Photoelectrochemical Water-Splitting using 3C-SiC

Pontus Höjer

Examiner, Mikael Syväjärvi
Supervisor, Jianwu Sun
Abstract

In 1972 Fujishima and Honda conceptualised a photoelectrochemical cell for hydrogen generation via PEC water splitting. Hydrogen as a clean energy carrier provides environmentally friendly energy storage solutions or can fuel certain applications. This idea has since then been further built upon with new materials and combinations with the aim of improving efficiency. In this project n-type cubic silicon carbide thick layers were grown by a sublimation method and characterised for water splitting performance. A generated photo-current density of 0.45 mA/cm² was measured with no bias between the working and counter electrodes.
To Elina
Abstract

In 1972 Fujishima and Honda conceptualised a photoelectrochemical cell for hydrogen generation via PEC water splitting. Hydrogen as a clean energy carrier provides environmentally friendly energy storage solutions or can fuel certain applications. This idea has since then been further built upon with new materials and combinations with the aim of improving efficiency. In this project n-type cubic silicon carbide thick layers were grown by a sublimation method and characterised for water splitting performance. A generated photo-current density of 0.45 mA/cm$^2$ was measured with no bias between the working and counter electrodes.
Acknowledgements

First of all, thanks to Jianwu, for providing supervision for this project and helping out a lot with the progression of it, and thanks to Mikael, for examining me. A great big thanks to Yuchen, for helping out with a lot of practical work, and Valdas, also for helping with a lot of things. Thanks to Ildiko, for assisting me with things regarding chemicals, and Rickard, for the microscopy run-through. Also, thanks to Roger and Rolf for helping out with some practical things.

Thank you all for helping me in my project work!
List of abbreviations

Here is a list defining some abbreviations and symbols that appear within this thesis, see table [1].
Table 1. A list of abbreviations.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABPE</td>
<td>Applied bias photon-to-current efficiency</td>
</tr>
<tr>
<td>APCE</td>
<td>Absorbed photon-to-current efficiency</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>C&lt;sub&gt;SC&lt;/sub&gt;</td>
<td>Capacitance over the space-charge layer</td>
</tr>
<tr>
<td>E&lt;sub&gt;C&lt;/sub&gt;</td>
<td>Conduction band energy</td>
</tr>
<tr>
<td>E&lt;sub&gt;fb&lt;/sub&gt;</td>
<td>Flat-band potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;V&lt;/sub&gt;</td>
<td>Valence band energy</td>
</tr>
<tr>
<td>e</td>
<td>Electron charge</td>
</tr>
<tr>
<td>HEC</td>
<td>Hydrogen evolution catalyst</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-current efficiency</td>
</tr>
<tr>
<td>j</td>
<td>Current density</td>
</tr>
<tr>
<td>L&lt;sub&gt;D&lt;/sub&gt;</td>
<td>Carrier diffusion length</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal Hydrogen Electrode</td>
</tr>
<tr>
<td>OEC</td>
<td>Oxygen evolution catalyst</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
</tr>
<tr>
<td>PEC</td>
<td>Photoelectrochemical (water splitting)</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic (cell)</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>SCL</td>
<td>Space-charge layer</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>STH</td>
<td>Solar-to-hydrogen efficiency</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>V&lt;sub&gt;B&lt;/sub&gt;</td>
<td>Band-bending potential</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>W&lt;sub&gt;dep,acc&lt;/sub&gt;</td>
<td>Width of a depletion or accumulation layer</td>
</tr>
<tr>
<td>η&lt;sub&gt;e/h&lt;/sub&gt;</td>
<td>Carrier generation efficiency</td>
</tr>
<tr>
<td>η&lt;sub&gt;F&lt;/sub&gt;</td>
<td>Faradaic efficiency</td>
</tr>
<tr>
<td>η&lt;sub&gt;interface&lt;/sub&gt;</td>
<td>Carrier transport over an interface efficiency</td>
</tr>
<tr>
<td>η&lt;sub&gt;transport&lt;/sub&gt;</td>
<td>Carrier transport efficiency</td>
</tr>
<tr>
<td>μ&lt;sub&gt;e,h&lt;/sub&gt;</td>
<td>Carrier mobility</td>
</tr>
<tr>
<td>τ&lt;sub&gt;e,h&lt;/sub&gt;</td>
<td>Carrier lifetime</td>
</tr>
</tbody>
</table>
# Contents

1 Introduction .................................................. 1
   1.1 Research goals ........................................... 3

2 Methodology .................................................. 5

3 Theory .......................................................... 7
   3.1 The semiconductor ......................................... 7
   3.2 The cell .................................................... 11
      3.2.1 The working electrode ......................... 11
      3.2.2 The electrolyte .................................. 16
      3.2.3 The reference electrode .............. 16
   3.3 Efficiency ............................................... 17
      3.3.1 Diagnostics ....................................... 18
   3.4 Methods of measurement .................................. 20
      3.4.1 Open-Circuit Potential .................... 20
      3.4.2 Mott-Schottky ............................ 22
      3.4.3 Photo-current onset ................... 24
      3.4.4 Chronoamperometry .................... 26
      3.4.5 Gas chromatography .................. 26

4 Previous work ................................................. 29
   4.1 Semiconductors ........................................ 29
   4.2 Co-catalytic materials .................................. 32
      4.2.1 Hydrogen evolution catalysts ........ 32
      4.2.2 Oxygen evolution catalysts .......... 33
   4.3 Ohmic contacts .......................................... 37

5 Experimental procedures .................................... 39
   5.1 Sample preparation .................................... 39
      5.1.1 The 4H- and 6H-samples .......... 39
      5.1.2 Growth ......................................... 40
5.1.3 Polishing & cleaning .......................................... 40
5.1.4 Ohmic contact deposition on 3C-SiC ....................... 42
5.1.5 Ohmic contact deposition on 4H- and 6H-SiC ............... 42
5.1.6 Ohmic contact on Si ........................................... 43
5.1.7 Making the electrodes ........................................ 43
5.1.8 Co-catalyst deposition ......................................... 44
5.2 Sample characterisation ........................................... 45
5.2.1 Optical microscopy ............................................. 45
5.2.2 IV measurements ............................................... 45
5.3 PEC measurements ............................................... 46
5.3.1 Mott-Schottky ................................................ 46
5.3.2 Open-Circuit Potential ........................................ 47
5.3.3 Photo-current onset .......................................... 47
5.3.4 Chronoamperometry ......................................... 47
6 Results and discussion ............................................ 49
6.1 Growth and preparation ......................................... 49
6.2 Ohmic contacts .................................................. 50
6.3 Mott-Schottky .................................................... 52
6.3.1 Si .......................................................... 52
6.3.2 3C-SiC ....................................................... 55
6.4 Open-Circuit Potential ........................................... 58
6.4.1 Si .......................................................... 58
6.4.2 3C-SiC ....................................................... 59
6.5 Photo-current onset .............................................. 59
6.5.1 Si .......................................................... 60
6.5.2 3C-SiC ....................................................... 60
6.5.3 6H-SiC ....................................................... 62
6.5.4 Co-catalyst deposition ........................................ 62
6.6 Chronoamperometry ............................................. 64
6.6.1 Si .......................................................... 64
6.6.2 3C-SiC ....................................................... 64
6.7 Summary ........................................................ 66
6.8 Sources of error ................................................ 67
7 Conclusions and future work ..................................... 69
7.1 Further improvements ......................................... 69
7.2 Summary ........................................................ 70
Bibliography .......................................................... 71
Chapter 1

Introduction

Over the past few hundreds of years earth has suffered the industrious nature of mankind in our endeavour to increase the standard of life for all human beings. During this time we have not until recently noticed the impact we have had on our planet. It is not a secret that energy-related issues are quite pronounced today, we are beginning to see the effects of a long time with unrestrained consumption of fossil fuels, such as global warming. The imprint we make on our planet is only one perspective, another is that the resources we expend to fuel the lifestyle that we have built for ourselves will soon be completely spent. Although we still have enough oil to keep our engines running we are starting to realise that it will run out eventually. In fig. 1.1, the world energy consumption can be seen to have an upwards trend which should not be surprising considering increased ubiquity of various power-consuming devices with both increased population and increased living standards all across the world.

Therefore, alternative sources of energy are necessary to develop for a sustainable future. Solar cells are the intuitive response to such an issue since around $3 \times 10^{24}$ joules of solar energy is received by the earth every year and only a fraction of this could cover the entire world’s energy consumption. Probably nobody has missed that the development of solar cells is underway [3], but where to store the generated electricity is a recurring issue. Comparing the specific energy of different ways to store energy one will see that chemical bond storage is more efficient than batteries, hydrogen being one of the energetically richest compounds with approximately 142 MJ/kg of specific energy. Therefore it would be a good idea to somehow store energy in chemical forms, as it is quite easy to both keep in tanks and transport for use when needed. This could both be used as fuel to drive machinery and as an alternative to backup generators in case
Introduction

Figure 1.1. On the left side: Trend of world energy consumption divided by energy source, given in million tonnes oil equivalent on the y-axis and year on the x-axis (from 1990 to 2015). Adapted from [1]. And to the right: The photoelectrochemical cell described by Fujishima and Honda, 1 is the TiO$_2$ electrode, 2 is the Pt electrode, 3 is an ion membrane and 4 & 5 is some external circuitry. [2]

of power failures. The question then is how to convert solar energy into chemically bound energy. [4]

In 1972 the ground-breaking article by Fujishima and Honda [2] was published describing their experiment using n-doped TiO$_2$ as a photo-anode, and Pt as a cathode, in an electro-chemical cell, see fig. 1.1. By irradiating this TiO$_2$ photo-anode with white light, water will be oxidised here and hydrogen ions will be reduced at the Pt electrode (more on this in chapter 3). The result of this reaction is water molecules splitting into hydrogen and oxygen, gases that can be collected through proper piping and then utilised for e.g. energy production. Thus, that article laid down the road for further development of photoelectrochemical (PEC) water-splitting cells which are continuously being researched still today (more on this under section 4).

It seems like cubic silicon carbide (3C-SiC) would fit this application very well due to its suitable opto-electronic properties. Recent developments in manufacturing 3C-SiC [5] makes it possible to perform measurements on the material in order to characterise its performance as the active material in a PEC-cell. And so, with this project an attempt is made to make a contribution to the ongoing research of PEC water-splitting devices by implementing cubic silicon carbide as the working electrode component.
1.1 Research goals

The purpose of this project is to develop efficient photoelectrochemical water-splitting photo-electrodes utilising 3C-SiC as the semiconducting material. The main goals of this project work are as follows:

- To grow samples of 3C-SiC and manufacture photo-electrodes of them.
- To characterise the photoelectrochemical water-splitting performance of the 3C-SiC photo-electrodes.
- To deposit some co-catalytic materials onto the photo-electrodes.
- To characterise the photoelectrochemical water-splitting performance of the 3C-SiC photo-electrodes with co-catalysts.

Ideally, an improvement of the performance of the photo-electrodes with the deposition of co-catalytic materials will be observed and perhaps be comparable to previous results of research performed on both SiC and on other semiconductor electrodes.
4

Introduction
Chapter 2

Methodology

The steps taken from the beginning of the project to the end are roughly described here as a general plan of action. Each step is motivated by the expected outcome of that particular event and its effect on the overall progression of the project.

In order to properly understand the subject and the task at hand a literature study was performed. This gave some information about what progress has been recently done in the field, with the purpose of thoroughly investigating several different approaches to inspire any decisions regarding project design. It also yielded some information about achieved performance of similar devices which can be used as a yardstick for the results of this project.

With a sufficient amount of information gathered about the subject the practical work started with growing samples of n-type 3C-SiC onto substrates of 4H-SiC using a sublimation method [5]. The samples were then visually examined to ensure actually being of 3C-type. This was done by optical microscopy since the optical properties of the distinct polytypes of SiC are different.

The samples of 3C-SiC were fashioned into photo-electrodes by mechanical polishing, chemical cleaning and addition of a backside ohmic contact. Ohmic contacts were also made on n-type 4H- and 6H-SiC which were then fashioned into electrodes. Some p-type Si-electrodes were made as well. Following the sample preparation, measurements of the photoelectrochemical water-splitting capabilities of the bare 3C-SiC and Si were performed with the aim of characterising the performance of the semiconductor alone and comparing results with the more well-known Si. Another benefit of doing measurements on Si was learning a bit about the practical methods. This was done using a solar simulator, a potentiostat and a small container...
Methodology

of aqueous 1 M NaOH electrolyte with a quartz window in it, referred to as the PEC cell. This is done in order to obtain a benchmark of the efficiency of the material for comparison between 3C-SiC and other semiconductors as well as comparison with itself when co-catalytic materials are added onto the electrodes.

After proper referential performance of the bare 3C-SiC had been recorded the co-catalytic materials were applied using electro-chemical deposition methods. This was done because it is well-developed by other researchers and thus recipes for depositing the chosen materials can be found in literature. This is advantageous both because it has a large potential to further the water splitting efficiency and enhance the stability of the semiconductor electrode. The recipes are not completely reproducible on a new material though, and some characterisation of co-catalyst deposition methods was performed on 6H-SiC since it is thought to closer resemble 3C compared to some other material. Since all SiC polytypes straddle the water-splitting potentials they are all in principle able to split water unbiased. After a good enough deposition method was discovered it was thought to be tried on 3C samples. Then the 3C-SiC with co-catalysts would have had their water-splitting performance characterised in the same manner as the bare material after which the results were to be compared.

