Advanced Photoanodes
for Photoassisted Water Electrolysis

by

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Abstract

With continuously growing energy demands, alternative, emission-free solar energy solutions become ever more attractive. However, to achieve sustainability, efficient conversion and storage of solar energy is imperative. Photoelectrolysis harnesses solar energy to evolve hydrogen and oxygen from water, thereby enabling energy storage via chemical means. Hematite or $\alpha$-Fe$_2$O$_3$ has emerged as a highly promising photoanode candidate for photoelectrochemical cells. While significant improvements in its performance have recently been achieved, it remains unclear why the maximum photocurrents still remain well below their theoretical predictions.

This study investigates the defect chemistry and conduction mechanism of hematite in order to understand and improve this material’s shortcomings. A defect model for donor doped hematite was derived and its predictions confirmed by the electrical conductivity of ilmenite hematite solid solution bulk samples as a function of temperature and oxygen partial pressure. The enthalpies of the Schottky defect formation and the reduction reaction for hematite were determined as 13.4 eV and 5.4 eV, respectively. In addition, a temperature independent value for the electron mobility of 0.10 cm$^2$/Vs for 1% Ti donor doped hematite was derived.

Furthermore, the electrical conductivity of nanometer scale, epitaxially grown thin films of the ilmenite hematite solid solution system was characterized by electrical impedance spectroscopy. This work reports a detailed correlation between the electrical conductivity of the undoped hematite, the 1 atom% Ti doped hematite and the thin films with higher ilmenite content and the conditions under which they were annealed ($20^\circ$C $\leq$ T $\leq$ 800$^\circ$C and $10^{-4}$ atm $\leq$ pO$_2$ $\leq$ 1 atm). Hematite’s room temperature conductivity can be increased from $\sim 10^{-11}$ S/cm for undoped hematite films by as much as nine orders of magnitude by doping with the Ti donor. Furthermore, by controlling the non-stoichiometry of Ti-doped hematite, one can tune its conductivity by up to five orders of magnitude. Depending on processing conditions, donor dopants in hematite may be compensated largely by electrons or by ionic defects (Fe
vacancies). The electron mobility of the film was determined to be temperature independent at 0.01 cm$^2$/Vs for the $<0001>$ epitaxial film containing a Ti donor density of $4.0 \times 10^{20}$ cm$^{-3}$.

Finally, the photoelectrochemical performance of these materials was tested by cyclic voltammetry and measurements of their quantum efficiencies. The 1% Ti doped hematite thin film exhibited the highest photocurrent density of these dense, thin films at 0.9 mA/cm$^2$ with an applied bias of 1.5 V vs. RHE. The IPCE of this sample reached 15% at wavelengths between 300 nm and 350 nm after an annealing treatment at 580°C for 36 h. The solid solution containing 33% ilmenite preformed nearly as well as the doped hematite. The performance decreased with higher ilmenite concentrations in the solid solution. For all samples containing any ilmenite, the onset potential shifted to lower values by $\sim 200$ mV after the annealing treatment. The increase in charge carrier density upon reduction of Ti doped hematite was confirmed by a Mott-Schottky analysis of the hematite/electrolyte interface. In contrast, only minor changes in the carrier density were observed when reducing an undoped hematite photoanode. Changes in slope of the Mott-Schottky plots revealed the presence of deep trap states in the hematite films. In-situ UV-vis spectroscopy displayed a pronounced optical signature corresponding to the existence of such deep levels.

These results highlight the importance of carefully controlling photoanode processing conditions, even when operating within the material's extrinsic dopant regime, and more generally, provide a model for the electronic properties of semiconducting metal oxide photoanodes.

Thesis Supervisor: Harry L. Tuller
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List of Publications


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Attaining a Ph.D. from MIT is a long journey with many ups and downs. In a buzzing environment of constant innovation and technical achievements driven by extraordinary people, you grow as a person as much as you grow professionally. As for any journey, it is the people and your interactions with them that enrich your experience. Celebrating the highs and commiserating during the lows built long lasting friendships and provided strength to tackle any difficult task. I would like to take this opportunity to express my gratitude to the people that have made the difference.

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Contents

Abstract 3

List of Publications 5

Acknowledgments 7

Contents 11

List of Figures 15

List of Tables 23

1 Introduction 25

1.1 Motivation . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 25
1.2 Alternative energy sources . . . . . . . . . . . . . . . . . . . . . . . . 28
1.3 Solar energy . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 29
1.4 Thesis outline . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 30

2 Background and Theory 33

2.1 The photoelectrochemical cell . . . . . . . . . . . . . . . . . . . . . . . . 34
2.1.1 Operation . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 34
2.1.2 Challenges . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 35
2.2 Photoanode studies . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 37
2.2.1 TiO$_2$ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 39
2.2.2 WO$_3$ . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 40
2.2.3 BiVO$_4$ .................................................. 41
2.2.4 Fe$_2$O$_3$ .................................................. 42

2.3 Objectives ................................................... 44
2.4 Ilmenite hematite solid solution (IHSS) ......................... 45

3 Experimental Methods ........................................ 51

3.1 Sample preparation ........................................ 52
3.1.1 Bulk samples .......................................... 52
3.1.2 Pulse laser deposition .................................. 53

3.2 Physical characterization .................................. 57
3.2.1 X-ray diffraction ....................................... 57
3.2.2 Optical absorption spectroscopy ......................... 59
3.2.3 Profilometry ............................................. 62

3.3 Electrical characterization ................................ 63
3.3.1 Bulk samples .......................................... 63
3.3.2 Thin films .............................................. 67

3.4 Photoelectrochemical characterization ....................... 69
3.4.1 The PEC cell .......................................... 69
3.4.2 Annealing ............................................... 71
3.4.3 Contacting .............................................. 71
3.4.4 Catalyst deposition .................................... 71
3.4.5 Photocurrent density measurement ...................... 72
3.4.6 IPCE measurement .................................... 73
3.4.7 Mott-Schottky measurement ............................ 77

4 Defect Chemistry of Hematite ................................ 79

4.1 Kröger-Vink notation ....................................... 80
4.2 Defect reactions ........................................... 80
4.3 Defect diagram ............................................ 83
4.3.1 Brouwer approximation for hematite: intrinsic case .... 83
4.3.2 Brouwer approximations for hematite with a donor dopant: extrinsic case 84

5 Results 87
5.1 X-ray diffraction 88
5.1.1 Targets 88
5.1.2 Pellets 89
5.1.3 Thin films 91
5.2 Absorption spectroscopy 95
5.2.1 Thin films for electrical characterization 95
5.2.2 Thin films for PEC measurements 97
5.3 Electrical conductivity 100
5.3.1 DC conductivity of bulk samples 100
5.3.2 ELS results for thin films 105
5.3.3 Conductivity of thin films 105
5.4 PEC performance 110
5.4.1 Hematite ilmenite solid solutions 110
5.4.2 Mott-Schottky analysis 122
5.4.3 Homojunctions 124

6 Discussion 127
6.1 Electrical characterization of the bulk samples 128
6.1.1 Electron mobility in polycrystalline bulk hematite 128
6.1.2 Thermodynamic parameters derived from the application of the defect chemical model 129
6.1.3 Phase stability 140
6.2 Electrical characterization of thin film specimens 144
6.2.1 Electron mobility in epitaxial thin films of hematite 145
6.2.2 Thin film conductivity after an anneal at 580°C 145
6.3 Photoelectrochemical performance 147
6.3.1 Change in performance due to composition 147
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>World Energy Source Distribution in 2009</td>
<td>26</td>
</tr>
<tr>
<td>1-2</td>
<td>CO$_2$ emissions and Kaya factors</td>
<td>26</td>
</tr>
<tr>
<td>1-3</td>
<td>Available exergy for renewable sources</td>
<td>28</td>
</tr>
<tr>
<td>2-1</td>
<td>Schematic of the operation of a photoelectrochemical cell</td>
<td>34</td>
</tr>
<tr>
<td>2-2</td>
<td>Number of photons in the solar spectrum (AM1.5) as a function of photon energy</td>
<td>36</td>
</tr>
<tr>
<td>2-3</td>
<td>Band edge positions of several semiconductors at pH 14</td>
<td>38</td>
</tr>
<tr>
<td>2-4</td>
<td>Hexagonal ordering of cations in ilmenite and hematite</td>
<td>45</td>
</tr>
<tr>
<td>2-5</td>
<td>Phase diagram of iron oxides</td>
<td>47</td>
</tr>
<tr>
<td>2-6</td>
<td>DC conductivity of samples with varying compositions of the IHSS system</td>
<td>48</td>
</tr>
<tr>
<td>2-7</td>
<td>Photocurrent densities of iron titanates</td>
<td>49</td>
</tr>
<tr>
<td>2-8</td>
<td>Nonstoichiometry of hematite as a function of oxygen partial pressure at high temperatures</td>
<td>50</td>
</tr>
<tr>
<td>3-1</td>
<td>PLD vacuum chamber used for thin film depositions</td>
<td>54</td>
</tr>
<tr>
<td>3-2</td>
<td>Transmission, reflection and absorption of an FTO coated quartz substrate</td>
<td>60</td>
</tr>
<tr>
<td>3-3</td>
<td>Dektak scan showing the step height of a hematite film on an FTO coated quartz substrate</td>
<td>62</td>
</tr>
<tr>
<td>3-4</td>
<td>Schematic of a bulk sample with Pt contacts</td>
<td>63</td>
</tr>
</tbody>
</table>
3-5 Bulk samples contacted with Pt wires mounted on alumina multi-bore tubes with thermocouples at each sample. ............................................. 65

