Study of solar cells by electron holography

DISSERTATION
zur Erlangung des akademischen Grades
Doctor rerum naturalium

(Dr. rer. nat.)

vorgelegt

der Fakultät für Mathematik und Naturwissenschaften
der Technischen Universität Dresden

von

M. Sc. Sandino del Busto, John William

Eingereicht am 10.02.2012

Die Dissertation wurde in der Zeit von November 2007 bis Dezember 2011 im Institut für Strukturphysik angefertigt

Betreuer: Prof. Dr. Hannes Lichte.
Dedicated to those who have to struggle in everyday life.
Abstract

Photovoltaic energy is the most promising future energy source. Therefore, strong efforts are made to improve their price-to-efficiency ratio. New technologies and materials are being involved in the production, such as poly-crystalline materials rather than mono-crystalline silicon. Some of these materials are based on copper-chalcopyrite with advantageous properties like directly tunable band gap, high absorption coefficients, low deposition temperatures, low-cost materials and capability of deposition on suitable materials. However, correlation between the thin film materials characteristics and device performance are not well understood, and increasing the efficiency needs an exhaustive comprehension of the different phenomena involved in their performance, such as role of defects, doping concentrations and potentials, which requires the development of innovative techniques for the characterization.

Electron holography in the TEM would be very helpful, because it allows the quantitative reconstruction of the complex object wave. The measurement of phase and amplitude of the wave makes it possible to determine the potential in the object studied. In this manner, electron holography is a powerful tool for materials characterization at nanometre scale because it relates potential distributions with structure. However, artefacts can be introduced in the measurement. Therefore, the procedure of acquisition, reconstruction and correction of artefacts of the electron holograms, fundamental for the interpretation of the results in terms of potential, are in detail presented.

Moreover, the object of study exhibits challenges to the technique because of their polycrystalline structure, which introduces dynamic interaction with the electron beam sometimes stronger than the desired one. Consequently it is necessary to have an adequate measurement procedure. To overcome this limitation, a characterization method including in-situ stimuli is proposed and applied to crystalline silicon and CIGS solar cells. For this, a suitable sample preparation procedure with Focused Ion Beam (FIB) milling, and a specially designed sample holder allowing illumination with light and biasing a TEM sample are developed and applied to solar cells.

As result of the work, it is shown that expectedly the electron illumination has an important influence. It produces larger generation rates than 1 sun standard illumination. As counterpart, the recombination processes occurring at the surface of the small and thin sample tend to reduce the potential generated by the illumination. As consequence, only the p-n junction potential is usually measured. To produce an appreciable effect by illumination with light, the TEM lamella must be thicker, and the illumination intensity of the light must be strongly increased.

This thesis realises the first extensive study of the application of electron holography to the measurement of potentials in solar cells applying in-situ illumination and biasing. The experimental findings were corroborated by simulation calculations. They show that the processes in the objects are essentially correctly understood, however, quantitative interpretation is not yet sufficiently accurate.
Kurzfassung


Ein spezielles Problem von polykristallinen Materialien ist die Tatsache, dass durch unterschiedlich orientierte Kristallite unterschiedliche Innere Potentiale gemessen werden können. Darüber hinaus besteht die Gefahr, dass die Elektronen mit unterschiedlichen Körnern in unterschiedlicher Weise dynamisch wechselwirken; dies führt zu Phasendifferenzen, die erheblich stärker sein können als die eigentlich interessanten Halbleiterpotentiale. Deshalb werden die holographischen Untersuchungen so modifiziert, dass die Objekte in-situ, beispielsweise unter Anlegen elektrischer Spannungen ("biasing") oder Beleuchtung mit Licht, untersucht werden. Die hierzu nötigen neuen Präparationsverfahren für die Objekte werden entwickelt. Ebenso werden neue in-situ Objekthalter entwickelt, die diese Parameter gezielt zu verändern gestatten.


Diese Dissertation realisiert die erste umfassende Studie über die Anwendung von Elektronen-Holographie für die Messung von Potenzialen in Solarzellen unter Anwendung von Biasing und in-
Nomenclature

ACTF Amplitude Contrast Transfer Function
CIGS Cu(In,Ga)Se$_2$
DR Depletion Region
EELS Electron Energy Loss Spectroscopy
FEG Field Emission Gun
LED Light Emitting Diode
MTF Modulation Transfer Function
PCTF Phase Contrast Transfer Function
PECVD Plasma-Enhanced Chemical Vapour Deposition
PGA Phase Grating Approximation
QNR Quasi Neutral Region
SEM Scanning Electron Microscope
SNR Signal to Noise Ratio
TEM Transmission Electron Microscopy
WKB Wentzel-Kramers-Brillouin
WTF Wave Transfer Function
## Constants

<table>
<thead>
<tr>
<th>Notation</th>
<th>Description/meaning</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_b$</td>
<td>Boltzmann constant</td>
<td>$1.38 \times 10^{-23} \frac{J}{K}$</td>
</tr>
<tr>
<td>$e$</td>
<td>Electron charge</td>
<td>$1.60 \times 10^{-19} \text{C}$</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
<td>300K</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck constant</td>
<td>$6.63 \times 10^{-34} \text{J s}$</td>
</tr>
<tr>
<td>$m_o$</td>
<td>Electron rest mass</td>
<td>$9.11 \times 10^{-31} \text{Kg}$</td>
</tr>
<tr>
<td>$\pi$</td>
<td>Number Pi</td>
<td>3.1415</td>
</tr>
<tr>
<td>$\varepsilon_o$</td>
<td>Vacuum permeability</td>
<td>$8.85 \times 10^{-12} \frac{\text{C}}{\text{V m}}$</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of light</td>
<td>$3 \times 10^8 \frac{\text{m}}{\text{s}}$</td>
</tr>
<tr>
<td>$\lambda_e$</td>
<td>Electron wavelength (200keV)</td>
<td>2.5 pm</td>
</tr>
</tbody>
</table>

## Symbols used in electron microscopy

<table>
<thead>
<tr>
<th>Notation</th>
<th>Description/meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e$</td>
<td>Relativistic mass of the electron</td>
</tr>
<tr>
<td>$P$</td>
<td>Momentum</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Relativistic factor</td>
</tr>
<tr>
<td>$v_e$</td>
<td>Speed of the electrons</td>
</tr>
<tr>
<td>$V$</td>
<td>Potential</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$C$</td>
<td>Contrast</td>
</tr>
<tr>
<td>$q$</td>
<td>2D coordinates in reciprocal space</td>
</tr>
<tr>
<td>$r$</td>
<td>2D coordinates in real space</td>
</tr>
<tr>
<td>$q_c$</td>
<td>Carrier frequency of holographic interference fringes</td>
</tr>
<tr>
<td>$U_f$</td>
<td>Biprism voltage</td>
</tr>
<tr>
<td>$U_e$</td>
<td>Acceleration voltage of the electrons</td>
</tr>
<tr>
<td>$r_f$</td>
<td>Filament radius</td>
</tr>
<tr>
<td>$\psi_{\text{obj}}$</td>
<td>Part of the electron wave travelling through the sample</td>
</tr>
<tr>
<td>$\psi_{\text{ref}}$</td>
<td>Part of the electron wave travelling in the vacuum</td>
</tr>
<tr>
<td>$A_{\text{obj}}$</td>
<td>Object wave amplitude</td>
</tr>
<tr>
<td>$A_{\text{ref}}$</td>
<td>Reference wave amplitude</td>
</tr>
<tr>
<td>$\lambda_{\text{inel}}$</td>
<td>Inelastic mean free path</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Interaction constant</td>
</tr>
<tr>
<td>$V_{\text{MIP}}$</td>
<td>Mean inner potential</td>
</tr>
<tr>
<td>$\text{FT}$</td>
<td>Fourier transformation</td>
</tr>
<tr>
<td>$\text{FT}^{-1}$</td>
<td>Inverse Fourier transformation</td>
</tr>
<tr>
<td>$I_{\text{in}}$</td>
<td>Inelastic intensity</td>
</tr>
<tr>
<td>$\lambda_{\text{EELS}}^{\text{inel}}$</td>
<td>Inelastic mean free path for Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>Notation</td>
<td>Description / meaning</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Superposition angle produced by the biprism</td>
</tr>
<tr>
<td>$w_{hol}$</td>
<td>Width of the hologram</td>
</tr>
<tr>
<td>$j_{bc}$</td>
<td>Electron illumination current density</td>
</tr>
<tr>
<td>$t_{opt}$</td>
<td>Optimal sample thickness</td>
</tr>
</tbody>
</table>

Symbols used for the description of the electric properties of semiconductors

Table 2:

<table>
<thead>
<tr>
<th>Notation</th>
<th>Description / meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_D(r)$</td>
<td>Donor density in the conduction band</td>
</tr>
<tr>
<td>$N_A(x)$</td>
<td>Acceptor density in the valence band</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Intrinsic density of charge</td>
</tr>
<tr>
<td>$N_C(T)$</td>
<td>Density of states in the conduction band</td>
</tr>
<tr>
<td>$P_V(T)$</td>
<td>Density of states in the valence band</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Energy of the Fermi level</td>
</tr>
<tr>
<td>$E_V$</td>
<td>Energy of the valence band</td>
</tr>
<tr>
<td>$E_C$</td>
<td>Energy of the conduction band</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Acceptor states energy</td>
</tr>
<tr>
<td>$E_D$</td>
<td>Donor states energy</td>
</tr>
<tr>
<td>$m_h^*$</td>
<td>Effective mass of holes</td>
</tr>
<tr>
<td>$m_e^*$</td>
<td>Effective mass of electrons</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>Relative dielectric constant of the semiconductor</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Photon frequency</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Light wavelength</td>
</tr>
<tr>
<td>$F_o(\lambda)$</td>
<td>Initial radiance</td>
</tr>
<tr>
<td>$G$</td>
<td>Generation rate</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field</td>
</tr>
<tr>
<td>Notation</td>
<td>Description / meaning</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------</td>
</tr>
<tr>
<td>$n$</td>
<td>Density of electrons in the conduction band</td>
</tr>
<tr>
<td>$p$</td>
<td>Density of holes in the valence band</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperate</td>
</tr>
<tr>
<td>$V$</td>
<td>Potential</td>
</tr>
<tr>
<td>$V_{bi}$</td>
<td>Built-in potential</td>
</tr>
<tr>
<td>$V_{bi}^*$</td>
<td>Initial built-in potential with stimulus</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Electron affinity</td>
</tr>
<tr>
<td>$V_C$</td>
<td>Contact potential</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Intrinsic charge density</td>
</tr>
<tr>
<td>$J_e$</td>
<td>Electron current density</td>
</tr>
<tr>
<td>$J_h$</td>
<td>Hole current density</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>Electron mobility</td>
</tr>
<tr>
<td>$\mu_h$</td>
<td>Hole mobility</td>
</tr>
<tr>
<td>$D_e$</td>
<td>Electron diffusion coefficient</td>
</tr>
<tr>
<td>$D_h$</td>
<td>Hole diffusion coefficient</td>
</tr>
<tr>
<td>$V_a$</td>
<td>Biasing voltage</td>
</tr>
<tr>
<td>$E_{f_n}$</td>
<td>Quasi Fermi level for electrons</td>
</tr>
<tr>
<td>$E_{f_p}$</td>
<td>Quasi Fermi level for holes</td>
</tr>
<tr>
<td>$p_{no}$</td>
<td>Minority carrier concentration in the n-doped region</td>
</tr>
<tr>
<td>$n_{po}$</td>
<td>Minority carrier concentration in the p-doped region</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>$E_{e-h}$</td>
<td>Energy to create an electron-hole pair</td>
</tr>
</tbody>
</table>
Contents

1 Introduction ........................................... 1

2 Basics of Solar Cells ................................. 5
   2.1 Introduction ..................................... 5
   2.2 Physics of solar cells ............................ 6
      2.2.1 Absorption of light ......................... 6
      2.2.2 Separation of charge ....................... 9
      2.2.3 Transport process ......................... 13
   2.3 Potential under biasing in darkness .......... 14
   2.4 Potential under illumination ................. 15
   2.5 Efficiency of solar cells ..................... 17
   2.6 Summary ....................................... 19

3 Potential measurement by electron holography ... 21
   3.1 Introduction .................................... 21
   3.2 Propagation of the electron wave through the object .... 22
   3.3 The phase problem in TEM ...................... 23
   3.4 Off-axis electron holography ................. 27
      3.4.1 Biprism .................................... 27
      3.4.2 Interference ................................ 30
      3.4.3 Reconstruction of the object wave from the hologram .. 31
      3.4.4 Problems and artefacts .................... 32
      3.4.5 Additional parameters ..................... 38
      3.4.6 Potential measurement .................... 42
   3.5 Summary ....................................... 44
# Application of electron holography on solar cells

4.1 Introduction .............................................. 45
4.2 Potential measurement in polycrystalline solar cells ................. 46
4.3 Measurement of the functional potential by means of in-situ stimulus ... 49
  4.3.1 Effects expected according to the stimulus applied .......... 52
4.4 Charge induced by the electron beam ................................ 54
  4.4.1 Quantification of charge induced by the electron beam ....... 54
4.5 Revision of noise problem .................................... 59
4.6 Summary .................................................. 62

# Design, construction, characterisation and application of a TEM holder for in-situ biasing and illumination

5.1 Introduction .............................................. 65
5.2 Holder design .............................................. 66
5.3 Designed holders .......................................... 69
5.4 Reduction of charge under illumination ............................. 76
5.5 Summary .................................................. 78

# TEM sample preparation for in-situ biasing and illumination

6.1 Sample preparation .......................................... 82
  6.1.1 Sample size and shape .................................. 83
  6.1.2 Sample preparation procedure ............................ 84
6.2 Artefacts introduced by the preparation ........................... 87
  6.2.1 Artefacts of the FIB milling process ....................... 87
6.3 Simulating p-n junction potentials in FIB lamellae .................. 91
6.4 Optimum thickness ......................................... 92
6.5 Sample preparation of CIGS solar cells ............................ 93
6.6 Summary .................................................. 96

# Measurement of built-in potential under in-situ illumination and bias of solar cells

7.1 Introduction .............................................. 97
7.2 Silicon solar cells ......................................... 98
  7.2.1 Sample ................................................ 98
7.2.2 Biasing ......................................................... 100  
7.2.3 Illumination ............................................... 106  
7.3 CIGS solar cells ........................................... 112  
7.3.1 Sample ................................................... 112  
7.3.2 Carriers generation by the electron beam .......... 113  
7.3.3 Calculation of $V_{MIP}$ and $\lambda_{inel}$ ............ 114  
7.3.4 Biasing ................................................... 115  
7.3.5 Illumination ............................................ 118  
7.4 Summary ..................................................... 118  

8 Summary ...................................................... 121  

A Parameters list .............................................. 125  

B Photovoltaic energy production panorama ............ 127  

C Angular distribution of LEDs illumination .......... 131  

D Types of solar cells - first and second generation  135
Chapter 1

Introduction

Photovoltaics is one of the most promising future sources of energy. Moreover, it could potentially cover the global consumption of energy\textsuperscript{1}.

Increasing the efficiency of multicrystalline solar cells \textsuperscript{2} is a major challenge where control of the following aspects \textsuperscript{38} is important: First, the solar cell must be a strong optical absorber guaranteeing an optimum light collection. Second, it must incorporate a built-in electric field, usually generated by means of a p-n junction, which guarantees optimum charge separation. Last but not least, it must allow the application of Ohmic electrical contacts to collect the charges.

Additional aspects, which limit the efficiency in a more realistic multicrystalline solar cell are \textsuperscript{21}:

1. Influence of grain boundaries on recombination, as well as current transport and diffusion/segregation.
2. Characteristics of the band-offset due to the difference between the electron affinities of absorbers.
3. Point defects affecting the device’s behaviour. This effect is not yet completely understood. It is usually considered empirically without knowledge of the active centres.

Therefore, a complete characterisation of the growing process correlated with the response and local device behaviour is necessary, as well as the understanding of local states and chemical profiles. It is also clear that the efficiency of the device is determined not only by the characteristic of its individual components, and hence a characterisation of the interplay of the different layers is necessary.

Aspects affecting the efficiency, the physical basics and technological issues are influenced by, e.g. material inhomogeneities on a nanometre scale hence have to be characterised accordingly \textsuperscript{21}.

Nowadays, for a comprehensive characterisation of solar cells different techniques are applied, for example: Scanning Probe Microscopy and related techniques (e. g. Atomic

\textsuperscript{1}In Appendix B a panorama of the photovoltaic energy consumption in the world is shown.

\textsuperscript{2}The efficiency is defined as the ratio between the electrical power given by the device and the light power received.
CHAPTER 1. INTRODUCTION

Force Microscopy), X-Ray Diffraction (XRD), Ellipsometry, Electron Microscopy (SEM, TEM), Auger Electron Spectroscopy, Secondary-Ion Mass Spectrometry (SIMS), Photoelectrons Spectroscopy, Photoluminescence (PL), Electron-Beam Induced Current (EBIC) and Small-Spot Light-Beam-Induced Current (LBIC), among others. With these techniques, it is possible to measure the physical properties of a solar cell such as roughness and morphology, electrical properties of the surface, electronic structure of the surface, crystalline phases in the solar cell structure, quantitative compositional information about the surface, doping distribution, contaminants in the surface and near-surface, alignment of energy bands, energetic and spatial distribution of the density at interfaces as well as defects and thickness of the layers.

These characterisation techniques, however, analyse only superficial or macroscopic electrical, optical and structural properties; they do not allow the direct measuring of local electric potentials in the bulk on a nanometre scale.

Local potential variations occur at the p-n junction, the surfaces as well as between and within the grains. The resulting potential distribution changes locally under illumination or charge transport and is the driving force for the carriers created by the illumination. Thus it plays a decisive role for solar cell efficiency [149][39].

Presently, electron holography is the only method which allows measuring the semiconductor potentials on a nanometre scale.

The Triebenberg-Lab (Technische Universität Dresden, Germany) has pioneered the measurement of potential distributions in semiconductors. Such measurements have been used in a large number of applications in micro-magnetics and micro-electrics at medium and atomic resolution [83, 141, 152, 129]. However, it has not yet been used for the characterisation of solar cells.

For application to multicrystalline solar cells, namely $Cu(In,Ga)Se_2$ known as CIGS, huge problems arise due to the unwanted signals from the grainy structure, possibly much higher than the desirable ones. Consequently, the final goal of the research project is to apply electron holography to measure local potential distributions in multi-crystalline solar cells.

To reach the goal, the following questions must be answered:

1. What is the basic physical principle of a solar cell?
2. What are the principal factors affecting the solar cell efficiency and how are they related to the potential distribution?
3. Is it possible to measure the potential distribution at p-n junctions in solar cells by electron holography?

---

3In this thesis three different types of potential measurement are distinguished: potential difference, potential variation and potential distribution. A potential difference is measured between two points. The second one, the potential variation, refers to dynamical measurement of the potential under an external influence, for example illumination or temperature variations. The last one, the potential distribution, refers to the measurement of spatial variations of potential.

4In this thesis the terms multicrystalline and polycrystalline are used indistinctly.
4. Is it possible to correlate the band structure in the solar cell with the measured potential?

5. What are the most suitable experimental conditions, e.g. sample orientation, acquisition time and so on, to measure this potential?

6. What are the necessary conditions in the sample preparation, e.g. optimal sample thickness, to measure the potential in solar cells?

Answers to these questions are given in the following.
Chapter 2

Basics of Solar Cells

2.1 Introduction

A solar cell is a device, which converts solar energy, i.e. photons, directly into electric energy. This process is based on the photovoltaic effect, which produces a built-in potential. Photons produce free charges, which are subsequently separated by a built-in electric field created in intentionally constructed inhomogeneous materials.

Figure 2.1 illustrates the basic components of a solar cell. A solar cell is structured in layers. The uppermost and lowermost layers serve as contacts to collect the charges generated by the solar radiation. In order to improve the transmittance of light to the inner layers of the cell, an optical window as the upper layer is used; in some solar cells this optical window also has conductive properties helping to collect the generated charges. The absorbent material contains a p-n junction providing an electric field for charge separation. Depending on the type of the solar cell the layers may have different disposition. In order to improve the performance, different doping of the materials or additional layers can be used.

Crucial points relating to the characteristics of these layers must be considered: The conductive contacts must be Ohmic contacts with the absorbent material layer for optimal charge conductivity. The optical window must be highly transparent to ensure that the light arrives in the absorbent material region of the solar cell; it must also have anti-reflective properties to avoid the reflection of the light at the surface of the absorbent material. The absorbent material must have an adequate band gap and a large absorption coefficient; additionally, it must provide an electric field, usually by means of a p-n junction, with a certain field profile to ensure the separation of the charges generated. In this layer, the diffusion length of the generated charges must be large enough to ensure that the charges reach the contacts. Indeed, the electrical and mechanical coupling between the layers is necessary to avoid losses.

Measuring the built-in potential distribution created by a p-n junction in the solar cell is a major challenge, because it plays a decisive role in the solar cell efficiency. It is usually calculated indirectly from other measurements such as Kelvin microscopy [52, 53].
CHAPTER 2. BASICS OF SOLAR CELLS

Figure 2.1: Structure of a solar cell. Left: picture of a c- silicon solar cell [20]. Right: schematic cross-section of the layers of a solar cell.

To understand the relationship between the built-in potential and the solar cell efficiency, the following aspects must be considered: The physics of the solar cells, the potential under biasing in darkness, the potential under illumination and the problems, which affect the efficiency of the solar cells. All these aspects are examined in this chapter.

2.2 Physics of solar cells

The whole process of converting light energy into electrical energy has different steps: absorption of the light, separation of charge and transport to the contacts.

2.2.1 Absorption of light

Photons arriving at the surface of the solar cell are absorbed only if they have an energy\(^1\) \(E = h\nu\) larger than the band gap energy \(E_g\) of the absorbent material\(^2\). During the absorption process the photon flux can transfer its energy to electrons. Electrons situated in the valence band can jump into the conduction band thereby creating electron-hole pairs. This transition can also occur into and out of intraband states. In these cases, photons with lower energy than the forbidden band gap are also absorbed. Figure 2.2 shows some photon absorption processes. These intraband states are generated by defects in the crystalline structure of the absorbent material\(^3\).

Transitions occurring between the valence band and the impurity state of acceptors with energy \(E_A\) or between the donors state with energy \(E_D\) and the conduction band are called intraband transitions. They do not contribute to the photovoltaic effect because the charges there cannot move through the material. These states also increase the recombination rate in the semiconductor.

\(^1\)\(h\) is the Planck constant and \(\nu\) is the photon frequency

\(^2\)In the following we will assume a basic band structure. With a valence band of constant energy \(E_V\), a conduction band with energy \(E_C\) as well as acceptor and donor states from the doping process with energies \(E_A\) and \(E_D\) respectively (Figure 2.2).

\(^3\)Here not all of the possible electronic transitions are described. A more complete description can be found, for example in Sze [126, p. 745].
2.2. PHYSICS OF SOLAR CELLS

Figure 2.2: Different electron-photon excitations in a semiconductor: Intrinsic excitation band to band between the valence band with energy $E_V$ and conduction band with energy $E_C$, extrinsic excitation between the valence band or conduction band and donor or acceptor states with energies $E_D$ and $E_A$, respectively.

The amount of light absorbed in a material is given by its absorption coefficient $\alpha$, which is dependent on the light wavelength $\lambda$. Figure 2.3 shows the absorption coefficient for crystalline silicon ($c-Si$) and CIGS.

![Figure 2.3: Absorption coefficients of $c-Si$ and CIGS.](image)

The larger the absorption coefficient, the better the absorption of the light and consequently the rate of charge generation is larger. If light hits the top surface with an initial radiance of $F_0(\lambda)$ (photons/(cm$^2$s)), this radiance decays exponentially with the distance $x$ of propagation into the medium according to:

$$F(\lambda, x) = F_0(\lambda) \exp \left[ -\alpha(\lambda) x \right].$$

(2.1)

In the following it is assumed that each absorbed photon with an energy of $E > E_g$ creates an electron-hole pair. The density of electron-hole pairs produced in the absorbent material is given by the generation rate $G(x)$, which is related to the flux by:

$^{4}$The absorption coefficient $\alpha$ describes the attenuation of the light propagating through a material.
\[ G(x) = -\sum_{\lambda} \frac{dF(\lambda x)}{dx} = \sum_{\lambda} \alpha(\lambda) F_{e}(\lambda) \exp[-\alpha(\lambda) x]. \] (2.2)

This equation gives the generated density of charge per second in the material.

Figure 2.4 shows the generation rate of electron-hole pairs as a function of the surface distance (depth) for \textit{c}-Si and \textit{CIGS} illuminated with a flux density (radiance) of $10^{18} \text{cm}^{-2}\text{s}^{-1}$ of 470 nm (blue) and 650 nm (red) photons. For a given area of the absorbent material, \textit{c}-Si solar cells must be thicker in order to generate approximately the same charge produced by thin \textit{CIGS}. The reason is the low absorption coefficient as a consequence of the indirect band gap of the silicon, which is one of the biggest problems in the reduction of costs in these types of solar cells. Therefore, in solar cells it is important to use materials with a large absorption coefficient. This allows to reduce the thickness of the absorbent material, and hence costs of production.

![Figure 2.4: Electron-hole pair generation rate in the absorbent material by a flux density of $10^{18} \text{cm}^{-2}\text{s}^{-1}$ of 470nm and 650nm photons. This effect clearly shows why \textit{c} – \textit{Si} solar cells must be thicker than \textit{CIGS} for the same amount of electron hole pairs to be generated.](image)

Equation 2.2 implies that the generation rate for each electron reaching the surface with larger energy than the band gap produces an electron hole pair. However, the energy $E > Eg$ is lost by thermalisation. Shockley and Queisser [114] calculate the ultimate efficiency of a solar cell considering the energy distribution of the solar radiation and assuming the energetic balance of the solar cell as a thermodynamic system. They report a maximum for $Eg = 1.1 \text{eV}$. The total energy produced by such a solar cell is 44% of the total energy incident from the sun. Because of the band gap the amount of energy lost is more than 55%. This is the maximum possible in these kinds of solar cells. Therefore in a more realistic description, the generation rate 2.2 must include a factor indicating the probability of electron-hole pair creation by photons with energy larger than the band gap.

8
2.2.2 Separation of charge

Once the electron-hole pairs are created, the electrons leave the valence band and jump into the conduction band. These charges must be transported in opposite directions to the contacts. This is achieved in most of the solar cells by means of an electric field $E$ created by a p-n junction.

A p-n junction is created if two semiconductors are in contact. However, they must have different doping concentrations, one with donor and one with acceptor doping.

The doping is conducted intentionally to introduce impurities or to create vacancies. Impurities create acceptor levels for holes in the valence band (p-material), if their number of valence electrons is smaller than the surrounding material. In this process a level close to the valence band inside of the forbidden band gap is created. A donor level for electrons in the conduction band (n-material) is created if the number of valence electrons of a doping substance is larger than the number of valence electrons in undoped material. Consequently, a new state close to the conduction band inside the forbidden band gap is created. In the case of vacancies the acceptor or donor states are created by intentionally changing the ratio between some of the component of the material, for example in CIGS the ratio $Cu/In$ is controlled by inducing defects in the crystal structure.

Because of this doping process the charge distributions of electrons and holes change and in consequence also, the Fermi level with energy $E_f$ of the doped materials changes. In the case of $p$-doped materials the Fermi level is located closer to the valence band. Likewise, in $n$-doped materials, it is located near to the conduction band (Figure 2.5). The most usual doping materials are phosphorous and boron. Phosphorous produces a donor state ($n$ doping) and boron produces an acceptor state ($p$ doping).

![Figure 2.5: Band structure of $n$-doped material (left) and $p$-doped material (right); $E_D$ is the energy of the donor state created by addition of impurities to the material, in this case the Fermi level moves closer to the conduction band. In a similar way, an acceptor impurity creates an acceptor state; here the Fermi level is located closer to the valence band.](image)

In solar cells two statistical distributions to describe the doping concentrations are used: the Fermi-Dirac and the Maxwell-Boltzmann distributions. On one hand the Fermi-Dirac distribution is used in high doping concentrations and high temperatures. On the other hand the Maxwell-Boltzmann distribution is used in low doping concentrations and low
temperatures, as approximation of the Fermi-Dirac distribution. For a detailed description see [126]; a detailed discussion regarding the use of each distribution in the description of the electron density is given in [5, p. 42].

If the Fermi level is localised inside the forbidden band gap and separated by more than $4k_b T \sim 0.13 \text{eV}$ from either band edge\(^5\), the semiconductor is called non-degenerated. In this condition, the charge distribution, as previously mentioned, can be described by the Maxwell-Boltzmann distribution.

According to this distribution, the electron density in the conduction band and the hole density in the valence band are given by:

$$n(r) = N_C \exp[-(E_C - E_f)/k_b T], \quad (2.3)$$

$$p(r) = P_V \exp[-(E_f - E_V)/k_b T] \quad (2.4)$$

with

$$n(r) \cdot p(r) = n_i^2. \quad (2.5)$$

Here $n_i$ is the intrinsic charge concentration, whilst $N_C(T)$ and $P_V(T)$ are the density of states in the conduction and valence bands, respectively, given by:

$$N_C(T) = 2 \left( \frac{2\pi m_e^* k_b T}{\hbar^2} \right)^{3/2} \sim 2.8 \times 10^{15} \text{cm}^{-3} \quad (2.6)$$

$$P_V(T) = 2 \left( \frac{2\pi m_h^* k_b T}{\hbar^2} \right)^{3/2} \sim 1.04 \times 10^{15} \text{cm}^{-3} \quad (2.7)$$

In these equations $m_e^*$ is the effective mass of the electrons in the conduction band and $m_h^*$ is the effective mass of holes in the valence band. The values for these parameters are given in Table A.2.

\(^5\)In this equation $k_b$ is the Boltzmann constant and $T$ is the temperature.

p-n junctions

In conditions of no illumination and no electrical biasing, the p-n junction potential is built-up as follows. Free mobile electrons from the $n$-doped region diffuse into the $p$-doped region and holes in the opposite direction. In consequence an electric field is created providing a drifting force produced by local charge concentrations. These two effects of diffusion and drift compensate each other, creating an equilibrium where the total current in the probe is zero. Following this, all the forces cancel making the Fermi level constant through the junction.
The transition region, where the band structure changes, is called the Depletion Region (DR). In this region an electric field exists. Such regions where the potential is constant are called Quasi Neutral Regions (QNR) (Figure 2.6).

In cases where the only difference between both materials is their charge carrier concentration, the junction is called homo-junction. Otherwise, if the contacted materials are different, it is a hetero-junction. In general, these two materials have different forbidden band gaps, electron affinities $\chi$, contact potentials $V_C$ and lattice constants. Figure 2.6 shows the p-n junction for a homo-junction and a hetero-junction.

Figure 2.6: Left: band structure of a p-n homo-junction. Right: example of a band structure of a hetero-junction. Two materials $a$ and $b$ are in contact, the material $a$ with band gap $E_{ga}$ and electron affinity $\chi_a$ and the material $b$ with band gap $E_{gb}$ and electron affinity $\chi_b$. The contact potential between the two materials is $V_C$. The solid lines indicate the conduction band $E_C$ and the valence band $E_V$.

In a hetero-junction solar cell, the material with the larger band gap is used as an optic window, whereas the material with the smaller band gap is the absorbent material. In CIGS based solar cells, the structure is given by the optic window consisting of $n^+$-doped ZnO and the absorber made of $p$-doped CIGS. In addition, to improve the electrical coupling between CIGS and ZnO, a buffer material like CdSe, $p$-doped, is commonly used.

**Potentials in homo-junctions - Shockley’s model**

The resulting equation containing the exponential term of the charge distribution depends on the potential $V$ itself and resembles the Poisson equation but with non-linear terms, which must be solved self-consistently:

$$\nabla V = \frac{e}{\varepsilon_o \varepsilon_s} (N_C(T) \exp[-(E_C - V_e)/k_b T])$$
$$+ \frac{e}{\varepsilon_o \varepsilon_s} (P_V(T) \exp[-(V_e - E_V)/k_b T] - N_D + N_A), \quad (2.8)$$

where $\varepsilon_o \varepsilon_s$ are the dielectric constant of vacuum and the relative dielectric constant of the semiconductor, respectively, and $N_A$ and $N_D$ are the acceptor and donor doping concentrations, respectively.
This equation can be solved analytically under non-degenerate doping conditions using the one-side abrupt junction approximation, according to Shockley’s model. With these approximations the potential difference through the junction, the so called built-in potential $V_{bi}$, follows as:

$$V_{bi} = \frac{k_b T}{e} \ln \left[ \frac{N_A N_D}{n_i^2} \right];$$  \hspace{1cm} (2.9)

here $n_i$ is the intrinsic charge concentration density. The width $W$ of the depletion region (DR) is:

$$W = \sqrt{\frac{2\varepsilon_s e V_{bi}}{e} \left( \frac{N_A + N_D}{N_A N_D} \right)}$$  \hspace{1cm} (2.10)

In this thesis, the solution of the Poisson equation (Equation 2.8) is obtained using a 3D Partial Differential Equation solver based on finite elements (FlexPDE [24]). A comparison of the analytical and numerical solutions of a p-n homo-junction with uniform doping $N_D$ and $N_A$ is shown in Figure 2.7.