(The co-catalyst deposition on 3C-SiC was ultimately not performed, due to not finding a working deposition method in time.)

This sequence of actions are meant to give a clear enough image of what type of material has been grown, how well it performs as a photo-electrode in water-splitting applications and how much it can be improved by application of co-catalytic materials.
Chapter 3

Theory

Here is a short description of the fundamental principles behind developing PEC water-splitting devices. Basically, a semiconductor emerged into an electrolyte and externally connected to a counter electrode can be driven by sunlight (in many cases also an external bias) to split water. Theoretically, either an n-type semiconductor can be used as an anode together with a metal cathode, or a metal anode with a p-type semiconductor as the cathode, or a combination of both with p-type and n-type semiconductors as cathode and anode respectively. In principle any of these configurations can be used, but for the scope of this project we will limit ourselves to the first suggestion of n-type semiconductor anode, however, the fundamentals behind PEC devices can be extended to any of these combinations.

The principles of solar-driven water-splitting is similar to that of a PV cell, and imagining the PV cell somehow integrated into the electrode configuration and serially connected with an electrolyte an attempt can be made to describe the PEC water-splitting process. The following chapter will briefly explain the details of this principle, mainly focusing on using 3C-SiC as a photoanode.

3.1 The semiconductor

When a semiconductor is put into an electrolyte electronic equilibrium will be reached by an electric current flowing through the junction between the two media. Equilibrium in this case will be when the electron Fermi level \((E_F)\) in the semiconductor matches the electrolyte redox potential \((E_{\text{redox}})\). The current will cause a space-charge layer (SCL) to appear at the junction, in the electrolyte it corresponds to a so called Helmholtz double layer due to charges attracted to the SCL, while in the semiconductor band-bending will
Figure 3.1. Image of the energy bands of an n-type semiconductor in contact with an electrolyte. A. Flat-band potential, no space-charge layer. B. Depletion layer, electrons have moved into the electrolyte, causing the bands to bend upwards. \( W_{\text{dep}} \) is the width of the layer and \( V_B \) is the potential drop over it, corresponding to the flat-band potential. In the electrolyte the Helmholtz double layer forms, \( H1 \) and \( H2 \). 

occur, depending on the position of the Fermi level \( [7] \). If the Fermi level happens to be equal to the flat-band potential (\( V_{FB} \) or, perhaps more commonly, \( E_{fb} \)), which is the potential in the semiconductor that corresponds to no potential drop over the SCL, the bands will not bend due to no excess charge in the junction. Otherwise, the electrons can either accumulate at or deplete from the semiconductor and cause an accumulation- or depletion-layer which will bend the bands accordingly, see fig. 3.1. The electrolyte charged layer consists of ions in the liquid attracted to the interface, however, this layer is usually very thin in comparison to the space charge layer in the semiconductor. So, the charged region in the semiconductor is the dominant factor in separating the photo-generated carriers. 

The width of this depletion layer can be calculated by:

\[
W_{\text{dep}} = \sqrt{\frac{2\varepsilon_s \varepsilon_0 V_B}{e N_D}} \tag{3.1}
\]

where \( \varepsilon_s \) is the permittivity of the semiconductor, \( \varepsilon_0 \) is the permittivity in vacuum, \( V_B \) is the drop in potential over the depletion layer, \( e \) is electronic charge and \( N_D \) is donor concentration.

Semiconductors with high carrier mobilities and long lifetimes, see eq. 3.7 later on, will experience a stronger separation of carriers in the depletion
3.1 The semiconductor

region, which affects the possibility of carrier recombination. Therefore it is quite necessary that the semiconductor has large enough mobility to efficiently separate its generated carriers. The reason why keeping the carriers from recombining is important can be seen in fig. 3.2 which shows a good overview of the principles behind PEC. Here an incoming photon can excite electron-hole pair with a certain efficiency $\eta_{e^-/h^+}$, the electron will then be positioned in the conduction band and the hole in the valence band, see fig. 3.2 and eq. 3.2:

$$\text{Semiconductor} + 4h\nu \rightarrow 4h^+ + 4e^- \quad (3.2)$$

where $h$ is Planck’s constant, $\nu$ frequency of the incident light and $h^+$ & $e^-$ are the hole and electron respectively, specially $h\nu$ denotes one photon. This will occur when the energy of the incident light, $h\nu$, is larger than the band-gap of the semiconducting material, $E_g$.

The holes can then participate, affected by some transport and interfacial transferring efficiencies, in the following reaction at the n-type semiconductor-electrolyte interface:

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2 \quad (3.3)$$

where $H_2O$, $H^+$ and $O_2$ are water molecules, hydrogen ions and oxygen molecules respectively. The hydrogen ions can then travel to the cathode through the electrolyte and there interact with the photo-generated electrons which have been transported there via external circuitry. And so, the following reaction will occur at the cathode:

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (3.4)$$

where $H_2$ are hydrogen molecules. The overall water-splitting reaction then looks like this:

$$4h\nu + 2H_2O \rightarrow 2H_2 + O_2 \quad (3.5)$$

This reaction, eq. 3.5 will only occur if the energy of the incident photons is enough to overcome the threshold energy required for water-splitting. The change in free energy for converting one water molecule into one hydrogen- and one half oxygen molecules, i.e. half of the reaction in eq. 3.5 is $\Delta G = 237.2$ kJ/mol, which would correspond to an energy per photo-generated electron of:

$$E_e = \frac{\Delta G}{2N_A} = h\nu = 1.23 \text{ eV} \quad (3.6)$$

where $N_A = 6,022 \times 10^{23}$ mol$^{-1}$ is Avogadro’s number. [6, 10]
Figure 3.2. Schematic image of the different processes occurring in a PEC cell with an n-type semiconductor working electrode. An incident photon, $h\nu$, excites an electron into the conduction band. The created hole will move to the electrolyte and the electron to the counter electrode and then contribute to their part in the redox reactions. Here $\eta$ denotes various efficiencies, OP denotes the over-potentials for the HER and OER half-reactions, 1.23 eV is the minimum thermodynamic energy required to split water and $E_F$ denotes the quasi-Fermi levels of the carriers, a notation sometimes used for carrier populations not in equilibrium. \[9\]

Thus, taking into consideration the reaction in eq. 3.5 alone, one would imagine water-splitting can be achieved by using a semiconductor with a band-gap of $E_g > 1.23$ eV just straddling the redox energy levels for splitting water. However, this is not the case, as this should also include loss mechanisms such as interfacial recombination and over-potentials, as seen in fig. 3.2, resulting in the band-gap of the semiconductor needing to be at least around 2 eV \[11\]. With too large band-gaps, however, the ability to utilise the visible light spectrum severely decreases due to a lower amount of incident photons fulfilling the requirement of having an energy higher than $E_g$, as mentioned earlier. This effectively limits the viable band-gap levels upwards as well, since too low photo-carrier generation makes the cell too inefficient a band-gap smaller than around 3.2 eV is preferred. \[11\] At wavelengths lower than around 450 nm the intensity of sunlight starts to
3.2 The cell

drop drastically and semiconductors with band-gaps in this region cannot reach very high levels of PEC water-splitting efficiency (this can be seen later on in fig. 4.2).

To summarise this, specific electronic properties are required for a semiconductor to be a viable choice in a PEC-cell. It needs to at least have good enough transport-properties and a suitable band-gap.

3.2 The cell

Since the electrodes work in an aqueous electrolyte under illumination it is critical that all materials involved, especially the semiconductor at the working electrode (WE), are chemically stable and does not significantly corrode. This puts additional requirements on the choice of materials that are suitable for the application. This also applies to the other parts inside the cell, such as the counter electrode (CE). The CE can also be made much bigger than the WE since it implies that the performance of the cell is not limited by the reaction at the CE.

3.2.1 The working electrode

Choosing the semiconductor material for the working electrode is only the first step, actually manufacturing an electrode out of it is the next. In order to do so the semiconductor sample should first be made in the appropriate dimensions.

Thickness

The optimum thickness of the semiconductor should in terms of carrier transport be equal to the sum of the width of the space-charge layer and the majority carrier diffusion length. This is done using eq. 3.1 together with:

\[ L_D = \sqrt{\frac{\mu \tau k_B T}{e}} \]  

(3.7)

where \( \mu \) is the carrier mobility, \( \tau \) is the carrier lifetime, \( \frac{k_B T}{e} \) is the product of the Boltzmann constant and the temperature divided by the electronic charge. Thus the width of the semiconductor should be:

\[ W = L_D + W_{dep} = \sqrt{\frac{\mu \tau k_B T}{e}} + \sqrt{\frac{2 \epsilon_s \epsilon_0 |V_B|}{e N_D}} \]  

(3.8)

A calculation of this with a range of appropriate values for the different material properties can give an approximation of how thin the sample needs
to be made. However, there are some practical considerations to take into account here as well since it might be difficult to handle samples that are much thinner than around 300 µm. In table 3.1 some constant values are listed.

Table 3.1. Values used in calculating optimal sample thickness.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_0$</td>
<td>$8.854\times10^{-12}$</td>
<td>F/m</td>
</tr>
<tr>
<td>$k_B$</td>
<td>$1.38\times10^{-23}$</td>
<td>J/K</td>
</tr>
<tr>
<td>$T$</td>
<td>298</td>
<td>K</td>
</tr>
<tr>
<td>$e$</td>
<td>$1.602\times10^{-19}$</td>
<td>C</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>9.72</td>
<td>-</td>
</tr>
</tbody>
</table>

In fig. 3.3 some plots of the depletion layer width against doping concentration and diffusion length against lifetime can be seen. It is clear that for the diffusion length and depletion region to be as large as possible the doping of the semiconductor has to be low, the Schottky-barrier towards the electrolyte has to be high, the carrier lifetime has to be long and the carrier mobility has to be high. Even if all these parameters are at some reasonably good value, seen in table 3.2, the optimal sample thickness will be around 91 µm.

Figure 3.3. Some calculations based on the values of table 3.1, the axes are logarithmic. Left: A plot of depletion region width vs. doping concentration for several values of the potential drop over the SCL. Right: A plot of carrier diffusion length vs. carrier lifetime for several values of carrier mobility.

By looking at the plots in fig. 3.3 a large range of resulting thicknesses can be seen, so the useful thickness of a sample is heavily influenced by the
Table 3.2. A calculation of optimal sample thickness, using reasonable parameter values.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_D$</td>
<td>$10^{16}$</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>320</td>
<td>cm$^2$/Vs</td>
</tr>
<tr>
<td>$\tau$</td>
<td>10</td>
<td>$\mu$s</td>
</tr>
<tr>
<td>$V_B$</td>
<td>1</td>
<td>eV</td>
</tr>
</tbody>
</table>

carrier transport properties of the material.

A reason to want the samples to be as thick as possible is that in order to also have optimal optical properties the sample thickness should be around the same as, or thicker than, the light penetration depth:

$$\delta = \frac{1}{\alpha(\lambda^{-1})}$$  \hspace{1cm} (3.9)

where $\alpha$ is the absorption coefficient which is proportional to the inverse of the wavelength, $\lambda$. An illustration is made in fig. 3.4 showing some schematic of penetration depths in relation to diffusion length and depletion layer width. Here light with wavelengths larger than $\lambda_2$ will excite carriers which are too far away to participate in any water-splitting.

Figure 3.4. An illustration of penetration depth in relation to the diffusion length and depletion layer width. In this case $\lambda_1 > \lambda_2 > \lambda_3$, some light with short wavelength, like $\lambda_1$, might only penetrate a short distance into the material, and only light with wavelength up to $\lambda_2$ is useful while light with $\lambda_3$ goes through the material.
In fig. 3.5 A) a plot over the absorption coefficient and penetration depth in 3C-SiC can be seen, this 3C was grown by Solangi and Chaudhry [12] using chemical vapour deposition (CVD). In the same figure B) is a sample used for comparison which has a slightly higher doping and thickness. Similar results have also been gotten by e.g. Sridhara et al. [13]. It can be seen that for wavelengths close to the band-gap value the penetration depth is fairly large, which implies losses of light that goes all the way through the samples. Defects or doping might increase the absorption coefficient and reduce the light lost.

![Figure 3.5](image)

**Figure 3.5.** A plot of the light absorption coefficient $\alpha$, the red lines, on 3C-SiC for two samples. The blue lines instead show the penetration depth from eq. 3.9. 

A) Sample of 8 $\mu$m thickness with a so called buffer layer, with $5 \times 10^{16}$ cm$^{-3}$ doping. B) Sample of 10.7 $\mu$m thickness, with $6.9 \times 10^{16}$ cm$^{-3}$ doping. [12, 13].

In this application only visible light and only wavelengths corresponding to above band-gap illumination are interesting, limiting the reasonable wavelength range to about 390-525 nm for 3C-SiC with its band-gap of approximately 2.36 eV. In fig. 3.5 it seems like the penetration depth of light with an energy of 2.36 eV is in the region of around 80-150 $\mu$m.

One way to attempt to optimise the light absorption efficiency while also properly utilising the transport properties of the materials is through nano-structuring. As schematically shown in fig. 3.6 nano-wires can be
3.2 The cell

![Figure 3.6](image)

**Figure 3.6.** An illustration of the benefits of nanowire-structure on the surface of the working electrode. $L_D$ is the diffusion length of minority carriers and $\delta_{\lambda}$ is the penetration depth of light with that particular wavelength, in this case $\lambda_1 > \lambda_2 > \lambda_3$.

made such that their thicknesses allows for the minority carrier diffusion length to always be within range of the edge of the wire, i.e. the wire diameter should be equal to $2L_D$. If the length of the wires also match the penetration depth of the light this ensures a large portion of the light can be absorbed to create useful carriers that can participate in reactions at the semiconductor surface. Of course, consideration also has to be taken of the majority carriers ability to transport themselves to the contact-interface. Another property that can be improved by this is the reflected light losses, by making a nano-wired structure some trenches between the wires are also implicitly made, which traps incoming light by it hitting multiple surfaces.