3-6 IV sweeps of a hematite bulk sample at different temperatures exhibiting ohmic behavior ................................................................. 66

3-7 Schematic of a potentiometric oxygen sensor ........................................ 67

3-8 IDE on a thin film sample for electrical characterization ........................................ 68

3-9 Design of the PEC cell used for this study ........................................... 70

3-10 Typical thin film sample and assembled cell for PEC measurements ........... 72

3-11 Schematic of the experimental setup to measure the performance of a PEC cell under simulated sunlight ........................................... 73

3-12 Illustration of the experimental setup to measure the external quantum efficiency of a photoanode ........................................... 74

3-13 Spectral power density of the Xenon lamp of the IPCE setup: various calibration curves measured on different days ........................................ 75

3-14 Raw data as collected with the IPCE setup: the current is recorded as the light is chopped at constant time intervals and the wavelength is scanned allowing for the determination of the photocurrent as a function of wavelength. ........................................ 76

4-1 Intrinsic case: Defect diagram depicting the pO$_2$ dependence of various charge carriers in the different regimes ........................................... 86

4-2 Defect diagram depicting the pO$_2$ dependence of various charge carriers in the different regimes ........................................... 86

5-1 X-ray diffraction patterns of the (FeTiO$_3$)$_{1-x}$(Fe$_2$O$_3$)$_x$ targets produced for PLD ........................................... 89

5-2 X-ray diffraction patterns of the (FeTiO$_3$)$_{1-x}$(Fe$_2$O$_3$)$_x$ pellets produced for electrical characterization ........................................... 90

5-3 X-ray diffraction patterns of the (FeTiO$_3$)$_{1-x}$(Fe$_2$O$_3$)$_x$ thin films on sapphire substrates ........................................... 91
5-4 High resolution XRD scans of the epitaxially grown hematite thin film on sapphire.  

5-5 High resolution XRD scans of the epitaxially grown Fe$_{1.98}$Ti$_{0.02}$O$_3$ thin film on sapphire.  

5-6 High resolution XRD scans of the epitaxially grown Fe$_{1.67}$Ti$_{0.33}$O$_3$ thin film on sapphire.  

5-7 High resolution XRD scan of the highly textured Fe$_{1.33}$Ti$_{0.67}$O$_3$ thin film on sapphire.  

5-8 High resolution XRD scans of the epitaxially grown FeTiO$_3$ thin film on sapphire.  

5-9 Absorption spectroscopy results, absorption coefficient and Tauc plots for the epitaxially grown IHSS thin films.  

5-10 Absorption spectroscopy results, absorption coefficient and Tauc plots for the IHSS thin films prepared for PEC measurements.  

5-11 DC conductivity of α-Fe$_2$O$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1050°C.  

5-12 DC conductivity of Fe$_{1.98}$Ti$_{0.02}$O$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1050°C.  

5-13 DC conductivity of Fe$_{1.67}$Ti$_{0.33}$O$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1050°C.  

5-14 DC conductivity of Fe$_{1.33}$Ti$_{0.67}$O$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1030°C.  

5-15 DC conductivity of FeTiO$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1030°C.  

5-16 Nyquist plots of hematite and Fe$_{1.98}$Ti$_{0.02}$O$_3$.  

5-17 Conductivity of the Fe$_{1.98}$Ti$_{0.02}$O$_3$ and hematite thin films as a function of temperature at different partial pressures of oxygen.  

5-18 Conductivity of the Fe$_{1.67}$Ti$_{0.33}$O$_3$ and hematite thin films as a function of temperature at different partial pressures of oxygen.
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-19</td>
<td>Conductivity of the Fe_{1.33}Ti_{0.67}O_{3} and hematite thin films as a function of temperature at different partial pressures of oxygen.</td>
</tr>
<tr>
<td>5-20</td>
<td>Conductivity of the FeTiO_{3} and hematite thin films as a function of temperature at different partial pressures of oxygen.</td>
</tr>
<tr>
<td>5-21</td>
<td>PEC performance of as-deposited and annealed undoped hematite thin films.</td>
</tr>
<tr>
<td>5-22</td>
<td>Quantum efficiencies and absorption of the as-deposited and annealed hematite thin films.</td>
</tr>
<tr>
<td>5-23</td>
<td>PEC performance of undoped hematite, hematite catalyzed by CoPi and hematite in the presence of a hole scavenger.</td>
</tr>
<tr>
<td>5-24</td>
<td>PEC performance of as-deposited and annealed 1% Ti doped hematite thin films.</td>
</tr>
<tr>
<td>5-25</td>
<td>Quantum efficiencies and absorption of the as-deposited and annealed 1% Ti doped hematite thin films.</td>
</tr>
<tr>
<td>5-26</td>
<td>PEC performance of as-deposited and annealed Fe_{1.67}Ti_{0.33}O_{3} thin films.</td>
</tr>
<tr>
<td>5-27</td>
<td>Quantum efficiencies and absorption of the as-deposited and annealed Fe_{1.67}Ti_{0.33}O_{3} thin films.</td>
</tr>
<tr>
<td>5-28</td>
<td>PEC performance of as-deposited and annealed Fe_{1.33}Ti_{0.67}O_{3} thin films.</td>
</tr>
<tr>
<td>5-29</td>
<td>Quantum efficiencies and absorption of the as-deposited and annealed Fe_{1.33}Ti_{0.67}O_{3} thin films.</td>
</tr>
<tr>
<td>5-30</td>
<td>PEC performance of as-deposited and annealed ilmenite thin films.</td>
</tr>
<tr>
<td>5-31</td>
<td>Quantum efficiencies and absorption of the as-deposited and annealed ilmenite thin films.</td>
</tr>
<tr>
<td>5-32</td>
<td>Mott-Schottky plots of undoped and doped hematite thin films measured after different annealing treatments.</td>
</tr>
<tr>
<td>5-33</td>
<td>Energy band schematic of a BiVO_{4} and 1% W doped BiVO_{4} homojunction.</td>
</tr>
<tr>
<td>5-34</td>
<td>PEC performance of the 1% Ti doped Fe_{2}O_{3} homojunctions compared to that of the doped and undoped hematite thin films.</td>
</tr>
</tbody>
</table>
5-35 Quantum efficiencies and absorption of the 1% Ti doped Fe$_2$O$_3$ homojunctions. .......................................................... 126

6-1 Conductivity dependence of bulk hematite on temperature. ....... 131
6-2 Conductivity dependence of bulk Fe$_{1.67}$Ti$_{0.33}$O$_3$ on temperature. ... 133
6-3 Conductivity dependence of bulk Fe$_{1.33}$Ti$_{0.67}$O$_3$ on temperature. ... 134
6-4 Conductivity dependence of bulk FeTiO$_3$ on temperature. ............ 134
6-5 Conductivity of bulk Fe$_{1.67}$Ti$_{0.33}$O$_3$ as a function of pO$_2$ including fits based on the transition between Regime II(i) and Regime III(i). ....... 138
6-6 Conductivity of bulk Fe$_{1.33}$Ti$_{0.67}$O$_3$ as a function of pO$_2$ including fits based on the transition between Regime II(i) and Regime III(i). ....... 138
6-7 Conductivity of bulk FeTiO$_3$ as a function of pO$_2$ including fits based on the transition between Regime II(i) and Regime III(i). ....... 139
6-8 Conductivity of bulk Fe$_{1.98}$Ti$_{0.02}$O$_3$ as a function of pO$_2$ including model conductivity for the intrinsic case. ......................... 140
6-9 X-ray diffraction patterns of the (FeTiO$_3$)$_{1-x}$(Fe$_2$O$_3$)$_x$ pellets after an anneal at 1000°C. ................................................. 141
6-10 X-ray diffraction patterns of the annealed (FeTiO$_3$)$_{0.33}$(Fe$_2$O$_3$)$_{0.67}$ pellet before and after polishing. ......................... 142
6-11 X-ray diffraction patterns of the annealed (FeTiO$_3$)$_{0.67}$(Fe$_2$O$_3$)$_{0.33}$ pellet before and after polishing. ......................... 143
6-12 X-ray diffraction patterns of the annealed FeTiO$_3$ pellet before and after polishing. ......................... 143
6-13 Conductivity of the Fe$_{1.98}$Ti$_{0.02}$O$_3$ and hematite thin films as a function of temperature at different partial pressures of oxygen, in comparison to room temperature conductivity after an anneal at only 580°C. ... 146
6-14 PEC performance of the reduced photoanodes of various compositions. 148
6-15 Current densities for 1% Ti doped hematite as a function of wavelength at a constant applied bias of 1.5 V vs. RHE calculated from the IPCE values of each sample and normalized to match the spectral irradiance of the solar simulator.