![Comparison between the results of using the 3D solution of the Poisson equation by the program FlexPDE and the 1D Shockley model. The insert shows the resulting grid and an image of the potential distribution in the centre slice of the block.](image)

Figure 2.7: Comparison between the results of using the 3D solution of the Poisson equation by the program FlexPDE and the 1D Shockley model. The insert shows the resulting grid and an image of the potential distribution in the centre slice of the block.

The 3D finite element modelling also makes it possible to calculate the p-n junction, incorporating the effect of doping gradients and additional layers. These factors will become important in the study of effects due to sample preparation by using the Focused Ion Beam (Chapter 6).
2.2. PHYSICS OF SOLAR CELLS

2.2.3 Transport process

Up to this point, only equilibrium situations have been considered. However, when the p-n junction is biased or illuminated, the equilibrium is shifted. In this situation the local charge concentration is not only determined by the local potential and equations relating the total electron and hole currents but also by the equation relating the total electron and hole currents.

The electric field generated in the junction forces the electrons and holes to move thus generating a current. This current is referred to as drift current. In the same way, the difference of charge concentrations produces a diffusion of charges. In consequence, the current is controlled by drift and diffusion, and is described by the current density equations.

Two transport equations defining the current densities of electrons \( J_e(r) \) and holes \( J_h(r) \) are defined:

\[
J_e(r) = e \mu_e n(r) E(r) + eD_e \nabla n(r) \tag{2.11}
\]
\[
J_h(r) = e \mu_h p(r) E(r) - eD_h \nabla p(r) \tag{2.12}
\]

In these equations \( \mu_e \) and \( \mu_h \) are the mobilities and \( D_e \) and \( D_h \) the diffusion coefficients for electrons and holes respectively. The drift of charge is due to electric fields. In general the charge current is affected by lattice vibrations, impurities, other carriers, surfaces (grain boundaries and interfaces) and material imperfections. The mean influence of these parameters is included in the mobilities \( \mu_e \) and \( \mu_h \) for electrons and holes.

As previously indicated, diffusion transport is produced by local variations of carrier concentration in the material and is described by the mass transfer equation, Fick’s law. Local variations of carrier concentrations can occur because of recombination processes, injection or generation of charge and spatially varying doping concentration. The diffusion process attempts to compensate gradients of carrier concentrations whereby carriers displace from regions of higher density into regions of lower density.

The diffusion coefficient in non-degenerated semiconductors is correlated with the mobility through the Einstein relation:

\[
D_{e,h} = \frac{k_B T}{e \mu_{e,h}} \tag{2.13}
\]

Two additional equations describing semiconductors under illumination or biasing are the Poisson and the continuity equations.

The Poisson equation relates the potential distribution \( V(r) \) to the space-charge density \( \rho(r) \):

\[
\text{div}(\varepsilon_0 \varepsilon_s \text{grad}(V(r))) = -\rho(r) \tag{2.14}
\]

here given by:
CHAPTER 2. BASICS OF SOLAR CELLS

\[ \rho(r) = e[N_d(r) - N_a(r) - n(r) + p(r)] \]  
(2.15)

This density of charge in general depends on position. \( N_d(r) \) and \( N_a(r) \) are the donor and acceptor densities, \( n(r) \) is the electron density in the conduction band and \( p(r) \) is the hole density in the valence band.

As a consequence of charge conservation, the continuity equation serves as a boundary condition for drift and diffusion and describes the change in the number of carriers in a determined region.

\[ \frac{dn(r)}{dt} = \frac{dn(r)}{dt} \bigg|_{rad} + \frac{1}{e} \nabla \cdot J_e(r) - R_e(r) \]  
(2.16)

\[ \frac{dp(r)}{dt} = \frac{dp(r)}{dt} \bigg|_{rad} + \frac{1}{e} \nabla \cdot J_h(r) - R_h(r) \]  
(2.17)

\( \frac{dn(r)}{dt} \bigg|_{rad} = \frac{dp(r)}{dt} \bigg|_{rad} = G(r) \) consider the process of charge generation due to radiation, whereas \( R_e \) and \( R_h \) describe the process of electron and holes recombination.

The substitution of transport equations 2.11 and 2.12 into the continuity equations 2.16 and 2.17 results in two coupled equations; the transport equations:

\[ -\mu_e E(r) \cdot \nabla n(r) - \mu_e n(r) \nabla \cdot E(r) - D_e \Delta n(r) - R_e(r) + G(r) = 0 \]  
(2.18)

\[ \mu_h E(r) \cdot \nabla p(r) + \mu_h p(r) \nabla \cdot E(r) - D_h \Delta p(r) - R_h(r) + G(r) = 0 \]  
(2.19)

These equations, written for steady state, that is \( \frac{dn(r)}{dt} = \frac{dp(r)}{dt} = 0 \), must be solved by the current and charge densities in the solar cell. For this, adequate boundary conditions are necessary.

2.3 Potential under biasing in darkness

The solution of biasing of an ideal p-n junction in low injection condition is calculated by Shockley [113]. According to his model, under forward or reverse biasing, the built-in potential is reduced or increased respectively in proportion to the applied voltage \( V_a \).

Then:

\[ V = V_{bi} \pm V_a \]  
(2.20)

When a voltage \( V_a \) is applied, the equilibrium is perturbed, and hence the minority carrier concentration on both sides of the p-n junction changes. This shifts the Fermi levels for minority electrons and holes between the band gap, \( E_{fn} \) and \( E_{fp} \) for electron and holes respectively.

The solution of the transport equations for electrons and holes in low-injection condition yields the current for electron and holes:
\[ J_n = \frac{eD_n n_{po}}{L_e} (\exp \left[ e \frac{V_a}{k_b T} \right] - 1) \] (2.21)

\[ J_p = \frac{eD_h p_{no}}{L_h} (\exp \left[ e \frac{V_a}{k_b T} \right] - 1) \] (2.22)

In this equation, \( p_{no} \) and \( n_{po} \) are the concentrations of holes in the \( n \) region and density of electrons in the \( p \) region, respectively, and \( L_e \) and \( L_h \) are the diffusion lengths for electron and holes; details can be found in [126, 3].

Evidently, the current in the p-n junction is dominated by the minority carriers. This fact will be fundamental for understanding the role of the recombination process in the solar cells efficiency.

The total current \( J = J_n + J_p \) is:

\[ J = J_o \left( \exp \left[ e \frac{V_a}{k_b T} \right] - 1 \right) \] (2.23)

which is the Shockley equation for an ideal diode.

In consequence, the saturation current \( J_o \) yields:

\[ J_o = J_n + J_p = \frac{eD_n n_{po}}{L_e} + \frac{eD_h p_{no}}{L_h} \] (2.24)

In this equation all the quantities \( D_e, D_h, p_{no}, n_{po}, L_h \) and \( L_e \) depend on temperature.

This model qualitatively describes the p-n junction under biasing. Nevertheless, it cannot describe quantitatively Si p-n junctions. They do not include surface effects due to charge trapped in ionized defects, which creates surface currents producing recombination of charge; this can have a density as large as the density of surface atoms (approx \( 10^{15} \) atoms/cm\(^2\)). In general, the procedure to neutralise the surface is called passivation and can be made by means of annealing with hydrogen [112]. Also in this model, tunnelling of carriers between states in the band gap is not considered. These effects will be studied in more detail in Section 2.5.

### 2.4 Potential under illumination

Once the photon is absorbed, an electron-hole pair is created, the charges are separated and transported outside of the DR into the QNR towards the contacts (Figure 2.8). The transport of charge in the DR and QNR regions obeys different physical processes; in the DR it is controlled mainly by drift and in the QNR by diffusion.

The minority charge concentrations are important for the efficiency of the solar cell. These charges determine the charge transport in the solar cell. If the minority charges recombine
before they can be transported through the p-n junction, the total number of charges collected effectively is reduced, and so is the efficiency.

Under illumination conditions the generation rate $G > 0$ contributes with additional mobile carriers, and hence the Fermi energy levels of minority electrons and holes are shifted. As a consequence, quasi-Fermi levels for electrons $E_{fe}$ and for holes $E_{fh}$ are created. The distance between these levels through the p-n junction, represents the open circuit voltage $V_{OC}$ generated by the solar cell (Figure 2.8).

The current generated reads:

$$J_{ph} = \int_{0}^{L} e \cdot G(x) dx$$  \hspace{1cm} (2.25)

In this equation $L$ corresponds to the thickness of the solar cell.

In case of biasing and illumination, in low injection conditions, one finds the superposition of the dark current and the illumination induced current: [109]:

$$J = J_o - J_{ph}$$  \hspace{1cm} (2.26)

Then:

$$J = J_o \left( \exp \left[ \frac{eV_a}{k_bT} \right] - 1 \right) - J_{ph}$$  \hspace{1cm} (2.27)

The $V_{OC} = V_a$ voltage occurs for $J = 0$, in consequence:

$$V_{OC} = \frac{k_bT}{e} \ln \left( \frac{J_{ph}}{J_o} \right)$$  \hspace{1cm} (2.28)
2.5 Efficiency of solar cells

The efficiency is the ratio between the power given by the device and the power received. It is a factor between 0 and 1 usually given as a percentage. In case of solar cells the efficiency is given by the relation between the maximum output power and the power at standard illumination Air Mass 1.5 Equivalent Sun\(^6\).

To measure the solar cell performance, the dark and illuminated J-V curves are studied (Figure 2.9).

![Diagram of J-V curves](image)

Figure 2.9: J-V curves showing the most important parameters determining the solar cells efficiency, \(V_{oc}\) open circuit voltage, \(J_{sc}\) short-circuit current density, \(V_{mp}\) maximum power voltage and \(J_{mp}\) current density at maximum power [109].

Important parameters of the illuminated J-V curve are the open circuit voltage, the short circuit current density, the maximum power voltage and the current density at this maximum power. The efficiency reads:

\[
\eta = \frac{P_m}{P_o} = \frac{V_{mp} J_{mp}}{P_o}
\]  

(2.29)

Unfortunately, a single p-n junction solar cell is not an ideal device. A theoretical calculus of the efficiency in such a device by Shockley & Queisser in 1961 [114] reveals the maximum efficiency in a single p-n junction solar cell. In this calculation the main factors considered are sun temperature, solar cell temperature, band gap, conversion rate of electron-hole pairs, geometry and transmittance. With these factors the efficiency is below 40%. This limit, known as the Shockley-Queisser limit, imposes a severe problem to photovoltaic energy. In the case of c-Si solar cells these low efficiencies make it necessary to use larger areas that unfortunately yields cost increases. Additionally, this limit indicates that a solar cell constructed with a unique p-n junction will have this as ultimate efficiency. The

Shockley-Queisser limit does not consider effects of light reflection on the surfaces and losses by recombination, which, in the case of Silicon solar cells, count with an additional 35% to the reduction of the efficiency.

For reducing the losses by reflection at the surface special treatments are made. For example, by etching of the surface, the reflectivity is reduced from 35% to 20% \[4\]. Moreover with the addition of anti-reflecting coatings, the reflection reduces to a few percent. Along with the effect of reflections in the surface, the recombination of the minority carriers plays a fundamental role in the solar cell efficiency. The solar cell once illuminated, is perturbed from their equilibrium condition, therefore it tends to restore it. This is made by means of recombination processes. In the indirect band gap the dominating recombination process is the Shockley-Read-Hall (SRH) mediated by traps in the band gap \[115, 45\]; in low injection conditions the recombination rates are:

\[
R_n = \frac{n_n - n_{no}}{\tau_n} \quad R_p = \frac{n_p - n_{po}}{\tau_p}
\]

(2.30)

for electrons and holes, respectively.

In these equations, \(p_{no}\) and \(n_{po}\) are the minority equilibrium carrier concentrations and \(\tau_p\) and \(\tau_n\) are the minority carrier lifetimes, which are connected with the diffusion length \(L_n\), \(L_p\) by means of:

\[
\tau_n = \frac{L_n^2}{D_n} \quad \tau_p = \frac{L_p^2}{D_p}
\]

(2.31)

If the recombination is increased in the material, the minority diffusion length is reduced. Consequently the minority carrier lifetime reduces as well. In result, the saturation current \(J_o\)

\[
J_o = qN_C N_V \left( \frac{1}{N_a} \sqrt{\frac{D_a}{\tau_e}} + \frac{1}{N_d} \sqrt{\frac{D_h}{\tau_h}} \right)
\]

(2.32)

increases with increase of recombination. Finally, the open circuit voltage \(V_{OC}\) is reduced.

Altogether, the equation describing the J-V curve can be written as:

\[
J = J_o \left( \exp \left[ \frac{e(V_a - IR_s)}{k_B T} \right] - 1 \right) - J_{ph} - \frac{V_a - IR_s}{R_{sh}}
\]

(2.33)

Figure 2.10 shows the circuit equivalent of the solar cell. The shunt resistance \(R_{sh}\) accounts for the effect of leakage of current by defects and the series resistance \(R_s\) for Ohmic loss at the surfaces.

In a solar cell, the recombination can cause an additional 25% of the efficiency reduction\[150\].

To overcome the limitations imposed by the Shockley-Queisser limit on the solar energy costs, two ways can be followed. The first is made by the so-called second generation solar
second way follows new concepts of solar cells, namely third generation solar cells.

Second generation solar cells include also some improvements, which attempt to go beyond the Shockley-Queisser limit. The use of Ga gradients changes the band gap making it possible to absorb a larger portion of the solar spectrum, and creates a larger depletion region, which increases the region where the electron-hole pairs are separated \[39\].

Third generation solar cells include the intermediate band solar cells \[95\], the multi exciton generation solar cells \[91\], and the hot carrier solar cells \[23\]. However, this issue is not directly related to the topic of this work and thus will not be further discussed.

### 2.6 Summary

This chapter shows the basics of the solar cells physics and in particular introduces the more basic equations. The effect of biasing in dark and illumination with light is also included. This physical concepts are fundamental for the understanding of the method of characterization described in Chapter 4 and for the explanation of the results.

In the chapter is also shown that the recombination processes play an important role in the efficiency and therefore their full characterization is necessary. In general, localized recombination processes produce a local variation of potential, therefore by measurement of the solar cell potential this effect must be visible. However, due to the reduction of the size of the solar cell and their preparation for TEM, it is expected that the recombination produces a reduction of the open circuit potential.
Chapter 3

Potential measurement by electron holography

3.1 Introduction

Transmission electron microscopes use fast electrons, which are scattered by potential distributions of thin objects, in order to deliver atomically resolved intensity distributions. As a consequence, in the image plane only the amplitude is acquired, whereas the phase of the electron wave is lost. Thus, potentials, which are phase objects, are almost invisible in normal TEM. The solution is to use a method allowing the measurement of the complete phase distribution of the electron wave, i.e. electron holography [33].

In modern microscopes, which are equipped with coherent electron emission guns like Schottky or Field Emission Guns (FEG), the electron beam produced is sufficiently coherent to create measurable electron interference patterns of the electron wave. That allows the realisation of Gabor’s idea [32] for the reconstruction of wave fronts. Moreover, thanks to the invention of the electrostatic biprism [85], off-axis electron holography was developed. With this invention, new insights into material properties have come to the fore, because a substantial part of the electron-object interaction modulating the phase of the electron wave, lost in normal microscopy, has become accessible. Since the birth of electron holography, this aspect has been used to measure potentials e.g. mean inner potential ($V_{MIP}$) [86, 49, 34, 67] of materials [137] or functional potential like that generated by p-n junctions [29, 28, 102].

Because electron holography offers this unique possibility for potential distribution imaging at nanometre scale, the holographically reconstructed wave in terms of amplitude and phase can play an important role for the solar cells characterisation.

Besides the phase, the amplitude $A_e(x, y)$ of the electron wave is of principle importance, because it is required for the determination of local object thickness $t(x, y)$, through which the electron wave passes, according to the following relation:

$$t(x, y) \propto -\ln A_e(x, y) \quad (3.1)$$
At the same time, knowing $t(x, y)$ makes it possible to determine the potential distribution $V(x, y)$ averaged along $z$, because it is related with the electron wave phase by means of:

$$
\varphi(x, y) \propto V(x, y) \cdot t(x, y)
$$

(3.2)

In this relation, the potential is assumed to be constant along the beam direction.

Therefore, the information of potential distribution coming from the built-in field in the solar cell can be recovered only from a correct measurement of phase and amplitude.

Measurement of amplitude and phase is affected not only by the electron microscope or by the object characteristics, but also by the experimental procedure employed (image acquisition time, field of view, adjustment of the microscope, etc.). For specific object orientation with respect to the electron beam, diffraction effects modulate amplitude and phase of the electron wave in a very complicated way depending on both thickness and orientation, making the interpretation of findings difficult. Therefore to obtain interpretable results, it is vital to have a full understanding of the experimental conditions in order to control or to avoid the mentioned effects.

Thus, in this chapter the electron-object interaction is described along with the electron holographical method. In addition, a discussion of the main factors affecting the measurement of the amplitude and phase is presented. Finally, an argumentation about the accuracy of the measurement of electrostatic potentials is introduced.

All aspects are fundamental for the unequivocal and quantitative interpretation of phase and amplitude in terms of the potential in solar cells.

### 3.2 Propagation of the electron wave through the object

The elastic electron-object interaction is determined by means of the object electrostatic potential. From the perspective of energy conservation, the electrons interact by means of two processes: elastic and inelastic scattering. The total energy of the electrons is conserved if they interact elastically. At inelastic interaction a certain amount of energy is transferred from the electron to the object. The inelastic interaction is characterised by the change of internal degree of freedom in the object e.g. through intra- and inter-band transitions or excitation of plasmons, phonons, secondary electrons, and others[103, p. 157].

The equation describing the elastic interaction of the electrons with the object is the relativistically corrected Schrödinger equation also known as the approximated Klein-Gordon equation, which includes all relevant features for elastic scattering in conventional TEM [79]:

$$
\left[ \frac{\hat{\mathbf{p}}^2}{2\gamma m_o} + V \right] \psi = E^* \psi.
$$

(3.3)
3.3. THE PHASE PROBLEM IN TEM

In this equation, \( \hat{P} \) is the momentum operator, \( \psi \) is the electron wave, \( V \) corresponds to the electrostatic potential of the object, \( \gamma = 1/\sqrt{1 - v^2/c^2} \) is the Lorentz factor, \( c \) is the speed of light in vacuum, \( v \) is the speed of the electrons, \( E^* = (E^2 - m_e^2c^4)/2\gamma m_e c^2 \) is the normalised reduced total energy of the electron, \( m_e \) and \( m_o \) are the electron masses relativistic and in rest, respectively\(^1\) (values for \( c, v_e \) and \( m_o \) are given in Appendix A).

The electron wave can be calculated from the Schrödinger equation by using several procedures namely the Bloch wave formalism or the multi-slice algorithm \(^55\). Solving both is strongly dependent on computing time and requires periodic objects or small volumes. As a consequence, the use of both is restricted mainly to high resolution electron microscopy. The simulation of large structures like p-n junctions would be a huge task. Moreover, it is not necessary, because a more simple procedure, which gives very good results, can be used.

This method consists of solving the Schrödinger equation in the Wentzel-Kramers-Brillouin (WKB) approximation. Details about the approximation and procedure of solving the semi-classic equations are found elsewhere \(^25, 147\).

As result for \( E \gg V \), it is obtained:

\[
\psi_e(x, y) \approx \psi_o \exp \left[ i \sigma \left( \int_{z_0}^{z} V(x, y, z') \, dz' \right) \right] = \psi_o \exp [i \varphi] \tag{3.4}
\]

This approximation is also called the Phase Grating Approximation\(^2\).

In this equation \( \sigma = 2\pi \cdot m_e \cdot e \cdot \lambda_e / h^2 \) corresponds to an interaction constant. \( \lambda_e \) is the relativistic corrected electron wavelength \(^3\), \( h \) the Planck constant and \( e \) the elemental electron charge. The value of this constant is \( \sigma = 0.00729 \, / \text{nm} \) for electrons accelerated to \( 200 \, \text{keV} \).

The model introduced here can be applied only to very thin samples (<20 nm) or weak scattering potentials, for example light materials \(^122, \text{P61}\). The model also requires, as previously mentioned, that the electrons interact elastically with the scattering potential, i.e. no energy loss.

However, the inelastic interaction can be incorporated, a-posteriori, by means of the Beer-Lambert-Bougert law in a phenomenological manner \(^43\). This topic is discussed in Section 3.4.4.

3.3 The phase problem in TEM

A modern Transmission Electron Microscope consists of an electron source, electromagnetic lenses, deflectors, stigmators, apertures and an image recording system.

\(^1\)The relativistically corrected electron mass is: \( m_e = \frac{E_o + E}{E_o} m_e \), where \( E_o = m_e c^2 \) and \( E = eU \) with \( U \) the electron acceleration voltage in the microscope; in the case of Triebenberg’s microscopes \( U=200 \, \text{kV} \).

\(^2\)Because all of the analysed samples in this thesis are non-magnetic, magnetic effects are not involved in the equations. If the reader is interested, more information can be found \(^74\).

\(^3\)\( \lambda_e = h \cdot c \cdot (2E \cdot E_o + E^2)^{-1/2} \)
There are different kinds of electron sources. However, for holography the key factors is spatial coherence, that is brightness, which is optimal in Schottky or Field Emission Guns (FEG). After the source, the emitted electrons are accelerated to an energy of 200 keV. In the microscope there is a series of magnetic lenses, deflectors and correctors, which are used to focus, deviate and correct the path of the electrons in the column. The lenses in the electron microscopes used in this work are arranged to form the following optical system: gun lens, condenser lens, objective lens, diffraction and intermediate lens and projection lens (see Figure 3.1). Finally, a CCD camera is used to record the image.

![Figure 3.1: Scheme of a transmission electron microscope in bright field mode. On the right the electron path through the different lenses is depicted. The angles are strongly exaggerated.](image)

The imaging process in TEM can be described according to Abbe's theory. In accordance with this imaging theory, the transfer of the object exit wave into the back focal plane is described by a Fourier transformation (Figure 3.2).
An image will have infinite resolution if all the spectral frequencies of the object contribute to the image formation. However, this is not possible because of the finite size of the objective lens, the presence of apertures in the diffraction plane and lens aberrations.

In the case of the objective lens, the imperfections of the magnetic lenses introduce optical aberrations. These are independent of the properties of the object and modulate the electron wave in Fourier space by the wave transfer function (WTF).

Therefore, the image wave reads as:

\[
\psi_{\text{im}}(\mathbf{r}) = \text{FT}^{-1} [\text{WTF}(\mathbf{q}) \ \text{FT}(\psi_{\text{obj}}(\mathbf{r}))],
\]

In this equation \(\psi_{\text{im}}\) and \(\psi_{\text{obj}}\) are the electron waves at image plane and object plane, respectively. \(\mathbf{q}\) denotes a 2D-vector in the reciprocal space \((q_x, q_y)\), \(\mathbf{r}\) is a 2D-vector in real space, and \(\text{FT}\) and \(\text{FT}^{-1}\) indicate the Fourier transformation and its inverse, respectively (Figure 3.2).

In general the wave transfer function is written as:

\[
WTF(\mathbf{q}) = \exp[-i \chi(\mathbf{q})] = \cos(\chi(\mathbf{q})) - i \cdot \sin(\chi(\mathbf{q})),
\]

where \(WTF(\mathbf{q})\) incorporates the coherent aberrations of the objective lens. The wave aberration function \(\chi(\mathbf{q})\) is a polynomial series of the aberration coefficients [135, 44, 77]. The transfer of the amplitude and phase of the electron wave is given by the functions \(\text{ACTF} = \cos(\chi(\mathbf{q}))\) and \(\text{PCTF} = \sin(\chi(\mathbf{q}))\) respectively. ACTF transfers object amplitude and phase information into image amplitude and image phase directly, and PCTF transfers object phase into image amplitude and vice-versa in dependence on the frequency and lens aberrations. Figure 3.4 shows this transference process.
In the case of only defocus $D_z$ and spherical aberration $C_s$, $\chi(q)$ reads:

$$\chi(q) = 2\pi k \left[ \frac{1}{4} C_s \left( \frac{q}{k} \right)^4 + \frac{1}{2} D_z \left( \frac{q}{k} \right)^2 \right]$$

(3.7)

where $k = 1/\lambda_e$.

The aberrations lead to a spatial frequency interdependence, intermixing amplitude and phase from the object plane into the image plane in a very complex manner.

In TEM, certain focus values can be defined, which make it possible to adjust this intermixing between phase and amplitude for a certain frequency range. A defocus, where this information transfer is optimised for phase contrast, is the so called Scherzer defocus $D_z^{\text{Scherzer}}$ [55, p. 23], which is defined by the expression:

$$D_z^{\text{Scherzer}} = -\sqrt{\frac{3 C_s}{2 k}}$$

(3.8)

Figure 3.3 depicts ACTF and PCTF for Scherzer defocus.

![Figure 3.3: Amplitude and phase transfer functions from the Phillips CM200 microscope operated in Lorentz mode in Scherzer focus $D_z = -5505$ nm, for electrons accelerated to 200 keV. The coefficient of spherical aberration is $C_s = 8000$ mm and convergence angle $\theta_c = 1$ mrad. The PCTF shows optimum phase contrast.](image)

Consequently, a highly doped p-n junction with a 100 nm wide depletion region imaged in Scherzer defocus of the Lorentz lens at Philips CM200 does not exhibit spatial phase
3.4. OFF-AXIS ELECTRON HOLOGRAPHY

variations above a length scale of 50nm (q=0.02 1/nm), i.e. such large area phase modulations are suppressed by transfer properties of the electron microscope 4.

Low frequencies corresponding to information produced by p-n junctions are not transferred into the amplitude image, Figure 3.4. And therefore in normal TEM this information is lost.

Figure 3.4: Transfer of amplitude and phase from the object to the detector. Because of the fact that the detector only measures the intensity, phase information is only partially transferred to the image depending on the properties of the PCTF. The complete phase acquisition is not possible in that way.

To solve this problem, a method allowing the measurement of the complete wave, that is amplitude and phase, must be applied. A method offering this possibility is off-axis electron holography.

3.4 Off-axis electron holography

3.4.1 Biprism

An interference pattern arises if electron waves are superimposed coherently at the image plane. This can be easily achieved in a TEM by means of a Möllenstedt biprism [85]. In Figure 3.5 the electron path created in the microscope by the biprism is depicted.

4The mixing of the phase and amplitude in a transfer system is given by the PCTF and ACTF. If the chromatic and spatial coherence of the electron source are considered, the resolution will be damped additionally by the so called envelope functions. Details regarding this are found in several theses and articles e.g. [44, 135, 77]
Fig. 3.5: Basic scheme of off-axis electron holography.

The biprism mounted above the first image plane close to the selected area diffraction aperture (see Fig. 3.1) superimposes two coherent partial waves, the reference wave $\psi_{\text{ref}}$ and the object wave $\psi_{\text{obj}}$, under a certain angle $\beta$ in the image plane, Fig. 3.6.

Off-axis holograms are characterised by two parameters [68]: fringe spacing $s = 1/|q_c|$ and hologram width $w_{\text{hol}}$, which are defined by the geometric position of the biprism in the path of rays in the transmission electron microscope. The geometry is illustrated in Fig. 3.6 in more detail.

The parameters $+q_c/2$ and $-q_c/2$ denote the position of the two virtual sources in the back focal plane corresponding to the tilt of the partial waves produced by the biprism. They are related to the superposition angle $\beta$ of the waves by:

$$q_c = k \cdot \beta$$  \hspace{1cm} (3.9)

With magnification of the objective lens:

$$M = \frac{a + b}{f}$$  \hspace{1cm} (3.10)
the fringe spacing related to the object plane is given by:

\[ s_{hol} = \frac{s}{M} = \frac{a + b}{2a \gamma_o U_f M} \]  

(3.11)

and the hologram width is:

\[ w_{hol} = \frac{w}{M} = \frac{2b \gamma_o U_f}{M} - 2r_f \frac{a + b}{a M} \]  

(3.12)

In these two equations \( \gamma_o \) is a constant of proportionality between the voltage and deflection angle \( \gamma \) of the electrons by the biprism, \( r_f \) radius of the biprism filament and \( U_f \) the biprism filament voltage.

For given lens excitations and acceleration voltage of the electrons, the parameters \( a, b, \) and \( \gamma_o \) are fixed; the first two are determined by the position of the biprism with respect to the back focal plane and the image plane, respectively [68], and the third one is a geometric parameter of the biprism dependent on its radius \( r_f \), the distance to the external grounded electrode \( r_2 \), and the acceleration voltage of the electrons [84]. The deflection angle \( \gamma \) is:
CHAPTER 3. POTENTIAL MEASUREMENT BY ELECTRON HOLOGRAPHY

\[
\gamma = \gamma_0 U_f = \pi \frac{U_f}{2 U_e \log(r_f/r_2)}
\]  

(3.13)

with \(U_e\) the acceleration voltage of the electrons in the electron microscope.

\[\begin{align*}
\psi_{\text{obj}} &= A_{\text{obj}} \exp \left[ i (2\pi \mathbf{q}_e \cdot \mathbf{r} / 2 - \varphi_{\text{obj}}) \right], \\
\psi_{\text{ref}} &= A_{\text{ref}} \exp \left[ -i (2\pi \mathbf{q}_e \cdot \mathbf{r} / 2 + \varphi_{\text{ref}}) \right];
\end{align*}\]

(3.14)

Figure 3.7: Effect of the Möllenstedt biprism on the electron path. Between the two images only the biprism voltage is changed. The left image shows electron paths produced with smaller biprism voltage than the case of the right image. With larger voltage the superposition angle \(\beta\) is increased. Therefore, fringe spacing decreases and hologram width increases.

3.4.2 Interference

In order to gain a better understanding, in this section a perfect microscope and a perfect sample are considered. The effects of lens aberrations, inelastic interactions, coherence of the electron source and MTF of camera are included later in Section 3.4.4 of this chapter.

The interfering waves, deflected by the electron biprism are:

\[\psi = \psi_{\text{obj}} + \psi_{\text{ref}}\]

(3.15)

The intensity, measurable by a detector follows as:
3.4. OFF-AXIS ELECTRON HOLOGRAPHY

\[ I = \psi \psi^* = (\psi_{\text{ref}} + \psi_{\text{obj}})(\psi_{\text{ref}} + \psi_{\text{obj}})^* = A_{\text{ref}}^2 + A_{\text{obj}}^2 + 2A_{\text{obj}}A_{\text{ref}} \cos(2\pi q_c \cdot r + \Delta \varphi) \]  

(3.16)

with \( \Delta \varphi = \varphi_{\text{ref}} - \varphi_{\text{obj}} \) and \( q_c \) the carrier frequency of the wave.

If the equation of the interference is rearranged to consider the contrast \( C = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \), the hologram intensity can be rewritten as:

\[ I = (A_{\text{ref}}^2 + A_{\text{obj}}^2) [1 + \text{C}_\text{amp} \cdot \cos(2\pi q_c \cdot r + \Delta \varphi)] \]  

(3.17)

with

\[ \text{C}_\text{amp} = \frac{2A_{\text{obj}}A_{\text{ref}}}{A_{\text{obj}}^2 + A_{\text{ref}}^2} \]  

(3.18)

\( \text{C}_\text{amp} = 1 \) if the amplitude of the object wave is equal to that of the reference wave; it is given only without object.

A real hologram presents several additional contributions affecting the contrast, which are considered in the subsequent sections of this chapter.

