
// Make functions known to Python module

static PyMethodDef TrpliMethods[] = {{ "fit_lifetime_image",
    fit_lifetime_image, METH_VARARGS }, { "fit_lifetime_pixel",
    fit_lifetime_pixel, METH_VARARGS }, { NULL, NULL, 0, NULL } /* Sentinel */
};

// Initialize the Python module

PyMODINIT_FUNC inittrpli(void) {
    (void) Py_InitModule("trpli", TrpliMethods);
    import_array();       // required for Numpy
}