6-16 Normalized current densities for doped hematite thin films at a constant applied bias and chopped AM1.5 illumination.

6-17 Extension of the depletion width as a function of the voltage drop across the space charge for different charge carrier concentrations.

6-18 Mott-Schottky plots of a 40 nm, 80 nm and 120 nm thick TiO₂ film on indium doped tin oxide.

6-19 Schematics of the band bending in the semiconducting photoanode at the liquid interface with and without the presence of deep trap states at low and high applied potentials.

6-20 In-situ optical transmission of the oxidized hematite thin film as a function of applied bias measured in the PEC cell.

6-21 Schematic of the energy levels of the oxidized hematite photoanode.

A-1 Power density spectra of the simulated sunlight reaching the photoanode in the PEC cell compared to the AM1.5G standard.

A-2 Integrated spectral irradiance of the AM1.5G standard between 300 nm and 600 nm.

B-1 SEM images of epitaxial undoped and 1at.% Ti doped hematite thin films on single crystal sapphire.

B-2 Cross-sectional profiles of epitaxial α-Fe₂O₃ thin films on single crystalline sapphire.

B-3 AFM phase angle images depicting the surface morphologies of epitaxial α-Fe₂O₃ thin films on single crystalline sapphire.

B-4 AFM image of the surface of an FTO coated quartz substrate.

B-5 AFM images depicting the surface morphologies of α-Fe₂O₃ thin films deposited by PLD onto FTO coated quartz.
C-1 Solutions for the electron concentration for the extrinsic and the intrinsic case as well as a superposition of the two ....... 180

D-1 An untreated and a heat treated Fe_{1.33}Ti_{0.67}O_{3} sample. .............. 183

D-2 XPS survey scans for the as-fabricated and the annealed sample. . . . 184

D-3 High resolution XPS data of the C1s, O1s, Fe2p3 and Ti2p peaks of the untreated and annealed Fe_{1.33}Ti_{0.67}O_{3} samples. ............... 185

E-1 Illustration of the experimental setup to measure the optical transmission through the PEC cell while applying a bias. .............. 187
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Unit cell dimensions, formula units per unit cell and the theoretical</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>densities of ilmenite and hematite.</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Composition, actual and theoretical density of all PLD targets.</td>
<td>53</td>
</tr>
<tr>
<td>3.2</td>
<td>Composition, dimensions and density of bulk samples for electrical</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>characterization.</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Composition and thickness of films fabricated by PLD for conductivity</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>measurements.</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Composition and thickness of films fabricated by PLD for PEC measurements.</td>
<td>57</td>
</tr>
<tr>
<td>3.5</td>
<td>Bulk sample dimensions relevant for electrical characterization.</td>
<td>64</td>
</tr>
<tr>
<td>4.1</td>
<td>Predicted charge carrier densities for each possible neutrality regime</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>for the intrinsic case.</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Predicted charge carrier densities for each possible neutrality regime</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>for the extrinsic case.</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Optical bandgaps of the epitaxially grown IHSS thin films on sapphire.</td>
<td>97</td>
</tr>
<tr>
<td>5.2</td>
<td>Optical bandgaps of the IHSS thin films used as photoanodes.</td>
<td>99</td>
</tr>
<tr>
<td>5.3</td>
<td>Charge carrier densities of the hematite and I2HSS thin film photoanodes.</td>
<td>123</td>
</tr>
<tr>
<td>6.1</td>
<td>Thermodynamic parameters controlling the charge carrier concentrations</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>based on fits to the bulk conductivity data.</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>Current density at a constant applied bias of 1.5 V vs. RHE for 1% Ti doped hematite.</td>
<td></td>
</tr>
<tr>
<td>6.3</td>
<td>Charge carrier densities of the hematite and I2HSS thin films on FTO coated quartz substrates as observed at low and high applied potentials.</td>
<td></td>
</tr>
<tr>
<td>6.4</td>
<td>Dielectric constant of hematite calculated from the Mott-Schottky data and the measured thickness of the thin films.</td>
<td></td>
</tr>
<tr>
<td>B.1</td>
<td>Roughness of hematite thin films grown by PLD on FTO coated quartz</td>
<td></td>
</tr>
<tr>
<td>D.1</td>
<td>Atomic concentration ratios based on survey spectra on the Fe\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{3} samples.</td>
<td></td>
</tr>
<tr>
<td>D.2</td>
<td>Atomic concentration ratios based on high resolution data of the Fe\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{3} samples.</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Motivation

Possible energy shortages and the impact of global warming on future weather patterns are of growing global concern. In 2007, the world’s energy consumption totaled $5.22 \times 10^{18}$ J, corresponding to a consumption rate of $16.6$ TW \cite{1}. The U.S. Energy Information Administration (EIA) predicts this number to grow by 49\% in the coming 25 years to a consumption rate of 24.7 TW. In 2010, 86\% of the world’s energy demand was covered by energy derived from fossil fuels (Figure 1-1) \cite{2}.

Fossil fuels have been the world’s most reliable energy source for the past one hundred years. These fuels are primarily in the form of oil, natural gas and coal. The total energy derived from these fuels is limited by the conventional and unconventional reserves present on the planet today. Nathan Lewis et al. estimate that current reserves have the ability to satisfy global demand for several hundreds of years at a consumption rate of up to 30 TW per year \cite{3}. Still, there is much concern about the continued exploitation of fossil fuels at such high levels, given likely impact on the environment and climate change and associated consequences.

The Intergovernmental Panel on Climate Change (IPCC) reports a 1 °C increase in the global average temperature from 1850 to 2000 as well as a significant increase in sea
level and decrease in the Northern hemisphere snow coverage during the last century [4]. The IPCC suggests a further increase of 1.8 °C to 4.0 °C in temperature during the next century depending on demographic, economic and technological developments across the world. The findings and predictions are strongly correlated to the emission of anthropogenic greenhouse gases, carbon dioxide being the main culprit. Figure 1-2 shows the increase of world wide carbon dioxide emissions based on four factors, where the carbon intensity is the amount of carbon dioxide emitted per unit of energy and the energy intensity corresponds to the consumption of energy per dollar of GDP.

Figure 1-1: World Energy Source Distribution in 2009 [2].

Figure 1-2: CO₂ emissions and Kaya factors, 1990-2035 (index: 2007 = 1.0). Adopted from [1].
Coal is the “dirtiest” of the fossil fuels producing 88.3 kg of carbon dioxide emissions per gigajoule of energy produced. Natural gas presents itself as the “cleanest” fossil fuel releasing only 50.3 kg/GJ [5]. Regardless, all energy derived from fossil fuels has greenhouse gas emissions as an undesired byproduct and poses a risk to the environment.

Fossil fuel dependence is linked to both national and economic security. Most of the world’s oil originates from members of the Organization of Petroleum Exporting Countries (OPEC), which include Iran, Iraq and Venezuela. Also, the EIA predicts the largest increases in natural gas production over the next quarter century in regions such as the Middle East, Africa and Russia. The United States, on the other hand, leads the consumption of both oil and natural gas and is second only to China in coal consumption for energy. Troubled political relations with many of the aforementioned countries create a strong incentive for the U.S. and other developed nations to be energy independent.

Considering economics, the recent recession demonstrated how closely energy consumption and energy prices are linked to overall economic development. Worldwide consumption decreased by 1.1% in 2009 [2]. The price of crude oil crashed to less than a fourth of its value within six months in 2008 and more than doubled again by 2010, showing high volatility. Fossil fuel dependence has a great impact on the economic performance of a nation.