### 3.4.3 Reconstruction of the object wave from the hologram

The process of hologram reconstruction by using the Fourier method developed by Wahl [138] is applied. The Wahl method uses the Fourier transformation of the recorded hologram given by Equation 3.30:

\[
\begin{align*}
FT(I) &= FT \left[ A_{\text{ref}}^2 + A_{\text{obj}}^2 \right] \\
&+ FT \left[ (A_{\text{ref}}^2 + A_{\text{obj}}^2) \cdot \text{C}_\text{amp} e^{i(\Delta \varphi)} \right] \otimes \delta(q - q_c) \quad \text{side band +1} \\
&+ FT \left[ (A_{\text{ref}}^2 + A_{\text{obj}}^2) \cdot \text{C}_\text{amp} e^{-i(\Delta \varphi)} \right] \otimes \delta(q + q_c) \quad \text{side band -1}
\end{align*}
\]  

(3.19)

The Fourier transformation produces three bands (regions). One of these is in the centre and is called the centre band; this band corresponds to the conventionally measured image in TEM in the spatial frequency domain. Two lateral bands (also called side bands) carry the information of the wave which is to be reconstructed. These two bands consist of exactly the same information, but one is the complex conjugate of the other.

The wave is recovered by centring the Fourier spectrum in the side band corresponding to the positive phase and masking it \((-q_c \text{ in this case})\). Following this, one finds by the inverse Fourier transformation:

\[ \Psi_{\text{obj}} = FT^{-1} \left[ FT \left[ (A_{\text{ref}}^2 + A_{\text{obj}}^2) \cdot \text{C}_\text{amp} e^{i(\Delta \varphi)} \right] \right] = 2A_{\text{obj}}A_{\text{ref}} e^{i(\Delta \varphi)} \]  

(3.20)
CHAPTER 3. POTENTIAL MEASUREMENT BY ELECTRON HOLOGRAPHY

Figure 3.8: Hologram (left) of an object and its Fourier transformation (centre) showing the centre and side bands.

The result is a complex image with information of the original wave multiplied with contrast coefficients and an additional phase shift coming from asymmetric spatial coherence of the electron source.

Figure 3.9: Images of amplitude and phase reconstructed from the hologram shown in Figure 3.8. Some of the artefacts induced are indicated in the image. These artefacts are studied in the next section.

3.4.4 Problems and artefacts

Off-Axis electron holography provides a rather direct access to amplitude and phase of the image wave. However, the measurement of potentials at microscopic level is influenced by some artefacts. In electron holography the strength of the method is at the same time its weakness. It is the sensibility to electric and magnetic fields.

In transmission electron microscopes there are several sources of electromagnetic fields, additional to that in the sample. Understanding of how these fields affect the measurement, is paramount for quantitative determination of potentials, for the interpretation of the results, and for establishment of the accuracy. Moreover, their comprehension establishes a milestone for the experiments.

The goal of this thesis is not to research such parameters as they have been studied exhaustively for several years in the Triebenberg group. Several articles and theses have been published [72, 147, 148]. Here, only a description of these factors is presented.
3.4. OFF-AXIS ELECTRON HOLOGRAPHY

All elements in the microscope and post image processing affect the interpretation of phase in terms of potential. A detailed list of the main elements influencing and introducing artefacts to the off-axis electron holography technique is shown in Figure 3.10.

Figure 3.10: Main artefacts in off-axis electron holography [72, 78]. A full comprehension of how these parameter affect the measurement is required for the interpretation of the electron wave in terms of potentials.

In the following, the influence of the above introduced sources of artefacts on fringe contrast is discussed in more detail.

Influence on fringe contrast

Factor $C$ in Equation 3.17 contains all of elements which affect the fringe contrast in the hologram acquired. These elements can be summarised in: degree of coherence of the source $\mu$, instabilities $C_{\text{inst}}$, MTF of the camera $C_{\text{MTF}}$ and inelastic processes in the object $C_{\text{in}}$ [74].

As a consequence, the contrast due to these factors is:

$$C \propto |\mu| C_{\text{inst}} C_{\text{MTF}} C_{\text{in}} C_{\text{amp}} \quad (3.21)$$

The effect of the amplitude previously discussed is incorporated in $C_{\text{amp}}$.

The degree of coherence $\mu$ between the waves determines the contrast. Usually $|\mu| < 1$ because the electron source is neither a point source nor is it strictly monochromatic. Instead, the electron source is an extended incoherent and quasi monochromatic source. Therefore, according to the Van Cittert-Zernike theorem the contrast is reduced by $|\mu|$, which corresponds to the normalised Fourier transform of the intensity distribution function of the source [12, p. 510]. Consequently there is a reduction in contrast when fringe spacing of the interference pattern is reduced due to an increase of superposition angle $\beta$ with increasing of biprism filament voltage under fixed parameters $a$, $b$ and magnification.
This is because the superposition distance between object and interference waves is increased and hence the spread of illumination angles generates stronger phase variations with the result of fringe contrast decay. Moreover, the illumination aperture can be decreased by spreading the beam further at the expense of intensity. A way to increase the current density for a certain contrast is given by means of elliptical illumination. Additionally, if the source is not symmetric, a phase factor has to be introduced determining finally the complex degree of coherence $\mu = |\mu| \exp(i\rho)$

Factor $C_{\text{inst}}$ includes all mechanical or electrical instabilities, namely instabilities of the biprism, thermal variations, air vibrations around the microscope, acoustic noise, variation of the lenses currents, magnetic fluxes and building instabilities. Many of these are minimized or suppressed by the special construction of the Triebenberg laboratory. Others such as the biprism instabilities are reduced by orienting the wire perpendicularly to the axis of the biprism holder. A way to determine their contribution is acquiring holograms with large recording time ($\sim 10$ s). If instabilities are not present, no reduction of the contrast is detectable.

In our laboratory Gatan slow-scan CCD cameras are used. These cameras detect electrons by means of a scintillator, which transforms the electrons into photons; this conversion prevents CCD detectors from being damaged by the high energetic electrons. These photons are conducted into the CCD chip by means of an optical fibre array. The spread in position of electron depends on scintillator thickness: electrons arriving at the scintillator create cascades of photons in a quasi-conical shape. The larger the scintillator thickness the larger is the spreading of the photons created. This is the reason for the Modulation Transfer Function of the camera (MTF). The main effect of the MTF on electron holography is the blurring of fringes by the convolution with the Fourier transform of the MFT. The effect leads to a limited transfer of certain spatial frequencies and therefore to reduction of the resolution. This effect is the main factor in the hologram contrast decreasing [79, p. 27], which is considered by the factor $C_{\text{MTF}}$. The electron waves interact with the sample elastically or inelastically. Only those, which are coherently emitted from the source and elastically scattered contribute to the fringe modulation of hologram. The inelastically scattered waves are mainly incoherent with respect to the reference wave [22] and hence do not modulate the phasing of the fringe pattern. The intensity of the object wave, after passing through the sample, hold the contributions of inelastic $(A_{\text{obj}}^{\text{inel}})^2$, and elastic $(A_{\text{obj}}^{\text{el}})^2$ electrons. The sum of these contributions is the total intensity $(A_{\text{tot}})^2$ arriving to the image plane, in consequence:

$$A_{\text{tot}}^2 = (A_{\text{obj}}^{\text{inel}})^2 + (A_{\text{obj}}^{\text{el}})^2$$  \hspace{1cm} (3.22)

and the coherent part contribution is:

$$A_{\text{coh}} = \sqrt{(A_{\text{obj}}^{\text{el}})^2}$$  \hspace{1cm} (3.23)

McCartney and Gajdardziska-Josifovska [81] study the role of the inelastic interaction on the hologram contrast. Similar to EELS, the total intensity can be expressed as:
3.4. OFF-AXIS ELECTRON HOLOGRAPHY

\[(A_{\text{inel}}^2) = A_{\text{tot}}^2 (1 - e^{-t/\lambda_{\text{inel}}}) \]  
\((3.24)\)

where \(\lambda_{\text{inel}}\) is the so-called inelastic-mean-free path of the electrons in the material and \(t\) the sample thickness. Then, the relationship between electrons that have suffered inelastic losses in the object and the total incident intensity is expressed as:

\[A_{\text{tot}}^2 e^{-t/\lambda_{\text{inel}}} = (A_{\text{obj}}^{\text{el}})^2.\]  
\((3.25)\)

The term 3.23

\[(A_{\text{obj}})^2 = (A_{\text{obj}}^{\text{el}})^2\]  
\((3.26)\)

corresponds to the amplitude of the wave measured by electron holography. Mostly, the total illumination on the sample is equal to that in the reference wave, then:

\[A_{\text{tot}} = A_{\text{ref}}\]  
\((3.27)\)

Finally, the reduction of the contrast due to inelastic interaction in the object \(C_{\text{inel}}\) can be written as:

\[C_{\text{inel}} = e^{-t/2\lambda_{\text{inel}}} = \frac{A_{\text{obj}}}{A_{\text{ref}}}\]  
\((3.28)\)

In general \(\lambda_{\text{inel}}\) is a material-specific property, but similarly to EELS, it has an angular dependence \(\lambda(\theta)_{\text{inel}}\). Therefore, their measuring is affected depending on the collection angle used in the electron microscope. In this situation, a certain amount of the elastic and inelastic intensities is scattered outside of this angle, and hence \(A_{\text{tot}} \neq A_{\text{ref}}\) i.e. the detected mean free path for the fraction of detected signal changes. The collection angle is determined by the diameter of the object aperture applied. In this thesis, the inelastically scattered contributions to high scattering angles (>10 mrad) are assumed small for the dominating energy loss.

The factor reducing the contrast by inelastic interaction is used to determine the thickness. As requirement, the sample must be in kinematic condition, the material must be homogeneous in the direction of the electron wave propagation \((z)\), and the mean free path \(\lambda_n\) of the sample must be known. The thickness is determined from the amplitude of the wave by means of:

\[t = -2\lambda_{\text{inel}} \ln \left( \frac{A_{\text{obj}}}{A_{\text{ref}}} \right) = -2\lambda_{\text{inel}} \ln (A_n)\]  
\((3.29)\)

where \(A_n\) corresponds to the normalised amplitude. Finally, the equation describing the hologram results:

\[I = (A_{\text{ref}}^2 + A_{\text{obj}}^2) \left[ 1 + |\mu| C_{\text{inst}} C_{\text{MTF}} C_{\text{inel}} \cdot \frac{2A_{\text{ref}}^2}{A_{\text{ref}}^2 + A_{\text{obj}}^2} \cos(2\pi q_e \cdot r + \Delta\phi + \rho) \right] \]  
\((3.30)\)
Artefacts

Some of the artefacts in the hologram like dead and hot pixels or Fresnel fringes are evident before the reconstruction 3.11. However, others are visible only after reconstruction, such as geometrical distortions and phase wrapping.

The detailed observation of recorded intensity distributions shows some defects of the camera pixels. Some of them are saturated and others inactive, which are known as hot and dead pixels, respectively. These pixels provoke huge 2D blurring function under the reconstruction process. Figure 3.11 shows some of these pixels before reconstruction.

Figure 3.11: Fresnel fringes as well as hot and dead pixels in the recorded hologram, which produce artefacts in the reconstructed wave.

The second artefact considered here corresponds to Fresnel diffraction of the electron beam at the edges of the biprism. It appears as a defocused shadow of the biprism filament.

Geometrical distortions and phase wrapping are shown in Figure 3.9. Geometrical distortions of the image are caused by the optical fibre coupling; the fibres are packed in a hexagonal bundle creating a “chicken wire”, which is slightly distorted producing fringe bending and hence artificial phase modulations. A last artefact considered here is “phase wrapping”. The wave is recovered by inverse Fourier transformation, which delivers an array of complex numbers. The phase of this wave is calculated by means of the arctangent function. Consequently the phase is only represented between 0 and $2\pi$, producing the so called phase wrapping effect. For absolute measurement, the phase has to be unwrapped. In some circumstances, due to low resolution of the hologram fringes, several steps of $2\pi$ may be overlapped. As a consequence, it is not possible to determine correctly the phase in absolute values, and singularities in the phase can also appear.
3.4. OFF-AXIS ELECTRON HOLOGRAPHY

Reduction of artefacts and contrast problems

In Triebenberg laboratory, several software tools on Digital Micrograph™ have been developed. The algorithms allow correcting several of the artefacts, e.g. hot and dead pixels, Fresnel fringes of the biprism and MTF of the camera. These are corrected before reconstruction. Details of these procedures can be found in [148, 147, 60, 77].

The distortions of the optical fibre can be removed by the acquisition of a second hologram without object (empty hologram), and the later division of the raw object wave by the reconstructed empty wave.

This second hologram is reconstructed in a similar way yielding:

$$\psi_{emp} = 2|\mu| C_{MTF} C_{emp} \cdot A_{ref}^2 e^{-i(\varphi_{ref})}$$ (3.31)

These two reconstructed waves are divided.

$$\psi_{rec} = \frac{\psi_{obj}}{\psi_{emp}} = \frac{|\mu| C_{MTF} \cdot C_{MTF} \cdot A_{ref}^2 \cdot e^{-i(\Delta \varphi - \rho)}}{|\mu| C_{MTF} \cdot A_{ref}^2 \cdot e^{i(\varphi_{ref} - \rho)} \cdot C_{MTF} C_{MTF} C_{MTF} e^{-i\varphi_{obj}}}$$ (3.32)

In general, the MTF cannot be corrected in this way, because of the convolution with the wave.

Finally, the original wave, with a normalised amplitude $A_n = C_{inel}$ is reconstructed (Equation 3.28), giving the final complex image of the object $\psi_{rec}$. In Figure 3.12 amplitude and phase images recovered after applying the procedure explained are shown.

![Figure 3.12: Images of amplitude (left) and phase (right) reconstructed from the hologram shown in Figure 3.8.](image)

In this thesis the following reconstruction procedure is used: Removing of the Fresnel fringes and dead and hot pixels, Fourier transformation of the hologram, identification and centring of the correct side band, selection and application of the mask, and finally, application of the inverse Fourier transformation. With this procedure the wave is recovered. The
same procedure is also applied to the empty hologram. A flowchart of the reconstruction process is shown in Figure 3.13.

Figure 3.13: Flowchart of the reconstruction process of a hologram using an empty hologram. The original holograms (a,b), show the effect of Fresnel diffraction at the biprism. To correct it, a mask in Fourier space is applied (c,d). After the holograms are inversely Fourier transformed (e,f), there is a clear reduction of the Fresnel fringes. In these images the hot and dead pixels of the camera are reduced by replacing them with the mean value of the neighbours. After Fourier transformation, the side band is masked out (g), centred (h) and inversely Fourier transformed to obtain the complex wave in real space. The object wave is divided by the wave reconstructed from the empty hologram. Finally, the object wave is obtained as amplitude and phase images (i, j).

### 3.4.5 Additional parameters

The main figures of merit determining the applicability of a hologram are: field of view, lateral resolution and signal resolution.

Electron holography requires the superposition of object and reference waves to perform
interference. This reference wave is usually passing through vacuum regions\(^5\). That means that the observation region in the object must be close to the vacuum, limiting the available region of interest on the one hand. On the other hand, the holographic field of view cannot be chosen freely because of its dependency on fringe spacing (Equation 3.12), which has to be well sampled by finite CCD pixels. The number of pixels of the camera and the demands on fringe sampling creates a limitation, one fringe must be sampled by at least 4 pixels of the CCD chip (Figure 3.11)[65]. The cameras installed in Triebenberg have 1024x1024 pixels. This means that no more than 256 fringes of the interference pattern can be recorded and reconstructed. The correlation between the width of the hologram (Equation 3.12) and the separation of the fringes (Equation 3.11), means that magnification and size of the CCD chip of the camera limits the field of view and resolution related to the object, in which holograms can be acquired.

In our Philips CM200FEGST/LL, by using the standard objective lens, a field of view of 30nm is achieved. By using the Lorentz lens a larger field of view up to 800nm is easily achieved\(^6\). On the other hand, in our Tecnai F20 Cs-corrected TEM under standard operation conditions, it is only possible to acquire high-resolution holograms with a field of view close to 10nm. Recently, studies of the TEM optics have led to the development of a larger variety of fields of view by changing the excitation of the diffraction lens in our CM200, or by using the transfer lens of the Cs corrector like a Pseudo Lorentz Lens (PLL) in combination with different excitations of the diffraction lens. Through employing these new lens configurations, the set of magnifications described in Table 3.1 in our electron microscopes can be easily realised [117, 116].

<table>
<thead>
<tr>
<th>Microscope</th>
<th>Configuration</th>
<th>(W_{\text{hol}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM200</td>
<td>DIF 90</td>
<td>20</td>
</tr>
<tr>
<td>CM200</td>
<td>DIF 50</td>
<td>70</td>
</tr>
<tr>
<td>CM200</td>
<td>DIF 30</td>
<td>200</td>
</tr>
<tr>
<td>CM200</td>
<td>DIF 10</td>
<td>60</td>
</tr>
<tr>
<td>CM200</td>
<td>Lorentz</td>
<td>800</td>
</tr>
<tr>
<td>Tecnai</td>
<td>PLL 75</td>
<td>150</td>
</tr>
<tr>
<td>Tecnai</td>
<td>PLL 50</td>
<td>700</td>
</tr>
<tr>
<td>Tecnai</td>
<td>PLL 26</td>
<td>3000</td>
</tr>
<tr>
<td>Tecnai</td>
<td>DIF 80</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3.1: Lens settings for electron holography in our laboratory. The parameters DIF and PLL are explained in [116, 117]. The numbers in DIF 90 or PLL 75 correspond to the percentage of the total excitation of the diffraction lens.

The hologram acquisition and reconstruction has a strong influence on the final lateral resolution of the image. According to the last discussion, each hologram fringe is sampled by 4 pixels. Additionally, in the Fourier transform of the hologram, the radius of the

---

\(^5\)In some occasions, if the reference wave cannot be acquired in the vacuum, thin objects like carbon foils are used, a drawback of this procedure is the increase of noise in the reconstructed wave image.

\(^6\)The Lorentz lens is a type of objective lens originally designed for investigation of magnetic specimens [153].
CHAPTER 3. POTENTIAL MEASUREMENT BY ELECTRON HOLOGRAPHY

centre band must be two times the radius of the side band. Consequently, the maximum reconstructable frequency \( q_{\text{max}} \) in the side band must fulfil the condition \( 3q_{\text{max}}^{\text{st}} \leq q_c \). This relation is true for strongly diffracting objects. For pure phase objects the relation \( 2q_{\text{max}}^{\phi} \leq q_c \) is sufficient in most cases. These relations are depicted in Figure 3.14.

Figure 3.14: Diameter of the mask used for hologram reconstruction. For strong diffracting objects the diameter of the mask must be smaller to \( q_{\text{mask}}^{\text{st}} \leq q_c/3 \) (left side band), else if the object is a pure phase object, this diameter is \( q_{\text{mask}}^{\phi} \leq q_c/2 \) (right side band). The logarithmic line scan along the line b-b shows the diameter of both masks.

A consequence of these values is that the diameter of the mask used to reconstruct the object wave must meet:

\[
q_{\text{mask}}^{\text{st}} \leq \frac{q_c}{3} \tag{3.33}
\]

in strong diffracting objects, and:

\[
q_{\text{mask}}^{\phi} \leq \frac{q_c}{2} \tag{3.34}
\]

in pure phase objects. In the case of the objects studied here, this diameter is between those two extreme values.

A second factor limiting the lateral resolution is the information limit, which is determined by the incoherent lens aberrations. As an example the information limit of the Phillips CM200 Lorentz and the Tecnai F20 Cs-corrected is calculated in medium resolution. In the Phillips CM200 Lorentz, the usual configuration using the Lorentz lens has an extremely large spherical aberration, approx. 8 m compared to \( \sim 2 \text{ mm} \) of a usual objective lens. Smaller spherical aberration implies an improvement of the information limit. Figure 3.15 shows the corresponding amplitude and phase contrast transfer functions giving an information limit of 2 nm at Scherzer defocus. The other parameters are shown in that figure also.
3.4. OFF-AXIS ELECTRON HOLOGRAPHY

In the case of the Tecnai in PLL mode the spherical aberration is close to 8 mm. In this case the amplitude and phase contrast transfer function, shown in Figure 3.15, indicate an information limit of ∼0.6 nm, at Scherzer defocus.

![ACTF and PCTF graphs for CM200 and Tecnai F20 microscopes](image)

Figure 3.15: WTF of the CM200 and the Tecnai F20 microscopes. The CM 200 is operated in Lorentz mode in the Scherzer focus \( D_z = -5505 \text{ nm} \), for electrons accelerated to 200 keV. The aberration is spherical aberration \( C_s = 8000 \text{ mm} \), and convergence angle \( \theta_c = 1 \text{ mrad} \). The Tecnai F20 Cs-corrected microscope is operated in PLL mode also in Scherzer focus \( D_z = -194.644 \text{ nm} \), for electrons accelerated to of 200keV; spherical aberration \( C_s = 10 \text{ mm} \) and chromatic aberration \( C_c = 41 \text{ mm} \). In both calculations a convergence angle of \( \theta_c = 1 \text{ mrad} \) is used.

The resolution is finally given by the smaller value of the information limit and the diameter of mask used in the hologram reconstruction.

The mask for the reconstruction has a strong effect in real space, because of the convolution with its inverse Fourier transform, inducing a point-spread function with many side-lobes depending on the mask shape applied. In order to avoid this, the masks for the wave reconstruction must have soft edges, i.e. no abrupt ending. In the Triebenberg’s software four different masks can be applied: Butterworth, Fourier transformation of the Hanning window, \( \text{Sinc} \) and \( \text{Sinc}^2 \). In this thesis, the \( \text{Sinc} \) mask is used in the way that one of the roots corresponds to the position of the centre band, realising a separation of the side band due to removal of centre band.

Noise determines the minimal measurable potential differences and also indicates the experimental conditions for biasing or illumination, which are necessary to obtain significant
results. All of the elements in and around the microscope play a more or less fundamental role in restricting the detection limit, as already considered for the hologram fringe contrast. Moreover, the hologram measurement is a statistical process, where each electron contributes with a signal at a certain position at the detector. Therefore the shot noise also contributes to the detection limit. Extensive studies regarding the noise have been conducted by Lichte [71, 70, 69].

The contrast in Equation 3.17 is one of the determinant factors in the signal resolution and consequently also spatial resolution. An image with high spatial resolution also has contributions from high frequency noise. As a result, images with larger spatial resolution are also noisier.

Shot noise in amplitude and phase has been studied by Harscher and Lichte [46]. They show that amplitude and phase noise are affected by the contrast $C$ (Equation 3.17), and by the number $N_{rec}$ of electrons per reconstructed pixel [71]. According to Harscher the standard deviation of contrast is:

$$\sigma_C = \sqrt{\frac{2 - C^2}{N_{rec}}}$$

resulting in a standard deviation of phase:

$$\sigma_\varphi = \frac{1}{C} \sqrt{\frac{2}{N_{rec}}}$$

and of amplitude:

$$\sigma_A = \sqrt{2 N_{rec}}$$

Reducing the noise in the reconstructed wave means increasing the number of electrons in the image and/or increasing the contrast. To increase the number of electrons, two options can be employed: the first is to increase the electron beam flux at the expense of coherence, and the second is to extend the recording time. Large fluxes can damage the sample and also induce charging of the object, which produces electric fields around the sample. Extending the recording time, could blur the object image due to sample and biprism drift hence results in reduction of the contrast through thermal and mechanical instabilities.

Formánek [25] estimates the influence of the exposure time and drifting on contrasts. However these values are strongly dependent on the microscope and laboratory conditions and therefore cannot be applied to any laboratory. In the next chapter this important problem is again analysed in more detail.

### 3.4.6 Potential measurement

The electrostatic potential of the sample is produced by several sources in the object, namely potential from the atoms, local compositional variations due to diffusion and
segregation at interfaces, change of bonds and strain of the lattice, doping potentials, contact potentials, displacement of atoms at interfaces and defects, compensating charges and Schottky effect. Very undesirable are those produced by local charging of the object produced by the electron beam.

The contribution of the atoms in a solid including the bonding is called mean inner potential \( V_{MIP} \). The origin of this potential is the superposition of atomic potentials and local concentrations of charge in the material due to the bonding of the solid. The atomic potential can be approximated by Wentzel \([145, 57]\) as:

\[
V(r) = \frac{Z e^2}{4\pi \varepsilon_0 r} \exp[-br],
\]

(3.38)

\( Z \) is the atomic number, \( e \) the electron charge, \( \varepsilon_0 \) the dielectric constant in the vacuum, \( r \) distance from the nucleus, and the exponential describes the screening of the nucleus by the electrons. A complete list of atomic potentials has been compiled by Lubk from the parameters given by Weikenmeier & Kohl \([144]\) in a much more complicated parametrisation.

In case of a homogeneous crystalline structure, the mean inner potential is calculated as the average of the atomic potentials over the volume of the unit cell \( \Omega \). The value for silicon is roughly \( V_{MIP} = 12 \, \text{V} \).

It is important to note that the built-in potential of p-n junctions \( V_{pn} \approx 1 \, \text{V} \) is much weaker than that from the atomic potential contribution in silicon. The scattering on that part of the total potential can be treated as a perturbation within the Phase Object Approximation (POA). The sample must be sufficiently thick to increase the signal stemming from the built-in potential.

For the measurement of p-n junctions or other functional potentials, samples with a thickness between 200nm to 400nm must be used. An increase in thickness increases the phase shift, but, alas, also the inelastic scattering, and also alters the effect of dynamic scattering processes in a non-linear manner. Consequently, the object must be oriented with respect to the electron beam in such a way that signals coming from dynamic scattering conditions are eliminated \([26]\). This aspect will be studied in detail in Section 4.2 of the next chapter.

A simple way to calculate the potential is to assume that the potentials is homogeneous in beam direction (z coordinate). In this case the Equation 3.32 with the phase 3.4:

\[
\Psi_{rec} = C_{inel} \exp \left[ i \sigma \left( \int_{z_0}^{z} V(x, y, z') \, dz' \right) \right]
\]

(3.39)

can be written as:

\[
\Psi_{rec} = C_{inel} \exp \left[ i \sigma V(x, y) \, t(x, y) \right],
\]

(3.40)

i.e. the potential projection can be simplified to a product:
\[ \varphi(x, y) = \sigma \cdot \bar{V}(x, y) \cdot t(x, y) \] (3.41)

Inserting thickness \( t \) from (3.29) one obtains for the object potential average \( \bar{V}(x, y) \)
along \( z \)-direction:

\[ \bar{V}(x, y) = -\frac{\varphi(x, y)}{\sigma \cdot 2 \cdot \lambda_{\text{inel}} \cdot \ln (A_n(x, y))} \] (3.42)

### 3.5 Summary

In this chapter the interaction between the electron wave and the object has been described,
showing that the electrons change their phase by interaction with the electromagnetic
potential in the object. As a simplified approximation, the Phase Grating Approximation
has been introduced. Under this approximation the electron wave propagating through
the sample experiences a phase shift by means of the projection of the potential in the
direction to the electron path.

\[ \Psi_{\text{rec}}(x, y) = A_n^{\text{el}} \exp \left[ i \sigma \left( \int_{z_0}^{z} V(x, y, z') \, dz' \right) \right] = A_n^{\text{el}} \exp [i \varphi] \] (3.43)

To fulfill this approximation, the object must not be oriented with respect to the electron
beam in dynamic conditions because then amplitude and phase differ considerably from
POA and hence interpretation is very difficult. If the sample is oriented with one of the
crystalline axes parallel to the electron beam ("zone axis"), dynamic diffraction is increased.
Therefore the sample should be oriented far off any crystalline orientation. In addition, a
complete description of off-axis holography has been made including the reconstruction
method as well as the problems encountered when measuring some of the induced artefacts.
Some of the artefacts induced by the camera, the biprism Fresnel diffraction or phase
wrapping are presented. Some of these artefacts and problems can be reduced during
reconstruction through the application of algorithms used for the reconstruction.

Finally, it is described, how the potential can be measured by electron holography. The
assumptions for these measurements are that the sample must be homogeneous in the
direction of the electron wave propagation and in non dynamic conditions. Only under
these situations the measured phase is proportional to the potential. Additionally, to
obtain the potential in the object, the amplitude related to the thickness by an exponential
absorption law must be normalized. For this normalization, a second hologram without
object is acquired. Finally, the potential distribution averaged along \( z \):

\[ \bar{V}(x, y) = -\frac{\varphi(x, y)}{\sigma \cdot 2 \cdot \lambda_{\text{inel}} \cdot \ln (A_n)} \] (3.44)

results.
Chapter 4

Application of electron holography on solar cells

4.1 Introduction

Electron holography has proved to be a powerful method to measure potentials and carrier doping concentrations in semiconductors. Several groups have demonstrated that p-n junction potentials can be detected [83, 31, 15, 101, 102]. Meanwhile, off-axis electron holography is widespread in the semiconductor industry for device characterisation [19]. Difficulties in sample preparation and poor experimental conditions have delayed quantitative measurements until recently [82, 98, 130, 63]. Large progress has been made particularly in the field of preparation methods [27, 141, 142], optical set-ups [117], sample orientation avoiding dynamic conditions [26] and in-situ biasing [129]. Moreover, in order to provide detailed 3D information of the built-in potential, holographic electron tomography has been developed and successfully applied [147, 134].

However, although off-axis electron holography has proved to be a powerful technique for the measurement of potentials with nanometre resolution, the technique has not yet been applied to solar cells. To develop a systematic study of solar cells by electron holography, it is necessary to understand the particular problems pertaining to the measurement of potentials within this kind of devices. Difficulties related to the method have already been demonstrated in the previous chapter. However, solar cells present additional difficulties, which are shown and discussed in this chapter.

As previously mentioned, some of the more promising solar cells have a polycrystalline structure. Therefore, in this chapter the problems, regarding the measurement of the electric potential distribution on polycrystalline solar cells, are discussed. This polycrystalline structure generates the problem that it is not possible to orientate all grains of the solar cell in non dynamic diffraction, and therefore potential measurements in terms of functional fields by means of normal electron holography are nearly hopeless. A solution is proposed applying in-situ stimulus to the sample inside the TEM column and measuring the material response. A discussion about the effects of the electron beam in generating electron-hole pairs in silicon solar cells and a continuation on the study of noise close the chapter.
4.2 Potential measurement in polycrystalline solar cells

To illustrate the difficulties in the measurement of potentials in polycrystalline solar cells, images of the reconstructed amplitude and phase of a Mo/CIGS/CdS/ZnO thin film solar cell are shown in Figure 4.1.

Figure 4.1: Reconstructed wave, amplitude (left) and phase (right) of a CIGS solar cell. In the images the different layers of the solar cell are indicated, also a grain boundary and precipitates are visible. This local variation of composition makes the interpretation of the phase image and the amplitude in terms of potential and thickness difficult.

The Mo back contact layer is not visible because it is located far away of the field of view. In the CIGS layer a grain boundary and precipitates are visible. The latter could stem from local changes of composition, impurities of the sample or Cu$_2$Se precipitates frequently observed in this kind of objects [56, p. 163]. The sample was prepared for TEM-investigation using the traditional cross-sectional method, in which a Dimple Grinder and argon ion polishing are applied to finish the sample. This method is used mainly for high-resolution TEM, because it produces thin samples with low surface damage. However, it has the drawback of creating a sample of non-uniform thickness. The argon ion beam etches the surface in a non uniform manner. Details about this sample preparation method can be found for example in [87].

If the sample contains local variations of composition or precipitates, it is very difficult to calculate the individual mean inner potentials $V_{MIP}$ or the inelastic mean free path $\lambda_{inel}$ from amplitude and phase (see Figure 4.1). Therefore, the local thickness cannot be calculated, and it cannot be determined whether the sample has functional potentials$^1$. Therefore, holographic analysis of the potential structure in polycrystalline materials is very difficult, because of the peculiar dynamic phase shifting effects, which arise from the granular structure. Unfortunately, these effects strongly influence the measured results. They occur between and within differently orientated grains and arise from thickness.

$^1$for explanation of $V_{MIP}$ and $\lambda_{inel}$ see Chapter 3
4.2. POTENTIAL MEASUREMENT IN POLYCRYSTALLINE SOLAR CELLS

variations or from local composition with different mean inner potentials. The arising unwanted phase modulations can be much stronger than the desired ones from doping.

As a consequence, the development of a method to separate the additional contributions from desired ones, i.e. the $V_{MIP}$ and inelastic effects from the functional potentials in the solar cell, is essential. Such a method is explained in section 4.3.

Dynamic condition

Assume that the Phase Grating Approximation is locally valid under non-dynamic conditions and no other potential than the mean inner potential $V_{MIP}$ is present.