**Backside contact**

It is important to minimise the electronic losses between the substrate and the actual electrode connection. This can be done by applying an ohmic contact to the backside of the sample. Typically, the semiconductor needs to enrich the interface with majority carriers and for this to happen the work function of the contact material should be lower than in the semiconductor for n-type, and analogously reversed for p-type. Commonly used as a low work function contact material is aluminium. This is a rule of thumb, however, since the metal can induce some electron states in the band-gap
that can cause anomalous effects, such as Fermi-level pinning. It is especially important to verify the linear relation between current and potential that characterises ohmic behaviour in order to be sure that no Schottky barrier is present. Such a barrier could reflect carriers back into the semiconductor instead of transporting them through the contact which will severely affect the performance of the device.

3.2.2 The electrolyte

Regarding the electrolyte it can be chosen so as to the greatest extent not destroy the electrodes, depending on their material. The electrolyte should also not absorb light in the same spectral range as the WE as well as not chemically interfere with anything in the cell and have sufficient ionic conductivity, usually at concentrations above around 0.1 M in an aqueous solution. [9]

3.2.3 The reference electrode

As reference electrode one with a known potential should be used, to which the different measurements can be related to. There are many different reference electrodes available, which one is best depends on the situation. The standard hydrogen electrode (SHE) is defined as 0 V at a hydrogen ion activity of $H^+ = 1$. Zero potential in this case is the point at which hydrogen gas evolution can occur, see fig. 3.2 and thus water oxidation occurs at 1.23 V relative to this. The normal hydrogen electrode (NHE) is defined as 0 V at a hydrogen ion concentration $H^+ = 1$, thus it is close to the SHE at low concentrations. The reversible hydrogen electrode (RHE) standard is useful when comparing measurements done in different electrolytes since it is independent of pH-level. Normally an electrode is affected by the pH in a way described by the Nernst equation:

$$E_{\text{redox}} = E_{\text{redox}}^0 + \frac{RT}{zF} \ln \left( \frac{a_{\text{ox}}}{a_{\text{red}}} \right) \quad (3.10)$$

where $E_{\text{redox}}^0$ is the standard redox potential in the electrolyte, $R$ is the ideal gas constant, $T$ is the temperature, $z$ is the number of electrons involved in the reaction, $F$ is Faraday’s constant, $a_{\text{ox}}/a_{\text{red}}$ is the activity of oxidised/reduced species which at low concentrations can be substituted by the actual concentrations. What this means for the PEC cell is a Nernstian bias of roughly 59 mV per unit difference in pH levels. The RHE is thus defined as having its potential in such a way as to compensate this:

$$E = 0V - 0.059 \times pH \quad (3.11)$$
3.3 Efficiency

Commonly used as reference is the silver/silver chloride electrode (Ag/AgCl), which works in solutions of a wide pH range. It can be kept in different concentrations of potassium chloride (KCl) in order to have the silver chloride concentration at a stable level, for instance the solution may be saturated with KCl. In saturated KCl the electrode potential is \( E = +0.197 \, \text{V vs SHE} \). This means at around \( pH \approx 13.6 \) the difference between Ag/AgCl in saturated KCl and RHE will be approximately 1 V, as seen in fig. 3.7.

![Figure 3.7. An illustration of the pH-dependency of the Ag/AgCl-sat. KCl electrode in relation to the RHE, at around 13.6 pH the difference is approximately 1 V.](image)

3.3 Efficiency

It is useful to define some way to measure the efficiency of a PEC cell, the ultimate measurement determining the performance of the cell is of course solar-to-hydrogen efficiency (STH). STH is measured when the WE is exposed to AM 1.5 G (Air Mass 1.5 Global illumination, a solar irradiation standard mimicking sunlight with an incident angle of \( \approx 42^\circ \) above the horizon and power density of \( \approx 100 \, \text{mW/cm}^2 \)) and the system is unbiased in a 2-electrode setup. Also the WE and CE must be kept at the same pH-level as there might otherwise be small additional potential difference between the two as described by the Nernst equation above, see eq. 3.10. This is normally not an issue but can be taken into account when using a setup with different compartments for the different electrodes, which is still possible by paying close attention to each pH level. With these things...
taken into account the STH efficiency is defined as the chemical energy in the generated hydrogen divided by the energy of the incident sunlight:

\[
\text{STH} = \frac{p_{H_2} \text{ (mmol/s)} \times \Delta G \text{ (J/mol)}}{P_{\text{total}} \text{ (mW/cm}^2\text{)} \times A \text{ (cm}^2\text{)}} \quad (3.12)
\]

with \(p_{H_2}\) denoting the hydrogen production in mmol per second, \(\Delta G\) is the change in Gibbs free energy per mol, \(P_{\text{total}}\) is the illumination power density and \(A\) is the illuminated area of the electrode [9]. An alternative definition can also be provided utilizing the fact that produced power can be described with voltage, current and faradaic efficiency:

\[
\text{STH} = \frac{|j_{SC} \text{ (mA/cm}^2\text{)}| \times 1.23 \text{ (V)} \times \eta_F}{P_{\text{total}} \text{ (mW/cm}^2\text{)}} \quad (3.13)
\]

where \(j_{SC}\) is the short-circuit photo-current density, the 1.23 V is the water splitting potential and \(\eta_F\) is the faradaic efficiency for hydrogen evolution [9]. This does not require actually measuring the produced amount of hydrogen, but instead relies on the faradaic efficiency which is thus the ratio of separated carriers that are actually used for water splitting, as such it is less accurate.

### 3.3.1 Diagnostics

It is also useful to define some diagnostic efficiencies to use as tools in determining performance of the device as they can be used to probe some specific properties, which might be beneficial in order to understand and improve the materials.

#### ABPE

By applying a bias between the WE and CE the applied bias photon-to-current efficiency (ABPE) can be measured, which does not really reflect an actual solar-to-hydrogen process due to changed properties under bias. With an applied bias \(V_b\) eq. 3.13 can be modified to:

\[
\text{ABPE} = \frac{|j_{\text{ph}} \text{ (mA/cm}^2\text{)}| \times (1.23 - |V_b|) \text{ (V)} \times \eta_F}{P_{\text{total}} \text{ (mW/cm}^2\text{)}} \quad (3.14)
\]

where \(j_{\text{ph}}\) is the photo-current density, \(\eta_F\) is the faradaic efficiency for hydrogen evolution and \(P_{\text{total}}\) is the illumination power density. This should be measured under the same conditions as STH (AM 1.5 G) and can be used to characterize e.g. photo-response efficiency under bias. [9]
IPCE

Incident photon-to-current efficiency (IPCE) is another diagnostic efficiency measurement that describes the resulting photo-current from the incident light depending on wavelength, it can be used to estimate a maximum theoretical STH efficiency when measured unbiased. IPCE is centered around three basic processes in a PEC cell, $\eta_{e^-/h^+}$, the efficiency of electron-hole pair generation per incident photon, $\eta_{\text{transport}}$, the efficiency of transporting charge to the solid-liquid interface and $\eta_{\text{interface}}$, the efficiency of charge transfer at the interface (see fig. 3.2):

$$\text{IPCE} = \eta_{e^-/h^+} \ast \eta_{\text{transport}} \ast \eta_{\text{interface}}$$

which is identical to the external quantum efficiency (EQE) of a PV cell. It is clear that decent transport properties are required in order to make efficient PEC cells and also interfacial recombination is a common issue in these systems. Shining some monochromatic light onto the WE the IPCE can be calculated as:

$$\text{IPCE} = \left| \frac{j_{\text{ph}} \, (mA/cm^2)}{P_{\text{mono}}} \right| \ast \frac{hc \, (eV \ast nm)}{\lambda \, (nm)}$$

where $j_{\text{ph}}$ is the photo-current density, $hc = 1239.84 \, eV*nm$ is Planck’s constant times the speed of light, $P_{\text{mono}}$ is the incident light power density and $\lambda$ the wavelength of the incident light. This gives a measurement of electrons generated per photon in, as opposed to power generated per power in like STH gives. Assuming every generated electron is used for water-splitting this gives a theoretical maximum efficiency, with a known faradaic efficiency an estimate to the achievable STH might be made.

APCE

If more detailed studies on the inherent properties of a material is desired it can be useful to measure the absorbed photon-to-current efficiency (APCE) since the IPCE takes into account photonic losses such as from reflection. It is thus defined as IPCE but without the absorptance, the number of generated electron-hole pairs per incident photon, $\eta_{e^-/h^+}$:

$$\text{APCE} = \eta_{\text{transport}} \ast \eta_{\text{interface}}$$

which is identical to the internal quantum efficiency (IQE) of a PV cell. Usually absorbance is defined as the logarithm of the incident illumination intensity divided by the transmitted illumination intensity: $A = -log\left(\frac{I}{I_0}\right)$,
where $I$ is transmitted intensity and $I_0$ is incident intensity. Under the assumption that every absorbed photon generates an electron-hole pair it can be written:

$$\eta_{e^-/h^+} = \frac{I_0 - I}{I_0} = 1 - \frac{I}{I_0} = 1 - 10^{-A}$$  \hfill (3.18)$$

and so eq. (3.18) in conjunction with eq. (3.16) can be written as:

$$\text{APCE} = \frac{|j_{ph} \text{ (mA/cm}^2\text{)}| \times h\nu \text{ (eV} \times \text{nm})}{P_{mono} \text{ (mW/cm}^2\text{)} \times \lambda \text{ (nm)} \times (1 - 10^{-A})}$$  \hfill (3.19)$$

Even if ABPE, IPCE and APCE are useful diagnostic tools, the only true measurement of the performance of a PEC cell is the STH efficiency. In the following section different ways to measure different properties of the WE are described, but once again the only true measurement of the hydrogen generating performance will be the unbiased 2-electrode measurement, monitoring the generated hydrogen gas.

### 3.4 Methods of measurement

In order to make any photoelectrochemical measurements the flat-band potential ($E_{fb}$) of the photoelectrode should be determined as it is an indicator of whether or not the material can be used for water-splitting. For an n-type semiconductor the flat-band potential should be negative compared to the potential for hydrogen evolution, which is 0 V vs. RHE. Analogously, the flat-band potential of a p-type material should be positive compared to the potential for oxygen evolution, 1.23 V vs. RHE. $E_{fb}$ can be found, or at least estimated by several experimental techniques such as illuminated open-circuit potential (OCP), Mott-Schottky (M-S) and photo-current onset (j-V) measurements. The flat-band potential should be independent of method used to measure it, but each technique has its errors in estimation which limits both the accuracy of any single method as well as the agreement of the results from the different methods.

#### 3.4.1 Open-Circuit Potential

By shining light onto the WE with sufficient intensity and energy, $h\nu > E_g$, to be able to generate enough carriers to compensate for the band-bending at the surface $E_{fb}$ can be estimated. In fig. 3.8 a schematic drawing of the band structure of a semiconductor in contact with an electrolyte can be seen, with the estimate of the flat-band potential shown.
The safest way to achieve this is by plotting OCP versus illumination intensity in order to find the appropriate intensity at which the potential saturates. However, increasing the light intensity increases the rate of possible sample oxidation, so it is not always appropriate to do this. Also, for an n-type material the potential shift during the OCP should be negative otherwise it implies the bands bending the wrong way, see fig. 3.8, and analogously OCP should shift positively for p-type materials. Using a sample with low defect density and not too fast recombination rate the measured potential between the WE and a reference under sufficient illumination is an estimate of the flat-band potential. The reliability of this estimate is dependent on the quality of the sample, drifts in the photo-current response can be caused by e.g. corrosion or slow adsorption processes at the semiconductor surface as well as heating due to the light source. Generally, a fast response to turned on light is an indicator of higher quality material. Also, defects in the material can cause high recombination rates which will counteract the band-flattening effect and thus require more intensive illum-
nation. If the light is not intense enough to flatten the bands the resulting measurement of the flat-band potential will be an underestimation, see C in fig. 3.8. In fig. 3.9 an example of a chopped light OCP measurement is seen, done for one insufficient light intensity. 

Figure 3.9. An example of measured open-circuit potential on a p-type Si sample, with time in seconds on the x-axis and potential in mV vs. RHE on the y-axis. The potential of light on estimates the position of the flatband potential as \( \approx 370 \) mV vs. RHE. The power is, however, insufficient for flattening the bands and so this underestimates \( E_{fb} \). To get a better approximation a scan over increasing light intensities could also be done.

3.4.2 Mott-Schottky

Measuring the space-charge layer capacitance over a scanned range of applied potentials can be used to determine the flat-band potential according to the Mott-Schottky relation:

\[
\frac{1}{C^2_{SC}} = \frac{2}{\epsilon_r \epsilon_0 A^2 e N_{dopant}} (E - E_{fb} - \frac{k_B T}{e}) \tag{3.20}
\]

where \( C_{SC} \) is the capacitance of the space-charge layer, \( \epsilon_r \) is the semiconductor permittivity, \( \epsilon_0 \) is the vacuum permittivity, \( A \) is the area of the sample surface, \( e \) is the electronic charge, \( N_{dopant} \) is the dopant concentration, \( E \) is an applied potential, \( k_B \) is Boltzmann’s constant and \( T \) is the temperature. Using this it is possible to determine the flat-band potential
3.4 Methods of measurement

as well as the dopant concentration of the semiconductor, assuming the measurement is successfully performed. Along with knowing the band-gap of the material it is then possible to see if the band structure of the material is appropriate for water-splitting. 