Although fossil fuels present a reliable energy source, they do so at the cost of the environment due to the high carbon dioxide emissions. The desire to be energy independent for security reasons also drives the search for fossil fuel alternatives. Hence, clean and renewable energy sources are under intense investigation.
1.2 Alternative energy sources

Nuclear power is a carbon neutral source of energy and already accounts for more than five percent of today’s total global consumption (Figure 1-1). However, uranium resources are limited, similar to those of fossil fuels. Global uranium reserves can only maintain the current production rate and prices for the next one hundred years [6]. Even if technological innovation reduces uranium extraction costs and improves energy efficiency, the usage of nuclear power faces further impediments. Breeder reactors have a high capital cost, present safety concerns and their lifetime is limited. Public protests and the fear of nuclear proliferation also hinder the implementation of new nuclear power plants. Finally, the largest concern relates to the radioactive waste and the disposal thereof due to the unknown longtime consequences.

Figure 1-3: Available exergy for renewable sources. Exergy is the maximum useful work derived from the respective energy sources [7].

Thus, the focus turns to renewable energy sources. Here, the most attractive and carbon neutral sources include solar irradiation of the earth’s surface, wind energy, heat retractable from the earth’s mantel, i.e. geothermal energy, and hydroelectricity. Figure 1-3 compares the sustainable power production for these renewable sources and compares them to the global energy consumption rate per year. It becomes immediately apparent that the sun’s energy is the most plentiful resource. In fact, the amount of solar energy that reaches the earth’s surface within one hour is nearly equivalent to the energy consumed globally in 2007 [1-3].
1.3 Solar energy

Several technologies exist that capture solar radiation and convert it to useful energy. The most widely implemented type is photovoltaic. Such systems are comprised of multiple solar cells connected in series to comprise a module, which in turn is installed to form an array with several more modules to increase the total power output to a desired wattage. The cells absorb the sun’s photons and convert their energy into an electrical current supporting a load. The relatively low conversion efficiency of this process is a key limiting factor for solar cells. The high materials-, production- and installation costs of cells and modules drive the high prices for electricity originating from solar power. The cost of electricity generated from fossil fuels is between 1 c/kWh and 8 c/kWh, where coal is the cheapest and oil the more expensive fuel [8]. Natural gas falls between the two. Wind and nuclear powered electricity cost 5 c/kWh to 7 c/kWh, where nuclear is slightly more expensive. In comparison, solar electricity has a price of 25 c/kWh to 50 c/kWh. Currently, governments provide incentives for investing in photovoltaics with policies and subsidies in order to lower their country’s carbon footprint. However, ultimately, the technology must improve such that solar can become an economically competitive energy source without subsidies.

Solar thermal power offers a lower cost alternative to photovoltaics at 10 c/kWh to 15 c/kWh [8]. Unlike photovoltaics, electricity is not generated directly from sunlight. Instead, sunlight is concentrated and focused onto a working fluid in order to produce thermal energy. In the case of high solar concentrators, the heat can be employed in a steam turbine or heat engine to produce electricity.

Global production capacity of solar power more than tripled between 2007 and 2009 from 7.3 GW to 23 GW, which proves the immense interest in converting this vastly available resource into useful energy [2]. But even if the current technology improves and fossil fuel prices increase such that solar energy becomes economically feasible, there is one further problem: the sun does not shine 24 hours per day. Consequently, solar energy requires storage in order to be collected in excess while the sun shines.
and to be dispatched at night, wherever power may be needed.

Photoelectrochemistry (PEC) offers a means of capturing sunlight and converting it to chemical energy instead of electrical or thermal energy, as is the case for photovoltaics and solar concentrators, respectively. In photoelectrolysis, absorbed light provides the energy required to e.g. split water into hydrogen and oxygen. Hydrogen serves as an energy fuel, while oxygen may be released into the environment without concerns. The sun’s energy is stored in the hydrogen bonds, which have a higher bond strength than those in water molecules. In order to dispatch this energy again, one can have hydrogen recombine with atmospheric oxygen to form water in a fuel cell and generate electricity or even burn the hydrogen to generate heat or mechanical energy. Thus, photoelectrolysis enables solar energy storage. Furthermore, it allows for carbon neutral production of hydrogen.

1.4 Thesis outline

Following this introductory chapter, the operation of a PEC cell will be explained in Chapter 2 including its challenges and limitations. Current photoanode materials are discussed with special attention on hematite. The possibilities of an ilmenite hematite solid solution (IHSS) as photoanode are considered in detail. The experimental methods employed to fabricate several types of samples of the IHSS system are described in Chapter 3 along with various characterization techniques. Chapter 4 details the derivation of the defect model for undoped and donor doped hematite in order to understand which charge carrier species controls conductivity at a given temperature and partial pressure of oxygen. Chapter 5 summarizes the results of the DC conductivity measurements of the bulk samples, the electrical impedance spectroscopy of the thin films and the PEC performance of the IHSS thin film photoanodes. In addition, a Mott-Schottky analysis for the hematite and doped hematite anodes is presented as well as the performance of a doped and undoped hematite homojunction photoanode. The PEC characterization described in Section 3.4 was performed in collaboration
with Prof. Roel van de Krol, Dr. Fatwa Abdi and Dr. Peter Bogdanoff at the Solar Fuels Institute at the Helmholtz Zentrum Berlin during two visits in July 2013 and February 2014. The results are discussed in further detail and in relationship to one another in Chapter 6. Finally, Chapter 7 lists the key findings and suggests future directions.
Chapter 2

Background and Theory

In this chapter, the operation of a PEC cell is explained. The PEC cell is limited by several factors, generally pertaining to the material properties of the photoanode, such as the bandgap and electronic transport properties. These will be discussed in detail in the following sections. Afterwards, current photoanode materials are reviewed by relating their properties to their PEC performance. Hematite, as a key candidate material, is discussed in detail and the ilmenite hematite solid solution system is introduced.
2.1 The photoelectrochemical cell

2.1.1 Operation

Splitting water requires two simultaneous half-cell reactions. In an electrochemical cell, water oxidation occurs at the anode, yielding oxygen, while protons are reduced at the cathode to produce hydrogen \[9\]

\[
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4e^- + \text{O}_2 \quad E_{\text{ox}}^\circ = -1.23 \text{ eV} \quad (2.1)
\]

\[
4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2 \quad E_{\text{red}}^\circ = 0 \text{ eV} \quad (2.2)
\]

Thermodynamically, the minimum applied potential required to drive the overall reaction, 1.23 V, is equal to the sum of the listed half-cell potentials in Eq. 2.1 and Eq. 2.2. These are listed for standard conditions and versus the normal hydrogen electrode (NHE). This reaction potential corresponds to the change in Gibbs free energy.

\[\text{Figure 2-1: Schematic of the operation of a photoelectrochemical cell.}\]

In order to produce hydrogen and oxygen, a PEC cell operates as demonstrated in Figure 2-1. First, incident photons are absorbed by the semiconducting anode. Their energy promotes electrons from the valence band (VB) to the conduction band (CB) to create electron-hole pairs. A Schottky contact between the anode and the
electrolyte creates an electric field that accelerates the excited electrons towards the back contact. From there, they travel to the counter electrode where they recombine with protons to form hydrogen gas. On the anode side, holes move from the valence band to the semiconductor/electrolyte interface to oxide water and produce oxygen. This completes the overall reaction. An applied bias can assist the water splitting process [10].

2.1.2 Challenges

The physical properties of the semiconducting anode and its interaction with the liquid electrolyte present several challenges. Theoretically, the bandgap of the semiconductor must at least be larger than the redox potential required for water cleavage, 1.23 eV. A bandgap between 1.9 eV and 2.0 eV, however, is suggested in order to overcome thermodynamic losses and overpotentials to guarantee fast reaction kinetics [11,13]. On the other hand, the solar spectrum limits the bandgap maximum. Only photons higher in energy than the energy difference between the valence and conduction band of the semiconductor can contribute to water oxidation. Figure 2-2 shows the photon flux based on the earth’s surface irradiation by the sun. It becomes apparent that strong visible absorption of light by the photoanode is desired, i.e. a relatively small bandgap of less than 2 eV, to ensure that the maximum number of available photons assist in the water splitting process. Furthermore, the alignment of the conduction and valence band edges with those of the redox potentials in the electrolyte is important. The valence band must lie below the oxidation level of water, such that holes can be injected into the H\textsubscript{2}O/O\textsubscript{2},H\textsuperscript{+} level to generate oxygen gas. Additionally, the conduction band must be positioned above the reduction potential H\textsuperscript{+}/H\textsubscript{2} to enable injection of electrons to produce hydrogen. If this is not the case, an applied potential can align the bands appropriately. However, this decreases the overall efficiency of the cell.