In consequence, from the equations for thickness 3.29:

$$t = -2\lambda_{inel} \ln \left( \frac{A_{obj}}{A_{ref}} \right) = -2\lambda_{inel} \ln (A_n)$$

(4.1)

and phase 3.41:

$$\varphi(x,y) = \sigma \cdot \bar{V}(x,y) \cdot t$$

(4.2)

the product between $V_{MIP}$ and $\lambda_{inel}$

$$V_{MIP} \lambda_{inel} = -\frac{\varphi}{2 \sigma \ln (A_{obj}/A_{ref})}$$

(4.3)

must be constant, because $V_{MIP}$ and $\lambda_{inel}$ are two constants dependent only on material properties. Therefore the product must be also constant and independent of thickness. Consequently, a database of the product $V_{MIP} \lambda_{inel}$ of different materials can be used as a criterion to determine, if a wave image is acquired under dynamic conditions or not.

On the other hand, if the sample is measured in kinematic conditions, the product can be used to construct a composition map. However, a difficulty arises from the noise. In general, amplitude images are noisier than phase images and, because taking the logarithm of the amplitude increases the noise, it is difficult to specify a threshold value for distinguishing between specific materials. But if low noise images in non dynamic conditions can be acquired, composition maps could be established.

As an example the image wave, amplitude and phase, from Figure 4.1 is used. In these images local validity of the Phase Grating Approximation is assumed, and thus the calculated product $V_{MIP} \lambda_{inel}$ must be constant in these regions. Figure 4.2 shows regions where this assumption is valid (boxes 1, 2 and 3). Some statistical spread of the value is expected due to the intrinsic noise of the image. Area 1 (CIGS) presents a good example of a local kinematic situation. On the other hand in areas 2 and 3, it is clear that other effects, dynamic or changes in composition, are present.
CHAPTER 4. APPLICATION OF ELECTRON HOLOGRAPHY ON SOLAR CELLS

Figure 4.2: Measured product of $V_{MIP}$ and $\lambda_{inel}$ from amplitude and phase (Figure 3.12). In this image, regions where the measured product $V_{MIP}\lambda_{inel} = \text{constant}$ are found (areas 1 to 3), but also regions where effects of dynamic interaction can be found (areas 4). On the right side, the histograms of the product in each one of the areas indicated by boxes 1 (CIGS), 2 (CdS) and 3 (ZnO) are shown. In the histogram of area 1 the small statistical spread around a mean value indicates a good approximation to kinematic situation, whereas in the histograms of areas 2 and 3 the dispersion of the values indicates additional phases or dynamic conditions.

In the image it is clear that at the interfaces or close to the vacuum, the measured product $V_{MIP}\lambda_{inel}$ does not have a constant value. This can be due to dynamic interactions, local changes of composition or functional potentials. The product must have a determined value given by $V_{MIP}$ and $\lambda_{inel}$. In this case, the sample is highly expected to be in kinematic conditions. However, there is still an uncertainty, because the measured product could also give equal values for different non-kinematic orientations: it is only a necessary condition but not a sufficient one. Further systematic studies of this product are necessary.

In those regions, where the product is constant and either $V_{MIP}$ or $\lambda_{inel}$ is known beforehand, the other one can be determined from the product (Equation 4.3). Consequently the potential in these regions can be calculated (see equations 4.1 and 3.4). If both ($V_{MIP}$ and $\lambda_{inel}$) are unknown, they can be determined measuring the thickness distribution by means of another method like CBED or EELS [11] and using this information by inverting the equations 4.1 and 3.4 or by theoretical calculations. A method to calculate the $V_{MIP}$ could be, e.g., DFT. But, in general, DFT calculations can be intricate and time consuming; and determination of the experimental data requires precise knowledge of the sample characteristics. DFT calculations must include surface effects and granular structure of the material, to adjust with the experimental results. Despite of these difficulties, DFT has been applied successfully to several materials giving a good agreement with the
4.3 Measurement of the functional potential by means of in-situ stimulus

In a non-magnetic sample with a p-n junction, the phase measured by electron holography is proportional to:

\[ \varphi = \sigma \int \nabla(V(x, y, z)dz = \sigma \int (V_{MIP}(x, y, z) + V_{bi}(x, y, z)) dz \] (4.4)

In this equation \( V_{bi} \) describes the solar cell functional potentials with \( t \) corresponding to the sample thickness.

Under in-situ biasing or illuminating with light only the p-n junction potential changes, while the \( V_{MIP} \) remains constant. Therefore, biasing or illuminating with light allows the separation of the potential variations at the p-n junction from the inner potentials, grain orientation effects and sample preparation artefacts. Thus, it yields unique and quantitative information about the functional potentials, see Figure 4.3. Therefore, two conditions should be fulfilled: First, the material should not be modified upon biasing or illuminating with light and second, the electron illumination conditions must be kept stable during the whole experiment in order to maintain the same electron-object interaction. This last condition must be fulfilled, because the dynamic interaction is very sensitive to small changes of electron illumination direction with respect to the sample. To verify if the sample or the electron illumination changes, one way is to compare the reconstructed amplitudes. They must not change during the experiment.

Figure 4.3: Left: band structure after applying a voltage across a homo p-n junction solar cell. The p-n junction potential changes proportionally to the biasing potential \( V_a \). Right: effect of illumination with light on the band structure of the solar cell. If no external load is applied to the solar cell, the separation of the generated electron-hole pairs produces an open circuit voltage \( V_{oc} \).
CHAPTER 4. APPLICATION OF ELECTRON HOLOGRAPHY ON SOLAR CELLS

Figure 4.4: Sequence followed to acquire, process and compare the holograms in the in-situ experiment. 1. Acquisition and reconstruction of the holograms with and without stimulus, respectively. 2. Determination and correction of the displacement of the images with and without stimulus, respectively. 3. Subtraction of phase images with and without stimulus. 4. Determination of the thickness from the reconstructed amplitude (average of \(A\) and \(B\)). 5. Calculation of the potential distribution. The most important condition for this experiment is that the amplitude images, with and without stimulus, must not change.

In order to quantitatively compare images with and without stimulus, the following procedure described in Figure 4.4 is proposed. The method consists of a series of steps to obtain information of functional potential of the sample. It follows:

1. Two holograms with and without stimulus are acquired, each one of them with a respective empty hologram. This can give rise to large displacement of the object. Therefore special care has to be taken about the relative position of the images, because these two images have to be aligned later: Strong displacements reduce the finally overlapping area. In addition, for an artefact-free comparison later on it is important to use the same imaging conditions, as far as possible. For each set of object holograms, empty holograms are also acquired without changing the illumination with light and/or biasing conditions. To improve the signal to noise ratio...
in the holograms, large exposure times are used (from 6 to 10 seconds). Subsequently, each hologram is reconstructed in amplitude and phase according to the method explained in Section 3.4.3 using the respective empty hologram.

2. Determination of the image displacement from the amplitude images. After each object hologram an empty hologram is acquired. Therefore, normally there is a displacement of the holder with respect to the position of illumination. If a dramatic displacement occurs after each acquisition, it is necessary to correct it by means of the object goniometer (compustage). Fine corrections of the displacements are calculated by cross-correlating the two amplitude images using a script implemented in the Triebenberg software. Following this, the calculated displacement data $\Delta x, \Delta y$ are used\(^2\) to correct the displacement between the images.

3. Subtraction of phase images with and without stimulus. After subtraction, the resulting phase image contains only the information about the stimulus applied.

$$\varphi_{B-A} = \sigma \int_0^t (V_{MIP} + V_{bi}^s) \, dz - \sigma \int_0^t (V_{MIP} + V_{bi}) \, dz = \sigma \int_0^t (V_{bi}^s - V_{bi}) \, dz. \quad (4.5)$$

$V_{bi}^s$ corresponds to the built-in potential with stimulus, it is $V_{bi}^s = V_{bi} - V_a$ under biasing\(^3\) and $V_{bi}^s = V_{bi} - V_{OC}$ (note that $V_{OC} > 0$) under illumination with light\(^4\).

4. Thickness determination. In regions, where the sample is not dynamic, the thickness is determined from the amplitude image. In $c$–silicon and in amorphous materials, it is feasible to orient the full sample in non-dynamic conditions, and therefore the thickness map can be determined for the whole image. On the other hand, in polycrystalline solar cells only local kinematic regions can be obtained. In regions, where the sample is dynamic, the thickness needs to be extrapolated.

5. Calculation of potential distribution averaged along $z$ using the expression:

$$\Delta V = \frac{\varphi_{A-B}}{\sigma t}. \quad (4.6)$$

The main assumption in this equation is that the projected potential in the direction of the electron beam is constant, which is not always valid. These are the cases with samples prepared using FIB, because of the damage in the surface of the samples inflicted by the ion beam or with sample with variation in composition.

In this thesis, this procedure is initially applied to well defined systems in order to gauge the possibilities, as well as to understand the difficulties and to establish a standard procedure. Because of their well known properties $c$–silicon\(^5\) solar cells are selected. With the knowledge acquired using $c$–silicon solar cells, the method is later applied to CIGS solar cells.

\(^2\)In objects with soft variations in the contrast, no satisfactory results are obtained when using automatic alignment, e.g. cross correlation. In this case, a manual determination of the displacement data is necessary.

\(^3\)Positive potential is assumed for forward biasing.

\(^4\) $V_{OC}$ and $V_a$ are defined in Chapter 2.

\(^5\)The $c$–silicon solar cells are supplied by the “Fraunhofer ISE” (Fraunhofer-Institut für Solare Energiesysteme)
4.3.1 Effects expected according to the stimulus applied

The correct interpretation of the measurements needs understanding of the stimulus effects in terms of potential changes. An adequate quantification of the effects also determines the grade of precision needed, to detect the potential variations. Therefore, a brief discussion regarding the effects of illuminating and biasing is presented in the following section.

Potential variation in the solar cell under illumination with light

It is known that illumination of solar cells with light generates electron-hole pairs, which are separated by the p-n junction and hence produce an effective potential. This generated potential reduces the built-in potential of the p-n junction and is referred to as open circuit voltage ($V_{oc}$) in the literature. In normal conditions of operation\(^6\) and with highly efficient solar cells, the potential $V_{oc}$ generated is close to the values indicated in Table 4.1.

<table>
<thead>
<tr>
<th>Type of solar cell</th>
<th>p-n junction potential ($V_{pn}$)</th>
<th>Typical experimental open circuit voltage ($V_{OC}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c - silicon$</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>CIGS</td>
<td>1.0</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 4.1: Typical p-n junction ($V_{pn}$) and open circuit ($V_{oc}$) potentials of some of the solar cells studied in this thesis. Open circuit values are given for the air mass 1.5 sun standard illumination. This illumination is defined in Section 2.5.

According to these data, the potential changes, i.e. the open circuit potentials ($V_{oc}$), are larger than 0.6 Volt. If larger illumination intensity is applied, a larger potential $V_{OC}$ is expected. But in any case, it is limited by the built in potential ($V_{bi}$).

Potential variation by biasing of the solar cell

Biasing of solar cells produces a potential variation proportional to the potential applied ($V_a$). This potential variation increases when the p-n junction is reverse biased and reduces when it is forward biased. The details of biasing are discussed in Section 2.3.

---

\(^6\)These conditions are defined by low temperatures (T<350K), low illumination conditions (< 10sun), zero current and low recombination rate.
Figure 4.5: Effect of biasing on the band structure of a solar cell. Left, forward bias; here the p-n junction potential is reduced by the same amount as the applied potential. Centre, zero bias; no changes in the band structure. Right, reverse bias; the potential in the p-n junction is increased by the applied voltage. Electron holography measures the potential with reference to the vacuum, in these images this potential is represented by the (blue) line at the top of the images.

To apply biasing inside the TEM, it is necessary to have an adequate TEM sample holder with a proper sample. In Chapter 5 a complete description of the holder is presented and in Chapter 6 an appropriate sample preparation is described.

Correlation of the measured potential and band structure

The band structure defines the functional built-in fields in the solar cells. They are determinant for the charge transport and separation of the electron-hole pairs generated by the illumination with light. Therefore, measuring the band structure in the solar cells helps to specify one of the main parameters, which rules the solar cell efficiency. The band structure in a hetero-junction has additional parameters, which are determined by properties like band gap, contact potentials, as well as doping concentrations.

The phase difference measured from a hologram and acquired at non-dynamic interaction gives a measure of the projected potential in the sample. It means that the mean inner potentials in solids, surface effects, polycrystalline structures and grain boundaries must be measured. Anyhow these effects are small compared with the bulk potentials. For example, calculations of $V_{MIP}$ in semiconductors show at surfaces values close to 0.2 V \[52\]. Moreover $p-$ and $n-$doped materials can not be distinguished if not in contact. The concentration of the doping elements ($\sim 1 \times 10^{19}$ cm$^{-3}$) is small with respect to the number of atoms in host material ($\sim 1 \times 10^{22}$ cm$^{-3}$). Therefore their contribution to the total $V_{MIP}$ is insignificant. Electron holography measures consequently the built-in potential created by the differences of doping only when they are in contact, producing the built-in potential $V_{bi}$. But in principle it would be possible to measure the electron affinity or the work function. These two are surface properties of the material, nonetheless, if the contributions from surface or grain structure are to be measured, a problem remains for the sample preparation. In most cases the damage induced by the preparation produces a larger signal than that from the described phenomena.
It seems that surface effects affect the measurement. Unfortunately these effects could not be studied in this thesis because it would demand a larger time effort. But due to the importance of this topic, it must be analysed in future.

Electron holography cannot be correlated with the band structure in general, i.e. discontinuities of the conduction and valence band remain invisible to the method. Still, parameters which contribute to the band structure, such as contact potentials and doping, can be measured.

4.4 Charge induced by the electron beam

In the proposed in-situ experiment, additional artefacts in the measurement can appear. One of the most prominent stems from the electron-hole pair generation in the sample by the electron beam. Since this effect is always present and could have a large influence in the analysis of the results, a detailed quantification needs to be carried out.

4.4.1 Quantification of charge induced by the electron beam

The electron beam used for imaging in the TEM, while passing through the sample also produces electron-hole pairs. These electron-hole pairs are produced by energy transfer from the electrons to the object, that is, inelastic interaction. Consequently, this generated charge changes the minority carrier density in a way similar to illumination with light. A quantification of these electron-hole pairs must be calculated and their influence on the potential must be evaluated.

In the literature, a number of previous studies have attempted to calculate the generated electron-hole pairs and to quantify their effect on the measured p-n junction potential by means of electron holography [16, 50, 25, p.84]. Cavalcoli et al. [16] calculate the generation rate per electron using the Bethe-Bloch equation. The calculations reported in the mentioned article give a value of $2.5 \times 10^{10}$ e-h pairs/s at 200 keV electrons and a beam current density of 3.2 mA/cm$^2$.

Houben et al. [50] specify additionally the effect of the electron illumination on grain boundaries and p-n junction potentials. For estimating the amount of electron-hole pairs generated they use the Bethe-Bloch equation as described in [6, p 132]. This equation gives the rate of energy transfer $|\frac{dE}{dz}|$ by a particle travelling through a material. An unfortunate aspect of this article is that the equation applied is not valid for electrons. In the original article, Barnetts’ et al. [6] indicate that the equation is only valid for “moderately relativistic charged particles other than electrons”. Nevertheless, the results of Houben et al. are presented to compare them with results of other authors.

According to Houben et al., the generation rate of electron-hole pairs is given by:

$$G_e = G_h = \frac{1}{2} \frac{j_{bc} |\frac{dE}{dz}|}{e E_{e-h}}$$

(4.7)
where \( j_{bc} \) is the electron illumination current density, and \( E_{e-h} \) is the energy necessary to create an electron-hole pair\(^7\). The factor \( 1/2 \) corresponds to the equipartition of the energy transfer into plasmon energy loss and electron-hole pair creation. Typical parameters for a \( c-silicon \) sample studied with electron holography are: \( j_{bc} = 1 \text{nA} \) in an area of 2 \( \mu \text{m} \) of diameter, \( E_{e-h} = 3.6 \text{ eV} \), and \( \left| \frac{dE}{dz} \right| = 786 \text{ eV/\mu m} \) yielding a generation rate of \( G = G_{n,p} = 8.6 \times 10^{23} \text{e-h pairs/cm}^3\text{s}. \)

Also Formánek \[27\] makes an estimation of the number of electron-hole pairs per incoming electron. The basic calculation consists in comparing a semi-empiric value determined by the division of the mean plasmon energy loss by the energy necessary to create an e-h pairs in silicon (3.6 eV) with the results of Cavalcioni et al.\[16\] and with the formula of Cabanel et al. \[13\]. From this method he estimates a value of 10e-h pairs per incident electron with an error in one order of magnitude, and calculates a corresponding generation rate of \( G = 6.2 \times 10^{20} \text{e-h pairs/cm}^3\text{s} \) with an electron current density of 0.3 mA/cm\(^2\). It is approx. 100 times smaller than the illumination conditions used in the calculation of Cavalcioni et al..

In the present thesis, the equation of Bethe-Bloch as reported in the article of Sternheimer et al. \[123\] is used. This equation gives the stopping power of electrons in different materials. To determine the electron dose, Figure 4.6 shows an example of typical hologram acquisition in our microscope CM200 Lorentz. The counts in the hologram in the vacuum region give a dose close to 1830 counts per pixel\(^8\). Because this intensity corresponds to the overlapping of two waves (empty wave and object wave) it is two times the illumination in the sample. At the area corresponding to one pixel, the sample is impacted with 890 electrons in 7 s.

\(^7\)The other terms in this equation have been previously defined (See list of symbols).

\(^8\)In the case of the camera mounted in this specific microscope (Phillips CM200) the gain i.e. counts per electron, is 0.971.
CHAPTER 4. APPLICATION OF ELECTRON HOLOGRAPHY ON SOLAR CELLS

Figure 4.6: Typical hologram of a $c-$ silicon sample taken in the CM200 Lorentz electron microscope. The inset shows the intensity along the arrow. The counts in the camera $n_{\text{vac}}$ in the vacuum are close to 1830 counts. The rate of conversion in the camera installed in this microscope is 0.97 electron/pixel, giving a number of approximately 1780 electrons per pixel. The acquisition time of this image was 7 s.

If this dose is divided by the calibrated area of one pixel, one obtains the number of electrons per unit area:

$$\frac{890 \text{e}^{-}}{(0.857725 \text{nm})^2} \sim 1.2 \times 10^{17} \text{e}^{-}/\text{cm}^2,$$

(4.8)

divided by the recording time (7 s) and multiplied for the electron charge, it yields a current density of:

$$j_{\text{sc}} = 2.8 \text{mA/cm}^2.$$

(4.9)

With this value for current density $j_{\text{sc}}$ and with the value of stopping power calculated for silicon impacted with electron at 200keV\textsuperscript{9} of $\left| \frac{\text{d}E}{\text{d}x} \right| = 5.23 \times 10^6 \text{eV/cm}$, the electron-hole pair generation rate can be calculated.

$$G_e = G_h = R \cdot \frac{j_{\text{bc}}}{e E_{e-h}}$$

(4.10)

The difficulty for a precise calculation lies in estimating the ratio between the electron-hole pairs created and other concurrent inelastic processes with respect to the total energy

\textsuperscript{9}In the calculation a Si density of 2.33 g/cm$^3$ is used.

\textsuperscript{10}Calculated using the program ESTAR of the National Institute of Standards and Technology (NIST). This program can be accessed on line via the address http://physics.nist.gov/PhysRefData/Star/Text/ESTAR.html
transferred to the object. Therefore the parameter $R$ taking into account this ratio is included.

Table 4.2 shows a comparison of generation rates calculated by the mentioned authors. For a better comparison, the results are recalculated using the same electron current density of this thesis. For the calculation of this thesis the value for $R = 0.5$ as given by Houben et al. [50] is used.

This ratio between the electron hole-pair generated and the other concurrent inelastic processes represented in the factor $R$ needs to be discussed. It can be assumed that half of the electrons impacting the sample produce electron-hole pairs. However, the amount of inelastically scattered events should destroy completely the contrast because almost no elastically scattered electron remains to contribute to the interference. The solution of this apparent paradox are the cascade processes produced by high energetic inelastic processes, which decay in a manifold of low energetic processes, for example in electron-hole pairs. In this case the energy loss of one single electron produces a large amount of electron-hole pairs.

<table>
<thead>
<tr>
<th>Work</th>
<th>Generation rate e-h pairs/(cm$^3$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cavalcòli[16]</td>
<td>$8.6 \times 10^{22}$</td>
</tr>
<tr>
<td>Houben[50]</td>
<td>$7.5 \times 10^{23}$</td>
</tr>
<tr>
<td>Formánek[25]</td>
<td>$6.5 \times 10^{21}$</td>
</tr>
<tr>
<td>This work</td>
<td>$1.3 \times 10^{22}$</td>
</tr>
</tbody>
</table>

Table 4.2: Comparison of calculations of e-h pairs generated by the electron beam made by different authors. For comparison, the values were recalculated using the electron current density of this thesis.

Certainly the values of Table 4.2 are extremely large. A way of estimating the influence on the potentials in solar cells is to compare them with the generation rate produced by the illumination with light. Figure 4.7 shows the comparison with respect to the standard illumination 1 sun.
Figure 4.7: Comparison between electron-hole pair generation by light (blue line) and the range of values given by the different calculations (filled band) with a line (red) indicating the value calculated in this thesis. The generation rate by light is calculated using the green (\(\lambda = 535\text{nm}\)) absorption value. A strong influence from the electron beam is to be expected on the measurement of potentials in solar cells.

All these results indicate that the electron-hole pairs generated by the electron beam are an extremely important factor when measuring p-n junction potentials by electron holography. This effect is even more relevant for materials with low doping concentrations (~10\(\times\)10\(^{-17}\) cm\(^{-3}\)). In this case, the built-in potential by doping is in high injection conditions, because the injection of electron-hole pairs exceeds the doping concentrations (n and p regions). Here the physics of the solar cells must be re-evaluated. Also a large effect is expected in the case of in-situ experiments with illumination and biasing, since the solar cell is illuminated by the electrons. In this case smaller potentials are expected than predicted by theory. A comparison of theoretical results with experimental results is presented in Formánek’s work [25]. He shows that the potential drop across the p-n junction is reduced by the electron illumination. In a p-n junction with a theoretical potential drop of 1.0 V, the measured values are in the range of 0.7 V to 0.8 V. In this experiment, electron current densities of 2 \(\times\) 10\(^{-3}\) A/cm\(^2\) and 3 \(\times\) 10\(^{-5}\) A/cm\(^2\) are used. For a typical electron current density used to acquire holograms in this thesis (2.8 \(\times\) 10\(^{-3}\) A/cm\(^2\)), Formánek reports a reduction in p-n potential of 0.3 V. Also Houben et al. [50] simulate the p-n junction under different electron illumination conditions. They indicate that a significant reduction in the junction voltage (close to 50%) is recorded for generation rates in the TEM larger than 1 \(\times\) 10\(^{23}\) cm\(^{-3}\)s\(^{-1}\) for doping concentrations below 1 \(\times\) 10\(^{17}\) cm\(^{-3}\). However in the same article a reduction of 20% under low generation rates with the same doping concentration is reported.

As a consequence, e-h pair generation under electron illumination must produce a potential reduction of the p-n junction. Despite it, experiments of potential measurements by electron holography rarely consider this effect and in most of the cases it is simply ignored [42, 131, 101]. An explanation is that the surface of the sample prepared for TEM is not passivated, i.e. it is a defect-rich surface. In such a case the sample suffers from a large rate of surface recombinations. The net effect of this layer leads to a reduction of the open circuit
4.5 Revision of noise problem

In Section 3.4.5 is shown that noise effects can be described by the standard deviation of phase:

\[ \sigma_\varphi = \sqrt{\frac{2}{C^2 \cdot N_{\text{rec}}}} \]  

(4.11)

and amplitude:

\[ \sigma_a = \sqrt{N_{\text{rec}}} \]  

(4.12)

which is described by a Poisson distribution with the mean corresponding to the intensity.

The detection limits are given by the number of electrons per reconstructed pixel \( N_{\text{rec}} \) and the contrast \( C \). The contrast cannot be increased experimentally beyond a certain limit (≈ 0.3) (see previous chapter). In addition the acquisition time cannot be increased indefinitely. A way to solve this problem is to acquire series of holograms under the same conditions. Subsequently these holograms are reconstructed identically and the resulting waves aligned and averaged. Finally averaged images of amplitude and phase are obtained. Under this procedure the reduction of noise is proportional to \( 1/\sqrt{N} \) where \( N \) is the number of holograms averaged.

Figure 4.8 shows the effect in the standard deviation of amplitude and phase with the acquisition and reconstruction of a single hologram and three holograms. The image waves as amplitude and phase images for both cases are shown. The data clearly demonstrate a reduction of the noise.
CHAPTER 4. APPLICATION OF ELECTRON HOLOGRAPHY ON SOLAR CELLS

Figure 4.8: Comparison of reconstructed image wave as amplitude and phase of a single reconstructed hologram (top) and from three (bottom) holograms. The images show standard deviation calculated in the vacuum region in the inset boxes. With three images, a noise reduction of 38% in phase and 40% in amplitude is obtained, close to the theoretical value of $\sqrt{3}$. In these images the acquisition time of each hologram is 7 sec.

Figure 4.9: Images of the thickness calculated from the amplitudes in Figure 4.8. The standard deviation, calculated in the area of the boxes shows a noise reduction of 72.5% close to the theoretical value of 73.2%. Right; profile along the arrows shows the effect of averaging of the images. The profile corresponding to the averaging of three images shows a clear reduction of noise in the thickness.

From the amplitude images and using Equation 4.1, the thickness is calculated (Figure 4.9).
4.5. REVISION OF NOISE PROBLEM

The standard deviation in thickness calculated using error propagation of the Equation 4.1 is given by:

$$\sigma_t = 2\lambda_{inel} \frac{1}{A_n} \sigma_{A_n} \quad (4.13)$$

The absolute standard deviation in the thickness increases with respect to the amplitude because of $2\lambda_{inel}A_n^{-1} \gg 1$. However, the acquisition of hologram series reduces the noise of the thickness proportional to $\sqrt{N}$; figure 4.9 shows a standard deviation close to the theoretic value.

Finally, the potential is calculated using phase and thickness (Figure 4.10) by means of equation 3.42.

$$\bar{V}(x,y) = -\frac{\varphi(x,y)}{\sigma \cdot 2 \cdot \lambda_{inel} \cdot \ln (A_n(x,y))} \quad (4.14)$$

![Single hologram and Three holograms](image)

Figure 4.10: Images showing the potential distribution in the sample of $c-silicon$. With the acquisition of series of holograms the noise is reduced.

The potential distribution shows a noise reduction close to 2 for acquisition and averaging of three images. The precision of the potential measurement, assuming a Signal to Noise Ratio (SNR) of three, is close to 1.8V. This precision is still too low for the measurement of potential variations expected in solar cells, whether biased or illuminated. Therefore in this thesis, larger series of holograms are taken, also with larger exposure times.

An example of a potential reconstructed from 9 holograms is shown in 4.11. The standard deviation of the potential in terms of the standard deviation of phase $\sigma_\varphi$ and thickness $\sigma_t$ calculated from the series by means of the equation yields:

$$\sigma_V = \frac{1}{\sigma_t} \sqrt{\sigma_\varphi^2 + \frac{1}{4t^2} \sigma_t^2}. \quad (4.15)$$

Applying this equation, a standard deviation in the potential of 0.04V is measured. With SNR=3, a detection limit of 0.12 V results.
CHAPTER 4. APPLICATION OF ELECTRON HOLOGRAPHY ON SOLAR CELLS

4.6 Summary

In this chapter the problem of potential measurement in polycrystalline solar cells has been discussed. The main problems arise from the object itself, the sample preparation and from the interaction of the electrons with the object. The random orientation of the grains, inhomogeneous composition and ill-defined geometry make it impossible to utilise the usual holographic technique. Therefore an in-situ method is proposed with in-situ illuminating and biasing of the solar cell. With this method, separation between the functional potentials and the additional contributions to the phase is feasible.

However, calculations show that the effect of the electron-hole pair generation by the electron illumination must have a strong influence. The illumination produced by the electrons is stronger than that of the standard 1 sun. At the surface of the \( c - \text{silicon} \) solar cell, the e-h pair generation rate by the electrons is 5 times larger than 1 sun light with typical electron illumination conditions for the acquisition of holograms in the electron microscope. At 200nm depth this ratio is 6.5 times.
Finally a brief discussion about the signal to noise ratio in the measurement of potential was presented, which shows the necessity to acquire series of holograms in order to reduce noise. The possibility to reduce noise by increasing the electron illumination intensity is avoided. Because calculations of the effects of illumination with larger intensities show larger electron-hole pairs generation and also larger sample charging probability. The electron illumination reduces the open circuit voltage, creates stray fields and induces currents.
Chapter 5

Design, construction, characterisation and application of a TEM holder for in-situ biasing and illumination

5.1 Introduction

In-situ TEM experiments are becoming an exciting field of research. In general, in-situ TEM allows real time observations of the interplay between processes, properties and micro-structure relationships in materials. In addition to the possibility to measure the structure by normal TEM, they allow determining changes in the potential under external modifications in holography.

In-situ experiments in TEM have been performed since the conception of microscopy. At the beginning simple experiments were conducted: heating, cooling or the study of the damage made by the electron beam \[146\]. In addition a number of pioneers realised more complex procedures, such as biasing of p-n junctions \[29, 28\].

These types of experiments have gained importance with the improvement of microscopes and in understanding of object-electron interaction, as well as an increased interest of the semiconductor industry, amongst others. Nowadays it is possible to strain the sample by means of an indenter manipulated by piezoelectric elements \[92\], to apply electric fields \[62\], to magnetise the sample by using the TEM lens \[108\], to bias\[140, 129, 90\], to cool, to heat \[119\] or to illuminate. New developments make it possible also to introduce gas in the sample region (environmental microscopy) \[30\]. These dynamic stimuli of object functions have been applied in different studies like catalytic process, semiconductor p-n junctions, hardness, and others \[17\].

However, performing TEM in-situ experiments requires highly demanding techniques. Indeed, TEM specific aspects such as the high vacuum present in the column, the small space around the specimen, displacement and tilting of the holder, charging problems coming from the presence of isolating materials close to the observation area or from the
sample itself, position and finally orientation of the specimen with respect to the stimulus applied. Besides, in electron holography, the geometry and orientation of the object with respect to the electron biprism is an important aspect. An optimal orientation of the interference fringes with regard to the object is a decisive aspect in the quality of the data.

Any electromagnetic field produced by the sample or by any element around modulates the phase of the electron wave and creates artefacts in the measurement. Furthermore, to apply illumination or biasing simultaneously with holography is a demanding experiment. The development and tuning of the sample holder is one the most demanding tasks in this project, and a considerable amount of time is required to design, construct and test the holder.

Some companies sell very expensive holders for electrical biasing, which use a small movable needle manipulated mechanically or driven piezoelectrically to contact the sample. This principle is also used for tension or stress measurements. However, holders for illumination and simultaneous biasing are not on the market. There are only a limited number of publications reporting experiments with illumination [111].

Therefore the holder had to be constructed in the Triebenberg laboratory. This chapter focuses on the description of the design and characterisation of the holder head. Aspects of special attention are: effects of charging by the electron beam, space limitations in the TEM column and characterisation of the source of optical illumination, namely LED or a LASER.

From the test of the different developed holders, it is clear that using a LASER as a source of illumination has proved to be the best solution. This holder allows the measurement of the potentials with minimal artefacts.

Finally, an example of the effects of high optical illumination for reduction of charging induced by the electron illumination in an isolating ZnO nano-wire is presented and discussed.

5.2 Holder design

For the in-situ experiments, a modified holder with a hollow shaft, compatible with our microscopes\(^1\), is used (See figure 5.1). This holder allows installing vacuum-tight isolated feed-throughs. With their help the electrical connections and the insertion of an optical fibre into the column are realised. In addition, because of the high vacuum requirements of the Schottky Field Emissions Guns (FEG) used in our laboratory,\(^2\) it is necessary to take special care of a reliable vacuum sealing of all components.

---

\(^1\)The microscopes used in Triebenberg are a Phillips CM200 Lorentz and a Tecnai F20 Cs.

\(^2\)The normal vacuum in the source regions is approximately \(10^{-8}\) Pa, being the highest vacuum in the microscope. Through the column, there are differentials of pressure, which are created by the different apertures in the column. In the sample region the vacuum is approx \(2.76 \times 10^{-5}\) Pa which is three orders of magnitude worse than at the gun.
5.2. HOLDER DESIGN

Figure 5.1: Holder with a hollow shaft. By means of the feed-through items in the head arranged around the object can be controlled from outside hence allow in-situ experiments.

Space for the object and in-situ setup is rather limited. The Philips CM200 Lorentz and the Tecnai F20Cs TEMs have super-twin objective lenses, which have a gap between the magnetic pole pieces at the sample position of 5.4mm. Moreover, the diameter of opening of the specimen stage, into which the holder is inserted, is only 5mm.