$C_{SC}$ can be quite difficult to determine due to non-ideality of the sample and measurements over several frequencies may need to be performed in order to yield good enough results. The frequency dependency of the flat-band potential is partly due to $C_{SC}$ consisting of capacitive contributions both from the double-layer and surface states. This would imply some difficulties in using eq. 3.20 however, the different capacitances can be seen as in a serial connection and thus the smallest usually dominates the overall response. This is not always the case, but often the space charge region will be dominant. The frequency dependency can induce either the same slope but different $E_{fb}$ for different measurements or different slopes with the same $E_{fb}$. The latter can yield decent values for $E_{fb}$ but with inaccurate estimates of carrier concentration and can be caused e.g. by surface states or irregularities in the semiconductor sample. Other causes of shifting flat-band potential include voltage drops over contacts or the Helmholtz layer. [9, 14] In fig. 3.10 some M-S plots can be seen, to the left an example of the first type of frequency, to the right an example of the second.

![Figure 3.10. An example of M-S measurements on a) a p-type 4H-SiC sample and b) an n-type Fe$_2$O$_3$ sample. The two plots perfectly showcases the two types of frequency dependency. Adapted from 2.](image)

Ideally, an equivalent circuit model can be formulated for the working electrode, simplified to a resistor and a capacitor connected in series. The resistor then contains the accumulated resistance over the bulk of the semiconductor, the electrolyte and any wiring in series, while the capacitor consists of the space-charge layer capacitance, $C_{SC}$, as above. Ideally $1/C_{SC}^2$ over a potential range shows a linear dependency, at $1/C_{SC}^2 = 0$ the value at the line intersection with the x-axis will be $E_{fb} + k_B T/e$ and the slope of the line is dependent on $N_{dopant}$ as in eq. 3.21:

$$N_{dopant}(cm^{-3}) = \frac{1.41 \times 10^{32}(cm \ast F^{-2} \ast V^{-1})}{\epsilon_r \ast A^2(cm^3) \ast \text{slope}(F^{-2} \ast V^{-1})}$$

which is retrieved from eq. 3.20 with appropriate substitutions. Appropriate values for $\epsilon_r$ can be found in literature for the material in question and the surface area should be carefully calculated as to not induce to much error in $N_{dopant}$, which should typically give a value around $10^{15} - 10^{18}$ cm$^{-3}$. [9]

Using eq. 3.21 and line fitting on the different frequency-curves measured with the Mott-Schottky method in fig. 3.10 a range of values for doping concentration and flat-band potentials can be found, see table 3.3.

**Table 3.3.** An example of calculated doping concentration and flat-band potential from the left side in fig. 3.10 which can be done using eq. 3.21 [9]

<table>
<thead>
<tr>
<th>Freq. (kHz)</th>
<th>Doping (cm$^{-3}$)</th>
<th>$E_{fb}$ (mV vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$4 \times 10^{17}$</td>
<td>1620</td>
</tr>
<tr>
<td>10</td>
<td>$3 \times 10^{17}$</td>
<td>1700</td>
</tr>
<tr>
<td>20</td>
<td>$3 \times 10^{17}$</td>
<td>1850</td>
</tr>
</tbody>
</table>

### 3.4.3 Photo-current onset

The ability of a semiconductor to split water without an external bias can be evaluated by measuring generated photo-current under illumination over a range of potentials. This gives information about the potential for photo-current onset, the amount of photo-current generated at a certain potential and can also be used to estimate the flat-band potential. In a three-electrode setup scanning from small reverse bias to forward, for an n-type semiconductor, can be done to identify the potential at which the current starts being generated, i.e. the photo-current onset. It is possible to deteriorate an electrode through anodic stripping by forward biasing larger than $E_{fb}$ for p-type, and analogously reversed for n-type, so the scanning range should be carefully set. Increasingly positive (for n-type) bias will
3.4 Methods of measurement

increase the electric fields over the space-charge layer, thus increasing the photo-current. The photo-current onset is the potential at which the carriers start driving the evolution reactions at the electrodes, this potential is offset from $E_{fb}$ by the over-potentials for the appropriate reaction. In fig. 3.11 an example of photo-current of an n-type sample is shown.

Figure 3.11. An example of what a photo-current onset measurement can look like with current on the y-axis and bias voltage on the x-axis, on a p-type Si sample. The light was chopped during the measurement, revealing a slight trend in the dark current. It looks like the onset potential is around -0.2 V vs. RHE.

In reality it may not be accurate, since $E_{fb}$ is an interfacial property and depends not only on the semiconductor but also on the electrolyte, interfacial effects can shift the onset to some other potential. The error induced can be quite large and may for instance be caused by some change in the over-potentials for water-splitting. Reduction of the over-potentials is a commonly targeted property when applying co-catalytic materials to the semiconductor in order to shift the onset to more cathodic (for n-type) potentials. The application of co-catalytic materials should ideally yield more accurate results for $E_{fb}$ by reducing over-potentials, however, the effect the co-catalyst can have on the semiconductor-electrolyte interface may shift $E_{fb}$ unpredictably. [9]
To summarise this, the j-V measurement is primarily done to find the onset potential as well as a measure of the maximum amount of photo-current that can be generated by the material. This is commonly used to compare different samples, with or without co-catalytic materials, as it is easy to see the differences in photo-current generation and onset potential.

3.4.4 Chronoamperometry

For determining the STH efficiency of a PEC cell with eq. 3.13 the short-circuit current density is required, which can be measured by chronoamperometry (CA). This is a technique usually used for time-resolved measurements of current under a pulsed bias, but for the PEC cell pulsed light is used instead and without any external bias. Chronoamperometry is performed in a 2-electrode setup, as opposed to the 3-electrode setup used in all other measurements, now the reference electrode contact is connected to the counter electrode instead. The photo-current can then be measured over the two electrodes under illumination with no applied bias, which will be the true generated photo-current from water-splitting, assuming there are no side-reactions generating any current. In fig. 3.12 an example of a CA measurement performed on a p-type Si sample is seen, this measurement is biased due to the inability of Si to split water unbiased. Ideally the part of the plot where there is light on should be flat, but in reality there are sometimes some rise- and recovery-times, depending on the carrier transport properties of the material. By monitoring the generated hydrogen gas from this and using eqs. 3.12 and 3.13 the faradaic efficiency of the cell can be retrieved as well as the real STH efficiency.

3.4.5 Gas chromatography

In order to actually measure the STH efficiency of the PEC cell the generated hydrogen has to be detected. Gas chromatography is an analytical technique used to determine presence and relative concentrations of different gases in a mixture. It requires the use of a gas chromatograph, which is an instrument adapted to the use of this technique. The basic principle is that the gas mixture to be analysed is injected into the system via a carrier gas, commonly used are inert or nonreactive gases such as He, N or Ar. The gas mixture is led into what is called an analyser column, which is a long tube commonly made of glass with some polymer coating on the inside, usually called the stationary phase. The gas will interact with the column and under heating the different compounds in the gas will elute at different times, called retention times. Each unique compound will corre-
3.4 Methods of measurement

Figure 3.12. An example of what a chronoamperometric measurement can look like on a p-type Si sample, biased by -2 V, with photo-current density on the y-axis and time on the x-axis.

Spond to a specific retention time, and this is what the analytical strength of gas chromatography is based on. The gas at the end of the column is detected, usually with a thermal conductivity detector (TCD). This method is highly resolved, and so chemically and physically similar compounds can be detected, but it is also fast and results can be obtained in minutes.

Using this technique together with those mentioned earlier a thorough analysis of the water-splitting capabilities of a PEC cell is possible to make, taking into consideration most of the important parameters of this application.
Chapter 4

Previous work

The basic goal of this technology, as mentioned earlier, is to use a semiconductor to split water into hydrogen and oxygen, from which the hydrogen gas can be gathered and used as a container of clean energy. The working principle behind it is that photo-generated carriers in the semiconductor can be used to oxidise water molecules and then reduce the resulting hydrogen ions. There are different ways to achieve this, either by using an n-type semiconductor as a photo-anode to drive an oxygen evolution reaction (OER), or by a p-type semiconductor as a photo-cathode to drive a hydrogen evolution reaction (HER). This report focuses on the n-type variation and oxygen evolution. The semiconductor used should fulfil some criteria, for instance its band-gap should straddle the redox-potentials of water-splitting (strictly, one would include over-potentials and other losses here) while it also should efficiently absorb visible light. This is described in simplicity under section 3. In this section some previous research in this field is presented.

4.1 Semiconductors

Common issues with existing technology include efficiency, the devices are just not performing well enough for commercial applications, but also stability, device performance is usually greatly reduced over time. This presents some demands on the properties of the semiconductor, firstly, it should have a suitable band-gap to efficiently absorb visible light to drive the water-splitting process, see fig. for the band positions of some commonly used semiconductors. Secondly, it should be a very durable, chemically stable material in order to prolong the lifetime of the device. Thirdly, its band edges should appropriately straddle the redox-potentials of water-splitting,
Figure 4.1. Band positions at pH = 1 (CB edge = red, VB edge = green) of some semiconductors in relation to the normal hydrogen electrode (NHE), as well as the redox potentials of water-splitting. Adapted from [4].

as described earlier. [15] It is also important for the semiconductor to have good ability to transport charges in order to let the photo-generated minority carriers reach the interface between the electrolyte and semiconductor before recombination happens. With all this in mind, there are a few semiconductors that more or less fulfil these requirements.

WO$_3$, Fe$_2$O$_3$, TiO$_2$ and BiVO$_4$ are all examples of well-known candidates for the photo-anode position, and much research has been done regarding their use in PEC devices [16, 17]. For instance the research on TiO$_2$ began in the 1970’s [2], as mentioned earlier, and has been a go-to working-electrode ever since and is continuing to be one of the most viable materials in PEC devices due to high photo-stability as well as being non-toxic and not too expensive [18, 19]. WO$_3$ emerged later than TiO$_2$ but has been shown to possess decent photo-catalytic qualities as well as being chemically stable (in acidic media at least), non-toxic and not expensive [20, 21]. BiVO$_4$ is a promising n-type semiconductor which has band-gap with a very suitable size of 2.4 eV (see fig. 4.1) [22]. Fe$_2$O$_3$ possesses great ability to absorb light in the visible spectrum, see fig.4.2, is chemically stable and also a cheap material [23].
4.1 Semiconductors

Figure 4.2. The solar spectrum together with the theoretical maxima in photo-generated current and STH efficiency base on the band-gap values of a few semiconductors and the assumptions that all light possible is absorbed and used for water splitting, the pink dot approximately marks the position of 3C-SiC. Adapted from [24, 25].

However, there are issues with each one of them. TiO$_2$ for instance has inherent problems with carrier recombination and proper utilisation of the solar spectrum, both of which will affect performance. These types of problems can sometimes be counteracted by some modification or addition to the semiconductor material. Alternatively an external electrical bias can be applied to help drive the wanted reactions, but then part of the point with this technology is lost. In fig. 4.1 it can be seen that BiVO$_4$, WO$_3$ and Fe$_2$O$_3$ are not perfectly fit for water-splitting as their conduction band edges are not positioned to accommodate the reduction potential within their band-gaps. Fe$_2$O$_3$ has generally bad opto-electronic properties resulting in poor efficiency [23]. The performance of BiVO$_4$ in water-splitting applications is primarily limited by its recombination losses due to poor electron-hole separation [26, 22]. TiO$_2$ straddles the redox potentials, but its band-gap
is quite large making its visible light absorption abilities insufficient for efficient water-splitting, as mentioned earlier. In fig. 4.2 the theoretically calculated maximum efficiency of some semiconductors is shown, it can be seen that TiO$_2$ is in the lower end of the efficiency spectra. Due to these imperfections in regard to the criteria mentioned earlier some semiconductors work in PEC devices on their own, others do not, in either case performance can be greatly altered in several ways, e.g. by nano-structuring or doping, for example it has been shown that N-doped TiO$_2$ nano-particles increased visible light absorption compared to un-doped nano-particles [27]. C-doped TiO$_2$ nano-tube arrays were shown to greatly increase the sunlight absorption efficiency of the material [28], H-treated (by annealing in an H-ambience) TiO$_2$ nano-wire arrays have also been shown to increase absorption efficiency as well as achieving a decent solar-to-hydrogen (STH) efficiency under bias of 1.1% [29]. Similar progress has been made regarding improving the weaknesses of the other semiconductors as well.

3C-SiC on the other hand, has a band-gap of about 2.36 eV and very well-positioned with regard to the potentials of water-splitting, see fig. 4.1. This size of band-gap is suited to utilise an appreciable portion of visible sunlight, see fig. 4.2 all the while not being too small to accommodate the water-splitting process. The optimal band-gap for water-splitting has been calculated to about 2.03 eV [11], which is close to that of 3C-SiC. In addition it exhibits good transport properties and is a chemically stable material with high durability which fits the application, however, surface oxidation is a known issue in anodic SiC. This has been proven for 6H-SiC to be suppressed by e.g. application of co-catalytic materials [30].