While the band gap size and alignment requirements may dictate the most restrictive limitations for a PEC system, several other factors can greatly influence the efficiency
Figure 2-2: Number of photons in the solar spectrum (AM1.5) as a function of photon energy. Flux regimes relevant for photoelectrolysis are indicated. Figure adopted from [11].

of a cell. For instance, charge carrier separation and transport are crucial. Long diffusion lengths, facilitated by high carrier mobilities, allow more holes to arrive at the solid/electrolyte junction without recombination, enabling water oxidation. This is generally achieved by increased metal 3d orbital overlap in the conduction band, typical of oxide semiconductors, and oxygen 2p or 2p-3d hybrid orbital overlap in the valence band. Doping of the semiconductor can also significantly alter the charge carrier lifetime and transport properties. While donors and acceptors usually lie near the conduction band and the valence band, respectively, deeper levels serve as recombination centers and can degrade the overall performance of the device.

Corrosion resistance of the semiconductor in the electrolyte, both in the dark and under photo-illumination, is another critical constraint for material selection. Side reactions at the solid-electrolyte interface that involve charge transfer can alter the chemical composition and thus the electronic properties of the semiconductor. To be electrochemically stable, the semiconductor’s enthalpy of reduction must lie above that of water reduction and the enthalpy of oxidative decomposition must be below that of water oxidation [11]. Consequently, many of the materials used in other
solar applications including CdS, GaAs and GaP are not suitable for PEC cells. Semiconducting oxides appear most favorable as anode materials for photoelectrolysis [13].

Good PEC cell performance dictates low overpotentials. Efficient hole transfer from the anode to the electrolyte is necessary for two reasons. First, hole accumulation in vicinity of the interface leads to enhanced electron-hole recombination due to the decrease in electric field at the interface. Second, high hole concentrations can lead to dissolution of the anode if the holes are not active in water oxidation [13]. Here, catalysts containing transition metals such as Ru, Mn, Ir and Co have been shown to increase the kinetics of hole transfer across the semiconductor/electrolyte interface to maintain a stable semiconducting anode and to promote water oxidation [14–17].

In summary, the properties of the semiconducting anode and its interaction with the electrolyte primarily govern the efficiency of a photoelectrolysis cell. Bandgap size and alignment, charge transport and anode stability are all materials’ properties. Tuning these properties presents a huge opportunity to increase the efficiency of PEC cells. Furthermore, good catalysts are required to enhance charge transfer from the anode to the electrolyte for effective water oxidation. Finally, it is desirable to implement low cost materials as electrodes and catalysts to manufacture a cell that is both efficient and economically viable.

2.2 Photoanode studies

In the early 1970’s, Fujishima and Honda presented the first functional photoelectrolysis cell to produce hydrogen. They showed that one could split water at an estimated quantum efficiency of ten percent with an n-type TiO$_2$ rutile single crystal anode and a Pt counter electrode [18, 19]. This was achieved with the addition of Fe$^{3+}$ ions to the electrolyte promoting the water oxidation reaction. The overall efficiency was 0.4% [20]. Fujishima and Honda’s discovery stirred great interest and today, many
investigations are underway to find better photoanodes and catalysts to improve PEC cell performance.

![Figure 2-3: Band edge positions of several semiconductors at pH 14 in relation to the water oxidation and reduction potentials as well as other common redox couples (Courtesy of Roel van de Krol).](image)

The primary selection criteria for photoanode materials are the materials' bandgaps and conduction and valence band edge positions relative to the water reduction and oxidation potentials. Figure 2-3 shows the energy band positions of several photoactive materials at pH 14. The redox potentials for water splitting reactions shift by $-59 \text{ mV/pH}$ and so do most band positions for the oxide materials [21]. If the bandgap of an anode material does not contain both the oxidation and the reduction potential of water, then an external bias can assist the water splitting reaction. Generally, the conventional photovoltaic materials would corrode in a PEC cell and/or are expensive, such as GaInP$_2$ and CuInS$_2$ [13]. Therefore, the attention turns to the more stable and cheaper metal oxide semiconductors. The following sections provide a short review of recent progress for the key candidate materials.
2.2.1 TiO$_2$

TiO$_2$ has been studied the longest as a photoanode material. Its large bandgap yields high stability. However, the bandgap of 3.0 eV for rutile or 3.2 eV for anatase limits charge excitation by absorption of light to wavelengths shorter than 415 nm or 390 nm, respectively [22,23]. Consequently, most solar flux photons do not carry sufficient energy to promote electron-hole pair creation in intrinsic TiO$_2$ and the theoretical solar-to-hydrogen conversion efficiency (power out/power in) is limited to 2.2% [24]. A common approach to sensitize the absorption of TiO$_2$ to the visible spectrum is to dope the material with transition metals. Maruska et al. observed absorption in the visible for TiO$_2$ doped with V, Cr, Mn, Fe, Co and Ni [22]. However, the resulting photocurrent depends strongly on the dopant. They postulate that the excited carriers undergo localized d-d transitions at Fe, Co and Ni impurities and therefore contribute few free carriers, which limits additional photocurrent. Mn dopants create a deep level and therefore result in slow response times. Cr doped TiO$_2$ shows a photocurrent onset at 520 nm and is superior to the other dopants in the visible, but its performance diminishes in the UV. Doping with Cr$^{3+}$ ions requires oxygen defects or a change of oxidation state to Cr$^{6+}$ for some dopant ions in order to maintain charge neutrality in the TiO$_2$ lattice [25]. In either case, recombination centers for electron-hole pairs are generated and result in the degradation of the photoresponse. In summary, substitutional doping on Ti$^{4+}$ sites with transition metals exhibits greater absorption in the visible spectrum but does not result in higher photocurrents for water splitting due to the formation of recombination centers.

Anion doping presents an alternative doping approach. Anions influence the position of the valence band, which for TiO$_2$ is far below the oxidation potential of water in the electrolyte. Asashi et al. have computed the density of states in anatase for substitutional doping of C, N, F, P and S on the O$^{2-}$ site [23]. Both nitrogen and sulfur show favorable mixing with the O 2p band and raise the valence band position. The photoactivity of TiO$_2-x$N$_x$ was tested by the decomposition of methylene blue and the material was active at wavelengths below 500 nm [26]. Lindgren et al. em-
ployed TiO$_{2-x}N_x$ (rutile) in a PEC cell and observed photocurrents at wavelengths below 550 nm, but the incident photon to current efficiency (IPCE) decreased for the doped samples compared to the undoped samples in the UV \[27\]. This decrease in IPCE is attributed to Ti$^{3+}$ states due to N doping and slow hole transport in the nitrogen band, both of which cause carrier recombination. Another study observed the photoactivity of TiO$_2$ doped with C by examining its ability to oxidize pollutants in the air or water \[28\]. A better photoresponse was observed for the C-doped TiO$_2$; however, carbon solubility was so low that the bandgap did not decrease to values below 3 eV. While both C and N doping show some photoactivity in the visible, their effects remain limited.

Nanostructures of titania have generated much interest as photoanode candidates due to the large surface to volume ratio and size-effects arising in the nano-regime. The gain in surface area allows more light absorption and provides more surface reaction sites over thin films or bulk material. Nanofractals of TiO$_2$ have better absorption coefficients, as these structures contribute to extensive light scattering. Additionally, nanofractals decrease the transport distance for holes to the solid-electrolyte interface \[13\], \[29\]. Co-doping these fractals with Fe and Cr results in photoactivity starting at 600 nm. Although the structures degrade under photoillumination in water or O$_2$ atmosphere, it exemplifies the effect of nanostructures.

### 2.2.2 WO$_3$

Tungsten oxide is another well-studied and understood photoanode material \[16\], \[30\]. Its bandgap is indirect, but at $\sim$ 2.6 eV. Therefore, WO$_3$ can capture a greater portion of the solar spectrum than TiO$_2$ and can reach a theoretical solar-to-hydrogen conversion efficiency of 4.8\% \[31\]. While the conduction band of WO$_3$ is slightly more positive than the hydrogen evolution redox potential (see Figure 2-3) and an external bias is required to assist the water splitting reaction, the material benefits from good charge carrier transport with a charge carrier mobility of 10 cm$^2$/Vs \[21\] and a diffusion length of $\sim$ 150 nm \[31\].
Santato et al. have reported the best performance to date of a WO$_3$ photoanode with a photocurrent density of 2.5 mA/cm$^2$ at 1.23 V vs. RHE [30]. The high photocurrent density is attributed to a mesoporous, nanostructured anode resulting in a high active surface area for light absorption and water oxidation. The same group also shows enhancement in the IPCE due to silver nanoparticles on the surface of the WO$_3$. These particles cause light scattering and reflection increasing the absorption of the photoanodes as well as surface plasmons [32]. Similarly to TiO$_2$, WO$_3$ photoanodes have been doped with C and N in order to raise the valance band and increase the fraction of solar photons capable of generating electron-hole pairs in this material [31]. However, success has been limited and while absorption became possible at longer wavelengths, the photocurrent density decreased with anion doping.