Furthermore, the position of the elements along the holder arm is also restricted. The specimen must be positioned in a specific place for imaging in the microscope. The maximum lateral displacements, allowed by the computer controlled stage (Compustage) are 1mm from the centre of the image in each direction x and y.\(^3\)

There is no degree of freedom of vertically positioning the specimen inside the gap of the pole pieces, because the sample needs to be placed in a specific reference plane (eucentric plane), where the calibrations of the microscope are defined\(^4\) [146]. The movement range of the holder along the optical axis is mechanically limited\(^5\). These restrictions define the tolerance in positioning the object in all dimensions. Additionally, the sample must be oriented with respect to the electron beam at non-dynamic diffraction conditions. Some orientation values for this tilting are given in the work of Formánek \[26, p 67\]; usually the tilting of the object to reduce dynamic diffraction effects should be made in \(\alpha\) and \(\beta\) directions (See Figure 5.2), however the holder applied here only allows tilting in \(\alpha\) direction.

---

\(^3\)The observation area is limited to 4mm\(^2\), in case of the usual circularly shaped holder this area is 3.1mm\(^2\).

\(^4\)Eucentric plane is a normal plane to the optical axis, which contains the holder axis as well as the tilt axis. For specimen located at this plane the image is in focus at the optimum value of the objective current.

\(^5\)In the Triebenberg microscopes this range is \(\pm 375\mu m\).
Figure 5.2: Space available for the holder with respect to the pole pieces of the objective lens, considering also the tilting angles $\alpha$ and $\beta$. In the holder designed in this thesis, the sample can be tilted only in $\alpha$ direction.

An important factor dominating the arrangement of all elements in the holder is the biprism direction, which is not freely selectable as desired for achieving the best interference contrast. In the CM200 microscope, which is used for the first measurements\textsuperscript{6}, the direction of the biprism creates the interference pattern of best fringe contrast oriented 30 degrees with respect to a line perpendicular to the holder axis. As a consequence, the arrangement of all the elements in the holder head should follow this orientation (see Figure 5.3).

Figure 5.3: Sketch showing the position and orientation of the LED as illumination source, contacts and sample in the holder head. The angle of 30° indicates the direction of the interference fringes.

The holder head fixes the specimen in the position of observation. Four copper wires are provided, two to connect the sample and two for the LEDs.

\textsuperscript{6}At the moment of construction of this holder. The microscope Tecnai F20, which does not have a Lorentz lens, does not have the lens configuration to acquire medium resolution holograms.
5.3 DESIGNED HOLDERS

Special precautions with charging under the electron beam have to be taken. However, it was found that even in a holder with isolating materials far away from the electron beam, strong charging effects are detected.

The first holder head is constructed using a laminated plate normally used for printed circuit boards (see Figure 5.4). This is selected because of the ease of mechanising and performing electrical contacts. However, the plate charges and therefore induces strong deformations to the image. With this holder, it is impossible to acquire normal TEM images. From this “experience”, the material basis of the holder head is changed to bronze and all of the insulating plastic parts are reduced to the minimum. In elements such as LEDs with a plastic encapsulation, a covering with an organic transparent conductive layer “PEDOT”\(^7\) is applied to reduce or eliminate these charge effects.

![Figure 5.4: First head constructed from a laminated plate normally used for printed circuit boards. This holder has only contacts for biasing. Images a (back side), b and c (front side) show details of placing of the contacts and sample fixing in the holder head.](image)

Other problems arise from understanding of the difficulties encountered when attempting to measure the change of the p-n potential in the solar cell by illumination and biasing. Firstly, it is understood that more intensity of light than expected is necessary, whilst a second reason is the magnetic stray field from the current of the LED’s.

5.3 Designed holders

Holders with LED

The holder has four contacts, made of simple lacquered copper wires. Two of them are used to power the LED and the others to contact the solar cell specimen. The copper wires are contacted with a silver based conductive epoxy.

\(^7\)This conductive PEDOT (Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) was supplied by the “Institut für Angewandte Physik” (IAP) of the Technische Universität Dresden.
The use of LEDs as a source of illumination seems to be advantageous because of the small size and the ease of installation, contact and power inside the microscope. Several LEDs were tested. The first sources were small commercial high intensity LEDs with wavelengths in blue and red and luminous intensities of 60 cd and 120 cd. Such LEDs are encapsulated with a transparent plastic. To reduce charging of the plastic under the electron beam, the LED is carbon coated; only then acquisition of holograms with enough contrast was possible. However, after reconstruction of the phase images, it became evident that this charging is a dynamic process, which induces unpredictable electric field variations in the area of observation.

Calculation of the radiant intensity of these LEDs shows that they provide in the sample region a brighter illumination density than the sun radiance. Table 5.1 shows the calculation of the photon flux by square centimetre of the applied LEDs.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Flux density of photons/(cm²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular intensity</td>
<td>Wavelength</td>
</tr>
<tr>
<td>60mcd</td>
<td>468nm</td>
</tr>
<tr>
<td>120mcd</td>
<td>650nm</td>
</tr>
</tbody>
</table>

Table 5.1: Illumination given by some of the LEDs. The angles 120° and 90° correspond to the angular distribution of the selected LEDs. Figure C.1.

The radiance of the sun, according to the 1.5 air mass equivalent sun illumination standard is $2.83 \times 10^{17}$ cm⁻²s⁻¹. The selected LEDs provide a radiance smaller than the standard 1 sun. However, with this illumination an effect on the p-n junction potential is expected.

---

8Radiance and spectral radiance are radiometric figures of merit, which describe the amount of light that passes through or is emitted from a particular area, and falls within a given solid angle in a specified direction. In TEM it corresponds to the brightness of the electron beam.

9This flux density can be calculated using the total power emitted for the sun at 1.5 mass equivalent, approx 1kW/m², and dividing by the mean photon energy of the solar spectrum, 2.36eV.
The charge due to the encapsulated LEDs is clearly observable by the reconstruction of empty holograms with different illumination intensities. Figure 5.6 shows the effect of illumination in the contrast of the holograms (Figure 5.6, top). The charge fluctuates during exposure time decreasing fringe contrast and hence increasing the noise in the phase image.

To reduce this charge problem, the surface of the LED is covered again with an organic transparent conductive layer of PEDOT. This layer reduces the problem making it possible to take holograms with full illumination by the LED without loss of contrast. A second problem with LED as illumination sources is drifting of the electron illumination image and the holder. This occurs when the illumination intensity (current) in the LED is changed. The drift of the electron illumination seems to originate from changes of charge accumulated in poorly conductive materials in the holder. By LED illumination, the surface conductivity is enhanced, and hence charging is reduced. A possible application of this effect could be the discharging of samples. It is illustrated at the end of this chapter on ZnO nano-wires (Section 5.4). The drifting of the holder is attributed to heat dissipated from the LED, but the displacement is not so strong.

Figure 5.6: Phase images from empty holograms with their respective hologram fringe contrasts (insets), if the current in the LED is increased between 0mA and 20mA. The contrast of the images is reduced with the increase of the LED current.

Comparing the holograms with and without illumination, one finds that the illumination does not produce detectable changes in the p-n junction potential. Under illumination,
the solar cell must create an Open Circuit Voltage ($V_{OC}$) but due to the recombination on the surface of the sample, this potential is reduced. To compensate this, the illumination must be increased in order to increase the e-h pairs generation rate, and hence the $V_{OC}$ potential.

To quantify the effect of recombination, simulations with the program Afors-HET are made. In the simulation the solar cell is simulated as an abrupt junction n-p-p$^+$ using the parameters of Table A.2. Additionally, the p-doped layer is simulated with a large concentration of neutral defects ($1 \times 10^{17}$ cm$^{-3}$) in the centre of the band gap; this value is chosen to fix the minority carrier diffusion length with the thickness of the sample at approx. 400 nm. This value is based on the assumption that each charge arriving at the surface recombines. As result, the flux density necessary to flatten the potential is of the order of $1 \times 10^{20}$ photons/(cm$^2$s), more than 300 times the sun flux density (Figure 5.7).

![Figure 5.7: Variation of potential and band structure for a flux density of photons, left $1 \times 10^{17}$/ (cm$^2$s), right $3 \times 10^{20}$/ (cm$^2$s), with monochromatic radiation $\lambda = 650$ nm. The simulations are made by means of the program AFORS-HET [47].](image)

As a result of this analysis, it is decided to use sources of illumination with a stronger power. Finally after a large search, the most intense chip LED available in the world is found. This new chip LED offers an intensity of 0.5W/mm$^2$ in two colours blue and green (wavelengths of 535 and 450nm respectively). Figure 5.9 shows how the elements are mounted in the holder.

---

10 This LED was donated for this research by the company SemiLED in Taiwan.
5.3. DESIGNED HOLDERS

Figure 5.8: Calculation of the potential variation and band structure of an open circuit CIGS solar cell when a flux of photons is applied, left $4 \times 10^{20}/(\text{cm}^2\text{s})$, right $5 \times 10^{22}/(\text{cm}^2\text{s})$. Monochromatic radiation with $\lambda = 470$ nm is used. Simulations are made with the program AFORS-HET[47].

Figure 5.9: Holder with the chip LED. The inset shows the position of the chip LED in the head.

Table 5.2 shows the results of calculations of radiance for these LEDs. The flux density of photons given by these LEDs is two orders of magnitude larger than the sun. They offer a radiance smaller than the illumination needed to flatten the p-n junction potential but enough to see the illumination effect in the measurements of potential by holography.
CHAPTER 5. DESIGN, CONSTRUCTION, CHARACTERISATION AND APPLICATION OF A TEM HOLDER FOR IN-SITU BIASING AND ILLUMINATION

Characteristics

<table>
<thead>
<tr>
<th>Power</th>
<th>Wavelength</th>
<th>Flux density of photons/(cm²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5W</td>
<td>535nm</td>
<td>$1.35 \times 10^{20}$</td>
</tr>
<tr>
<td>0.5W</td>
<td>450nm</td>
<td>$1.13 \times 10^{20}$</td>
</tr>
</tbody>
</table>

Table 5.2: Calculation of the flux density of the chip LED. These LEDs exhibit an illumination angle of 180°; however, due to the proximity of the sample (between 0.5 and 1.0 mm), the illumination is supposed constant over the sample area (details in the appendix C where the illumination is calculated).

These chip LEDs were installed in the holder thanks to the help of the “Institut für Aufbau- und Verbindungstechnik der Elektronik” (IAVT) of the Technische Universität Dresden.

However, after the first test, it was clear that the strong currents in the LED of approx 0.5 A again cause unpredictable shifting of the illumination and larger heat dissipation increasing the shifting of the whole holder head. This drifting produces a change in the electron illumination conditions between both exposures with and without stimulus. This makes a direct comparison, in terms of the pure effect of illumination with light, difficult.

These newly introduced artefacts indicate that a radical change in the design of the holder head had to be considered.

**Holder with a LASER as light source**

Finally, to resolve the problems occurring with LEDs, namely heating of the sample and the holder, charging and strong electric currents close to the electron beam, a new illumination system using a LASER is implemented, where only the light beam enters the microscope.

In principle two different designs are possible: One illuminates the sample from outside by using a port of access at the object stage level usually used to install additional detectors like for EDX. The other one implies the modification of the holder incorporating an optical feed-through, using fibre optics to transport the light emitted by a LASER to the object area.

1. The first option turned out to be very problematic and was ruled out because:

   (a) the alignment of the illumination system needs a complex mechanical alignment stage with at least 4 degrees of freedom (x, y, α and β), this alignment must be made from outside and the object cannot be observed directly.

   (b) a very special lead glass for x-ray shielding is necessary; the thickness of this lead glass has to be very large; no supplier for a respective lead glass was found.

   (c) The light absorption in lead glass is strong, demanding usage of even stronger light sources;
2. Second option, which was finally selected, requires a feed-through, which allows inserting an optical fibre and electrical contacts into the holder maintaining the high vacuum in the column. This feed-through must be self-made because, again, no supplier for such devices was found.

In this holder the light is carried from a high intensity LASER to the sample through a multi-mode optical fibre of 2m length.

The LASER is a diode pumped solid state LASER “LRS-0532-PFH-01000” from LaserGlow company, Canada. It is a green LASER (wavelength 532nm) with a nominal maximum output power of 1W. The output power can be controlled electrically by means of an external voltage applied between 0V and 5V.

To corroborate the data given by the supplier, the output intensity of the LASER is measured with a power detector “Thorlabs PM100”\(^\text{11}\). A maximum intensity of 1.54W at a wavelength of 532nm is found. This power is reduced by approximately 35% by the optic fibre coupling system. Figure 5.10 shows two calibration curves made on the LASER in function of the voltage: one directly from the LASER and the other after the optical fibre coupling.

![Figure 5.10: Output power given by the LASER coupled with the optic fibre. The efficiency of the coupling system is close to 65%.](image)

The output illumination distribution is determined by the optical coupling system between the LASER and the optical fibre. To make sure that the LASER offers an appropriated illumination on the solar cell, the characteristics of the output illumination need to be determined.

The optical coupling system is designed to have the smallest possible aperture angle. The value of 30° (full angle) was corroborated later by direct measurements of the illumination cone. The illumination produced at the exit of the optical fibre has a Gaussian distribution.

\(^{11}\)These measurements were made in the IAP institute of the TU Dresden
Therefore, by using this illumination distribution and measuring the total power supplied by the LASER, the illumination is fully characterised. Detailed calculation of the illumination is shown in Appendix C.

Using these parameters, the illumination, at maximum power of the LASER in the sample, gives the results shown in Table 5.3.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Max flux density of photons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power after optic fibre</td>
<td>1.0 W</td>
</tr>
<tr>
<td>Wavelength</td>
<td>532 nm</td>
</tr>
<tr>
<td>30°</td>
<td>$1.1 \times 10^{20} \text{photons/cm}^2\text{s}$</td>
</tr>
</tbody>
</table>

Table 5.3: Illumination on the object, produced by the optical fibre coupled to the LASER.

This means, that the LASER gives a flux of photons equivalent to approximately 380 suns.

This holder avoids the artefacts of the LED’s and allows acquiring holograms free of currents and charging effects in the sample region. Something that remains is the heating of the holder by the LASER beam.

Figure 5.11: Holder with optical fibre for LASER illumination of the object. The inset details the position of the optical fibre and illumination cone produced by the illumination. The measured aperture angle is 30° (in the inset the illumination cone and the position of the optic fibre are drawn for the sake of clarity).

5.4 Reduction of charge under illumination

Surprisingly, the illumination reduces charging of the object under the electron beam. As an example of this illumination effect, phase images of a ZnO nano-wire are shown in Figure 5.12 with and without illumination. The left image shows the phase distribution around the nano-wire charged under the electron beam without light illumination. Conversely, the right image shows the same situation but with the illumination switched on. It is evident that the charging is strongly reduced.
In this experiment, the sample is illuminated with the highest power of the LED donated by SemiLEDS with an irradiance of 0.1 W/mm$^2$. For comparison, the sun irradiates 0.001 W/mm$^2$ that is only 1\% of this power density\textsuperscript{12}.

![Holographic phase images of a ZnO nano-wire under the electron beam, without illumination (left) and illuminated with the Chip LED as source (right). The profile at the centre shows a comparison between the phase of the sample illuminated and not illuminated. The reduction of the electric field around the illuminated sample is obvious.]

This effect is surprising because, according to the ZnO parameter data (A.3), the band gap of the material has a width of 3.4 eV, which is larger than the energy of the photons used in the green LED (wavelength 532 nm; photon energy equivalent 2.33 eV). Therefore one would not expect the photons to show any effect in the material. A similar situation occurs with the heating of the sample; in this case the thermal energy given to the electrons in the material is smaller than that given by the illumination.

The discharging process could be explained by the existence of free surface states with smaller activation energies, which absorb the photons with energy lower than the band gap, thus creating electron hole pairs and increasing the superficial conductivity.

The same experiment is repeated later with the LASER as source of illumination (Figure 5.13), with similar results. In this case the sample is irradiated with the maximum power of the LASER.

\textsuperscript{12}This experiment does not use the full power of the LED to avoid artefacts from heating or currents.
CHAPTER 5. DESIGN, CONSTRUCTION, CHARACTERISATION AND APPLICATION OF A TEM HOLDER FOR IN-SITU BIASING AND ILLUMINATION

Figure 5.13: Holographic phase images of a ZnO nano-wire illuminated with the LASER beam (left) and not illuminated (right). The profile shows a comparison of the phase of these two conditions (centre). The reduction of the electric field around the illuminated sample is evident.

The first example is compared with 3D simulations of equipotential lines produced by a charged nano-wire in Figure 5.14. In these simulations, a uniform density of carriers of \(2.6 \times 10^{17} / \text{cm}^3\) is introduced on the ZnO nano-wire, adjusting with the experimental data.

Figure 5.14: Simulated phase image made with the program FlexPDE of a ZnO nano-wire charged under the electron beam (left). Phase profile comparing experimental data and simulation (right). In the simulation, charge densities of \(1 \times 10^{17} / \text{cm}^3\) and \(6 \times 10^{16} / \text{cm}^3\) are used for non illuminated and illuminated situations, respectively.

Discharging is a very beneficial side-effect found during the measurement process of potentials in solar cells. Indeed, usually a sample charging under the electron beam is sputter-coated with a thin layer of amorphous carbon. This layer, however reduces the final resolution of the image by increasing the scattering processes.

5.5 Summary

This chapter summarises the experience in the fabrication of holders suitable for in-situ illumination and biasing. Considerations arising from the specific intention for the design of the holders are discussed and detailed. Each of the holders is optically characterised to establish precisely the targeted illumination conditions on the solar cell specimen.
As result of the experience, a holder is constructed, that uses a LASER-coupled optical fibre hence solves most of the artefacts. In this holder the illumination of the object can be performed without further load, such as holder charging or presence of magnetic fields from driving currents. Consequently cleaner results of the stimulus effects can be obtained.

Finally an unexpected effect of illumination in ZnO nano-wires is found. It shows that charging created by the electron beam is reduced under light illumination. This effect opens the door to further applications of the developed holder for discharging the specimen during sensitive phase measurements.
Chapter 6

TEM sample preparation for in-situ biasing and illumination

Sample preparation is one of the most crucial steps in any TEM analysis. Without good samples it is not possible to obtain satisfactory results. However, an adequate TEM sample preparation requires between 1 and 4 days and it is strongly demanding on the ability of the person in charge of the process. Here emerges the question: Why is it so difficult? A suitable sample should be electron transparent, much thinner than 1000 nm. For high resolution imaging the thickness must be even only few mono-atomic layers, between 5 to 10 nm. Preparation of such a sample combines, in an intrinsic relation art, craft and science. Therefore, from the practical side, TEM sample preparation should be easy, reliable and relatively fast.

There are several kinds of TEM sample preparation methods, and usually they are named according to the main thinning process used: ion polishing, dimpling, milling, cleaving, electropolishing, microtomy, and so on. The samples can be produced according to the way how they are sliced and viewed: in cross section\(^1\) and plain view \(^2\). The use of the technique of preparation and the direction of sectioning depends on the nature of the sample and the characteristics to be measured\(^3\).

In solar cells, many different kind of materials are used. In the case of this thesis, the solar cells investigated consist of different materials with different mechanical and chemical characteristics. Therefore as much as possible a universal technique, applicable to all of them, must be applied. A promising technique is Focused Ion Beam (FIB).

Focused Ion Beam is a TEM sample preparation technique, which uses Ga\(^+\) ions to etch the material. The focused Ga\(^+\) ions are used to sculpt the object in a uniform lamella with suitable thickness to be observed by TEM. Also with the help of different precursors conductive or isolating layers can be deposited. A detailed description of the working principle can be found in \([36, 59, 66]\).

\(^1\)cross section: orientation yielding a thin slice normal to the surface of the bulk material.
\(^2\)plain view: orientation yielding a thin slice parallel to the surface of the bulk material.
\(^3\)A very helpful web-page describing several preparation techniques can be found under: http://temsamprep.in2p3.fr/accueil.php?lang=eng
FIB has many advantages including reliability, high precision in the location of the area of interest and possibility to tackle almost all kinds of materials [36, 89]. The disadvantages stem from the origin of the milling process itself. The ion impact can lead to ion implantation and cause several types of damage to the remaining material, which in turn results in strong changes in structural and electrical properties of the sample surface [14, 104, 105].

FIB preparation is becoming one of the regular methods of sample preparation for TEM because it allows obtaining reproducible samples with a very homogeneous thickness. It has been applied to many sorts of materials with different characteristics such as mono-crystals [97], poly-crystals [100], polymers [106] etc. It is also used increasingly in medium resolution electron holography for its flexibility and reproducibility [64, 88, 133].

Despite the fact that there are several advantages of FIB, it is not an ideal preparation method. It inflicts several different types of damage to the sample surface, e.g. amorphisation, Ga implantation etc. [125, 104, 105, 89].

Solar cells have also been prepared for TEM, using normal cross section preparation to study structural properties in high resolution imaging [151, 2], using FIB to study thickness of the layers [21], or to measure the potential distribution by electron holography [118].

As previously mentioned, some studies have already attempted to analyse solar cells, and have also attempted to measure the potential in organic solar cells. However, these studies are concentrated mainly on the morphological and structural properties of the solar cells. Nevertheless, studies of the effects of illumination or in-situ biasing on solar cells have not yet been conducted.

This chapter describes in detail the procedure applied to prepare the solar cells especially the c – silicon solar cells selected for study in this thesis. There will be a brief description of the technique used as well as artefacts introduced by the technique and difficulties in their removal. Additionally, some simulations of the effects of preparation on the potential measurement in solar cells are included. Following this, a calculation of the optimal sample thickness for holography is conducted. Requirements for the sample preparation to measure the effect of biasing and illumination by electron holography will be discussed. Additionally, some necessary elements for the preparation of CIGS solar cells are outlined.

6.1 Sample preparation

The challenge is to use a sample preparation method, which allows unequivocally measuring their functional potentials by means of electron holography. It must also deliver reproducible and fast results as well as be applicable to a large variety of materials with different hardness, ductility and electrical properties. Additionally, it should be possible to prepare samples for in-situ experiments.

Preparing semiconductor samples for in-situ experiments by FIB has been applied for several years. The literature describes works, in which biasing of p-n junction is applied [129, 90]. However, to the best knowledge of the author, in-situ illumination of photovoltaic devices is not reported. In the work of Twitchett et al. [129] highly-doped epitaxially grown
p-n junctions are studied and a preparation method allowing to bias them is described. The method has the advantage of using a large area of contact. Another advantage is that it allows using home made holders. This original idea of preparation of Twitchett [129] is modified to apply both biasing and illumination in-situ.

Figure 6.1 shows the sample preparation used by Twitchett [129, 128, 130]. The sample is fixed with conductive epoxy and a lamella is formed by means of the FIB in one of the corners. The contact to bias the sample is made mechanically by means of a copper spring.

Figure 6.1: Method of preparation used by Twitchett [128]. a. Fixation of the sample in the holder by means of a dedicated TEM supporting grid. b. Geometry of the sample. Image adapted from [128].

From this the method of preparation for this work is derived by minor modifications.

In the method of Twitchett the electrical contacts with the material are made mechanically, covering the main parts of the surface. This makes the illumination of the solar cell impossible. Therefore, for our experiments the size of the top electric contact is reduced to offer a large area for illumination. Figure 6.2 shows a top view of a finished $c -$ silicon solar cell probe, with electrical contacts and FIB milled lamella in one of the corners.

6.1.1 Sample size and shape

Once the method of preparation is chosen, the geometry of the samples is defined. The space within the pole pieces of the TEM objective lens is extremely reduced, thus performing in-situ experiments is highly demanding. The gap between the upper and lower pole piece as well as the displacement range of the sample compustage limit the sample dimensions.

To preserve the possibility of using normal TEM holders, dedicated copper grids of 3mm diameter have been selected to fix the sample in the holder. However, due to the special disposition of the elements for biasing and illumination in the holder, only samples with a maximum of 1.7 mm in the diagonal direction may be accommodated. In any case the sample should be large enough to allow electric contacting and illumination. Different sample shapes are tested, not only to establish the maximum area to illuminate and contact, but also to reduce the FIB milling time. The amount of material removed in the milling process depends on the geometry and their removal may require hours of FIB
CHAPTER 6. TEM SAMPLE PREPARATION FOR IN-SITU BIASING AND ILLUMINATION

Figure 6.2: Sample preparation overview: The sample is cut in a triangular shape and glued with conductive epoxy on a dedicated copper TEM grid on top, it is possible to see the electric contact. In one of the corners, the lamella is milled by means of FIB.

milling. Image 6.3 shows a number of different tested shapes. Finally the triangular shape is selected, because it offers the best compromise between large area for illumination and short milling time.

Figure 6.3: Shapes used for the sample preparation showing the amount of material removed in the FIB milling process and area accessible to illumination. The small bright rectangle indicates the lamella. The triangular shaped sample c offers the best compromise between milling time and area accessible for illumination.

6.1.2 Sample preparation procedure

In essence, the sample preparation procedure consists of the following general sequence. Here the procedure is designed for application with \( c \)-silicon type solar cells. Differences for polycrystalline CIGS preparation are detailed in subsection 6.5.

The sample preparation consists of three steps as follows.

1. **Mechanical resizing and polishing of the solar cells:** Due to the fact that the specimen is usually made from a wafer of thousands of micrometres thickness and several cm of size, it must be cut to a large rectangle of approximately 2.0 mm width with a diamond cutter. Subsequently, the sample is sawed again by means of a
6.1. SAMPLE PREPARATION

tungsten wire saw, which uses boron carbide in glycerine suspension as abrasive agent. During sawing, the surface must be protected with low temperature wax to avoid damage of the surface (Figure 6.4). The resulting piece has very irregular lateral faces. Therefore the small triangle is polished with diamond paper to obtain shined and smoothed lateral surfaces. The final lateral dimensions of the triangular-shaped sample are approximately 1.2 mm on each side.

Figure 6.4: Resizing of the sample is made with a wire saw. To protect the sample from damage due to scratching, a protective film of wax is used on the surface. The original contacts of the solar cells can be seen.

2. Fixing of the triangularly shaped probe on a TEM dedicated copper disk and contacting: To fix the triangular piece of specimen on the holder, a normal TEM dedicated copper grid is used. The geometry of the grid is modified similarly to that used in wedge shaped samples. The disk is cut in a special geometry and folded at a right angle ensuring a proper positioning of the specimen with respect to the electron beam (Figure 6.5). The final lamella must have its surface normal to the electron beam. The specimen is fixed onto the copper disk with commercial conductive epoxy resin. The final electric contact from the top surface to the holder contact is made by means of a thin copper wire, diameter 100µm, which is glued with the same conductive epoxy (see Figure 6.2).
3. Lamella FIB milling of trian-gular-shaped sample: The final process is FIB milling (Figure 6.6). This FIB milling is conducted in a dual-beam Neon 40EsB FIB from Zeiss Company\(^4\). In all preparations of this thesis the milling energy of the \(Ga^+\) ions is 30 keV. However in some of the samples, low energy ions of 5 keV are used to reduce the amorphisation effects in the final stage of the milling. The FIB preparation consists of the following steps for the lamella construction: Selection of the area, deposition of a \(Pt\) layer protecting against \(Ga^+\) ions, lamella milling and etching of the window for the reference wave (Figure 6.6, f). In general, FIB milling of a lift-out lamella is a fast procedure, between 2 to 4 hours, however, due to the dimensions and geometry of the specimen, each lamella for this thesis required between 6 and 8 hours of FIB milling. Image 6.6 shows the complete FIB milling process.

- The region, where the lamella is desired to be milled, approx. 2 \(\mu\)m wide and approx. 40 \(\mu\)m long, must be protected with two \(Pt\) layers sequentially deposited from a precursor. The deposition of the first layer of platinum is triggered by an electron-beam. The idea of this layer is to prevent damage of the surface produced by the \(Ga^+\) ions (Figure 6.6 a). The thickness of this layer is a few tens of nm [127]. The second layer of \(Pt\) is deposited by means of the \(Ga^+\) beam to a thickness of approximately 5\(\mu\)m (Figure 6.6 b). With these two platinum layers, damage due to the \(Ga\) ions during the lamella preparation is prevented. In addition, this platinum layer will also be used as the top contact for biasing or for measuring the potential during the illumination. For this reason, the platinum is contacted with the top contact wire by means of the conductive epoxy.

- The lamella is constructed by removing the material which is adjacent to the platinum line (Figure 6.6 d). The beam milling current is reduced when the milling probe approaches the platinum bar: from 10 nA at 5 \(\mu\)m distance from the platinum bar to 500 pA at the border of the platinum bar (Figure 6.6 d,e). Afterwards, the angle

\(^4\)The preparation of the samples was conducted in the “Leibniz-Institut für Polymerforschung Dresden e.V”.

Figure 6.5: Position of the sample in the copper disc with respect to the electron beam.
6.2 Artefacts introduced by the preparation

The method of preparation induces several artefacts to TEM and holographic measurements. These artefacts can be distinguished as problems induced by the reduced size of the sample and those stemming from the FIB milling process. The effects due to the size of the sample will be studied in the next chapter (Chapter 7). In this chapter, the effects of the FIB milling process are studied in detail.

6.2.1 Artefacts of the FIB milling process

The artefacts produced by the FIB milling process mainly consist of damage of the surface by amorphisation and Ga implantation, curtaining and effects of the platinum layer protecting the lamella.
CHAPTER 6. TEM SAMPLE PREPARATION FOR IN-SITU BIASING AND ILLUMINATION

Damage of the surface

The gallium ions, which etch the lamella, also destroy and modify the lamella surface exposed to the ion beam. Structural changes of the milled surfaces [80, 104, 10, 35] and redeposition of the material removed in the preparation process [14] occur.

Various studies have measured the potential in p-n junctions and acquired high resolution TEM images of the region modified by 30 keV Ga ions. Indeed Lenk [64] and Wolf [147], through the use of electron holographic tomography measurements, find that a lamella fabricated by FIB milling is composed of three different regions: an amorphous layer of thickness $t_o \approx 20$ nm close to the surface, a second one with several defects in the structure of thickness $t_1 \approx 50$ nm, and the last one, the intact core, corresponding to the original untouched material without damage by $Ga^+$ ions (Figure 6.7).

Figure 6.7: Representation of the different layers created by the FIB preparation. $t_o$ and $t_1$ are the thickness of the amorphous layer and the transition layer, respectively.

In the same article by Lenk, the effect of the layers modified for the FIB preparation on the projected potential is analysed. The first layer is assumed electrically dead because of the amorphous structure. The second one, the so called transition layer, is a region, where the potential is linearly increasing from the dead layer to the potential of the bulk. The last one is the intact core, where material is unmodified. The equation describing the phase shift due to this three layers in terms of the potential is:

$$
\varphi(x, y) = \sigma \cdot [V_{MIP}(x, y) t + \Delta V_{pn} \cdot (t - 2t_o - t_1)]
$$

(6.1)

where $t$ is the total thickness of the object.

According to this model, during the travel through the sample, the electrons experience different potentials in the sample. In the dead layers, the potential is constant given by the mean inner potential MIP; in the transition layer it increases linearly to the core potential, which is given by $V_{MIP} + V_{pn}$. In $n$ regions $V_{pn}$ is larger than in $p$ regions, i.e. $\Delta V_{pn} > 0$ when going from $n$ to $p$ regions. The MIP is determined from the middle of the p-n junction.

$Ga$ in $Si$ has doping properties similar to boron and hence produces a highly $p$-doped region. EDX measurements show that the concentration of $Ga$ can be as large as 2.5% at 26 nm depth [104], in lamellae prepared with 30keV $Ga$ ions. The $Ga^+$ implantation occurs mainly where the lamella is directly milled. Under milling, part of the removed
material redeposits again. In regions, where the material redeposits, the concentration of Ga is almost 12%, however this gallium can also diffuse into the crystalline silicon increasing its concentration in regions close to the surface.

Atom probe measurements [127] show that the Ga deposition is strongly dependent on the acceleration voltage, which influences the depth of gallium deposition and its concentration. In the case of 30 keV, the concentration increases exponentially from 6% in the surface to 11% at a depth of 20 nm. Below this first layer a second region is found, where the concentration decreases exponentially to zero at a depth allocated about 50 nm down the surface. This second region corresponds to the so called transition zone, where the gallium damages the crystalline structure of the silicon and induces defects. This second region also represents a gallium doped region; if the gallium occupies a lattice position, it acts as p dopant. Usually a solid material has approximately $1 \times 10^{22} \text{cm}^{-3}$ atoms. If only 0.1% of gallium atoms in this area are electrically active, the gallium doping of the silicon lamella is around $1 \times 10^{19} \text{cm}^{-3}$. This means that this layer acts as highly p-doped. The absence of the stray electric field lines emerging from the p-n junction in electron holography measurements [139, 132, 121] could also be explained by the short-cut created by this quasi-metallic region with large concentration of Ga.