4.2 Co-catalytic materials

In order to facilitate reduction- or oxidation-reactions at the semiconductor surface co-catalytic materials can be applied to it, which aims to increase the water-splitting performance. The co-catalyst provides the working electrode with reaction sites, they promote separation of electrons and holes and interfacial charge transferring as well as lower the activation energy required for the evolution reactions [17]. They also serve to protect the semiconductor from e.g. oxidation, increasing the lifetime of the device.

4.2.1 Hydrogen evolution catalysts

Pt is a good hydrogen evolution catalyst (HEC), which can be used to further promote HER. Theoretically, Pt is the best existing catalyst for HER out of all elements due to it bonding to H with such ideal strength
4.2 Co-catalytic materials

that it easily both adsorbs and reduces \(H^+\), as well as releases \(H_2\) afterwards [16, 31]. To the right in fig. 4.3 the position of Pt in a so called volcano plot can be seen to be close to the summit, due to which Pt is one of the most promising elements for hydrogen evolution. This is based on calculated adsorption energies of hydrogen onto the elements plotted vs. measured exchange current [31]. Ni can be used as well, it’s cheaper than Pt but not as effective. Other options include Fe and Co, both with weaker results compared to Pt. Different metal alloys have been shown to increase performance due to several factors such as increased surface area originating from a change in morphology during co-deposition of the materials. Certain alloys such as Ni-Mo based compounds have been shown to work decently as catalytic materials. [16] Oxides of transition metals can be used as HEC’s as well, for instance RuO\(_2\), which has been shown to increase stability of certain photo-cathodes in comparison to those decorated with Pt. [32]

![Figure 4.3. So called volcano plots over a few co-catalytic candidates, the closer to the summit they are, the better they are expected to work. Left: Volcano plot of trends of oxygen evolution activity for some metal oxides, with over-potential on the y-axis. [33] Right: Measured exchange current density versus Gibbs free energy for hydrogen absorption for a few elements, the metals to the left of Pt in the plot bind H too hard, and the metals to the right too softly [31, 34].](image)

4.2.2 Oxygen evolution catalysts

Shifting focus to n-doped semiconductors, there are a great deal of co-catalytic materials to drive oxygen evolution reactions as well, oxygen evolution catalysts (OEC) can be used on a photo-anode to promote OER. Pt can be used also as an OEC and it has been shown to increase the performance of a 3C-SiC-based PEC water-splitting device, Ichikawa et al. [35], in
this case the Pt was applied by three-electrode electro-chemical deposition which is a method that can be used with a large range of materials for this purpose \cite{10}. An optimal nano-particle size was found with which an energy conversion efficiency of 0.52 % was reached (with bias). Also Song et al. \cite{36} showed that Pt nano-particles decorating the surface of an n-type 3C-SiC photo-anode can increase the efficiency of a PEC water-splitting device as well as suppress the corrosion of the SiC surface. The nano-particles were made by sputtering Pt onto the SiC surface and annealing it afterwards in order to form particles. It is important that the inter-particle distance is smaller than the minority carrier diffusion length in order to decrease the risk that the metal is acting as a recombination center, which could deteriorate device performance \cite{9}. Also, increased surface coverage will cause losses in the amount of light that actually reaches the semiconductor, however, high surface coverage can also be necessary to facilitate reactions at a catalyst site rather than at the semiconductor/electrolyte interface \cite{37}.

\[ \text{IrO}_2 \] is shown to be a quite good OEC, the same goes for RuO\(_2\) which can be used both as HEC and OEC \cite{10}. On the left of fig. 4.3 a similar volcano plot as on the right side is shown but for the oxygen evolution on metal oxides instead, close to the summit of this e.g. RuO\(_2\) is found and slightly down-hill from there IrO\(_2\). However, Ru and Ir suffers from the same condition as Pt, which is that they are expensive and can only be acquired in limited quantities. IrO\(_2\) onto semiconductors such as WO\(_3\) has been shown to greatly increase performance of the oxygen production at the working electrode by e.g. Spurgeon et al. \cite{37}. It was noted that the method of applying the catalyst is quite important in order to get the highest performance, the best deposition method tested was sputtering although further investigations could be done in atomic layer deposition to yield improved results. For thick layers excellent water oxidation abilities were observed, however, larger light absorption of the co-catalyst is naturally observed as well, which means back-light illumination is an option. With thick films the effects of the electrolyte-semiconductor junction were to some extent diminished as well and photoelectrochemical performance reduced. A reflection is made regarding the ideal OEC layer as being optically transparent, highly conformal and sufficiently thin or porous to let interfacial energetics be controlled by the electrolyte. Another method could be to deposit catalyst particles at reasonable distances to let the electrolyte-semiconductor junction be dominant, which is the most reasonable solution to escape the problems associated with full coverage of a thick layer. \cite{37} RuO\(_2\) nano-particles have also been shown to greatly improve photo-current generation when deposited onto e.g. WO\(_3\) \cite{38}. These
metal oxides yield good results, but are not suitable for future use due to their scarceness. CoOOH, NiOOH and FeOOH are some examples of oxy-hydroxides that can be made using more abundant elements as co-catalysts. It can be noted from the volcano-plot in fig. 4.3, the amount of common metal oxides that reside close to the summit as well. FeOOH deposited onto BiVO₄ has been shown to significantly increase photo-current as well as stability compared to only BiVO₄. The electro-deposited FeOOH increased the ability of the semiconductor to utilise the photo-generated holes for water oxidation to nearly 100% faradaic efficiency. The generated photo-current is both very high and exclusively due to water oxidation which yields high performance, making FeOOH a very interesting material to be used as a co-catalyst. CoOOH onto WO₃ nano-rods with about 500 nm diameter has been shown to increase photo-current as well as stability. Issues such as carrier recombination are partly addressed by this because the applied cobalt seems to be able to efficiently transport holes to the electrolyte, which will then increase faradaic efficiency and thus hydrogen generation. Other types of OEC’s based on Co has been used on WO₃ to suppress the formation of peroxides in order to increase efficiency of the oxygen evolution. Different forms of cobalt-based oxides, such as CoₓOᵧ and cobalt phosphates (sometimes denoted Co-Pi), have also exhibited excellent co-catalytic properties. Co-Pi has been shown to increase photo-currents on many semiconductors, e.g. BiVO₄. Importantly, it has been shown to have a reducing effect on the thermodynamic over-potentials in the water-splitting reaction, which leads to a shift of the photo-current onset. In a comparative study between Co-Pi and FeOOH onto BiVO₄ by Jia et al., it was noted that although Co-Pi shows superior short-term performance, the increased stability with FeOOH makes it perform better in the long run. The electro-deposition method of Co-Pi and photo-deposition of FeOOH in that case were the same methods as have been used in previous research on these materials.

Both Co-Pi and FeOOH are thought to be well-performing and the comparison between them is interesting. The method used to deposit FeOOH is usually electro-deposition under illumination, well described by Seabold and Choi. Then the WE is put into aqueous solution of 0.1 M FeCl₂ (pH 4.1) and has light shone on it. Seabold and Choi used light through AM 1.5 G and neutral density filters with an illumination intensity of 1.6 mW/cm². An applied bias is used to control the photo-current resulting from oxidation of Fe²⁺ to Fe³⁺, which then uses OH⁻ to precipitate onto the semiconductor surface as FeOOH. The current was manipulated into being 10 µA/cm² for 3 seconds, followed by 1 µA/cm² for 2 seconds which
was then repeated for 5.5 hours for optimal film thickness. Similar methods have also been tried by e.g. Lhermitte et al. in which the WE is emerged into the same 0.1 M FeCl$_2$-solution. In this case, however, the illumination intensity was kept at the normal AM 1.5 G standard, 100 mW/cm$^2$ and a bias of 0.4 V vs. Ag/AgCl was applied. By monitoring the current they could stop the deposition after 0.087 C of charge had passed through, taking around 5-10 minutes. An electro-chemical deposition process followed with the same principles, but in the dark and with a 1.2 V bias vs. Ag/AgCl for another 5-10 minutes, until 0.07 C charge passed through. The difference in time between the two methods is quite large, but since they are used on different semiconductors it can be hard to say exactly what the difference in result is. Possibly a slower deposition-rate gives the precipitated particles more time to form some certain structure as opposed to a more irregular film using faster deposition.

An advantage of Co-Pi over FeOOH is the ability to deposit the material onto an electrode in the absence of illumination. It can be deposited using a method tried by Kanan and Nocera. They used electro-chemical deposition by oxidation of a solution containing phosphate and Co$^{2+}$. The material was originally deposited onto Indium-tin oxide, but the method has later been reproduced onto e.g. WO$_3$ by Seabold and Choi. The method is realised by preparing a 0.5 mM solution of Co(NO$_3$)$_2$ (cobalt nitrate) in 0.1 M KPi (potassium phosphate) of pH 7.0. A voltage of 1.3 V (vs. NHE) is then applied over an 8 hour period, forming a dark coating on the substrate.

An advantage of FeOOH over Co-Pi is the reduced risk of having to handle dangerous metal salts during manufacturing of the co-catalysts. Also, alternative deposition methods of FeOOH also exist and have been proven to increase device performance. Kim et al. deposited a thin layer of FeOOH onto Fe$_2$O$_3$ by a precipitation method, instead of the commonly used electro-deposition. By immersing the WE, in this case consisting of Fe$_2$O$_3$ on glass, into a solution of 0.15 M FeCl$_3$ and 1 M NaNO$_3$ kept at 100 °C for 5 minutes a 2 nm thin layer of FeOOH was made on the surface of the electrode. The resulting generated photo-current was doubled and the onset potential negatively by 0.12 V as compared to the bare semiconductor. It is possible, however, that this method is only usable due to the structure of the Fe$_2$O$_3$ being fitting to accommodate the growth of a FeOOH layer on top, perhaps it is not applicable to just any semiconductor.

To summarise this, previous research has shown many different and viable combinations of semiconductors and co-catalysts, such as BiVO$_4$ with Co-Pi or FeOOH, that all serve to increase the performance of water-
splitting devices by varying degrees. These methods and results will serve as a foundation for the work done in this project as well as motivation of the choices made regarding the device-design.

4.3 Ohmic contacts

Some work has been done regarding ohmic contacts on 4H- and 6H-SiC, for example it is possible to make good quality contacts on the Si-faces of both polytypes by evaporating 100 nm Al onto them. On the C-face, however, some annealing usually has to be done. As performed by La Via et al. [49], ohmic contacts on 4H-SiC were made by depositing a 100 nm Ni-film followed by annealing at 950 °C in an inert ambient. The measured I-V characteristics shows completely ohmic behaviour. Furnival et al. [50] on the other hand, used sputter deposition of 5 nm Ti followed by 150 nm Ni on C-face 4H-SiC and annealing in vacuum at 1050 °C for 200 seconds. The current reported in this case was higher than for La Via et al., thus resulting in a lower resistance ohmic contact.

On 3C-SiC some work has been done using Al, Ti and Ni, e.g. by Li et al. [51] who deposited 100 nm Ni and 20 nm Ti by e-beam evaporation to produce contacts on a 3C-SiC transistor. Wan et al. [52] deposited 200 nm Ni followed by annealing at different temperatures between 500 and 1000 °C for 2 minutes in Ar. After this a 700 nm layer of Au was deposited on top, as well as phosphorous implantation and a Ni/Si bi-layer. They produced ohmic contacts with different resistances depending for different conditions such as annealing temperature and phosphorous implantation conditions. It was shown e.g. that pure Ni annealed at above 700 °C can form ohmic contact on the 3C.

More novel materials have also been shown to produce ohmic contacts on SiC, such as Ti₃AuC₂ [53]. However, in the method developed by Fashandi et al. [53] the contacts were annealed at 600 °C for 1000 hours, making it a not so convenient way to produce ohmic contacts.
Previous work
Chapter 5

Experimental procedures

In order to measure the different properties mentioned earlier proper preparations must be made. Firstly the samples of 3C-SiC were grown, after which they were polished and cleaned, had contacts deposited onto them and were manufactured into electrodes. After this the PEC cell could be prepared with electrolyte and measurements performed, all of this is described briefly in the following sections.

5.1 Sample preparation

Here the methods of manufacturing and preparing the samples on which to perform measurements are described. First, a number of 3C-SiC samples were grown and visually checked for appropriate crystal structure, which is possible due to the different bandgaps of the SiC polytypes giving 3C a yellow appearance as compared to the transparent but often more greyish look of 4H. More in detail observations were later made with an optical microscope. After growth the samples were polished in order to remove the substrate and then cleaned before ohmic contacts were deposited. Electrodes were manufactured out of some of the samples at that point to test the water splitting performance of bare Si, 3C-SiC and 6H-SiC, on some 6H-samples a co-catalyst deposition method was also tried later.

5.1.1 The 4H- and 6H-samples

The pieces of 4H- and 6H-SiC were cut from industrially produced wafers and previously polished when acquired. The 4H-samples were off-cut by 4° from the [0001]-direction and are the same as were used as substrate for 3C-growth, see chapter 5.1.2 The 4H-samples were polished on both faces
while the 6H were polished to the same degree as the 4H on its Si-face, but more coarsely so on its C-face.

5.1.2 Growth

The samples of 3C-SiC used in this project were grown using a sublimation method \cite{5, 54, 55}. In short, this was done by putting a sample of 4H-SiC with an approximate size of 1x1 cm, cut off-axis by 4° with respect to the [0001]-direction, inside a graphite crucible together with a piece of polycrystalline 3C-SiC as source material. Shown schematically in fig. 5.1 is the contents of the crucible, in the bottom a piece of tantalum is put which serves two purposes, firstly it absorbs excess carbon released in the sublimation process, secondly it promotes an even temperature profile within the crucible. On it the source material is placed and then the first graphite spacer with a hole in it to let material sublimate through. During sequential heating of the crucible up to around 1900 °C the source material sublimes onto the substrate and forms 3C-SiC, described well in \cite{54}.