2.2.3 BiVO$_4$

Bismuth vanadate, a ternary metal oxide semiconductor, is another material that has stirred a lot of interest as a good photoanode candidate. Its bandgap of $\sim 2.4$ eV yields a theoretical solar-to-hydrogen conversion efficiency of 9% [33, 34]. The conduction band just straddles the redox potential for hydrogen evolution, eliminating the need for an external bias in the ideal case (see Figure 2-3). The material is cheap and abundant but does suffer from poor electron transport and slow oxidation kinetics, requiring catalysts to assist in efficient photoelectrolysis.

The bulk electron conductivity has been identified as one of the major bottlenecks in the performance of BiVO$_4$ as a photoanode [35]. This limitation can readily be overcome by doping the material with Mo [36] or W [34] increasing the electron density and consequently, increasing the conductivity as well. Effective catalysis was achieved by the application of a cobalt phosphate catalyst or other oxygen evolution catalysts, such as Co$_3$O$_4$, RhO$_2$ and Pt [33]. The best performance with a BiVO$_4$ photoanode was reported by Abdi et al., who employ the concept of gradient doping in order to create band bending in the semiconductor, which enhances charge carrier separation [37]. The resultant photocurrent density at 1.23 V applied bias vs. RHE
amassed to 3.6 mA/cm\(^2\) and corresponds to approximately 50% of the maximum theoretical photocurrent density for BiVO\(_4\).

2.2.4 Fe\(_2\)O\(_3\)

Hematite or α-Fe\(_2\)O\(_3\) has a bandgap of 1.9 eV to 2.2 eV and absorbs light at wavelengths shorter than 560 nm to 650 nm \(^{38}\). Therefore, hematite can absorb more photons within the solar spectrum than any of the other photoanode candidate materials discussed above. However, it requires an applied potential to assist water cleavage as its conduction band lies below the potential for hydrogen reduction (see Figure 2-3). In the early 1980s, Shinar and Kennedy demonstrated that α-Fe\(_2\)O\(_3\) is stable in aqueous media over a wide pH range when investigating the competition of halide oxidation and water oxidation under photoillumination with an assisting applied bias \(^{39}\). They also summarized the effects of several dopants in polycrystalline hematite \(^{40}\). Ti, Sn and Zn are reported to serve as single electron donors, whereas Nb and Ta donate two electrons each to the Fe\(_2\)O\(_3\) conduction band. Ca, Cu, Mg and Ni serve as acceptor sites, while Mn and Cr introduce electron traps.

Fe\(_2\)O\(_3\) photoanodes are reported to suffer from short hole diffusion lengths (2 nm to 4 nm), bulk and/or grain boundary recombination and the presence of surface states \(^{41}\). In one of the first studies of nanocrystalline hematite, Grätzel et al. observed large differences in the IPCE between front and back illumination for 1 µm to 1.5 µm thick porous hemitate films consisting of nanoparticles with 25 nm to 75 nm diameter \(^{42}\). The low IPCE at wavelengths between 400 nm and 600 nm for samples illuminated at the substrate-hematite interface is explained by the short hole diffusion length and recombination sites within the nanoparticles. The introduction of iodine into the electrolyte improves the photoactivity of nanoparticulate Fe\(_2\)O\(_3\). It is speculated that iodine species donate electrons to the surface traps of the hematite, eliminating electron trapping from the conduction band. Still, IPCE values remain below one percent as grain or bulk recombination remains dominant.
More recently, Grätzel et al. have shown that Si doping can enhance the photoresponse for $\alpha$-Fe$_2$O$_3$ by 50% to 90% depending on the preparation method [43]. Silicon affects both the hematite morphology and its electrical conductivity. Si dopants sit substitutionally on the Fe$^{3+}$ sites and donate an extra electron increasing the charge carrier concentration. Additionally, Si$^{4+}$ has a smaller ionic radius than Fe$^{3+}$, such that Si dopants decrease the grain size resulting in a more finely structured nanomorphology of the hematite photoanode. Better photoactivity is achieved due to shorter hole diffusion distances to the solid/electrolyte interface and the increased number of water oxidation sites due to the greater surface area. The highest photocurrent density for hematite to date, $3.3 \text{ mA/cm}^2$ at $1.23 \text{ V vs. RHE}$, was achieved by these cauliflower-structured anodes with the addition of an IrO$_2$ oxidation catalyst [16]. Other studies showed that a 1 nm thick SiO$_2$ layer between the $\alpha$-Fe$_2$O$_3$ and the transparent conducting electrode results in preferential growth along the (110) direction for hematite [44]. This direction is also preferential for electronic transport and therefore charge carrier recombination is reduced. The same effect has been observed for 5 nm to 10 nm thick SnO$_2$ interfacial layers. Deposition of dense $\alpha$-Fe$_2$O$_3$ films onto these substrates induced a carrier density of $10^{20} \text{ cm}^{-3}$ for Si doped samples compared to $10^{17} \text{ cm}^{-3}$ for undoped samples [13]. This confirms that Si acts as a donor in hematite besides influencing its microstructure.

In order to overcome hematite’s limitations, a lot of interesting ideas have been developed in the last decade. Beermann et al. grew nanorods that eliminated grain boundaries while maintaining a high aspect ratio [45]. The diffusion distance for holes was dependent on diameter of the rods only, which could be kept small, thereby allowing hole transport to the surface prior to recombination with electrons. On the other hand, the nano rods could be grown in an orientation preferential to electron transport along their length, further reducing recombination. Photocurrent studies of these hematite anodes in a KI electrolyte solution (pH 6.8) showed a significant improvement in the IPCE. Wang et al. followed a similar approach in using TiSi$_2$ nanonets coated with $\alpha$-Fe$_2$O$_3$. In this case, the TiSi$_2$ served as a conductive backbone for the electron transport, while the thickness of the hematite coating could be
kept within the few nanometers to minimize recombinations due to the short hole diffusion length [46]. This concept was again applied for hollow Al doped ZnO nanorods coated by hematite [47]. In all cases, the PEC performance improved due to the nano-architectures optimized for charge carrier transport in hematite.

Light trapping strategies have been implemented in order to use small feature sizes without sacrificing absorption. Rothschild et al. have demonstrated high photocurrents (up to 4.0 mA/cm$^2$ at 1.63 V vs. RHE) for hematite photoanodes using resonant light trapping [48]. A reflective coating (Pt or Ag) creates an optical cavity within a thin film of hematite, enhancing electron-hole pair generation near the semiconductor/liquid interface, which also minimized the travel distance for holes. In addition, these films are mounted in a V-shaped fashion, allowing absorption of photons that were previously reflected at another surface. The same photocurrent density at an applied bias of 100 mV less, i.e. 4.0 mA/cm$^2$ at 1.53 V vs. RHE, was achieved by hematite “champion” nanosturctures [49]. Warren et al. attribute a reduction in photocurrent to high angle grain boundaries in hematite. They explain that a potential barrier at grain boundaries obstructs majority carrier transport. Moreover, this barrier also reduces the potential drop across the space charge region, thereby reducing the depletion width and driving force for charge carrier separation. Besides the key studies highlighted here, several others have considered different dopants and processing techniques for hematite photoanodes. A nice summary of these is presented in a recent review by Li et al. [50].

2.3 Objectives

Hematite is a photoanode material of choice, because of its abundance, non-toxicity and stability as well as the correct size in bandgap. Despite so many efforts to overcome hematite’s limitations, photocurrent densities of this material are still limited to a quarter of the theoretical photocurrent density of 12.6 mA/cm$^2$ (considering a bandgap of 2.1 eV) [16]. Hematite has the highest theoretical solar-to-hydrogen effi-
ciency at 15.5% compared to other candidate materials, but its true potential remains untapped. In this study, the solid solution of hematite and ilmenite, FeTiO$_3$, is considered as a photoanode material. The ilmenite hematite solid solution (IHSS) is equivalent to hematite with varying content of the Ti donor dopant ranging from 0% to 50%. The IHSS system is implemented as a model system in order to examine the electronic conduction mechanism in hematite and understand its defect chemistry. In addition, ilmenite has a larger bandgap than hematite and presents the possibility of bandgap engineering to raise the conduction band of the semiconductor above the redox potential of hydrogen evolution. The electrical conductivities of both bulk and thin film samples are examined and the PEC performance of optimized anodes is characterized.