One way to reduce this effect is using a low acceleration Ga ion beam. Thompson [127] studies the effect of reduction in acceleration energy of the gallium ions. In the case of 5 keV, the concentration of gallium is strongly reduced. In this case the maximum concentration is approximately 2% close to the surface. This concentration decreases exponentially to a maximum depth of 5 nm from the surface. These effects are also shown by several other authors [104, 105].

Assuming that the damaged layer is given by the Debye length $\lambda_D$ one can calculate the doping necessary to screen the electric field of the p-n junction:

$$p = \frac{\varepsilon_0 K_b T}{e^2 \lambda_D^2}$$

The symbols used here are already defined in Table A.2 and Table 0. According to this formula the Ga doping produced by the FIB milling is sufficient to screen completely the p-n junction potential.

In total, FIB preparation produces a new junction between the intact core and the surface, which has a gradient of concentration decreasing exponentially from the surface. This effect will be studied by means of simulation in Section 6.3 of this chapter.

**Platinum deposition**

Other artefacts arise from the Platinum deposited to protect the lamella from milling. In this thesis the Platinum is also used as contact to bias the solar cell. Consequently, it is necessary to know its electrical properties and chemical composition.

---

5The Debye length is defined by $L_D = \sqrt{\varepsilon_0 k_b T/e^2 N_B}$, where $N_B = N_a$ or $N_d$. It determines the penetration length of an electric field in a semiconductor.
Studies conducted by Vila [136] on both electron and ion assisted deposition of Platinum indicate that the Pt film has considerable impurities. The Pt content is found less than 27% of the deposited material (C concentration from the metal-organic precursor: >65%, Ga from the ion beam: 8%). In the same article, resistivity is found much higher than that reported for bulk Pt (0.01 mΩ·cm). It is between 100 and 500 times larger in ion assisted Pt deposition; at electron assisted deposition it is even between 100 to 1000 times larger than that deposited using Ga ions.

These results coincide with results of Thompson [127]. In his work, atom-probe analysis of Pt film deposited by Ga ions shows a composition of approximately 55% atoms of Pt, 20% atoms of C, and 25% atoms of Ga.

All these results show a complex material, with several impurities and a relatively low conductivity.

**Curtaining**

The phenomenon of “Curtaining” is an effect of the milling yield due to local variation of composition or surface topology hence throwing a shadow underneath. These effects produce a thickness variation in the sample. It can be reduced by changing the scanning frequency of the Ga beam [110]. On the other hand, if low energy milling is used (5 keV), curtaining is increased due to the poor optics of the FIB for these energies. As consequence of the curtaining, inhomogeneous stripes parallel to the surface in direction of the milling are produced. An example is given in Figure 6.8. In this case, the curtaining occurs by small particles on the surface of the solar cell.

![Figure 6.8: Holographic phase image showing the effect of curtaining in direction of the arrows. The phase variation perpendicular to the arrows arises from corresponding thickness variation of the lamella.](image)
6.3 Simulating p-n junction potentials in FIB lamellae

To analyse the effect of these artificial layers and their possible effects on the potential, 3D simulations are made by means of the partial differential equation solver program FlexPDE. Here the program is used to solve the non-linear Poisson equation for non-degenerate doped materials (Equation 2.14). The geometry used in the simulation is shown in Figure 6.9.

Figure 6.9: Geometry used in the program FlexPDE to simulate the effect of the preparation. The dimensions are in µm. Only half of the lamella is simulated to reduce calculation time. Left, general view of the geometry showing the different layers of the lamella. Right, cross section made in the plane a-a (z = 2). The numbers indicate: 1. Vacuum region, 2. Highly p-doped region, 3. c-silicon surface.

Two simulations are necessary to assess the effect of the Ga doped layer. The n and p regions in c—silicon have a uniform doping of $1.5 \times 10^{16} \text{cm}^{-3}$ and $3 \times 10^{19} \text{cm}^{-3}$, respectively. The length of the p region is 0.5 µm. Figure 6.9 shows the geometry and shows the p and n-doped regions used in the simulation. It also shows the highly $p^+$-doped region 2. In the first simulation, the potential in the lamella without damage of the surface is calculated (see Figure 6.10 a). It is clear that in cases where there is no layer screening the p-n junction potential, significant stray fields should leak out into vacuum. In the second simulation a highly $p^+$-doped material is added to the surface of the lamella (region 2 of Figure 6.9). The doping of this material is $1 \times 10^{20} \text{cm}^{-3}$ with a relative dielectric constant like silicon. The thickness of this layer is chosen as 50 nm.
CHAPTER 6. TEM SAMPLE PREPARATION FOR IN-SITU BIASING AND ILLUMINATION

Figure 6.10: Comparison of the effect of FIB preparation in top- (left) and side- (right) view. a. Lamella without amorphous layer. b. Effect of a highly $p^+$-doped region on the surface of the lamella. One can clearly see the reduction of the stray field in vacuum and of the effective potential below the surface of the lamella.

This high-doped material has two effects. First, the screening of the p-n junction potential prevents the p-n potential from reaching the vacuum. It is clear that the stray field around the lamella is absent. Second, the highly $p^+$-doped surface reduces the projected p-n junction potential. This could explain the result of reduction of the p-n junction potential measured by means of 2D electron holography [61].

6.4 Optimum thickness

When a hologram is recorded, it is important to have a large phase signal well above noise. The phase signal can be increased by using a large thickness. However, that also reduces the amplitude of the reconstructed wave due to inelastic interaction and large angle scattering. Therefore a trade-off between phase signal and noise can be found at an optimum thickness.

Several authors have proposed different solutions to the thickness optimisation problem. The usual method is to use the signal to noise ratio of the phase image $SNR_\varphi$, which can be written as [73]:

$$\frac{\varphi}{\sigma_\varphi} = SNR_\varphi = \frac{C}{\sqrt{\frac{N_{rec}}{2}}} \sigma V(x,y)t$$

where $\varphi$, $\sigma_\varphi$, $C$ and $N_{rec}$ have been already defined.

Error propagation gives the standard deviation of the potential:

$$\sigma(\varphi, t)_V = \left(\frac{\partial V}{\partial \varphi}\right) \sigma_\varphi$$
Finally the potential signal to noise ratio $SNR_V$ is related to $SNR_\varphi$ by:

$$SNR_V = \frac{V}{\sigma(\varphi, t)_V} = \frac{\left(\frac{\varphi}{\sigma_t}\right)}{(\sigma t)\sigma_\varphi} = SNR_\varphi$$  \hspace{1cm} (6.5)

With the contrast damping by inelastic scattering of the electrons in the material according to

$$C_{inel} = \exp \left[ -\frac{t}{2\lambda_{inel}} \right],$$  \hspace{1cm} (6.6)

the optimum thickness $t_{opt}$, yielding maximum $SNR_\varphi$, i.e,

$$\frac{dSNR}{dt} = 0,$$  \hspace{1cm} (6.7)

reads [102]:

$$t_{opt} = 2 \cdot \lambda_{inel}$$  \hspace{1cm} (6.8)

In this equation all the additional terms, $N_{rec}$, $\sigma$, and $V(x, y)$, are assumed to be independent of thickness. The assumption is that $\lambda_{inel}$ and $V(x, y)$ are constants in the direction of propagation of the electron wave, and therefore no effect of the damage layers is included. The mean free path for inelastic interaction $\lambda_{inel}$ depends on the material. Typical values are between 50 nm and 200 nm, meaning that the optimum sample thickness varies between 100 nm and 400 nm. In the case of silicon $t_{opt} = 200 nm \ [25, 34]$ results.

Lenk [61] proposes the expression:

$$t_{opt} = 2\lambda_{inel} + 2t_o + t_1,$$  \hspace{1cm} (6.9)

which includes the effect of a damage layer $t_o$ and transition $t_1$ layers. This expression is obtained by minimizing the detection limit of the potential $V_{det,lim}$ given by:

$$V_{det,lim} = SNR \sigma_\varphi 0.0073 (t - 2t_o + t_1) \exp (-t/(2\lambda_{inel}))$$ \hspace{1cm} (6.10)

### 6.5 Sample preparation of CIGS solar cells

In CIGS some of the constituent layers are mechanically unstable; they are sensitive to air exposition, fragile or ductile, or sensitive to liquids such as acetone and water, which are used in normal preparation. Therefore, it is necessary to modify the preparation. In the next section the peculiarities for CIGS solar cells preparation are explained.
Preparation procedure

When the preparation procedure described in the last section is applied to CIGS solar cells, part of the surface is peeled off from the glass substrate or micro-scratched during manipulation or transport (Figure 6.11). In these cases, in-situ experiments are completely useless because the performance of the solar cells is destroyed by short-circuits or by electrical discontinuities between the layers.

Figure 6.11: Damage of thin film solar cells during the preparation process

Additionally, the usual glass substrate of this solar cell represents a serious problem for electron holography. The glass is charged when exposed to the electron beam and therefore a strong electric field appears around the sample making it impossible to acquire holograms. For this reason it is necessary to use another substrate. The solution is to use a metallic substrate such as Ti and Steel. To preserve the electrical properties of the solar cells, a dry preparation is chosen. The normal substances used to clean the sample, such as acetone or solvents, are avoided.

Figure 6.12: Cutting a CIGS solar cell with metallic scissors bends the metal and peels off the CIGS solar cell from the metallic substrate. A solution consists of using a Ti substrate; in this case the sample is prepared by breaking the substrate with a sharp blade.

However, by using this substrate, a new problem emerges. The difference of ductility between the substrate and the solar cell means that the solar cell is lifted out from the substrate. The cutting process using scissors or metal cutters tends to bend the metallic
substrate of the solar cell. A solution is to use a sharp razor blade. In this case, the \( Ti \) is broken under pressure, and the solar cell is not peeled off from the substrate. Following this last step, the solar cells are further prepared according to the previously described process.

Another problem comes from the preparation in SEM. It is well known that this solar cell has a tendency to create \( Cu \) precipitates, and the additional energy deposited by the electron beam induces their growth. To avoid this a fluoride gas-assisted etching is used. Figure 6.13 shows images of the process in the SEM and Figure 6.14 shows the final preparation of this solar cell.

Figure 6.13: SEM images of \( Cu \) precipitates. To avoid this an atmosphere of fluoride is used.

Figure 6.14: Final preparation of the \textit{CIGS} solar cell.


6.6 Summary

This chapter analyses the problems and artefacts in the preparation of solar cells for in-situ experiments. A method of preparation based on the idea of Twitchett [128] is used and modified.

It is established that the FIB method causes several problems e.g. Ga implantation and damage of the surface. As a consequence of the Ga implantation, the surface is highly $p^+$-doped. Additionally, the ideal specimen is analysed. This optimum thickness has to include the effect of the damage layer produced during the FIB milling. A secondary effect of this damage layer is the reduction of the detection limit of holographic measurement. As seen in Figure 6.15, the use of low energy $Ga^+$ ions during the FIB milling improves the detection limit.

![Figure 6.15: Effect on the detection limit of the Ga energy during the FIB milling. The reduction of the damage layer reduces damping of the amplitude and therefore the detection limit of the potential is improved.](image)

Finally, some of the problems of preparation in other kinds of solar cells are discussed, showing that each type of solar cell must be prepared according to the specific mechanical and chemical properties.

The results of this chapter are fundamental for the interpretation of the results in the next chapter.
Chapter 7

Measurement of built-in potential under in-situ illumination and bias of solar cells

7.1 Introduction

This chapter focuses on the application of the in-situ methodology for measuring built-in potentials in two solar cell types: mono-crystalline silicon (c-silicon) and CIGS.

The samples for this study are supplied by the following institutions specialised in fabrication and characterisation of solar cells: the c-silicon solar cells by the “Fraunhofer Institut ISE” in Freiburg and the CIGS solar cells by the “Helmholtz Institut” in Berlin.

As previously mentioned the c-silicon solar cell is chosen because this material offers well established results in the measurement of p-n junction potentials by electron holography [9, 63, 128, 143]. Studying these solar cells determines the reliability of the method and helps to identify problems.

The chapter begins with c-silicon solar cells. A description of specific characteristics is presented. Additionally the results obtained under biasing and illumination are shown and compared with theoretical models and simulations.

Subsequently, CIGS solar cells are investigated, showing the influence of the grain structure on the projected potential. Also in these solar cells calculations of the electron-hole pair generation under electron illumination and of mean inner potential ($V_{MIP}$) and inelastic mean free path ($\lambda_{inel}$) for the different layers are specially included. These data are not yet reported in the literature.

The chapter ends with a recompilation of the results and a number of possible proposals to remove problems currently encountered.
7.2 Silicon solar cells

A high efficiency $c -$ silicon solar cell, basically a p-n junction like the one shown in Figure 7.1, has an efficiency close to 20%. Currently these devices incorporate several additional improvements to increase their efficiency, such as pyramidally textured surface, additional oxide surfaces to reduce superficial recombination processes, high doping close to the metallic contacts to reduce the Schottky effect, and intentional doping profiles to increase the built-in field for optimal charge separation (Figure 7.1).

![Figure 7.1: Scheme of a modern silicon solar cell (image adapted from [94]). This solar cell includes some special characteristics to improve the efficiency: pyramidally textured surface, $p^+$ doping close to the rear contact, and top and bottom passivation layers to reduce the effects of recombination at the surfaces. With these solar cells efficiencies close to 20% are achieved.](image)

7.2.1 Sample

In this thesis, two different lamellae, lamella A and lamella B, cut from the same solar cells wafer, are studied$^1$. The main characteristics and doping concentrations of this wafer containing the solar cell are described in Table 7.1. The solar cell studied has the same structure as the solar cell shown in Figure 7.1.

<table>
<thead>
<tr>
<th>Wafer doping</th>
<th>Top doping</th>
<th>Depth of p-n junction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p , 1.5 \times 10^{16} \text{cm}^{-3}$</td>
<td>$n , 1.6 \times 10^{20} \text{cm}^{-3}$</td>
<td>$0.3 \mu\text{m}$</td>
</tr>
</tbody>
</table>

Table 7.1: Doping characteristics of the $c -$ silicon solar cell studied. The p doping is established with boron and the n doping with phosphorous. The solar cell has the same characteristics as those displayed in Figure 7.1.

Each lamella (lamella A and lamella B) is prepared from a $c -$ silicon solar cell. The solar cell is fabricated on a wafer $p$ doped with a boron concentration of $1.5 \times 10^{16} \text{cm}^{-3}$. It is

---

$^1$The solar cells are fabricated on a wafer of several cm of radius, in this case it is 10 cm.
structured with a pyramidal surface created by means of chemical etching with \( \text{NaOH} \) on the plane \(<100>\) (Figure 7.2 b). This pyramids have a mean size of 10\(\mu m\), which are used to increase light absorption.

After the etching of the pyramidal structure, the high concentration \( n \) doping by phosphorous implantation is made. This doping concentration is measured by means of the superficial resistivity \((120\Omega \text{cm}^{-2})\) resulting from p-n junction 300 nm below the pyramidal textured surface.

On top of this pyramidal structure a layer of \( SiN:H \) is deposited by Plasma-Enhanced Chemical Vapour Deposition (PECVD) (Figure 7.2, right). This layer reduces the number of defects in the surface, serves as an antireflection coating and protects the solar cell against diffusion of other materials, mainly alkaline occurring in the next steps of the solar cell production [48]. Finally, the \( Al \) contacts are screen-printed on the \( c-Si \) surface directly. Figure 7.2 shows the complete structure and a detail below the \( Al \) layer.

Due to the impossibility of measuring the doping because of the pyramids, the doping profile is determined from the superficial conductivity and the expected depth of the p-n junction. The profile is fitted by an \( \text{erfc} \)-function (Figure 7.3). From this profile the potential through the p-n junction is calculated by means of the program Afors-HET. The result is shown in Figure 7.3.

The calculation shows that the p-n junction potential drops approximately 1 V across a
depletion region almost 800 nm wide. This potential distribution is calculated without considering the effect of the SiN:H layer.

7.2.2 Biasing

The first experiment described is a biasing experiment made on lamella A (see Figure 7.4). In this case the platinum of the lamella is not directly contacted with the top contact. The distance from the platinum used to protect the lamella to the contact is approx. 500 µm. The lamella is prepared according to the procedure explained in Chapter 6, including the low energy polishing. In Figure 7.4 SEM and TEM images of the lamella are shown.

The experiment is made by varying the biasing voltage in the following sequence: 0.0 V, 0.5 V, 1.0 V, -1.0 V, -0.5 V and 0.0 V. For each voltage 6 holograms are taken, which are subsequently evaluated according to the procedure described in Chapter 4.
Figure 7.4: Sample preparation of the lamella used for biasing. Images a and b show the position of the lamella in the sample. Here, the platinum is not in direct contact with the external contact. c and d show SEM and TEM images of the lamella. The pyramidal structure of the solar cell is clearly visible. The TEM image d shows position and field of view of the acquired holograms (approx. 1 \( \mu \text{m}^2 \)).

Image 7.5 (a) shows the biasing polarity applied to the solar cell. In this work a positive biasing potential is assumed as forward biasing. In the same figure (b), the J-V curve acquired during the TEM in-situ experiment reveals the typical behaviour of a diode. However, the current density is much smaller compared with a measurement made on the same solar cell but using a larger area of 1 cm\(^2\) without TEM preparation. The reduction of current density indicates that the sample preparation has a strong influence in that it reduces the amount of carriers contributing to the total current. It is due to the recombination at the lateral surfaces. The effect of surface recombination can be simulated by adding defects on the \( p \)-doped region. It is made by means of the program Afors-HET by increasing the carrier density on a defect localized in the centre of the band gap. Figure 7.5 (c) compares the curve J-V acquired during the in-situ experiment with the simulations. The effect of reduction of current density with increasing of defect carrier density is evident.
CHAPTER 7. MEASUREMENT OF BUILT-IN POTENTIAL UNDER IN-SITU ILLUMINATION AND BIAS OF SOLAR CELLS

Figure 7.5: a: Biasing polarity of the solar cells, positive values are taken as forward biasing. b: J-V curves before and after the TEM sample preparation, the current density is strongly reduced. c: Comparison of bias measurements with simulation. In the simulation the only parameter changed is the density of defects in the p-doped region. The reduced size of the TEM sample increases the probability of recombination in the lateral surfaces resulting in a decrease of the current density.

Figure 7.6: Phase image as colour map (right) showing the geometry of the lamella where the potential is measured. In the profiles along the arrows (1,2) the effect of biasing on phase is measured. With forward biasing the phase image tends to flatten indicating that the p-n junction potential is reduced. Otherwise under reverse biasing (negative potentials) the phase decreases. It indicates a potential increase in the n-doped layer with respect to the p-doped region.
Figure 7.6 shows the result of the biasing experiment in the reconstructed phase image. A clear variation in the phase correlated with the biasing potential is evident. Under forward biasing (positive potentials) the phase signal shifts up. It moves in the opposite direction under reverse biasing (negative potentials). This behaviour agrees with the theory of biased p-n junctions (Section 4.3).

In order to investigate, whether or not the images are acquired under kinematic conditions, the product between mean inner potential and the inelastic mean free path ($V_{\text{MIP}}\lambda_{\text{inel}}$) is calculated. As previously mentioned, if the only potential measured is the $V_{\text{MIP}}$, i.e. the object is in kinematic conditions, the product $V_{\text{MIP}}\lambda_{\text{inel}}$ must be constant. Indeed, the calculation in Figure 7.7 shows that, at 1.0 V forward biasing, the product of $V_{\text{MIP}}$ and $\lambda_{\text{inel}}$ is constant (Figure 7.7 bottom left). Thus, the measurement can be considered to be conducted under kinematic conditions. This is further supported by the invariance of the amplitude images under different biasing conditions.

Figure 7.7: Images showing the product $V_{\text{MIP}}\lambda_{\text{inel}}$ at different biasing condition in a $c-Si$ solar cell. Profiles (1,2) along the boxes in the direction of the arrows. At 1.0 V forward biasing the product is constant. On the other hand, with increasing reverse bias (-0.5 V and -1.0 V) the product is not constant. This result indicates that biasing produces local changes in the product $V_{\text{MIP}}\lambda_{\text{inel}}$.

On the other hand, under reverse biasing (negative potentials) the built-in potential is increased. In this condition, the product $V_{\text{MIP}}\lambda_{\text{inel}}$ is not constant (Figure 7.7).

At 1.0 V forward biasing the product $V_{\text{MIP}}\lambda_{\text{inel}}$ gives a value of $1130 \pm 30$ $\text{V nm}$. The thickness of the lamella is calculated from an image at the border of the lamella, acquired by SEM during the FIB milling. The thickness (Figure 7.8 right) measured is approximately 190nm. Using this value and calculating $\lambda_{\text{inel}}$ from:

$$\lambda_{\text{inel}} = \frac{t}{2\ln(A_n)}$$

(7.1)
\( \lambda_{inel} = 100 \text{ nm} \) is obtained, which agrees well with values reported in the literature (7.2).

<table>
<thead>
<tr>
<th>Reference</th>
<th>( \lambda_{inel} ) (nm)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wolf [147]</td>
<td>100</td>
<td>Electron holographic tomography</td>
</tr>
<tr>
<td>Formánek [25]</td>
<td>100</td>
<td>Electron holography of wedges</td>
</tr>
<tr>
<td>Chou and Libera [18]</td>
<td>88.6 ± 6.9</td>
<td>Electron holography of amorphous si-nanospheres</td>
</tr>
</tbody>
</table>

Table 7.2: Reported values of \( \lambda_{inel} \). In this thesis the value of 100 nm is found in good agreement with the ones measured by Wolf and Formánek. It is used for determination of the object thickness.

From the SEM and holography images it is clear that the sample does not show a uniform thickness. The lamella is getting thinner towards the top border (original surface of the solar cell), which coincides with the milling direction. (profile 2 Figure 7.8). Besides, in the direction perpendicular to the sample, a small variation of the thickness is also observable (profile 1 same figure).

The junctions between \( c - Si/SiN : H \) and \( SiN : H/Pt \) cannot be imaged edge-on due to the pyramidal surface. In the projection of the interface, there is an inter-mixing of both materials. For this reason the thickness calculated from amplitudes there is not correct. It can be seen in the equation for the thickness determination (Equation 4.1).

\[
t = -2\lambda_{inel} \ln (A_n)
\] (7.2)

Figure 7.8: Right: High resolution SEM image of the border of the lamella, a distance of 148.8 nm is measured. Due to the lamella orientation (projection angle \( \alpha \approx 50^\circ \)) the thickness is approximately 190 nm. Left: Thickness map from the amplitude image calculated using the value of \( \lambda_{inel} = 100 \text{ nm} \). Centre: line profiles in direction of the arrows 1 and 2 showing the thickness distribution of the lamella. The thickness reduces in direction of the platinum uniformly around a mean value close to 180 nm (profile 2).
Each material has its own mean free path, and hence the thickness in regions with different materials cannot be determined from Equation 4.1. Instead, the thickness at the interface is extrapolated from the silicon region. From the product $V_{\text{MIP}} \lambda_{\text{inel}} = 1130 \text{ Vnm}$ with $\lambda_{\text{inel}} = 100 \text{ nm}$ the value of $V_{\text{MIP}} = 11.3 \text{ V}$ is calculated.

For comparison of the value of $V_{\text{MIP}}$ measured here with values found in literature, Table 7.3 shows values of $V_{\text{MIP}}$ for silicon measured experimentally or calculated theoretically. A difficulty for the comparison arises from the diverse experimental measurement conditions, i.e. microscope used, sample geometry (thin film, wedge, spheres, etc.) and sample preparation method (FIB, cleaving, polishing, etc.). The value obtained in this thesis agrees with the experimental result of Wolf [147] and Rau et al. [101].

<table>
<thead>
<tr>
<th>Reference</th>
<th>MIP (V)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weickenmeier et al. [144]</td>
<td>13.8</td>
<td>Theoretic - Independent atom potential</td>
</tr>
<tr>
<td>Wolf [147]</td>
<td>11.4</td>
<td>Experimental - electron holographic tomography</td>
</tr>
<tr>
<td>Wolf [147]</td>
<td>13.4</td>
<td>Experimental - electron holographic tomography</td>
</tr>
<tr>
<td>Kruse et al. [58]</td>
<td>12.52 ± 0.7</td>
<td>Experimental - Electron holography</td>
</tr>
<tr>
<td>Kruse et al. [58]</td>
<td>12.57</td>
<td>Theoretic - Density Functional Theory (DFT)</td>
</tr>
<tr>
<td>Rau et al. [101]</td>
<td>11.9 ± 0.7</td>
<td>Experimental - electron holography</td>
</tr>
<tr>
<td>Kim et al. [54]</td>
<td>12.21 ± 0.02</td>
<td>Theoretic - DFT</td>
</tr>
</tbody>
</table>

Table 7.3: Different values of $V_{\text{MIP}}$ reported for $c - \text{silicon}$ in the literature. Differences between the results come from the diverse experimental conditions or varying assumptions used in the theoretic calculations.

This data dispersion indicates the necessity of controlling carefully the characteristics of the sample and the experimental conditions.

Knowing that the sample is under kinematic conditions one can calculate the potential distribution from phase and thickness. Now, because only the effect of biasing is of interest, the difference between potential images with respect to the non-biased image is calculated according to:

$$
\Delta V = V - V^\circ = -\frac{\varphi_{pn} - \varphi_{pn}^\circ}{2\sigma \ln(A_n)}
$$

Here $V$ and $V^\circ$ are the projected potentials with and without biasing. The results are shown in Figure 7.9.

The biasing effect follows the model shown in Section 2.3. The model indicates that the built-in potential is modified by the biasing potential. Forward biasing reduces the p-n
CHAPTER 7. MEASUREMENT OF BUILT-IN POTENTIAL UNDER IN-SITU ILLUMINATION AND BIAS OF SOLAR CELLS

junction potential. Consequently, these potentials in the profile graphics appear negative. On the other hand, reverse biasing increases the potential, therefore the potential difference with respect to the original p-n junction potential is positive.

Figure 7.9: Biasing effect on the potential distribution. Left, comparison of the profiles along the boxes in the direction of the arrows in the images. Forward biasing produces negative potentials with respect to the reference due to the reduction of the p-n junction potential. The minimum potential difference measured under forward biasing is -0.6 volts. This value corresponds to the potential drop in silicon. On the other hand, reverse biasing produces a positive potential because the potential is increased by the potential applied.

An interesting effect occurs under forward biasing. Theoretically the potential drop is limited by the p-n junction potential, which corresponds in these samples to 0.92 V. However, the potential is limited to approximately 0.6 V, that is 0.3 V smaller. This difference is similar in magnitude to the reduction of the p-n junction by the electron illumination reported by Formánek [25].

Additionally the potential in the SiN : H region is found to be larger than the applied voltage. This effect can be explained by the positive charging of the SiN : H layer under the electron beam. This induced charging produces an increase of the potential.

7.2.3 Illumination

The lamella A is not used for the illumination in-situ experiment because of the unwanted charging effect of the SiN : H layer. For this reason a new lamella (lamella B) was
This new lamella is constructed from the same solar cell wafer. The position of the lamella is directly at the contacting Al-fingers (Figure 7.10). Note that the Al-finger is removed before preparation of the lamella.

Figure 7.10: Preparation of the lamella B used for illumination. a: overview of the sample. b: region where the lamella is made. c: lamella with the window for holography. This lamella was soft polished with low energy $Ga^+$ ions (5 keV). d: measurement of lamella thickness. The projection angle here is 70 degrees; therefore the real thickness is approx. 440nm.

This lamella is made thicker to lower the effect of recombination at the lamella surface, which would reduce the open circuit voltage. According to the SEM image, this thickness is close to 440 nm (Figure 7.10 d). Calculation of the lamella thickness from amplitude images gives the same magnitude (Figure 7.11).
CHAPTER 7. MEASUREMENT OF BUILT-IN POTENTIAL UNDER IN-SITU ILLUMINATION AND BIAS OF SOLAR CELLS

Figure 7.11: Left: thickness map calculated from amplitude image. Right: Line profiles along the arrows a and b, respectively. The profile a shows a thickness variation between 400 and 450 nm \( \pm 10 \) nm. Because of the curtaining effect of the FIB preparation, the lamella does not show a uniform thickness along direction b (profile b).

The calculation of thickness was performed using 16 amplitude images yielding a standard deviation close to 2.5\%, corresponding approximately to \( \pm 10 \) nm (Figure 7.11 profile a). The lamella is illuminated with different laser intensities. The illumination conditions applied are indicated in Table 7.4.

<table>
<thead>
<tr>
<th>Excitation voltage (V)</th>
<th>Total illumination power (mW)</th>
<th>Photon flux density at the sample ( photons/(cm^2 ) s)</th>
<th>Equivalent suns</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0 V</td>
<td>1000</td>
<td>( 3.8 \times 10^{19} )</td>
<td>131.0</td>
</tr>
<tr>
<td>2.0 V</td>
<td>165</td>
<td>( 6.2 \times 10^{18} )</td>
<td>21.6</td>
</tr>
<tr>
<td>1.5 V</td>
<td>100</td>
<td>( 3.8 \times 10^{18} )</td>
<td>13.1</td>
</tr>
<tr>
<td>1.4 V</td>
<td>60</td>
<td>( 2.3 \times 10^{18} )</td>
<td>7.9</td>
</tr>
<tr>
<td>1.3 V</td>
<td>40</td>
<td>( 1.5 \times 10^{18} )</td>
<td>5.2</td>
</tr>
<tr>
<td>0.0 V</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7.4: Illumination applied to the sample in the in-situ illumination experiment.

The reconstructed phases under the different illumination conditions are shown in Figure 7.12.
7.2. SILICON SOLAR CELLS

Figure 7.12: Left: reconstructed phases under illumination. Right: line profiles along the arrows in the boxes of the phase images. The phase increases with increasing illumination intensity. The maximum phase difference between n and p doped regions is 2.7 rad. Beyond 165 mW the phase does not increase further, even if the intensity of the laser is 1000 mW.

In these images the phase is shifted with respect to a reference in the sample, which is chosen as 0 rad in the p-region. From phase and thickness, the potential variation is calculated (Figure 7.13) by means of Equation 3.42.

Figure 7.13: Potential variation in the lamella under increasing laser illumination intensity. The illumination unit is given in equivalent suns.

Figure 7.13 displays 3 interesting aspects:

1. The potential without illumination does not correspond to the full p-n junction potential (0.92 V), the value measured (0.2 V) can indicate that the larger thickness of the lamella effectively reduces the effect of the recombination process. Consequently, already the creation of electron-hole pairs under the electron illumination produces a built-in potential similar to light illumination.

2. The reduction of the potential close to the platinum is produced by the Schottky contact between silicon and platinum (Figure 7.14). According to Figure 7.14, the contact with the platinum bends the band structure of the n–doped silicon, producing a reduction of the potential.
CHAPTER 7. MEASUREMENT OF BUILT-IN POTENTIAL UNDER IN-SITU ILLUMINATION AND BIAS OF SOLAR CELLS

Figure 7.14: Contact between a metal with a larger work function $f_m$ than a $n-$doped semiconductor with work function $f_s$. The electrons flow from the semiconductor into the metal because of the lower energy of the Fermi level. This creates a depletion region in the semiconductor bending the band structure up until equilibrium is reached levelling out the Fermi levels of both materials (centre). The length of the band bending depends on the built-in voltage hence on the doping of the semiconductor. Additionally, the large amount of electron-hole pairs created by the illumination with the electron beam reduces the Schottky potential (right).

The Schottky barrier with the platinum has a height of 1.01 eV [99] without considering the quality of the platinum deposited using FIB. Figure 7.14 shows the modulation of the band structure with Pt-Si Schottky effect, and electron illumination. Finally, the potential measured in the microscope, without light illumination, has the shape measured Figure 7.13. The effects of electron illumination and Schottky barrier are simulated by means of the program SCAPS 2.8.06.. The result shown in Figure 7.15 correlates well with the measurement by electron holography, except that the width of the Schottky barrier measured is larger than predicted. Effect not yet explained.

3. The potential close to the platinum increases with growing laser intensity, this growth is approximately limited to 1.0 V, which corresponds to the complete p-n junction potential. The potential growth with increasing illumination can be explained by two different phenomena occurring simultaneously during illumination with the laser: The sample is heated and therefore the superficial conductivity is increased under illumination. The temperature growth increases in turn the recombination probability, which also reduces the open circuit voltage $V_{OC}$ and the projected potential increases.