It is noted that when grown in this fashion, the 3C-SiC will start at the edge of the revealed substrate and grow in the [1120]-direction, meaning that at any certain time the growth process will have produced a thicker layer on the first part of the sample than further towards the edge. Also, a transition layer, consisting of mixed SiC-polytypes, develops between the grown 3C-SiC and the substrate, making the samples look like in fig. 5.2. During polishing a large amount of the transition layer is removed, although unless the sample has been grown thick enough there will be some area on the sample with slightly lower coverage of 3C-SiC \cite{54}. This implies that different parts of a grown sample might have different properties due to this different crystallography.

5.1.3 Polishing & cleaning

As mentioned in section 3.2.1 there is an optimal thickness for the samples. Considering also the limitation on the sample thickness of around 300 µm due to handling difficulties at lower values, the suggested thickness for these samples will be around that value. The thickness of the grown samples was in the range of 800-1100 µm approximately.

The samples were glued backside-up onto a holder and placed in a rotating wheel in a sample polishing-machine. The samples were then polished against pads of varying coarseness, starting with 70 µm down to 1 µm, making sure with each increasingly smooth pad to polish away at least the thickness corresponding to the coarseness of the last. This ensured a
5.1 Sample preparation

Figure 5.1. Left: Schematic image of the crucible used for growth of 3C-SiC. A slice of tantalum is placed in the bottom with a piece of SiC source material on top. The substrate is placed with its silicon-terminated face downwards, onto which the 3C structure is grown, sandwiched between two graphite spacers. Right: A fully grown sample of 3C-SiC on a 4H-SiC substrate.

smoothly polished surface on the backside of the samples onto which an ohmic contact could be deposited. The samples were polished down to thicknesses between 300 and 350 µm, measured with a micrometer. After the polishing the samples were removed from the holders by heating them until the glue melted. The samples were then put in acetone and boiled for some minutes, then taken out and rubbed with acetone and then boiled once more. The boiling then continued with ethanol after which standard RCA1 and RCA2 cleaning followed. This is basically done by bathing the samples first in a solution of ammonia (NH₃) and hydrogen peroxide (H₂O₂) and then in a solution of H₂O₂ and hydrochloric acid (HCl). These steps are made to ensure sufficient removal of glue residue leftover from the polishing process. In fig. 5.3 a polished, cleaned sample is seen, clearly visible are the domain boundaries that appear during growth between the differently oriented 3C-SiC areas. Also, towards the further end of the sample it is getting more transparent, indicating lower coverage of 3C-SiC in this area.
Figure 5.2. A schematic image of a cross-section of a 3C-SiC sample grown on 4H-SiC, it is then polished from the bottom up to the line. The cubic layer grows with a transition layer between it and the substrate [54], after polishing there is still some transition material left if the sample has not grown thick enough.

5.1.4 Ohmic contact deposition on 3C-SiC

Just prior to the deposition of ohmic contacts on the backside of the samples they were immersed in a hydrofluoric acid (HF) solution for 2 minutes in order to remove any surface oxidation that might have occurred. The samples were then fixed on a sample holder and placed inside a vacuum chamber together with aluminium (Al) and gold (Au) sources for evaporation. The vacuum chamber was connected to a device calibrated for metal evaporation within the system such that desired thicknesses could be input and applied power for the evaporation is set automatically. The resulting contacts were made of a 200 nm layer of Al on the backsides of the samples with a 20 nm layer of Au on top to prevent oxidation.

5.1.5 Ohmic contact deposition on 4H- and 6H-SiC

Ohmic contact deposition onto 4H- and 6H-SiC was done in order to characterise co-catalyst deposition methods before trying them on 3C-SiC. The contacts were deposited as dots at first, between which I-V-curves were measured in order to characterise their behavior. Before any deposition the same cleaning routine as on 3C was used.

Si-face

Contacts on the Si-face of the 4H- and 6H-samples were made by evaporation deposition of 100 nm Al.
5.1 Sample preparation

Figure 5.3. A sample after polishing and cleaning, with the yellow colour of 3C-SiC clearly visible. Also noticeable are the multiple domain-boundaries visible as lines along the growth direction, as well as the increasing transparency towards the lower edge of the sample, indicating a thinner layer of the 3C-SiC on this area.

C-face

On the C-face of the 4H- and 6H-samples several different method-parameters when applying contacts were tested. Nickel was applied in varying thicknesses in the range 100-130 nm and different amounts of annealing were tested at between 930-950 °C.

5.1.6 Ohmic contact on Si

The Si samples were provided with a 200 nm Al contact.

5.1.7 Making the electrodes

The samples with deposited contacts on their backsides could be made into working electrodes by gluing them onto a piece of glass using copper tape. On some samples silver paste was used to further secure good contact between the copper and semiconductor. The whole electrode was then covered in epoxy resin, see fig. 5.4, apart from the front surface of the semiconductor, which is supposed to be in contact with the electrolyte, and the end of the copper tape, which is connected to a potentiostat.
5.1.8 Co-catalyst deposition

The co-catalytic materials to be explored were chosen as FeOOH and Co-Pi (cobalt phosphate). Co-Pi has recently been shown to increase water-splitting performance, see chapter 4.2, also reducing the over-potentials when used on BiVO$_4$ which is a material of similar bandgap to 3C-SiC. The performance of cobalt-phosphates on other semiconductors have also yielded good results in general, so its overall good performance paired with the specific ability to reduce the over-potentials and thus shift the photocurrent onset is what motivates its use in this project. The other material, FeOOH, has also been shown to increase the performance of many semiconductors, including BiVO$_4$. It is more widely researched than Co-Pi and its overall good performance together with the specific ability to drastically increase the efficiency of oxygen evolution motivates the use of this co-catalyst in this project. Both co-catalysts were thought to be deposited using simple electro-deposition recipes found in literature. Unfortunately, the deposition of Co-Pi was later omitted due to lack of time.

FeOOH

The FeOOH was deposited using a method based on what has been tried by Seabold and Choi [39], see section 4.2.2. They used photoelectrochemical deposition by oxidation of Fe(II) ions to Fe(III) that precipitates onto the
5.2 Sample characterisation

The samples were characterised using different methods, such as optical microscopy, along the way from growth to complete electrode. Most importantly perhaps is the visual characterisation performed with the naked eye. From this the coverage of 3C-SiC can be determined due to its yellow colour, but also the amount of growth-domains on the surface as well as major defects and contaminants such as carbon particles. Other methods, such as electron microscopy, could also be utilised to get more thorough information about the samples.

5.2.1 Optical microscopy

The samples were examined in an optical microscope as a part of the growth process in order to keep track of roughly how many domain boundaries were present in a sample, how well the 3C coverage was, basically performing a similar analysis as with the naked eye except more in detail. It was also a good opportunity to see if there was anything unusual about a particular sample, any strange surface formations etc.

5.2.2 I-V measurements

In order to characterise the performance of the deposited ohmic contacts I-V measurements were performed. This was performed using a simple 2-
Experimental procedures

point setup, applying a bias over the sample and recording the resulting current with the intent of finding the linear, typically ohmic behaviour.

5.3 PEC measurements

The PEC setup consisted of a cell with a quartz window in its side and a lid with several holder positions for electrodes. The cell was filled with a 1 M NaOH solution of pH≈13.6 as electrolyte. Through the lid the electrodes were placed, the working electrode facing the quartz window, and the counter- and reference electrodes close by, see fig. 5.5. As Pt electrode was used as a counter and the Ag/AgCl in sat. KCl was used as reference.

![Figure 5.5. A schematic drawing of the PEC cell, the Working electrode is marked with W, the reference R and the counter C. In a 3-electrode setup all electrodes are connected, but in a 2-electrode setup the reference is instead connected to the counter electrode.](image)

The electrodes were connected to a Versastat 3 potentiostat, which in turn was connected to a computer with the Versastudio v.2.44.4 software on it. Before measurements on bare 3C-SiC started, several runs on Si was done to get good referential plots on all the different kinds of measurements. After some measurements on bare 3C-SiC had been performed, measurements on 6H followed, together with attempts of co-catalyst deposition.

5.3.1 Mott-Schottky

Mott-Schottky measurements were performed with a 3-electrode setup, where the capacitance over the working electrode was measured over a range of potentials. This was then repeated for several different frequen-
cies of that AC-potential. The purpose was to get estimates of the doping concentration and flat-band potentials, as described under chapter 3.4.2.

5.3.2 Open-Circuit Potential

The open circuit measurements were also performed using a 3-electrode setup, but instead the potential change over time was monitored with and without AM1.5G illumination. The purpose of this was to get an estimate of the flat-band potential, as described under chapter 3.4.1.

5.3.3 Photo-current onset

Once again, the 3-electrode setup was used to measure the photo-current onset. The generated photo-current in the dark, under AM1.5G illumination and under chopped illumination was then monitored for a range of applied potentials. The purpose was to determine the onset potential of the device as well as monitor the photo-current density at different applied voltages, as described under chapter 3.4.3.

5.3.4 Chronoamperometry

For the chronoamperometry measurements a 2-electrode setup was used, as opposed to every other measurement which uses the 3-electrode setup. The generated photo-current was then measured over time under chopped AM1.5G illumination, the process is described in short under chapter 3.4.4.
Experimental procedures
Chapter 6

Results and discussion

In this chapter the results of the preparation and measurements on the different samples are presented and discussed. Firstly, the results of the growth are briefly presented followed by any other preparation procedures worth mentioning, such as ohmic contact deposition. After that the results from the different types of PEC measurements are presented and discussed. All the different measurements were performed on 3C-SiC and p-Si, while 6H-SiC is also shown for the j-V part due to the co-catalyst deposition experiments.

6.1 Growth and preparation

The grown samples all looked different from each other, each had its own unique defects and degrees of 3C coverage, which probably affects PEC measurements. Usually the samples were visually examined to be completely covered in 3C-SiC, or possibly with some thinning coverage towards the end of the sample along the growth-direction. The amount of domain-boundaries was observed as between 2 and 6 for an average sample, see fig. 6.1. Other characteristics of the samples, such as a terrace forming right at the beginning of the sample in the growth direction, are also visible in fig. 6.1. Overall the quality of the samples produced seemed decent, with little major defects visible to the naked eye and mostly covered in 3C-SiC. The polishing yielded a backside surface which looked completely smooth and was not further examined afterwards. The results of the cleaning processes performed in order to remove the glue and other contaminations were not further scrutinised either. Fabricating of the electrodes was usually not any concern quality-wise, however, occasionally an electrode would not work which could be due to some bad adhesion to the copper
contact, or possibly some improper coverage of the epoxy resin. In general the production of electrodes was relatively problem-free.

Figure 6.1. A few micrographs of the grown samples. **Top left:** An image of the terrace formed at the start of the sample in the growth-direction, notably there are some stacking faults visible as geometric shapes. **Top right:** An overview image of a sample, visible are the domain boundaries as thick lines in the growth direction, as well as some carbon particle contamination as the black dot. **Bottom left:** An area of a sample near its edge, many small black dots probably due to carbon dust contamination as well as two larger carbon particles are visible, also, more defects in the form of lines. **Bottom right:** A relatively clean and seemingly fault-free area, however, the lines indicating some stacking-faults are still visible.

### 6.2 Ohmic contacts

The contacts made on the C-face of 6H-SiC using 130 nm Ni followed by annealing in nitrogen ambient at 930 °C for 4 min showed completely ohmic behaviour, as seen in fig. 6.2. This contact was made on the 6H-samples later used for testing the co-catalyst deposition. The contacts on the 3C-SiC samples were made with 200 nm Al and 20 nm Au on top and exhibited nearly ohmic behaviour, as seen in fig. 6.3. The resistivity of the contacts can be evaluated, but it was not done in this project.
6.2 Ohmic contacts

Figure 6.2. An I-V measurement made on the deposited Ni-contact on the C-face of 6H-SiC. The behaviour is characteristically ohmic.

Figure 6.3. An I-V measurement made on the deposited Al/Au-contact on 3C-SiC. The behaviour is nearly ohmic.
6.3 Mott-Schottky

Here the results of the Mott-Schottky measurements on the bare Si and 3C-SiC materials are shown and discussed.

6.3.1 Si

Some Mott-Schottky measurements on two p-type Si can be seen in figs. 6.4 and 6.5 with corresponding calculations performed in tables 6.1 and 6.2 respectively. In the images the frequency of each measurement is written in kHz next to its corresponding curve. Curiously the two different samples seem to each exhibit one of the two types of frequency dependency described in chapter 3.4.2. The measurements seen in fig. 6.4 seems to give a value of the flat-band potential of around 320 mV vs. RHE, but with a larger spread of the doping concentration. The straight line in the image is a line fit of the linear region of the 100 kHz curve. The measurement seen in fig. 6.5 thus gives a spread in the values of the flat-band potential, but gives a value of the doping concentration of around high $10^{14}$ cm$^{-3}$. The doping concentration of these Si samples is thought to be in the region of low $10^{15}$ cm$^{-3}$ and the flat-band potential of p-Si is usually slightly lower than what is measured here [56], but still these values seem to be within a reasonable range.
An M-S measurement on Si (exposed sample area = 0.162 cm$^2$). The straight line is a line fit of the linear region of the 100 kHz curve.