2.4 Ilmenite hematite solid solution (IHSS)

![Hexagonal ordering of cations in ilmenite, FeTiO$_3$, and hematite, $\alpha$-Fe$_2$O$_3$. Figure adopted from [51].](image)

Titanium acts as a donor when introduced into the hematite lattice. The low intrinsic conductivity of hematite is one of its limitation as a photoanode. Ti doped hematite preforms better as a photoanode than undoped hematite [40,52,54]. Large quantities
of titanium can be incorporated into the hematite lattice. When Ti cations replace 50% of the Fe cations, the ilmenite compound is formed. Hematite crystallizes in the corundum structure, where the oxygen ions are hexagonally close-packed and the iron cations fill two thirds of the octahedral sites [55]. In the ilmenite structure, half of the iron cations are replaced by titanium cations and alternating layers of iron and titanium are formed between oxygen planes. An illustration of both the ilmenite and hematite lattices is presented in Figure 2-4. Table 2.1 lists relevant parameters. Also, adding ilmenite to hematite forming a solid solution has the potential to stabilize the hematite phase in lower partial pressures of oxygen. At high temperatures (\(\sim 1000^\circ\)), hematite will transition to the magnetite phase below \(10^{-6}\) atm oxygen partial pressure (see Figure 2-5). In order to determine the conductivity mechanism and equilibrium charge carrier concentrations, however, a wide range of oxygen partial pressures must be accessible. This is particularly important at high temperatures, as kinetics are limiting charge carrier equilibration at lower temperatures. Therefore, stabilization of the hematite phase at lower oxygen partial pressures and high temperatures is desired.

Table 2.1: Unit cell dimensions, formula units per unit cell, \(Z\), and the theoretical density, \(\rho\), of ilmenite and hematite [56].

<table>
<thead>
<tr>
<th></th>
<th>ilmenite</th>
<th>hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>FeTiO(_3)</td>
<td>Fe(_2)O(_3)</td>
</tr>
<tr>
<td>(Z)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>(a)</td>
<td>5.089 Å</td>
<td>5.038 Å</td>
</tr>
<tr>
<td>(c)</td>
<td>14.092 Å</td>
<td>13.772 Å</td>
</tr>
<tr>
<td>(V_{uc})</td>
<td>316.01 Å(^3)</td>
<td>302.72 Å(^3)</td>
</tr>
<tr>
<td>(\rho)</td>
<td>4.789 g/cm(^3)</td>
<td>5.255 g/cm(^3)</td>
</tr>
</tbody>
</table>

The IHSS system has previously been studied for applications in spintronics [60,61]. The resistivity is reported to decrease from \(10^5\) \(\Omega\) cm for pure ilmenite to \(10^\Omega\) cm for a 50% ilmenite 50% hematite solid solution at room temperature (Figure 2-6(a)). At elevated temperatures, the solid solutions with increasing hematite content also exhibit lower resistivities. Figure 2-6(b) shows a reduction in activation energy as the temperature becomes lower. The change in activation energy occurs at different tem-
temperatures for the different compositions. While the activation energies for the three examined solid solutions are similar, they are significantly lower compared to that of the pure ilmenite sample. The trend of decreasing resistivity, as more hematite is added, was reported again for thin films of this solid solution by Zhou et al. [62].

Also, a transition from p-type to n-type behavior is observed based on Seebeck voltage measurements on bulk samples of varying compositions. Solid solutions containing more than 30% ilmenite are behaving as p-type semiconductors [63, 64]. The magnetic nature also changes across the range of different compositions. Both hematite and ilmenite are antiferromagnetic materials, but between 5% to 50% ilmenite content, the IHSS exhibits ferromagnetic behavior [61, 65]. There is discrepancy in the literature about the bandgap of ilmenite. The bandgap for bulk samples of ilmenite has been reported at values as low as 2.5 eV [62, 66]. The bandgap has also been reported at values as high as 3.5 eV for samples fabricated in low partial pressures of oxygen and for stoichiometric epitaxial films [66, 67].

Based on the properties of ilmenite, the results of first studies of the IHSS system
and the vast interest in hematite as a photoanode, the solid solution of ilmenite and hematite is a good model system to study the defect chemistry and conduction mechanism in a semiconducting metal oxide serving as a photoanode. While hematite has been studied extensively as a photoanode material (as discussed in Section 2.2.4), little work has been done to study the other end member of the IHSS system as a photoanode. In the 1970’s, Ginley and Butler measured photocurrents during water electrolysis using different iron titanates as photoanodes (Figure 2-7). These measurements also tested the effectiveness of single crystalline ilmenite. Ginley and Butler concluded that based on its performance, ilmenite was inferior to hematite as a photoanode material. Additionally, they determined an indirect bandgap for ilmenite of $\sim 2.2 \text{eV}$. 

Hematite’s shortcomings as a photoanode have been circumvented with clever de-
Figure 2-7: The square of photocurrents of iron titanates as a function of applied potential in 1 M NaOH illuminated with monochromatic light of 330 nm. Adopted from [68].

signs. The origin of the detrimental charge carrier transport and the band alignment limitation have not been addressed directly. Instead, the addition of donor dopants and favorable nanostructures have been implemented. Nanostructures significantly reduce the distance holes must travel as well as providing a large active surface area. On the other hand, little has been done to adjust the band alignment. Here, the solid solution of ilmenite and hematite provides both the opportunity of bandgap engineering and the investigation of the defect chemistry of these materials.

Little is known about the conduction mechanism and charge carrier dynamics in hematite. Early studies indicate that hematite is dominated by electronic compensation with intrinsic electrons and holes being the majority defects above 1100°C. Oxygen vacancies and iron interstitials are listed as probable ionic defects [70]. In the 1990’s, Dieckmann presented a more detailed study on hematite’s defect chemistry [69]. He confirmed that the majority defects at elevated temperatures are intrinsic electronic defects, i.e. electrons and holes. In addition, Dieckmann showed
Figure 2-8: Nonstoichiometry of hematite as a function of oxygen partial pressure at high temperatures. The fit corresponds to oxygen vacancies being the majority ionic defect in a regime where intrinsic electronic disorder dominates. Adopted from [69].

that, in this regime, doubly ionized oxygen vacancies are the predominant ionic defect. Thermogravimetric analysis revealed a $-1/2$ power dependence between the deviation from oxygen stoichiometry, $\epsilon$, and the oxygen partial pressure as indicated by the fit in Figure 2-8. Based on the temperature dependence of $\epsilon$ at a given partial pressure of oxygen, it was possible to determine the formation energy of an oxygen vacancy as 3.393 eV (given that the electron and hole concentrations are approximately equal). In this work, Dieckmann’s contributions will be used in order to derive the enthalpy of reduction for pure hematite in Chapter 6 in addition to characterizing the electronic properties of the IHSS model system.
Chapter 3

Experimental Methods

This chapter describes the preparation of all samples discussed in this thesis and their characterization. First, we consider the preparation of bulk samples used as targets for pulse laser deposition (PLD) of thin films as well as bulk samples for electrical characterization. Several compositions of the ilmenite hematite solid solution system are fabricated by traditional ceramic processing. Second, we discuss the fabrication of thin films for both electrical and PEC characterization, followed by an explanation of the physical sample characterization including X-ray diffraction (XRD) and optical absorption spectroscopy. Finally, electrical characterization of both bulk and thin film samples and PEC performance of the films are described in detail.
3.1 Sample preparation

3.1.1 Bulk samples

Bulk samples were prepared using traditional ceramic processing techniques. Ilmenite hematite solid solutions (IHSS) of varying compositions were prepared by mixing the end members of the solid solution, iron (III) oxide (Alfa Aesar, 99.945\% purity) and iron (II) titanium oxide (Alfa Aesar, 99.8+\% purity) at appropriate ratios. For good mixing, the powders were filled into a bottle containing zirconia milling media and a 1:1 water to isopropanol solution. The container was then placed onto a JRM ball mill (Paul O. Abbé Inc., Little Falls, NJ) for 24 hours at 300 rpm. Afterwards, the wet slurry was dried under a hood on a hot plate set to 150 °C until all moisture had evaporated. Next, the powder was sieved with a Retsch (Haan, Germany) test sieve (ASTM E11, 75\µm). Finally, the powder was pressed into a green pellet using a Carver 3925 hydraulic press (Wabash, IN).

To produce dense bulk samples, the green pellets were then calcined and sintered in an MTI (Richmond, CA) GSL1700X tube furnace while flowing argon (UHP, Airgas), with exception of the pure hematite pellet, which was exposed to air during this process. Calcination occurred at 650°C, 750°C and 900°C and sintering at 1200°C. Each temperature plateau was held for 2 hours and the heating and cooling rate was constant at 3 °C/min.