To show the effect of temperature, the solar cells potential is calculated by means of the program SCAPS (Figure 7.16). The simulation shows the same behaviour found experimentally, namely the increase of the built-in potential in the solar cell under illumination.
7.2. SILICON SOLAR CELLS

Figure 7.15: Simulation of the effect of electron illumination on the potential. In this simulation 1, 10 and 100 AM1.5 sun equivalent flux densities are used. According to the simulation with an illumination of 100 suns the potential is reduced to 0.4 V being close to the potential measured.

Figure 7.16: Effect of the temperature on the built-in potential of the solar cells. The built in potential increases with the temperature.

It is also interesting to note that the potential, with an illumination larger than 25.6 suns (165 mW), corresponds to the full p-n junction potential, i.e. the amorphous layer shows no influence in the measurement. This effect, also observed by McCartney et al. [82], could be due to the low energy Ga ions used in the preparation.
CHAPTER 7. MEASUREMENT OF BUILT-IN POTENTIAL UNDER IN-SITU ILLUMINATION AND BIAS OF SOLAR CELLS

7.3 CIGS solar cells

During measurement of the potentials in CIGS under illumination and biasing some artefacts could not be avoided; one of the most severe is that under in-situ illumination the dynamic conditions during the experiment change because of the unwanted heating by the laser beam. It violates one of the “sine qua non” conditions necessary to interpret the results of the in-situ experiment in terms of functional potentials.

As shown in Chapter 6, the CIGS solar cells present problems starting with the moment of the preparation for the in-situ experiment, because of the damage of the surface, peeling off and possible short circuiting, which impede the experiments of illumination and biasing.

In this section the calculation of the generation rate produced by the electron illumination in each layer of the CIGS is made, measurements of \( V_{MIP} \) and \( \lambda_{inel} \) are also included. Images of biasing are presented and analysed showing the problem of measuring the potential; also possible solutions to the measurement of the potential are presented.

7.3.1 Sample

These solar cells are also based on p-n junctions, but to avoid contact problems between the CIGS and the ZnO, an additional layer of CdSe is used as a buffer layer.

Figure 7.17: TEM micrograph of a CIGS solar cell in cross section, showing the composition by the different layers.

The structure of these solar cells from the substrate to the surface is given by the sequence of layers: Mo/Cu\((\text{In}_{x}, \text{Ga}_{1-x})\)Se\(_2\)/CdSe/ZnO. The molybdenum, with a thickness of 1\(\mu\)m as the back electric contact, is deposited by sputtering and shows a columnar growth. \( \text{Cu} \left(\text{In}_{x}, \text{Ga}_{1-x}\right)\text{Se}_2 \) is a polycrystalline material with a grain size variation between tens of nanometres and micrometers controlled by the parameters during the preparation and by the \( \text{In}/\text{Ga} \) ratio [1, 7]; this layer is the absorbent layer and is prepared typically with a thickness of 1\(\mu\)m. It is \( p \)-doped and the doping concentration depends on the \( \text{Cu}/\text{In} \)
ratio; in the best solar cells the doping concentration is close to $10^{17}\text{cm}^{-3}$; in the sample studied, here the thickness of this layer is 1.8 µm. CdSe is, as already mentioned, a buffer layer. However, because of the toxicity of Cd, several other materials are tested. The layer usually shows a thickness between 20 nm and 50 nm and the doping type is $n$ with a concentration of carriers of $1 \times 10^{15}\text{cm}^{-3}$. ZnO has a high $n$ doping and allows an Ohmic contact with the metallic grid deposited on the top to collect the electrons. This material must have a large forbidden band gap in order to be transparent to the photons and consequently allows the photons to be trapped in the absorbent material. The thickness of the layer is close to 1µm. A list of the parameters of the different layers is presented in Appendix A. Nowadays, these solar cells are amongst the most investigated because of their formidable efficiency close to 20%. However, there are several open questions concerning how the high performance is related to the role of grain boundaries, gradient of $Ga$ and concentration of $Cu$. Some models of the grain boundary potentials have been proposed [37] as well as some schemes of the device band structure [51].

Several samples of CIGS have been studied in this thesis, most of them prepared on a substrate of glass. However the main problem with this substrate is charging induced under the electron beam. This charging produces such strong stray fields that no holograms could be acquired. For this reason a sample prepared on a substrate of Ti is finally used. This solar cell is prepared for the in-situ experiment following the procedure discussed in Section 6.5. Figure 7.18 shows the lamella with an approximate thickness of 190 nm (Figure 7.18 d). Because of the larger atomic masses of the atoms in CIGS the mean free path is smaller in consequence the sample must be thinner.

As already mentioned in the sample preparation section (6.5), this lamella is prepared during the FIB milling within an atmosphere of fluoride to avoid the formation of precipitates of $Cu$.

### 7.3.2 Carriers generation by the electron beam

Similarly to silicon, the beam electrons produce electron-hole pairs in CIGS. For their calculation a similar procedure as for $c-silicon$ is used (Section 4.4). Applying the same electron illumination:

$$J_{bc} = 2.8 \times 10^{-3} \frac{\text{A}}{\text{cm}^2} = 175 \frac{e^-}{\text{s} \cdot \text{nm}^2},$$

(7.4)

together with the calculation of the stopping power $|\frac{dE}{dx}|$, the calculated generation rate of electron-hole pairs 4.10:

$$G_e = G_h = 0.5 \cdot \frac{j_{bc} |\frac{dE}{dx}|}{e E_{e-h}}$$

(7.5)

in the different layers of the CIGS solar cell is shown in Table 7.5. The value of $E_{e-h}$ is assumed as 2 times the band gap.
CHAPTER 7. MEASUREMENT OF BUILT-IN POTENTIAL UNDER IN-SITU ILLUMINATION AND BIAS OF SOLAR CELLS

Figure 7.18: SEM images showing the preparation of the CIGS solar cell sample. a: overview of the solar cell, some regions of the lamella are peeled off during the preparation. b: Image of the lamella, the different layers of the solar cell are indicated. c: overview of the lamella. d: Close-up of the lamella showing the thickness, (close to 190 nm after correcting projection effects).

| Layer | Generation rate $1/(\text{cm}^3\text{s})$ | $|\frac{dE}{dx}|$ eV/nm |
|-------|------------------------------------------|---------------------|
| CIGS  | $2.12 \times 10^{24}$                    | 0.174               |
| CdS   | $1.55 \times 10^{22}$                    | 0.177               |
| ZnO   | $1.42 \times 10^{22}$                    | 0.197               |

Table 7.5: Generation rate of electron hole pairs by the electron beam in the layers of a CIGS solar cell. The values of $|\frac{dE}{dx}|$ are calculated by means of the program “ESTAR” of the National Institute of Standards and Technology [93]. The generation rate for CIGS is two orders of magnitude larger than the generation rate for silicon. And because of the low doping of the CIGS and CdS, the electron illumination has a larger effect in the p-n junction potential measurement.

7.3.3 Calculation of $V_{MIP}$ and $\lambda_{inel}$

Figure 7.19 shows amplitude, phase and $V_{MIP}\lambda_{inel}$ images.
Figure 7.19: Images of amplitude (left), phase (centre) and the product $V_{MIP}\lambda_{inel}$ (right). The profiles are measured along the boxes 1 and 2 along the arrows shown in the left image. The phase image is unwrapped, but due to the abrupt end of the sample to the vacuum, the automatic unwrapping algorithm fails. Therefore, the absolute value was calculated knowing the approximate thickness from SEM and an approximate value for $V_{MIP} = 15$ V. The value of $\lambda_{inel} = 45$ nm is calculated for that thickness. A value for the product $V_{MIP}\lambda_{inel} = 660$ V nm is measured, resulting in a value for $V_{MIP}$=14.4 V for CIGS.

A product of $V_{MIP}\lambda_{inel} = 660$ V nm in CIGS is found. From this, $\lambda_{inel} = 45$ nm and $V_{MIP} = 14.4$ V are obtained. For ZnO the values measured are: $V_{MIP} = 18.6$ V and $\lambda_{inel} = 32$ nm. The layer of CdS shows strong dynamic contrast, unavoidable due to the small grain sizes. This fact makes it impossible to interpret the amplitude image in terms of thickness and therefore also the phase images in terms of potential. Therefore, no values are given.

7.3.4 Biasing

The biasing is made by varying the voltage in the following sequence: 0.0 V, 0.2 V, 0.4 V, 0.6 V, 0.8V, 1.0 V, 0.0 V, -0.2 V, -0.4 V, -0.6 V, -0.8 V and -1.0 V. Figure 7.20 shows the curve J-V acquired before and after the preparation. The preparation produces a small parallel resistance. Similarly to the $c – silicon$ solar cell the recombination increases for CIGS solar cells. As result the current density is reduced and simultaneously the J-V curve is flattened showing a linear tendency.
Figure 7.20: Current density vs. voltage curve of the CIGS solar cell before and after preparation; the preparation destroys the diode characteristic of the solar cell.

The biasing polarity applied to the solar cell is the same as that applied to $c$–silicon solar cells. With a positive biasing potential a forward biasing is produced. Figure 7.21 shows the effect of biasing on the amplitude. The main problem here is the change of the dynamic condition with each biasing voltage applied, i.e. the sample reacts dynamically on the biasing voltage. This effect is produced by stress between the grains; the grain bending and tilt change during the experiment produce unavoidable contour lines, which are also very sensitive to the electron beam tilting. Also, the phase of the electron wave is changed, which may hide the comparably small phase changes from potential variations.
Figure 7.21: Images showing the biasing effect on amplitude images. The dynamic conditions change during the experiment; the lines are used to visualise the movement of the contour lines indicated by the arrows.

Figure 7.22 shows the biasing effect on phase differences related to the unbiased one (0.0 V). From the images it is clear that the phase cannot be correlated with the potential because of the strong dynamic effects. One can only say that the phase is changing with the voltage applied. With forward biasing the phase is positive, and negative with reverse biasing. However, the positive phase at -0.2 V cannot be understood with the theory. This is an indication of charging effects. The electron beam produces a positive charging of the platinum by scattering of secondary electrons, and, because of the biasing, the p-n junction is increased; the charge accumulates in the platinum producing a local electric field. An indication of this stray field around the sample is the phase signal in vacuum regions. The measurements show indeed that at CIGS the phase in vacuum is not constant, indicating the presence of fields around the lamella.
CHAPTER 7. MEASUREMENT OF BUILT-IN POTENTIAL UNDER IN-SITU ILLUMINATION AND BIAS OF SOLAR CELLS

Figure 7.22: Subtraction of phase images. Here the image with a biasing potential of 0.0 V is selected as reference. Due to the strong dynamic conditions, the subtraction of the phases does not represent the potentials in the solar cells. However, there is a correlation between the applied biasing voltage and the variation of the phase.

7.3.5 Illumination

Unfortunately, under illumination the CIGS lamella solar cell is heated, which provokes a variation of the orientation of the sample, with respect to the electron beam. The results are not worth showing nor further discussing.

7.4 Summary

This chapter presents the results of applying in-situ illumination and biasing in $c-\text{silicon}$ and CIGS solar cells for the measurement of the potentials. Here the artefacts summarised in the chapters 3, 4 and 6 produce severe difficulties of interpretation. As consequence, the interpretation of the findings in terms of the functional potentials is very demanding.

For example, the J-V curves acquired during the biasing of the $c-\text{silicon}$ and CIGS samples indicate that the size of the sample plays an important role. In the TEM solar cell
samples there are two competitive effects: the recombination and the generation rate. The TEM fabrication of the sample introduces defect-rich lateral surfaces, which produce a large charge recombination. This effect is increased by the damage introduced by the FIB milling on the lamella surfaces. This recombination process reduces the built-in potential $V_{OC}$ created under illumination, whether by electrons or by light. As a result the potential measured is closer to the original one of the p-n junction produced by doping. A way to reduce the effect of the recombination can be increasing the sample thickness. Then the travelling distance until recombination is increased. A second possible solution is to use a surface treatment like fluorisation, which reduces recombination. A difficulty of this second procedure is transport and installation of the sample in the holder. In the first case, the sample needs to be protected from oxidation carrying it in an adequate atmosphere, liquid or gaseous, which, however, is not compatible with the preparation method and holder.

Another problem shown here and not yet resolved, is the measurement of potential in poly-crystalline solar cells. This type of solar cells shows dynamic conditions temporally changing. Also an adequate preparation less destructive is necessary. The sample must be reduced in size without infringing so much damage. Here an option could be laser cutting. For the lamella preparation, low energy FIB milling ($\sim 1$ kV Ga ions) has shown extraordinary results in the reduction of the surface damage. This low energy preparation has been also used in CIGS solar cells [107] showing that this low energy does not give rise to precipitation of Cu in the surface. The use of fluoride can be abandoned.

To realise the measurement of potentials in poly-crystalline solar cells, a precise control of the sample orientation is necessary. This control is improved by the use of Cs corrected microscopes, because the blurring of the image produced by the aberrations of the Lorentz lens is reduced and a better control of the sample orientation is possible.

Finally, values for $V_{MIP}$ and $\lambda_{inel}$ for the main of the materials studied were estimated:

<table>
<thead>
<tr>
<th>Material</th>
<th>$V_{MIP}$</th>
<th>$\lambda_{inel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c-\text{Si}$</td>
<td>11.3</td>
<td>100</td>
</tr>
<tr>
<td>CIGS</td>
<td>14.4</td>
<td>45</td>
</tr>
<tr>
<td>ZnO</td>
<td>18.6</td>
<td>32</td>
</tr>
</tbody>
</table>

The value for CdS could not be calculated because of the strong dynamic conditions showing up in this layer.
Chapter 8

Summary

This thesis contributes to reveal, to identify and to quantify the influences affecting the measurement of potentials in solar cells by electron holography and hence establishes the fundamental elements for the possible application to solar cells questions. To obtain quantitative measurements, the influence of the most critical points was analysed in detail, for example:

- Physical principle of a solar cell and the main factors affecting its efficiency.
- Electron-object interaction.
- Electron wave interference, which is the basic of the electron holographic technique.
- Reconstruction of phase and amplitude from the hologram acquired.
- Measurement of potential from the amplitude and phase.
- Noise and the relation with hologram acquisition.
- Sample preparation methodology for adapted geometry, at optimal thickness of the lamellae.
- Details of the holder developed and employed.

The phase of the electron wave is affected by the interaction with the electromagnetic potential in the object and it can be interpreted in terms of projected potential only if the sample is imaged in kinematic conditions. But, this situation is mainly valid in normal electron holographic method, if the object studied is easily orientable, e.g. at mono-crystalline or amorphous materials. However, measuring potentials in materials, which not always can fully be oriented kinematically, like the polycrystalline structure of the CIGS solar cells, is not easily possible. To solve this problem, a method using in-situ stimuli, to separate the information between the inner potentials and the functional potential, was proposed. This method compares the holograms acquired under change of in-situ stimuli of the object, namely illumination and biasing. For the application, a holder
allowing illumination and biasing of the solar cell at recording electron holograms was designed, constructed, characterised and employed. At the same time, a suitable sample preparation by means of FIB milling was devised. This method was finally applied to two kinds of solar cells: c- silicon, as material for the characterisation of the technique, and a CIGS solar cell as a possible target device. For that, two lamellae of c-silicon and a lamella of CIGS solar cells were used.

Aspects influencing the method like electron-hole pair generation caused by electron beam illumination, signal to noise ratio problem, and surface recombination were analysed and determined in detail. The calculation of the electron-hole pair generation by electron illumination shows that it must produce an open circuit voltage larger than the one produced by 1 sun standard illumination. In consequence, the potentials measured by electron holography should be smaller. This suggests the use of low electron illumination. However, it is clear that a compromise between low electron illumination and larger illumination time must be found for a sufficient count number. It was shown that the larger the count number in the detector the larger the precision in the measurement is.

On the other hand, another competitive effect, i.e. the recombination, plays a decisive role. A solar cell illuminated tends to create a built-in potential $V_{OC}$, which reduces the p-n junction potential. But because of the damage introduced in the surface by TEM preparation and FIB milling, the number of recombination centres increases hence reduces the amount of minority carriers. Thus the $V_{OC}$ is reduced or compensated.

Additionally, it is established that the FIB milling implants Ga ions damaging the surface and doping it highly $p^+$. Also it was shown that the CIGS solar cells suffer from Cu precipitation when prepared by FIB milling. To avoid this, a fluoride atmosphere is applied. However, the effects are not completely understood. A better solution could be the use of low energy Ga ions of approx. 1 keV.

An interesting effect found is the reduction of object charging under the electron beam by illumination with light. This effect will help to acquire images without the use of carbon coating for discharging, which is usually used successfully but at the disadvantage of blurring the image. To increase the discharging effect, it is suggested to apply light with an energy larger than the band gap of the sample. In the case of the material studied, ZnO, this would be larger than 3.6 eV.

In addition a method was proposed to determine, whether or not the sample is in kinematic conditions. It consists in the evaluation of the product $V_{MIP} \lambda_{inel}$. If the sample is in kinematic conditions, the product should be constant in a material. In fact, this was found experimentally in many cases. However, systematic studies with larger variations of angle and thickness are necessary, because data of these two constants found in the literature have been determined under different experimental conditions. In this thesis, the following values for c-Si, CIGS and ZnO were evaluated.

<table>
<thead>
<tr>
<th>Material</th>
<th>MIP $V$</th>
<th>$\lambda_{inel}$ $\text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>11.3</td>
<td>100</td>
</tr>
<tr>
<td>CIGS</td>
<td>14.4</td>
<td>45</td>
</tr>
<tr>
<td>ZnO</td>
<td>18.6</td>
<td>32</td>
</tr>
</tbody>
</table>
Finally, this thesis shows the first results ever of potential distribution measurement under biasing and illumination of real solar cells. It was found that effects of these specific stimuli can be measured by electron holography. With these measurements information of recombination in the surface, contact potentials and effects of temperature could be determined. Simulation calculations show qualitative agreement with the experimental results, indicating that the phenomena are in principle understood. For quantitative interpretations of the findings a better control of the object parameters has to be established.
Appendix A

Parameters list

Physical constants used in this work

<table>
<thead>
<tr>
<th>Name</th>
<th>Notation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann constant</td>
<td>$k_b$</td>
<td>$1.38 \times 10^{-23} \frac{J}{K}$</td>
</tr>
<tr>
<td>Electron charge</td>
<td>$e$</td>
<td>$1.60 \times 10^{-19} C$</td>
</tr>
<tr>
<td>Absolute temperature</td>
<td>$T$</td>
<td>300K</td>
</tr>
<tr>
<td>Planck constant</td>
<td>$h$</td>
<td>$6.63 \times 10^{-34} J s$</td>
</tr>
<tr>
<td>Rest electron mass</td>
<td>$m_o$</td>
<td>$9.11 \times 10^{-31} Kg$</td>
</tr>
<tr>
<td>Number Pi</td>
<td>$\pi$</td>
<td>3.1415</td>
</tr>
<tr>
<td>Vacuum permeability</td>
<td>$\varepsilon_o$</td>
<td>$8.85 \times 10^{-12} \frac{C}{V m}$</td>
</tr>
<tr>
<td>Speed of light</td>
<td>$c$</td>
<td>$3 \times 10^8 \frac{m}{s}$</td>
</tr>
<tr>
<td>Electron wavelength (200keV)</td>
<td>$\lambda_e$</td>
<td>0.0025 nm</td>
</tr>
</tbody>
</table>

Table A.1: Constants used [124]

Silicon and SiN:H parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Notation</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron effective mass</td>
<td>$m_e^*$</td>
<td>1.08$m_o$</td>
</tr>
<tr>
<td>Holes effective mass</td>
<td>$m_h^*$</td>
<td>0.56$m_o$</td>
</tr>
<tr>
<td>Forbidden band Gap (eV)</td>
<td>$E_g$</td>
<td>1.12</td>
</tr>
<tr>
<td>Holes mobility (cm$^2$/Vs)</td>
<td>$\mu_h$</td>
<td>424.62</td>
</tr>
<tr>
<td>Electron Mobility (cm$^2$/Vs)</td>
<td>$\mu_e$</td>
<td>1106.51</td>
</tr>
<tr>
<td>Holes lifetime (s)</td>
<td>$\tau_h$</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Electron lifetime (s)</td>
<td>$\tau_e$</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Intrinsic density of charge (cm$^3$)</td>
<td>$n_i$</td>
<td>$1.01 \times 10^{-16}$</td>
</tr>
<tr>
<td>Silicon relative permeability</td>
<td>$\varepsilon_{s-si}$</td>
<td>11.8</td>
</tr>
<tr>
<td>Silicon density (g/cm$^3$)</td>
<td>$\rho_{si}$</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Table A.2: List of parameters of silicon
## CIGS solar cells parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ZnO</th>
<th>CdS</th>
<th>OVC</th>
<th>CIGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (cm)</td>
<td>5 x 10^{-5}</td>
<td>5 x 10^{-6}</td>
<td>5 x 10^{-6}</td>
<td>2 x 10^{-4}</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>10</td>
<td>11</td>
<td>11.9</td>
<td>12</td>
</tr>
<tr>
<td>Electron affinity (eV)</td>
<td>4.4</td>
<td>4.2</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>3.4</td>
<td>2.4</td>
<td>1.35</td>
<td>1.15</td>
</tr>
<tr>
<td>effective conduction band density (cm^{-3})</td>
<td>2 x 10^{18}</td>
<td>2 x 10^{28}</td>
<td>2 x 10^{18}</td>
<td>2 x 10^{18}</td>
</tr>
<tr>
<td>effective valence band density (cm^{-3})</td>
<td>2 x 10^{18}</td>
<td>2 x 10^{18}</td>
<td>2 x 10^{18}</td>
<td>2 x 10^{18}</td>
</tr>
<tr>
<td>effective electron mobility (cm^{2}/Vs)</td>
<td>20</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>effective hole mobility (cm^{2}/Vs)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>doping concentration acceptors (cm^{-3})</td>
<td>0</td>
<td>0</td>
<td>1 x 10^{15}</td>
<td>1 x 10^{16}</td>
</tr>
<tr>
<td>doping concentration donors (cm^{-3})</td>
<td>1 x 10^{18}</td>
<td>1 x 10^{15}</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>electron thermal velocity (cm/s)</td>
<td>1 x 10^{7}</td>
<td>1 x 10^{7}</td>
<td>1 x 10^{7}</td>
<td>1 x 10^{7}</td>
</tr>
<tr>
<td>hole thermal velocity (cm/s)</td>
<td>1 x 10^{7}</td>
<td>1 x 10^{7}</td>
<td>1 x 10^{7}</td>
<td>1 x 10^{7}</td>
</tr>
<tr>
<td>Layer density (g cm^{-3})</td>
<td>5.7</td>
<td>4.8</td>
<td>2.328</td>
<td>2.328</td>
</tr>
</tbody>
</table>

Table A.3: List of parameters of CIGS Solar cells
Appendix B

Photovoltaic energy production panorama

The photovoltaic effect was discovered by Becquerel in 1839 [8]. The idea of creating a “battery” from this process was first proposed by Alfred Smee [120] by looking at some biological specimens.

After discovery of photoconductivity in selenium by Willoughy Smith in 1873 this material was used to make some devices which produce a photo-current. In 1876, William Adams and Richard Day found a photo-current in a sample of selenium contacted with two heated platinum contacts. In 1883 Charles Fritts, credited with creating the first true photovoltaic solar cell, produced a device using selenium pressed between gold and another metallic contact. In this first attempt the conversion efficiency\(^1\) was lower than 2%. In the following years, the photoelectric effect was also seen in copper-copper oxide, copper-lead sulphide and copper-thallium sulphide contacts.

Only later in 1914 Goldman and Brodsky explained the working process of these solar cells indicating that it is mainly due to the rectification produced in the interface between the semiconductor and the metal, thus making a differential conductivity of the charge in one of the contacts. In the 30’s the theory of the contact of metal-semiconductor devices was developed by Schottky and Mott, amongst others. However, due to the low efficiency and high cost of those devices, there was no interest in producing energy through the photovoltaic effect.

This panorama changed in 1950 with the work of Gerald Pearson, Darril Chaplin and Calvin Fuller in the Bell laboratories (USA), who started with an idea of Rusell Ohl \(^2\) the study of mono-crystalline silicon. In 1954 they presented the first practical solar cell with an efficiency close to 6%. This work was possible because of the better rectifying properties of the p-n junction compared to the Schottky barrier and the better photoelectric behaviour. In the 50’s decade the efficiency increased reaching 14% in 1960 by Hoffman electronics.

\(^1\)The efficiency is the ratio between the energy given by the device and the energy received from the sun in this case.

\(^2\)Rusell Ohl discovered the p-n junction and patented the modern solar cell [96].
Despite this progress photovoltaic solar energy was so expensive that it was used mainly in such regions where conventional energy was not accessible, for example for telecommunications and aeronautical applications.

In 1954, solar cells based on CdS were developed reaching an efficiency of 6% and after that, theoretical works showed that p-n junction of different materials like GaAs, InP and CdTe would have larger efficiencies. Despite this research, silicon was the foremost, mainly due to the advances in the silicon technology of the electronic industry.

In the 70’s the members of the OAPEC (Organization of Arab Petroleum Exporting Countries) proclaimed an oil embargo. Then the developed countries depending on the oil supply decided to invest in alternative sources of energy. As a result efforts to promote research of photovoltaic energy were undertaken by creating strategies to produce photovoltaic devices and materials cheaply and to improve their efficiency. These strategies to lower the costs include the use of chemically produced materials, exchange of silicon with other thin film materials or the use of organic materials. Strategies for increasing efficiency include tandem and multiple band gap designs. Although some of the first earth applications were made in Japan, Niger, and the USA, solar energy is used mainly in those places where energy production and transport are very difficult. None of these strategies was a widespread commercial development. In this period, the understanding of the photovoltaic science was routed.

Later in 1984 the first high-efficient silicon solar cells were developed at the University New South Wales in Australia with an efficiency of more than 20%.

Nowadays new material solar cells have a similar performance as silicon solar cells at a strong reduction of costs. Besides, there is a renovated interest in developing photovoltaic energy mainly due to the increase in the costs of traditional fossil combustibles and also due to the controversial discussion around nuclear energy production after the problems with the thermonuclear reactor of Fukushima Japan.

**Current photovoltaic energy production**

These days the global consumption of energy, Figure B.1, is approximately $15 \times 10^{16}$ W·h [www.eia.doe.gov/iaa] with a growth rate of 4% per year. The renewable energies (geothermal, wind, solar energy, wood) contribute with only $1.5 \times 10^{16}$ W·h around 10%, to this global consumption and this tendency has been constant over the past 20 years.

Of this amount of energy, photovoltaic energy installed in 2008 was $12 \times 10^{12}$ W (source: http://www.iea.org/stats/renewdata.asp?COUNTRY_CODE=29), which is less than 0.01% of the global energy consumption. Despite this panorama, in the last 10 years photovoltaic energy has had an incredible growth with an average rate of 20% per year. Growth was encouraged by public subsidies and environmental problems coming of traditional sources of energy as coal, gas and oil. Recent developments increase the efficiency and reduce of costs as well as the scale economy.

If we look at the progress made in the last 5 years in global production of photovoltaic energy and projecting it to 2015, this tendency indicates that in 2015 the production of
Figure B.1: a. World marketed energy consumption, b. Production in 2008 by fuel type. Source Energy Information Administration, International energy annual 2006, website www.eia.doe.gov/iea

Photovoltaic energy will be bigger than that of nuclear sources. Figure B.2 shows this tendency and data of photovoltaic energy production since 1999.

Figure B.2: Global photovoltaic energy production, data taken of www.solarbuzz.com

Solar energy shows advantages with respect to other sources of energy, i.e. it be produced during the day everywhere in the word depending on the geographical position and environmental conditions. Moreover, it could potentially cover the global consumption of energy.

Ideally, solar cells should be a not-contaminant device; however some potentially dangerous elements for the environment and public health are used during their manufacturing. Nowadays, big efforts are being made to reduce or avoid this problem.
Appendix C

Angular distribution of LEDs illumination

In this thesis several sources of illumination are used, i.e., LEDs as well as optic fibre coupled with a LASER. In this segment of the thesis, the properties of these illumination sources are calculated.

The first calculation shows the characterization of the illumination from two commercial LEDs, in second instance the unencapsulated LED from SEMILED and finally the illumination from the LASER.

Table C.1 shows the characteristics of the different light illumination sources used in this thesis are analysed.

<table>
<thead>
<tr>
<th>Source</th>
<th>Illumination power</th>
<th>Wavelength</th>
<th>Area</th>
<th>Illumination characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Encapsulated red LED</td>
<td>60mcd (~ 8.8 \times 10^{-4} W)</td>
<td>468 nm</td>
<td>point source</td>
<td>120° co-sinusoidal</td>
</tr>
<tr>
<td>Encapsulated blue LED</td>
<td>120mcd (~ 1.8 \times 10^{-3} W)</td>
<td>650 nm</td>
<td>point source</td>
<td>120° co-sinusoidal</td>
</tr>
<tr>
<td>Chip green LED</td>
<td>~ 0.5 W</td>
<td>532 nm</td>
<td>1 mm²</td>
<td>Plain</td>
</tr>
<tr>
<td>LASER/optic fibre</td>
<td>~ 1 W</td>
<td>532 nm</td>
<td>point source</td>
<td>Gaussian distribution</td>
</tr>
</tbody>
</table>

Table C.1: Characteristics of the diverse sources of illumination used in this thesis.
LED illumination

The illumination of commercial LEDs can be determined from data of luminous intensity $I_v$ in units of candela\(^2\), the angular distribution of the illumination and change of the intensity radiated with the current.

However to compare it, this units must be worked out in radiometric units. For monochromatic radiation the conversion between luminous and radiometric units is given by:

$$I_r(\lambda) = \frac{1}{683 \cdot \text{sr}} \cdot \frac{I_v(\lambda)}{y(\lambda)}$$  \hspace{1cm} (C.1)

Here $I_r$ is the radiant intensity \(^3\), defined as the power emitted in a certain solid angle. In SI it corresponds to Watt per steradian $\Omega$. $y(\lambda)$ is the luminous efficiency, a dimensionless function defined between 0 and 1.

To calculate the energy emitted from the LED and absorbed by the solar cell, it is necessary to calculate the number of photons per area $A$ and per second. That is the photon flux density:

$$\Phi_{ph} = \frac{P_r}{E(\lambda) \cdot A}$$  \hspace{1cm} (C.2)

In this thesis, the photon flux density $\Phi_{ph}$, is calculated in units of photon number per second and square centimetre\(^4\); in this equation $P_r$ corresponds to the electromagnetic energy (photons) per second emitted by the LED. $E(\nu) = h\nu_{ph} = hc/\lambda_{ph}$ is the energy of each photon emitted, and $A$ is the area irradiated. For the calculations this area is assumed 1mm\(^2\).

The total power radiated is then:

$$P_r = \int I_r \, d\Omega$$  \hspace{1cm} (C.3)

Typical intensity distributions for commercial LEDs with viewing angles of 120° and 90°\(^5\) are shown in the figure C.1. These intensity distributions of 120° and 90° are approximated to co-sinusoidal and polynomial distributions, respectively.

1The luminous intensity is the luminous flux emitted from a point per unit solid angle into a particular direction. The luminous intensity is the official base unit for light. http://www.schorsch.com/en/kbase/glossary/luminous-intensity.html

2Candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency $540 \times 10^{12}$ Hz and that has a radiant intensity in that direction of 1/683 W/sr.

3Radiant intensity is the radiant flux radiated from a point on a light source into a unit solid angle in a particular direction. Unit of radiant intensity is Watt per Steradian (W/sr). http://www.schorsch.com/en/kbase/glossary/radiant-intensity.html

4These units are chosen because the AforsHET uses it, however they change from program to program.

5Angle of viewing corresponds to the maximum angle at which a display can be viewed with acceptable visual performance, in LEDs this angle corresponds to the 50% of the maximum intensity radiated.
Table C.2: Illumination properties of the LEDs analyzed

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Flux density photons/(cm²s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luminous intensity $</td>
<td>I_v</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>60</td>
<td>468</td>
</tr>
<tr>
<td>120</td>
<td>650</td>
</tr>
</tbody>
</table>

Figure C.1: Angular distribution of the illumination of two LEDs with viewing angle of 120° (a) and 90° (b).

Under the assumption of rotational symmetry around the axis, the expression for the illumination for co-sinusoidal illumination, 120° illumination angle, is given by:

$$I_r = \frac{1}{683 y(\lambda)} \frac{I_v \cos(\varphi)}{n_1}$$

(C.4)

where $n_1$ is a normalization constant equal to $\frac{32400(\pi-2)}{\pi}$, $\varphi$ is the angle of incidence and $I_v$ is the luminous intensity in units of candela.