**Table 6.1.** Calculated values for doping concentration $N_D$ and flat-band potential $E_{fb}$ (vs. RHE) for a p-type Si sample at a few different AC frequencies, see fig. 6.4. The calculations were performed using a linear fit to find the slope of the curves, which was used with $\epsilon_r = 11.68$ in eq. 3.21 (the Mott-Schottky relation) to calculate these values.

<table>
<thead>
<tr>
<th>Freq. (kHz)</th>
<th>Doping (cm$^{-3}$)</th>
<th>$E_{fb}$ (mV vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.33*10$^{17}$</td>
<td>320</td>
</tr>
<tr>
<td>5</td>
<td>7.46*10$^{16}$</td>
<td>330</td>
</tr>
<tr>
<td>10</td>
<td>2.22*10$^{16}$</td>
<td>320</td>
</tr>
<tr>
<td>20</td>
<td>3.54*10$^{15}$</td>
<td>310</td>
</tr>
<tr>
<td>50</td>
<td>6.02*10$^{14}$</td>
<td>330</td>
</tr>
<tr>
<td>100</td>
<td>2.71*10$^{14}$</td>
<td>370</td>
</tr>
</tbody>
</table>
Figure 6.5. An M-S measurement on Si (exposed sample area = 0.159 cm$^2$).

Table 6.2. Calculated values for doping concentration $N_D$ and flat-band potential $E_{fb}$ (vs. RHE) for a p-type Si sample at a few different AC frequencies, see fig. 6.5.

The calculations were performed using a linear fit to find the slope of the curves, which was used with $\epsilon_r = 11.68$ in eq. 3.21 (the Mott-Schottky relation) to calculate these values.

<table>
<thead>
<tr>
<th>Freq. (kHz)</th>
<th>Doping (cm$^{-3}$)</th>
<th>$E_{fb}$ (mV vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.43*10$^{15}$</td>
<td>170</td>
</tr>
<tr>
<td>5</td>
<td>7.35*10$^{14}$</td>
<td>220</td>
</tr>
<tr>
<td>10</td>
<td>4.08*10$^{14}$</td>
<td>250</td>
</tr>
<tr>
<td>20</td>
<td>2.40*10$^{14}$</td>
<td>275</td>
</tr>
<tr>
<td>50</td>
<td>1.62*10$^{14}$</td>
<td>315</td>
</tr>
<tr>
<td>100</td>
<td>1.39*10$^{14}$</td>
<td>350</td>
</tr>
</tbody>
</table>
6.3 Mott-Schottky

6.3.2 3C-SiC

The M-S plots measured on bare 3C-SiC samples largely followed the first frequency dependency described in chapter 3.4.2, meaning that they mostly showed similar slopes but with a varying x-axis intersection and thus different $E_{fb}$. In figs. 6.6 and 6.7 a few Mott-Schottky measurements for two pieces of 3C-SiC from the same sample are shown. The different frequencies at which the lines are measured are written in kHz in the image. In tables 6.3 and 6.4 the results of some calculations of doping concentration and flat-band potentials can be seen. It seems like the doping concentration is slightly less frequency-dependent than the flat-band potential in both cases, which also agrees with the first type of dependency as stated earlier.

The frequency-dependency of the Mott-Schottky measurements results in that the flat-band potential cannot be very accurately determined this way, the variation is much larger than that observed previously for Si. This is probably due to some surface states, insulating layer, capacitative interference from the Helmholtz layer or various other reasons, all of which affect the equivalent circuit model which has been assumed as the Mott-Schottky relation. [57]

A few of the electrodes seemed to break down electrically after some M-S measurements, a guess is that the Schottky barrier breaks down due to an inappropriate voltage range, this was mostly observed at higher frequencies. This caused the capacitance measurements to only become noise. It also seems to affect the electrode permanently through all the following measurements. The electrodes are denoted A, B and C in the following sections and they originate from different parts of a 3C-SiC sample, where A is thought to be the best part in terms of 3C-coverage, B originates from the worst part and C some intermediate. The measurements on B and C are not shown in some cases due to their poor performance, C is often seen performing worse than B as well which might be attributed to the break down mentioned earlier.
Results and discussion

Figure 6.6. A Mott-Schottky measurement of $C_{SC}^{-2}$ against $V$ (vs RHE) on a 3C-SiC sample (with a surface area of 0.114 cm$^2$), the labels in the figure are the AC frequencies of each particular line in kHz.

Table 6.3. Calculated values for doping concentration $N_D$ and flat-band potential $E_{fb}$ (vs. RHE) for a 3C-SiC sample (which is denoted as the A-sample) at a few different AC frequencies, see fig. 6.6. The calculations were performed using a linear fit to find the slope of the curves, which was used with eq. 3.21 (the Mott-Schottky relation) to calculate these values.

<table>
<thead>
<tr>
<th>Freq. (kHz)</th>
<th>Doping (cm$^{-3}$)</th>
<th>$E_{fb}$ (mV vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.58*10$^{17}$</td>
<td>-10</td>
</tr>
<tr>
<td>5</td>
<td>1.01*10$^{17}$</td>
<td>-80</td>
</tr>
<tr>
<td>10</td>
<td>8.86*10$^{16}$</td>
<td>-130</td>
</tr>
<tr>
<td>20</td>
<td>6.68*10$^{16}$</td>
<td>-180</td>
</tr>
<tr>
<td>50</td>
<td>4.13*10$^{16}$</td>
<td>-300</td>
</tr>
<tr>
<td>100</td>
<td>2.56*10$^{16}$</td>
<td>-425</td>
</tr>
</tbody>
</table>
6.3 Mott-Schottky

Figure 6.7. A Mott-Schottky measurement of $C_{SC}^{-2}$ against $V$ (vs RHE) on a 3C-SiC sample (with a surface area of 0.078 cm$^2$), the labels in the figure are the AC frequencies of each particular line in kHz.

Table 6.4. Calculated values for doping concentration $N_D$ and flat-band potential $E_{fb}$ (vs. RHE) for a 3C-SiC sample (which is denoted as the B-sample) at a few different AC frequencies, see fig. 6.7. The calculations were performed using a linear fit to find the slope of the curves, which was used with eq. 3.21 (the Mott-Schottky relation) to calculate these values.

<table>
<thead>
<tr>
<th>Freq. (kHz)</th>
<th>Doping (cm$^{-3}$)</th>
<th>$E_{fb}$ (mV vs. RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.52 \times 10^{17}$</td>
<td>-20</td>
</tr>
<tr>
<td>5</td>
<td>$1.14 \times 10^{17}$</td>
<td>-40</td>
</tr>
<tr>
<td>10</td>
<td>$1.0 \times 10^{17}$</td>
<td>-75</td>
</tr>
<tr>
<td>20</td>
<td>$7.97 \times 10^{16}$</td>
<td>-120</td>
</tr>
<tr>
<td>50</td>
<td>$4.94 \times 10^{16}$</td>
<td>-200</td>
</tr>
<tr>
<td>100</td>
<td>$3.1 \times 10^{16}$</td>
<td>-300</td>
</tr>
</tbody>
</table>
6.4 Open-Circuit Potential

Here the results of the open-circuit potential measurements on the bare Si and 3C-SiC materials are shown and discussed.

6.4.1 Si

In fig. 6.8 some measurements of the open-circuit potential on p-Si are shown. The flat-band potential is approximated as around 370 mV vs. RHE for both the samples, which although assumed to be an underestimate seems to agree reasonably well with the results from the M-S measurements.

Figure 6.8. An OCP measurement using chopped AM 1.5 G illumination on p-Si comparing two different samples, in a 1 M NaOH electrolyte.
6.4.2 3C-SiC

The open circuit potential measurements performed on 3C-SiC should yield a more accurate, though underestimated, value of the flat-band potential than the M-S measurements did. In fig. 6.9 an OCP measurement with chopped light over a short period of time are shown that is made on the A-piece of a 3C-sample. The A-piece has the typical look of an OCP-measurement, and the potential step can be seen as approximately -350 mV thus approximating the flat-band potential as $\approx 400$ mV vs. RHE. It does, however, appear to have a slow recovery time after the light is turned off, indicating long carrier lifetimes which is positive with regards to the discussion on transport properties in chapter 3.2.1. The B-, and C-pieces did not give any comparable results, and appeared to be useless at this point.

The approximation of the flat-band potential is clearly an underestimate here since its value should be negative of 0 V vs. RHE, as mentioned in chapter 3.4.1.

![OCP - 3C-SiC A](image)

**Figure 6.9.** An OCP measurement on the A-sample with AM 1.5 G illumination in 1 M NaOH electrolyte. At the lower part of the figure the light is on, at the top it is off.

6.5 Photo-current onset

Here the results of the photo-current onset measurements on the bare Si and 3C-SiC materials as well as the attempted co-catalyst-deposited 6H-electrodes are shown and discussed. It can be noted that all the images
of j-V measurements have LSV (Linear Scan Voltammetry) written in the title, which is the type of scan used to perform such a measurement.

6.5.1 Si

The j-V measurements performed on p-type Si showed a large generated photo-current, see fig. 6.10, but at an onset potential negative of 0 V vs. RHE, indicating that the material is not suited for unbiased water-splitting. This is expected since the band-gap of Si is very small at \( \approx 1.2 \) eV, thus it can not be expected to straddle the redox-potentials of water-splitting. The high current is also expected due to the small band-gap and thus high utilisation of the solar spectrum.

![Image](image_url)

**Figure 6.10.** A j-V measurement on another sample of p-type Si, with a surface area of 0.159 cm\(^2\). The scan-rate is 20 mV/s, performed in a 1 M NaOH electrolyte. Also, some bubble formation can be spotted as small steps in the illuminated current, independently of the applied bias.

6.5.2 3C-SiC

Photo-current onset measurements were performed on bare 3C-SiC. On the A-piece, as mentioned in chapter 6.4, the A-measurement shown in fig. 6.11 was done.

A few runs in the dark showed great consistency in generated dark photo-current, which is expected. By running the same measurement several times it was noticed that the first measurement is slightly different from
6.5 Photo-current onset

the others as it dips down a bit in current after the onset potential. This might be due to some dirt on the surface or some other effect caused by the first rays of light. Apart from this there seems to be great consistency in generated photo-current under illumination as well, although a slight decay over time can be noted. The onset potential appears to be around 0.4 V vs. RHE and a photo-current density around 1 mA/cm$^2$ at 1.23 V vs. RHE.

In fig. 6.11 also some photo-current measurements made on the B- and C-pieces of the sample are shown, possibly strengthening the idea that the 3C-coverage plays a major role in how well the electrode performs. The curve originating from piece A exhibits a much higher generated photo-current than the other two pieces. Notably, however, the onset potential is approximately the same for every piece. But in this measurement piece C appears to behave completely normal apart from the fairly low generated current even though it was considered destroyed earlier. Compared to piece B, which originates from what is thought to be the worst area of the sample in terms of 3C-coverage, it seems to show slightly worse performance though.

Figure 6.11. A comparison between photo-current measurements from different pieces of the same sample. The red, blue and green represents pieces A, B and C respectively as before. The scan rate of these measurements was 20 mV/s, performed in a 1 M NaOH electrolyte.
6.5.3 6H-SiC

Some measurements performed on the Si-face on 6H-SiC, as to see the effects of the co-catalytic materials deposited on the samples. However, a comparison can also be made between the different SiC polytypes. In fig. 6.12 a j-V measurement on a 6H sample can be seen. The generated photo-current is notably about 3 orders lower than what is measured for 3C. Its relatively poor performance is expected due to a larger band-gap.

![Graph showing LSV of 6H-SiC](image)

**Figure 6.12.** A photo-current onset measurement performed on the Si-face of a 6H-sample (sample area = 0.197 cm$^2$). The scan rate of this measurement was 10 mV/s, performed in a 1 M NaOH electrolyte.

6.5.4 Co-catalyst deposition

The co-catalyst deposition was first attempted on 6H-SiC, in order to find a good enough recipe to use for 3C.

**First deposition attempt**

The first attempt of deposition of FeOOH onto 6H-SiC was performed with the general setup as described in chapter 5.1.8 except an attempt here was made to find an appropriate generated current by scanning over a bias between 0 and 1 V vs. Ag/AgCl with 10 mV/s scan-rate. With this method there is little control over the deposition rate as there is continuous deposition during the potential scan. What is noted during the subsequent
j-V measurements is altered performance of the material, see fig. 6.13, which indicates that at least some deposition occurred. In the plot some runs comparing bare and covered 6H-SiC are shown although it should be noted that no true comparison is possible to make between the bare 6H and the co-catalyst-covered due to a prolonged time between the measurements which could have some effect on the performance.

![Graph showing j-V measurements on 6H-SiC](image)

**Figure 6.13.** A few j-V measurements on 6H-SiC (sample area = 0.197 cm²) with and without FeOOH-deposition, performed in a 1 M NaOH electrolyte with a 20 mV/s scan rate. The measurement on the bare material was not done in conjunction with the deposition, but a few days earlier, which is why no true comparison can be made between the different curves. The different "runs" refer to subsequent j-V measurements performed on the same sample.

At first, an increase in generated photo-current density was noted for the red curve, however, immediately subsequent photo-current measurements (the green curve) yielded a significant decrease until the current was non-existent.

A possible reason for this is that since this measurement (as well as all previous ones) has been done in an aqueous 1 M NaOH electrolyte something similar as studied by e.g. Tolchev et al. can be occurring. In this case it is possible for FeOOH to transform into Fe₂O₃ in a NaOH ambient with applied heat. Fe₂O₃ has bad carrier transport properties, as mentioned in chapter 4, and can serve to reduce the current generated if applied onto the surface of 6H-SiC. So it is hypothesised that a combination of applied bias and illumination quickly degrades the applied co-catalyst material in the present electrolyte, although no other measurements have been made to confirm this.
Second deposition attempt

By preparation of a 0.1 M KH$_2$PO$_4$ (pH $\approx$ 7) electrolyte [39, 46] the 6H-SiC had its photo-current measured in this new ambient. This was followed by the deposition procedure described in chapter 5.1.8, where repeatedly some j-V measurement was performed in sequence with a deposition period. The result was not entirely conclusive, the performance is somehow altered by the deposition process compared to the bare 6H but it is difficult to determine if there is an improvement or not, over several consecutive measurements it seems like the actual photo-current is reduced indicating that the co-catalytic layer might have become too thick, or perhaps insulating. It is possible that too much material was deposited as the deposition current was initially much higher than expected.

It is possible to instead do a chronopotentiometric deposition sequence in which a fixed current is kept by a varying bias to avoid to large current deviations. In that case a more controllable and lower current can be used and perhaps a more easily defined deposition rate can be worked out. In any case further exploration is required in order to develop a well-working co-catalyst deposition method.

6.6 Chronoamperometry

Here the results of the chronoamperometry measurements on the bare Si and 3C-SiC materials are shown and discussed.

6.6.1 Si

The chronoamperometric measurements performed on Si can be seen in fig. 6.14. There is no notable current generated at 0 bias, which is expected from this material. At a large negative bias between the WE and CE a large current density is generated.

6.6.2 3C-SiC

In fig. 6.15 some chronoamperometry measurements performed on different pieces of the same 3C-sample can be seen. There is a certain decay in current density visible over time for all the pieces. As expected, the A piece yields a much higher current than the other two, and C performs worse than B possibly due to electrical break-down, as mentioned earlier. An unbiased current density of above 0.4 mA/cm$^2$ is a quite decent result compared to many other semiconductors. The stability in the measurement is not
Figure 6.14. A CA measurement on p-Si (sample area = 0.162 cm$^2$) unbiased and at -2 V, performed in a 1 M NaOH electrolyte.

Figure 6.15. Chronoamperometry measured unbiased under chopped AM 1.5G illumination in a 1 M NaOH electrolyte. As before the red, blue and green represents pieces A, B and C respectively.

excellent though, showing a 10% decrease in current over two minutes. This is probably due to oxidation of the semiconductor surface, causing an insulating layer to form. A photo-current density of 0.45 mA/cm$^2$ inserted in eq. 3.13 together with an assumed faradaic efficiency of $\eta_F = 1$ yields
an STH efficiency of \( \approx 0.55 \% \). This value is not accurate though, since reasonably \( \eta_F \) will be less than one.

6.7 Summary

To summarise the results of this project briefly, 3C-SiC seems to be able to split water although there are some features that can probably be improved upon further. The flat-band potential has not been accurately determined by any measurement method, but it is clear that it is positioned in a way that allows for water-splitting. The doping concentration of the grown 3C seems to be somewhere around the high end of \( 10^{16} \) or the low end of \( 10^{17} \) cm\(^{-3} \), which are values within reason for these samples though complementary measurement methods can be used to verify this. The photo-current onset potential is fairly high, indicating large over-potentials for the water-splitting reactions, which is something that can be improved by e.g. co-catalysts. Stability is not very well explored in this project, which is one property other materials excel at, e.g. \( \text{Fe}_2\text{O}_3 \) \(^{59}\). However, this property is also one to be improved by co-catalysts.

The generated photo-current density in an unbiased 2-electrode setup is quite large for a low band-gap material with such low amount of research performed on it. This result is promising for future improvements of 3C-SiC for water-splitting applications.

Few people seem to do the unbiased 2-electrode measurements, so it is difficult to make exact comparisons, however, the reason that there are not many referential values of this is because few bare semiconductor electrodes can actually yield any significant photo-currents unbiased. Table 6.5 contains some referential photo-current density values on some commonly researched semiconductors. One can note e.g. the current generation of \( \text{BiVO}_4 \) in an unbiased 2-electrode setup. The biased performance of the bare semiconductors can also be noted and compared to the 1 mA/cm\(^2\) generated by 3C-SiC at 1.23 V vs. RHE.

It seems like 3C-SiC is definitely a contender in this field, by matching other bare semiconductors in photo-current generation under bias, while exceeding them in unbiased 2-electrode measurements. What needs to be further examined is the faradaic efficiency, no gas generation was measured within this project, in order to properly characterise the hydrogen-generating ability of 3C-SiC.
6.8 Sources of error

A great many things influences this type of device since it has so many different components. Largely due to human errors the performance of the electrodes produced in this project are probably not as high as it possibly could be.

To begin with, the growth of the samples was probably not done in an optimal fashion. Increased coverage of 3C-SiC can be achieved, which is thought to increase the performance of the electrode as compared to having a large amount of transition layer. The polishing of the samples might not yield a perfectly uniform or flat surface on the backside, which could in some way affect the performance due to creating a non-uniform contact interface. After polishing there is also some glue residue left on the sample front-side which may be insufficiently cleaned off before proceeding with the measurements, which could potentially decrease performance.

The ohmic contacts made on the 3C-SiC were not completely ohmic, some Schottky barrier was present which will then affect the transport properties and decrease performance. The deposition of the contacts was

Table 6.5. A few values of photo-current generation for some commonly researched materials. The values are attempted to be kept to the same reference as much as possible. * These reference-electrodes have been calculated to RHE by the author of this report.

<table>
<thead>
<tr>
<th>WE</th>
<th>Co-catalyst</th>
<th>$j$ (mA/cm$^2$)</th>
<th>$\eta_F$</th>
<th>Electrolyte</th>
<th>Bias (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiVO$_4$</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>0.1 M KOH (pH 13)</td>
<td>1.23 vs. RHE</td>
<td>[60]</td>
</tr>
<tr>
<td>BiVO$_4$</td>
<td>ZnFe$_2$O$_4$/Co$^{2+}$</td>
<td>2.8</td>
<td>-</td>
<td>0.1 M KOH (pH 13)</td>
<td>1.23 vs. RHE</td>
<td>[60]</td>
</tr>
<tr>
<td>BiVO$_4$</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>0.1 M KH$_2$PO$_4$ (pH 7)</td>
<td>1.2 V vs. RHE</td>
<td>[59]</td>
</tr>
<tr>
<td>BiVO$_4$</td>
<td>FeOOH</td>
<td>1.7</td>
<td>-</td>
<td>0.1 M KH$_2$PO$_4$ (pH 7)</td>
<td>1.2 V vs. RHE</td>
<td>[59]</td>
</tr>
<tr>
<td>BiVO$_4$</td>
<td>-</td>
<td>0.55</td>
<td>-</td>
<td>0.1 M acetic acid (pH 3)</td>
<td>1.2 vs. RHE*</td>
<td>[60]</td>
</tr>
<tr>
<td>BiVO$_4$</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>0.1 M sodium acetate (pH 5)</td>
<td>1.2 vs. RHE*</td>
<td>[60]</td>
</tr>
<tr>
<td>BiVO$_4$</td>
<td>Co-Pi</td>
<td>0.1</td>
<td>-</td>
<td>0.5M Na$_2$SO$_4$ (pH 7)</td>
<td>0.8 vs. RHE*</td>
<td>[59]</td>
</tr>
<tr>
<td>BiVO$_4$</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
<td>0.5M Na$_2$SO$_4$ (pH 7)</td>
<td>0.8 vs. RHE*</td>
<td>[59]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>0.8 vs. RHE</td>
<td>[59]</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>-</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>1.2 vs. RHE</td>
<td>[59]</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>-</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>1.4 vs. RHE</td>
<td>[59]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>-</td>
<td>1.1</td>
<td>-</td>
<td>(pH 4.7)</td>
<td>1 vs. RHE*</td>
<td>[62]</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>-</td>
<td>0.65</td>
<td>-</td>
<td>1 M NaOH (pH 13.6)</td>
<td>1.2 vs. RHE</td>
<td>[59]</td>
</tr>
<tr>
<td>W/Mo-BiVO$_4$</td>
<td>-</td>
<td>0.04</td>
<td>0.9</td>
<td>0.1 M Na$_2$SO$_4$ (pH 7)</td>
<td>0 WE-CE</td>
<td>[52]</td>
</tr>
<tr>
<td>BiVO$_4$/p-Si</td>
<td>CoPi</td>
<td>0.16</td>
<td>-</td>
<td>0.1 M KPO (pH 5.5)</td>
<td>0 WE-CE</td>
<td>[53]</td>
</tr>
<tr>
<td>3C-SiC</td>
<td>-</td>
<td>0.45</td>
<td>-</td>
<td>1 M NaOH (pH 13.6)</td>
<td>0 WE-CE</td>
<td>This</td>
</tr>
</tbody>
</table>
also imperfect and did not always cover all of the areas it needs to on the backside of some samples. The gluing of the samples onto pieces of glass in the electrode-making process was also made imperfectly, perhaps sometimes not establishing contact on the appropriate areas. The same can be said about the epoxy resin, perhaps the surface coverage of the electrode is not ideal, perhaps some areas were left uncovered that should be covered and vice versa. It is also possible that the un-even epoxy made some areas of the sample unusable during water-splitting due to increased trapping of gas bubbles along the edges. The slightly transparent epoxy made calculations of the area of the sample more difficult as well, which doesn’t affect the performance but it affects all calculations of current densities and doping concentration from the Mott-Schottky relation. The area calculations may have been incorrect for other reasons as well, such as the sample not being exactly flat.

During the PEC measurements it is possible that the working electrode was not positioned exactly at such an angle and at such a distance away from the light source that the incident light represented the AM 1.5 G spectrum. The electrolyte might not be perfectly made either, perhaps its pH-value is slightly different than what is thought thus altering the Nernstian potential, or perhaps it has some contaminants which affects the water-splitting process. The same can be said about the cell itself which could have some contaminants in it.

To summarise this, it is evident that great care has to be taken during every step of manufacturing the electrodes and performing measurements to ensure that everything is made in optimal conditions. This has been quite difficult during this project, mainly due to inexperience, but most likely improvements can be made in this regard.
Chapter 7

Conclusions and future work

Here the conclusions that can be drawn from this project are presented together with a brief review of how 3C-SiC performs compared to other semiconductors as well as an outlook on what may be improved in the future.

The performance of other water-splitting devices greatly exceeds what has been presented in this project. The highest STH efficiency reported for any type of cell is to the best of my knowledge 24.4% [64]. However, this is performed on a multi-junctioned cell of several materials which easily gets higher efficiencies. For the single-material cells as in this project, possibly with a co-catalytic layer on top, the performance is at a whole other level with only a few percent in efficiency. For example, bare BiVO$_4$ only shows a few $\mu$A/cm$^2$ at 1.2 V vs. RHE, improved to around 1.65 mA/cm$^2$ with the application of a FeOOH co-catalyst [39]. These numbers are not far from what is shown on bare 3C-SiC in this project and improvements can probably be made, since 3C is relatively little researched compared to BiVO$_4$.

7.1 Further improvements

To improve the performance of 3C-SiC in PEC water-splitting many changes can be made, first of all more caution should be taken to ensure practical details turn out in an optimal way, a discussion on this can be found in chapter 6.8. Apart from that there are many other things that have not been addressed properly in this project if maximum water-splitting performance is desired. For example, surface structuring, as briefly mentioned in chapter 3.2.1, can be done to further improve the cell. The 3C-SiC samples are somewhat transparent, which means not all light is absorbed, which
Conclusions and future work

might be improved by this. This is partly due to the below-band-gap wavelengths, however, it is clear from the calculations performed in chapter 3.2.1 that a perfect match between carrier transport properties, light penetration and sample thickness is unlikely, perhaps some effort can be made in this regard.

Certain structuring of the co-catalytic material is also a possible point of improvement, no work is done in this project regarding the manner in which these materials are deposited onto the semiconductor. Of course there are also a large number of co-catalytic materials not explored at all, perhaps not the optimal choices were made in this project. The co-catalysts chosen here were not thoroughly characterised, since no successful deposition was made. The doping of the semiconductor has not been explored either, p-type might give different results and should be tested. There are also interesting possibilities to explore using for example intermediate bands.

The parts of the PEC cell that are not the working electrode, i.e. the counter electrode, the reference electrode and the electrolyte, can all probably be optimised further as well. Perhaps not much can be done with the reference and counter electrodes, but the electrolyte at least can be experimented with to make the interfacial carrier transitions and transport to the counter electrode easier.

The most reasonable point of improvement is proper sample handling and the application of co-catalytic materials to address critical factors such as device stability.

7.2 Summary

To give some final summary on this project, it seems as if 3C-SiC is fit for photoelectrochemical water-splitting applications. Although not exhibiting record-breaking performance, it seems to hold a high standard as compared to other common materials in the early stages of their development. Notably it exhibits an exceptionally high unbiased photo-current density in the 2-electrode setup, mimicking the real intended application. What has been presented in this project is also, to the best of my knowledge, the best recorded performance of 3C-SiC, surpassing that of e.g. Yasuda et al. [15], Ichikawa et al. [35] and Song [8]. The performance can most likely be further improved by application of co-catalytic materials, although it was not shown in this project it can be a focal point for future work.
Bibliography