For illumination of 90°, the expression is:

$$I_r = \frac{1}{683 y(\lambda)} \frac{I_v(1 - \varphi/2\pi)}{n_2}$$

(C.5)

with the normalization constant $n_2 = 2700\pi$.

With these equations and integrating the luminous intensity over the exposed area of 0.5 mm² an the solar cell and a distance from LED to the sample surface of 1.5 mm, one obtains the photon fluxes in Table C.2.

**Chip-LED illumination**

Due to the close distance between chip LED and sample surface, the illumination can be considered uniform. Accordingly, the following photon fluxes (Table C.3) are obtained assuming an exposed area of 0.5 mm² and a LED-sample distance of 0.5 mm.
Characteristics | Max flux density
---|---
Power $P_r$ (W) | Wavelength $\lambda$(nm) | photons/cm²s
0.5 | 535 | $1.35 \times 10^{21}$
0.5 | 450 | $1.13 \times 10^{20}$

Table C.3: Calculation of the radiance of the chip LED’s. These LEDs exhibit an illumination angle of 180°; however, due to the proximity of the sample, the illumination is supposed constant over the sample area.

**LASER/Optic fibre illumination**

The measured illumination distribution of the optic fibre follows a Gaussian spatial distribution (see Figure C.2). Taking that into account when integrating the luminous intensity over the exposed area of 0.5 mm² on the solar cell at a distance of 3 mm, the following photon fluxes are obtained (Table C.2).

Characteristics | Max flux density
---|---
Power $P_r$ (W) | Wavelength $\lambda$(nm) | photons/cm²s
1.0 | 532 | $1.1 \times 10^{20}$

Table C.4: Illumination on the sample region by the optical fibre coupled with the LASER.

Figure C.2: Distribution of illumination with the LASER after the optic fibre. It corresponds to a Gaussian function.
Appendix D

Types of solar cells - first and second generation

Solar cells are the elemental constituents of a solar panel, inside of which they are connected in series and parallel to give certain output voltage and current. Currently the commercial panels are divided into two types, silicon based panels and chalcogenide based ones. Figure D.1 shows some commercial panels and their corresponding efficiencies.

The solar cells classified by the material used to absorb the light are shown in Figure D.2. Historically the most often used material is silicon which dominates the global production of solar panels with more than 46% of the world production. Three types of silicon solar cells are produced: mono-crystalline with efficiencies close to 25% but at the same time high costs, poly-crystalline used in applications of low power consumption and thin films. Another materials group used to produce solar cells is the chalcogenide based structure; in this group the most important are the $CdTe$ and $Cu(In, Ga)SeS$ ($CIGS$), which are being extensively studied because of their large efficiencies with relatively small use of material, mainly due to their direct band absorption. A third group consists of III-V compounds $GaAs$ and $InP$, which offer the best efficiency whose costs are also the largest. The newest group is based on polymers, which offer low efficiencies and also have stability problem but are cheaper and easier to produce.
APPENDIX D. TYPES OF SOLAR CELLS - FIRST AND SECOND GENERATION

Figure D.1: Types of silicon and chalcogenide commercial solar photovoltaic panels and their efficiencies in 2009 [41]

Figure D.2: Types of solar cells and their efficiencies for the years of 2009 and 2008 in brackets, data from [40]
Bibliography


137


[24] FlexPDE 5.1. PDE Solutions Inc.


[66] Li, J., Malis, T., and Dionne, S. Recent advances in FIB-TEM specimen preparation techniques. *Materials Characterization* 57(1) (2006), 64.70.


[94] Nicholas, S. UNSW hits 19.4 percent on mass-produced solar cell. p-v magazine (online), July 2011.


[96] Ohl, R. Light-sensitive electronic device (patent n. 2402662), June 1946.


BIBLIOGRAPHY


List of Figures

2.1 Structure of a solar cell. Left: picture of a \( c-Si \) solar cell [20]. Right: schematic cross-section of the layers of a solar cell. 

2.2 Different electron-photon excitations in a semiconductor: Intrinsic excitation band to band between the valence band with energy \( E_V \) and conduction band with energy \( E_C \), extrinsic excitation between the valence band or conduction band and donor or acceptor states with energies \( E_D \) and \( E_A \), respectively.

2.3 Absorption coefficients of \( c-Si \) and \( CIGS \).

2.4 Electron-hole pair generation rate in the absorbent material by a flux density of \( 10^{18} \) cm\(^{-2}\)s\(^{-1}\) of 470nm and 650nm photons. This effect clearly shows why \( c-Si \) solar cells must be thicker than \( CIGS \) for the same amount of electron hole pairs to be generated.

2.5 Band structure of \( n \)-doped material (left) and \( p \)-doped material (right); \( E_D \) is the energy of the donor state created by addition of impurities to the material, in this case the Fermi level moves closer to the conduction band. In a similar way, an acceptor impurity creates an acceptor state; here the Fermi level is located closer to the valence band.

2.6 Left: band structure of a \( p-n \) homo-junction. Right: example of a band structure of a hetero-junction. Two materials \( a \) and \( b \) are in contact, the material \( a \) with band gap \( E_{ga} \) and electron affinity \( \chi_a \) and the material \( b \) with band gap \( E_{gb} \) and electron affinity \( \chi_b \). The contact potential between the two materials is \( V_C \). The solid lines indicate the conduction band \( E_C \) and the valence band \( E_V \).

2.7 Comparison between the results of using the 3D solution of the Poisson equation by the program FlexPDE and the 1D Shockley model. The insert shows the resulting grid and an image of the potential distribution in the centre slice of the block.

2.8 Process of charge separation in a solar cell with a \( p-n \) junction.

2.9 J-V curves showing the most important parameters determining the solar cells efficiency, \( V_{oc} \) open circuit voltage, \( J_{sc} \) short-circuit current density, \( V_{mp} \) maximum power voltage and \( J_{mp} \) current density at maximum power [109].
2.10 Equivalent circuit of a solar cell. $R_{sh}$ is the shunt resistance produced by leakage of carriers by recombination, and $R_s$ is the resistance produced by loss in the surface. The numbers indicate: 1 the ideal diode, 2 load external resistance, and 3 the current source.

3.1 Scheme of a transmission electron microscope in bright field mode. On the right the electron path through the different lenses is depicted. The angles are strongly exaggerated.

3.2 Abbe’s imaging of a perfect crystal.

3.3 Amplitude and phase transfer functions from the Phillips CM200 microscope operated in Lorentz mode in Scherzer focus $D_z = -5505$ nm, for electrons accelerated to 200 keV. The coefficient of spherical aberration is $C_s = 8000$ mm and convergence angle $\theta_c = 1$ mrad. The PCTF shows optimum phase contrast.

3.4 Transfer of amplitude and phase from the object to the detector. Because of the fact that the detector only measures the intensity, phase information is only partially transferred to the image depending on the properties of the PCTF. The complete phase acquisition is not possible in that way.

3.5 Basic scheme of off-axis electron holography.

3.6 Electron paths with positive potential at the biprism.

3.7 Effect of the Möllenstedt biprism on the electron path. Between the two images only the biprism voltage is changed. The left image shows electron paths produced with smaller biprism voltage than the case of the right image. With larger voltage the superposition angle $\beta$ is increased. Therefore, fringe spacing decreases and hologram width increases.

3.8 Hologram (left) of an object and its Fourier transformation (centre) showing the centre and side bands.

3.9 Images of amplitude and phase reconstructed from the hologram shown in Figure 3.8. Some of the artefacts induced are indicated in the image. These artefacts are studied in the next section.

3.10 Main artefacts in off-axis electron holography [72, 78]. A full comprehension of how these parameter affect the measurement is required for the interpretation of the electron wave in terms of potentials.

3.11 Fresnel fringes as well as hot and dead pixels in the recorded hologram, which produce artefacts in the reconstructed wave.

3.12 Images of amplitude (left) and phase (right) reconstructed from the hologram shown in Figure 3.8.
3.13 Flowchart of the reconstruction process of a hologram using an empty hologram. The original holograms (a,b), show the effect of Fresnel diffraction at the biprism. To correct it, a mask in Fourier space is applied (c,d). After the holograms are inversely Fourier transformed (e,f), there is a clear reduction of the Fresnel fringes. In these images the hot and dead pixels of the camera are reduced by replacing them with the mean value of the neighbours. After Fourier transformation, the side band is masked out (g), centred (h) and inversely Fourier transformed to obtain the complex wave in real space. The object wave is divided by the wave reconstructed from the empty hologram. Finally, the object wave is obtained as amplitude and phase images (i, j). .................................................. 38

3.14 Diameter of the mask used for hologram reconstruction. For strong diffracting objects the diameter of the mask must be smaller to \( q_{mask}^{st} \leq q_c/3 \) (left side band), else if the object is a pure phase object, this diameter is \( q_{mask}^{ph} \leq q_c/2 \) (right side band). The logarithmic line scan along the line b-b shows the diameter of both masks. .................................................. 40

3.15 WTF of the CM200 and the Tecnai F20 microscopes. The CM 200 is operated in Lorentz mode in the Scherzer focus \( D_z = -5505 \) nm, for electrons accelerated to 200 keV. The aberration is spherical aberration \( C_s = 8000 \) mm, and convergence angle \( \theta_c = 1 \) mrad. The Tecnai F20 Cs-corrected microscope is operated in PLL mode also in Scherzer focus \( D_z = -194.6 \) nm, for electrons accelerated to of 200 keV; spherical aberration \( C_s = 10 \) mm and chromatic aberration \( C_c = 41 \) mm. In both calculations a convergence angle of \( \theta_c = 1 \) mrad is used. .................................................. 41

4.1 Reconstructed wave, amplitude (left) and phase (right) of a CIGS solar cell. In the images the different layers of the solar cell are indicated, also a grain boundary and precipitates are visible. This local variation of composition makes the interpretation of the phase image and the amplitude in terms of potential and thickness difficult. .................................................. 46

4.2 Measured product of \( V_{MIP} \) and \( \lambda_{inel} \) from amplitude and phase (Figure 3.12). In this image, regions where the measured product \( V_{MIP}\lambda_{inel} = constant \) are found (areas 1 to 3), but also regions where effects of dynamic interaction can be found (areas 4). On the right side, the histograms of the product in each one of the areas indicated by boxes 1 (CIGS), 2 (CdS) and 3 (ZnO) are shown. In the histogram of area 1 the small statistical spread around a mean value indicates a good approximation to kinematic situation, whereas in the histograms of areas 2 and 3 the dispersion of the values indicates additional phases or dynamic conditions. .................................................. 48

4.3 Left: band structure after applying a voltage across a homo p-n junction solar cell. The p-n junction potential changes proportionally to the biasing potential \( V_a \). Right: effect of illumination with light on the band structure of the solar cell. If no external load is applied to the solar cell, the separation of the generated electron-hole pairs produces an open circuit voltage \( V_{oc} \). . 49
4.4 Sequence followed to acquire, process and compare the holograms in the in-situ experiment. 1. Acquisition and reconstruction of the holograms with and without stimulus, respectively. 2. Determination and correction of the displacement of the images with and without stimulus, respectively. 3. Subtraction of phase images with and without stimulus. 4. Determination of the thickness from the reconstructed amplitude (average of A and B). 5. Calculation of the potential distribution. The most important condition for this experiment is that the amplitude images, with and without stimulus, must not change. .......................................................... 50

4.5 Effect of biasing on the band structure of a solar cell. Left, forward bias; here the p-n junction potential is reduced by the same amount as the applied potential. Centre, zero bias; no changes in the band structure. Right, reverse bias; the potential in the p-n junction is increased by the applied voltage. Electron holography measures the potential with reference to the vacuum, in these images this potential is represented by the (blue) line at the top of the images. .......................................................... 53

4.6 Typical hologram of a $c$–silicon sample taken in the CM200 Lorentz electron microscope. The inset shows the intensity along the arrow. The counts in the camera $n_{vac}$ in the vacuum are close to 1830 counts. The rate of conversion in the camera installed in this microscope is 0.97 electron/pixel, giving a number of approximately 1780 electrons per pixel. The acquisition time of this image was 7 s. .......................................................... 56

4.7 Comparison between electron-hole pair generation by light (blue line) and the range of values given by the different calculations (filled band) with a line (red) indicating the value calculated in this thesis. The generation rate by light is calculated using the green ($\lambda=535$nm) absorption value. A strong influence from the electron beam is to be expected on the measurement of potentials in solar cells. .......................................................... 58

4.8 Comparison of reconstructed image wave as amplitude and phase of a single reconstructed hologram (top) and from three (bottom) holograms. The images show standard deviation calculated in the vacuum region in the inset boxes. With three images, a noise reduction of 38% in phase and 40% in amplitude is obtained, close to the theoretical value of $\sqrt{3}$. In these images the acquisition time of each hologram is 7 sec. .......................................................... 60

4.9 Images of the thickness calculated from the amplitudes in Figure 4.8. The standard deviation, calculated in the area of the boxes shows a noise reduction of 72.5% close to the theoretical value of 73.2%. Right; profile along the arrows shows the effect of averaging of the images. The profile corresponding to the averaging of three images shows a clear reduction of noise in the thickness. .......................................................... 60

4.10 Images showing the potential distribution in the sample of $c$–silicon. With the acquisition of series of holograms the noise is reduced. .......................................................... 61
4.11 Potential and standard deviation calculated from 9 holograms. The profiles show the values measured along the arrows. The sample is a p-n junction in a silicon lamella of 200 nm thickness (close to the optimum value). In this case a detection limit of 0.12 V is achieved. 62

5.1 Holder with a hollow shaft. By means of the feed-through items in the head arranged around the object can be controlled from outside hence allow in-situ experiments. 67

5.2 Space available for the holder with respect to the pole pieces of the objective lens, considering also the tilting angles $\alpha$ and $\beta$. In the holder designed in this thesis, the sample can be tilted only in $\alpha$ direction. 68

5.3 Sketch showing the position and orientation of the LED as illumination source, contacts and sample in the holder head. The angle of 30° indicates the direction of the interference fringes. 68

5.4 First head constructed from a laminated plate normally used for printed circuit boards. This holder has only contacts for biasing. Images a (back side), b and c (front side) show details of placing of the contacts and sample fixing in the holder head. 69

5.5 Holder constructed with a LED as a source of illumination. 70

5.6 Phase images from empty holograms with their respective hologram fringe contrasts (insets), if the current in the LED is increased between 0mA and 20mA. The contrast of the images is reduced with the increase of the LED current. 71

5.7 Variation of potential and band structure for a flux density of photons, left $1 \times 10^{17}/(\text{cm}^2\text{s})$, right $3 \times 10^{20}/(\text{cm}^2\text{s})$, with monochromatic radiation $\lambda = 650$ nm. The simulations are made by means of the program AFORS-HET [47]. 72

5.8 Calculation of the potential variation and band structure of an open circuit CIGS solar cell when a flux of photons is applied, left $4 \times 10^{20}/(\text{cm}^2\text{s})$, right $5 \times 10^{22}/(\text{cm}^2\text{s})$. Monochromatic radiation with $\lambda = 470$ nm is used. Simulations are made with the program AFORS-HET[47]. 73

5.9 Holder with the chip LED. The inset shows the position of the chip LED in the head. 73

5.10 Output power given by the LASER coupled with the optic fibre. The efficiency of the coupling system is close to 65%. 75

5.11 Holder with optical fibre for LASER illumination of the object. The inset details the position of the optical fibre and illumination cone produced by the illumination. The measured aperture angle is 30° (in the inset the illumination cone and the position of the optic fibre are drawn for the sake of clarity). 76

153
5.12 Holographic phase images of a ZnO nano-wire under the electron beam, without illumination (left) and illuminated with the Chip LED as source (right). The profile at the centre shows a comparison between the phase of the sample illuminated and not illuminated. The reduction of the electric field around the illuminated sample is obvious. ............................................. 77

5.13 Holographic phase images of a ZnO nano-wire illuminated with the LASER beam (left) and not illuminated (right). The profile shows a comparison of the phase of these two conditions (centre). The reduction of the electric field around the illuminated sample is evident. ............................................. 78

5.14 Simulated phase image made with the program FlexPDE of a ZnO nano-wire charged under the electron beam (left). Phase profile comparing experimental data and simulation (right). In the simulation, charge densities of $1 \times 10^{17}$/cm$^3$ and $6 \times 10^{16}$/cm$^3$ are used for non illuminated and illuminated situations, respectively. ............................................. 78


6.2 Sample preparation overview: The sample is cut in a triangular shape and glued with conductive epoxy on a dedicated copper TEM grid on top, it is possible to see the electric contact. In one of the corners, the lamella is milled by means of FIB. ............................................. 84

6.3 Shapes used for the sample preparation showing the amount of material removed in the FIB milling process and area accessible to illumination. The small bright rectangle indicates the lamella. The triangular shaped sample c offers the best compromise between milling time and area accessible for illumination. ............................................. 84

6.4 Resizing of the sample is made with a wire saw. To protect the sample from damage due to scratching, a protective film of wax is used on the surface. The original contacts of the solar cells can be seen. ............................................. 85

6.5 Position of the sample in the copper disc with respect to the electron beam 86

6.6 FIB process to prepare the sample: Selection of the area where the lamella will be milled (a), sequential platinum deposition assisted by electron beam (b) and $Ga^+$ ions (c); removal of material with low current ion beam (d and e); lamella finishing with low current Ga ions and opening the window for the reference wave (f). ............................................. 87

6.7 Representation of the different layers created by the FIB preparation. $t_o$ and $t_1$ are the thickness of the amorphous layer and the transition layer, respectively. ............................................. 88

6.8 Holographic phase image showing the effect of curtaining in direction of the arrows. The phase variation perpendicular to the arrows arises from corresponding thickness variation of the lamella. ............................................. 90
6.9 Geometry used in the program FlexPDE to simulate the effect of the preparation. The dimensions are in µm. Only half of the lamella is simulated to reduce calculation time. Left, general view of the geometry showing the different layers of the lamella. Right, cross section made in the plane a-a (z = 2). The numbers indicate: 1. Vacuum region, 2. Highly p-doped region, 3. c-silicon surface.

6.10 Comparison of the effect of FIB preparation in top- (left) and side- (right) view. a. Lamella without amorphous layer. b. Effect of a highly $p^+$-doped region on the surface of the lamella. One can clearly see the reduction of the stray field in vacuum and of the effective potential below the surface of the lamella.

6.11 Damage of thin film solar cells during the preparation process.

6.12 Cutting a CIGS solar cell with metallic scissors bends the metal and peels off the CIGS solar cell from the metallic substrate. A solution consists of using a Ti substrate; in this case the sample is prepared by breaking the substrate with a sharp blade.

6.13 SEM images of Cu precipitates. To avoid this an atmosphere of fluoride is used.

6.14 Final preparation of the CIGS solar cell.

6.15 Effect on the detection limit of the Ga energy during the FIB milling. The reduction of the damage layer reduces damping of the amplitude and therefore the detection limit of the potential is improved.

7.1 Scheme of a modern silicon solar cell (image adapted from [94]). This solar cell includes some special characteristics to improve the efficiency: pyramidal textured surface, $p^+$ doping close to the rear contact, and top and bottom passivation layers to reduce the effects of recombination at the surfaces. With these solar cells efficiencies close to 20% are achieved.

7.2 a: Overview of a c-silicon solar cell sample. b: pyramidal structure with a mean base size of 10 µm. Sequence in direction c shows the lamella; this lamella was constructed where the SiN:H layer was present. Sequence in direction d: contact of Aluminium (Aluminium finger); below the Al finger the SiN : H layer is removed to create an Ohmic contact with the silicon.

7.3 Left: doping profile of the c-silicon solar cell analysed. Right: band structure calculated from the doping concentration. A built-in potential of 0.92 V is expected.

7.4 Sample preparation of the lamella used for biasing. Images a and b show the position of the lamella in the sample. Here, the platinum is not in direct contact with the external contact. c and d show SEM and TEM images of the lamella. The pyramidal structure of the solar cell is clearly visible. The TEM image d shows position and field of view of the acquired holograms (approx. 1 µm²).
7.5 a: Biasing polarity of the solar cells, positive values are taken as forward biasing. b: J-V curves before and after the TEM sample preparation, the current density is strongly reduced. c: Comparison of bias measurements with simulation. In the simulation the only parameter changed is the density of defects in the p-doped region. The reduced size of the TEM sample increases the probability of recombination in the lateral surfaces resulting in a decrease of the current density.

7.6 Phase image as colour map (right) showing the geometry of the lamella where the potential is measured. In the profiles along the arrows (1,2) the effect of biasing on phase is measured. With forward biasing the phase image tends to flatten indicating that the p-n junction potential is reduced. Otherwise under reverse biasing (negative potentials) the phase decreases. It indicates a potential increase in the n-doped layer with respect to the p-doped region.

7.7 Images showing the product $V_{MIP}\lambda_{inel}$ at different biasing condition in a $c-\text{Si}$ solar cell. Profiles (1,2) along the boxes in the direction of the arrows. At 1.0 V forward biasing the product is constant. On the other hand, with increasing reverse bias (-0.5 V and -1.0 V) the product is not constant. This result indicates that biasing produces local changes in the product $V_{MIP}\lambda_{inel}$.

7.8 Right: High resolution SEM image of the border of the lamella, a distance of 148.8 nm is measured. Due to the lamella orientation (projection angle $\alpha \approx 50^\circ$) the thickness is approximately 190 nm. Left: Thickness map from the amplitude image calculated using the value of $\lambda_{inel} = 100$ nm. Centre: line profiles in direction of the arrows 1 and 2 showing the thickness distribution of the lamella. The thickness reduces in direction of the platinum uniformly around a mean value close to 180 nm (profile 2).

7.9 Biasing effect on the potential distribution. Left, comparison of the profiles along the boxes in the direction of the arrows in the images. Forward biasing produces negative potentials with respect to the reference due to the reduction of the p-n junction potential. The minimum potential difference measured under forward biasing is -0.6 volts. This value corresponds to the potential drop in silicon. On the other hand, reverse biasing produces a positive potential because the potential is increased by the potential applied.

7.10 Preparation of the lamella B used for illumination. a: overview of the sample. b: region where the lamella is made. c: lamella with the window for holography. This lamella was soft polished with low energy $Ga^+$ ions (5 keV). d: measurement of lamella thickness. The projection angle here is 70 degrees; therefore the real thickness is approx. 440nm.

7.11 Left: thickness map calculated from amplitude image. Right: Line profiles along the arrows a and b, respectively. The profile a shows a thickness variation between 400 and 450 nm $\pm 10$ nm. Because of the curtaining effect of the FIB preparation, the lamella does not show a uniform thickness along direction b (profile b).
7.12 Left: reconstructed phases under illumination. Right: line profiles along the arrows in the boxes of the phase images. The phase increases with increasing illumination intensity. The maximum phase difference between n and p doped regions is 2.7 rad. Beyond 165 mW the phase does not increase further, even if the intensity of the laser is 1000 mW. .................................................. 109

7.13 Potential variation in the lamella under increasing laser illumination intensity. The illumination unit is given in equivalent suns. ............................................................. 109

7.14 Contact between a metal with a larger work function $f_m$ than a $n-$doped semiconductor with work function $f_n$. The electrons flow from the semiconductor into the metal because of the lower energy of the Fermi level. This creates a depletion region in the semiconductor bending the band structure up until equilibrium is reached levelling out the Fermi levels of both materials (centre). The length of the band bending depends on the built-in voltage hence on the doping of the semiconductor. Additionally, the large amount of electron-hole pairs created by the illumination with the electron beam reduces the Schottky potential (right). ............................................. 110

7.15 Simulation of the effect of electron illumination on the potential. In this simulation 1, 10 and 100 AM1.5 sun equivalent flux densities are used. According to the simulation with an illumination of 100 suns the potential is reduced to 0.4 V being close to the potential measured. ............................................... 111

7.16 Effect of the temperature on the built-in potential of the solar cells. The built in potential increases with the temperature. ................................................................. 111

7.17 TEM micrograph of a CIGS solar cell in cross section, showing the composition by the different layers. ................................................................. 112

7.18 SEM images showing the preparation of the CIGS solar cell sample. a: overview of the solar cell, some regions of the lamella are peeled off during the preparation. b: Image of the lamella, the different layers of the solar cell are indicated. c: overview of the lamella. d: Close-up of the lamella showing the thickness, (close to 190 nm after correcting projection effects). 114

7.19 Images of amplitude (left), phase (centre) and the product $V_{MIP} \lambda_{inel}$ (right). The profiles are measured along the boxes 1 and 2 along the arrows shown in the left image. The phase image is unwrapped, but due to the abrupt end of the sample to the vacuum, the automatic unwrapping algorithm fails. Therefore, the absolute value was calculated knowing the approximate thickness from SEM and an approximate value for $V_{MIP} = 15$ V. The value of $\lambda_{inel} = 45$ nm is calculated for that thickness. A value for the product $V_{MIP} \lambda_{inel} = 660$ V nm is measured, resulting in a value for $V_{MIP}=14.4$ V for CIGS. ................................................................. 115

7.20 Current density vs. voltage curve of the CIGS solar cell before and after preparation; the preparation destroys the diode characteristic of the solar cell. ................................................................. 116
7.21 Images showing the biasing effect on amplitude images. The dynamic
conditions change during the experiment; the lines are used to visualise the
movement of the contour lines indicated by the arrows. . . . . . . . . . . . 117

7.22 Subtraction of phase images. Here the image with a biasing potential of
0.0 V is selected as reference. Due to the strong dynamic conditions, the
subtraction of the phases does not represent the potentials in the solar cells.
However, there is a correlation between the applied biasing voltage and the
variation of the phase. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 118

Source Energy Information Administration, International energy annual
2006, website www.eia.doe.gov/iea . . . . . . . . . . . . . . . . . . . . . . 129

B.2 Global photovoltaic energy production, data taken of www.solarbuzz.com . 129

C.1 Angular distribution of the illumination of two LEDs with viewing angle
of 120° (a) and 90° (b). . . . . . . . . . . . . . . . . . . . . . . . . . . . . 133

C.2 Distribution of illumination with the LASER after the optic fibre. It
corresponds to a Gaussian function. . . . . . . . . . . . . . . . . . . . . . 134

D.1 Types of silicon and chalcogenide commercial solar photovoltaic panels and
their efficiencies in 2009 [41] . . . . . . . . . . . . . . . . . . . . . . . . . . 136

D.2 Types of solar cells and their efficiencies for the years of 2009 and 2008 in
brackets, data from [40] . . . . . . . . . . . . . . . . . . . . . . . . . . . . 136
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Lens settings for electron holography in our laboratory. The parameters DIF and PLL are explained in [116, 117]. The numbers in DIF 90 or PLL 75 correspond to the percentage of the total excitation of the diffraction lens.</td>
</tr>
<tr>
<td>4.1</td>
<td>Typical p-n junction ($V_{pn}$) and open circuit ($V_{oc}$) potentials of some of the solar cells studied in this thesis. Open circuit values are given for the air mass 1.5 sun standard illumination. This illumination is defined in Section 2.5.</td>
</tr>
<tr>
<td>4.2</td>
<td>Comparison of calculations of e-h pairs generated by the electron beam made by different authors. For comparison, the values were recalculated using the electron current density of this thesis.</td>
</tr>
<tr>
<td>5.1</td>
<td>Illumination given by some of the LEDs. The angles 120° and 90° correspond to the angular distribution of the selected LEDs. Figure C.1.</td>
</tr>
<tr>
<td>5.2</td>
<td>Calculation of the flux density of the chip LED. These LEDs exhibit an illumination angle of 180°; however, due to the proximity of the sample (between 0.5 and 1.0 mm), the illumination is supposed constant over the sample area (details in the appendix C where the illumination is calculated).</td>
</tr>
<tr>
<td>5.3</td>
<td>Illumination on the object, produced by the optical fibre coupled to the LASER.</td>
</tr>
<tr>
<td>7.1</td>
<td>Doping characteristics of the $c-silicon$ solar cell studied. The p doping is established with boron and the n doping with phosphorous. The solar cell has the same characteristics as those displayed in Figure 7.1.</td>
</tr>
<tr>
<td>7.2</td>
<td>Reported values of $\lambda_{inel}$. In this thesis the value of 100 nm is found in good agreement with the ones measured by Wolf and Formánek. It is used for determination of the object thickness.</td>
</tr>
<tr>
<td>7.3</td>
<td>Different values of $V_{MIP}$ reported for $c-silicon$ in the literature. Differences between the results come from the diverse experimental conditions or varying assumptions used in the theoretic calculations.</td>
</tr>
<tr>
<td>7.4</td>
<td>Illumination applied to the sample in the in-situ illumination experiment.</td>
</tr>
</tbody>
</table>
7.5 Generation rate of electron hole pairs by the electron beam in the layers of a CIGS solar cell. The values of $\left| \frac{dE}{dx} \right|$ are calculated by means of the program “ESTAR” of the National Institute of Standards and Technology [93]. The generation rate for CIGS is two orders of magnitude larger than the generation rate for silicon. And because of the low doping of the CIGS and CdS, the electron illumination has a larger effect in the p-n junction potential measurement.

<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>Constants used [124]</td>
</tr>
<tr>
<td>A.2</td>
<td>List of parameters of silicon</td>
</tr>
<tr>
<td>A.3</td>
<td>List of parameters of CIGS Solar cells</td>
</tr>
<tr>
<td>C.1</td>
<td>Characteristics of the diverse sources of illumination used in this thesis.</td>
</tr>
<tr>
<td>C.2</td>
<td>Illumination properties of the LEDs analyzed</td>
</tr>
<tr>
<td>C.3</td>
<td>Calculation of the radiance of the chip LED’s. These LEDs exhibit an illumination angle of 180°; however, due to the proximity of the sample, the illumination is supposed constant over the sample area.</td>
</tr>
<tr>
<td>C.4</td>
<td>Illumination on the sample region by the optical fibre coupled with the LASER.</td>
</tr>
</tbody>
</table>
Index

7
ACTF, 25
Biasing, 14
Biprism, 27
c-Silicon solar cells, 98
Carrier current density equation, 13
CISG solar cells, 112
Contrast, 31, 33
Cross section, 81
Depletion Region (DR), 11
Detection limit, 41
Dynamic condition, 47
Efficiency, 17
127
54
Electron hole pairs induction, 54
Empty hologram, 37, 71
Generation rate (G(x)), 7
Hologram, 31
Hologram artefacts, 33
Illumination current, 16
Inelastic mean free path, 46
Mean inner potential, 43, 46
Minority carrier lifetime, 18
Noise, 59
noise, 42
Open circuit voltage, 52
PCTF, 25
23
Plain view, 81
Potential measurement, 42
Pseudo Lorentz Lens - PLL, 39
Quasi Neutral Region (QNR), 11
Recombination, 18
Sample preparation, 81
Scherzer defocus, 26
23
SemiLED, 72
Shockley-Queisser limit, 17
signal resolution, 42
Signal to Noise Ratio, 61
Spherical aberration, 26
54
Thickness, 35
Wave aberration function, 25
Wave reconstruction, 31
23
25
Acknowledgements

First of all I want to thank my lovely family, my wife Ingrid and my son Fabio, for the support, patience, and love, without them this thesis would have been meaningless. I am grateful to my “Doktorvater”, Professor Hannes Lichte, for the opportunity he gave me to work in this fascinating theme, for his trust, support, patience and incredible teaching capacity. I am thankful to all (former) members of the Triebenberg lab, Dorin Geiger, Michael Lehmann, Andreas Lenk, Axel Lubk, Heide Müller, Marianne Reibold, Falk Röder, Jan Sickmann, Sebastian Sturm, Karin Vogel and Daniel Wolf for their continuous support, fruitful ideas exchange and nice work atmosphere. A special acknowledge goes to Bernd Einenkel for his formidable capacity of translating my blueprints into real specimen holders. I am also thankful to the people who trusted in this project and supplied some of the studied samples: Daniel Abou-Ras from the Helmholtz Institut (Berlin) and Wolfgang Tress of the Institut für Angewandte Photophysik (TU Dresden). I am indebted to Petr Formánek and his assistant Michael Göbel who taught me the method of sample preparation by FIB milling. Last but not least I acknowledge the financial support of DAAD and the Universidad nacional de Colombia and Colciencias in form of the ALECOL scholarship.
Selbständigkeitserklärung


Dies ist mein erstes Promotionsverfahren.

Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

Dresden, der ________________

John William Sandino del Busto

Anerkennung der Promotionsordnung


Dresden, der ________________

John William Sandino del Busto