Targets

Targets are bulk samples prepared to be used as PLD source materials. They were pressed in a 1” diameter die at 15 kPSI for 2 min. After sintering, their top surfaces were polished with Leco silicon carbide polishing paper (Grit 600-1200) using a Struers (Ballerup, Denmark) Planopol machine. The targets prepared for this thesis are summarized in Table 3.1. The density was calculated from the targets’ mass and dimensions. One should note that the density is a lower bound as some targets were
chipped at the edges and therefore the calculated volume from the sample’s diameter and height is an overestimation to the true volume. Although the I98HSS target was prepared twice, it was too brittle each time and shattered, rendering it unsuitable for PLD. The theoretical densities for Fe$_2$O$_3$ and for FeTiO$_3$ are 5.255 g/cm$^3$ and 4.798 g/cm$^3$, respectively [56].

Table 3.1: Composition, actual and theoretical density of all PLD targets.

<table>
<thead>
<tr>
<th>target</th>
<th>composition</th>
<th>actual density g/cm$^3$</th>
<th>theoretical density g/cm$^3$</th>
<th>density %</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>Fe$_2$O$_3$</td>
<td>4.68</td>
<td>4.789</td>
<td>89.1</td>
</tr>
<tr>
<td>I2HSS</td>
<td>Fe$<em>{1.98}$Ti$</em>{0.02}$O$_3$</td>
<td>5.04</td>
<td>5.246</td>
<td>96.0</td>
</tr>
<tr>
<td>I33HSS</td>
<td>Fe$<em>{1.67}$Ti$</em>{0.33}$O$_3$</td>
<td>4.51</td>
<td>5.101</td>
<td>88.5</td>
</tr>
<tr>
<td>I67HSS</td>
<td>Fe$<em>{1.33}$Ti$</em>{0.67}$O$_3$</td>
<td>4.48</td>
<td>4.943</td>
<td>90.6</td>
</tr>
<tr>
<td>I98HSS</td>
<td>Fe$<em>{1.02}$Ti$</em>{0.98}$O$_3$</td>
<td>NA</td>
<td>4.798</td>
<td>NA</td>
</tr>
<tr>
<td>ilmenite</td>
<td>FeTiO$_3$</td>
<td>3.80</td>
<td>4.789</td>
<td>79.4</td>
</tr>
</tbody>
</table>

Pellets

Pellets are bulk samples prepared for electrical characterization. They were pressed in a 0.75” diameter die at 10 kPSI for 1.5 min. After calcining and sintering as above, a small rectangular sample was cut from each pellet with a diamond saw (Isomet 11-1180 by Buehler, Lake Bluff, IL). The resulting samples, along with their dimensions and densities, are listed in Table 3.2. The I98HSS pellet was too brittle and shattered when attempting to cut a small rectangular parallelepiped from it.

3.1.2 Pulse laser deposition

Pulse laser deposition or PLD is a fabrication technique for the preparation of metal oxide thin films of complex stoichiometry [71]. A laser, in this case a Coherent COMPex Pro 205 KrF eximer laser (Santa Clara, CA), emitting at a wavelength of 248 nm, is focused on a target inside a vacuum chamber and ablates the target so

---

1The hematite target was preexisting and not prepared by the author.
Table 3.2: Composition, dimensions and density of bulk samples for electrical characterization.

<table>
<thead>
<tr>
<th>sample</th>
<th>composition</th>
<th>width cm</th>
<th>height cm</th>
<th>length cm</th>
<th>actual density g/cm$^3$</th>
<th>density %</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>Fe$_2$O$_3$</td>
<td>0.578</td>
<td>0.295</td>
<td>1.805</td>
<td>5.14</td>
<td>97.8</td>
</tr>
<tr>
<td>I2HSS</td>
<td>Fe$<em>{1.98}$Ti$</em>{0.02}$O$_3$</td>
<td>0.333</td>
<td>0.260</td>
<td>1.300</td>
<td>4.85</td>
<td>92.4</td>
</tr>
<tr>
<td>I33HSS</td>
<td>Fe$<em>{1.67}$Ti$</em>{0.33}$O$_3$</td>
<td>0.292</td>
<td>0.255</td>
<td>1.625</td>
<td>4.78</td>
<td>93.7</td>
</tr>
<tr>
<td>I67HSS</td>
<td>Fe$<em>{1.33}$Ti$</em>{0.67}$O$_3$</td>
<td>0.392</td>
<td>0.285</td>
<td>1.400</td>
<td>4.28</td>
<td>86.7</td>
</tr>
<tr>
<td>I98HSS</td>
<td>Fe$<em>{1.02}$Ti$</em>{0.98}$O$_3$</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>ilmenite</td>
<td>FeTiO$_3$</td>
<td>0.295</td>
<td>0.240</td>
<td>1.555</td>
<td>3.74</td>
<td>78.0</td>
</tr>
</tbody>
</table>

That a vapor plume of material is created just above it (Figure 3-1(a)). The substrate positioned in close proximity collects some of the material, allowing for thin film formation. While the ablation process is very complex and not fully understood, one attributes the transfer of the exact stoichiometry from the target to the substrate to the incredibly rapid thermal heating of the target’s surface causing such high evaporation rates that all constituents essentially evaporate at the same rate. The substrate can also be heated and rotated during deposition. As the Neocera PLD system (Beltsville, MD) possesses six target holders, deposition of multicomponent films is possible (Figure 3-1).

![Figure 3-1](image-url): A schematic illustration (a) and a photograph (b) of the PLD vacuum chamber used for thin film depositions in this thesis.
Samples for electrical characterization

Thin films for electrical characterization were deposited onto doubly polished 10 mm x 10 mm x 0.5 mm single crystal sapphire substrates of <0001> orientation (MTI Corporation). Single crystal sapphire was chosen to enable the ilminite hematite solid solution films to be grown epitaxially on this substrate [62,67]. The mismatch of the basal plane of hematite is 5.8% with that of sapphire, resulting in a compressive strain in the film. The strain relaxes through the formation of dislocations and surface modulation once the film becomes thicker than 20 nm [73]. For ilmenite, the mismatch is slightly larger at 6.9%.

Deposition parameters were adjusted from those previously established for various iron oxides grown with the same Neocera system by Tepper et al [74–76]. After loading the substrates and targets, the PLD chamber was evacuated until the base pressure reached 5 × 10⁻⁶ Torr with a Pfeiffer Vacuum turbo-molecular pump (model TMU 261 p, Nashua, NH). Afterwards, oxygen (UHP, Airgas) was introduced into the chamber and during deposition, the O₂ pressure was maintained at 7.5 mTorr. The substrate to target distance was 6.5 cm. The substrate temperature was raised at 15 °C/min to 500 °C and then at 10 °C/min to 650 °C, where the temperature was held during deposition. A shutter (Figure 3-1(b)) concealed the substrates during a preablation of the target with 2000 laser pulses at 8 Hz. Preablation removed contaminants from the target’s surface prior to the actual deposition. Films were typically grown with 100,000 laser pulses with a power of 300 mJ and a repetition rate of 25 Hz. After deposition, the films were held at the deposition conditions for at least one additional hour prior to cooling at equivalent rates to heating above. Table 3.3 lists the samples produced for electrical characterization.

Samples for PEC measurements

Thin films of the same compositions as above were also deposited on quartz substrates coated with fluorine doped tin oxide (FTO) for PEC measurements (Section 3.4).
Table 3.3: Composition and thickness of films fabricated by PLD for conductivity measurements.

<table>
<thead>
<tr>
<th>thin film composition</th>
<th>thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite Fe$_2$O$_3$</td>
<td>162 ± 15</td>
</tr>
<tr>
<td>I2HSS Fe$<em>{1.98}$Ti$</em>{0.02}$O$_3$</td>
<td>215 ± 15</td>
</tr>
<tr>
<td>I33HSS Fe$<em>{1.67}$Ti$</em>{0.33}$O$_3$</td>
<td>105 ± 15</td>
</tr>
<tr>
<td>I67HSS Fe$<em>{1.33}$Ti$</em>{0.67}$O$_3$</td>
<td>124 ± 11</td>
</tr>
<tr>
<td>ilmenite FeTiO$_3$</td>
<td>156 ± 14</td>
</tr>
</tbody>
</table>

quartz substrates with dimensions of 25 mm x 12 mm x 1 mm were polished on both sides and originated from ESCO Optics (Oak Ridge, NJ). The FTO coating, with a specified surface resistivity of 15 Ω/sq, was performed by Solaronix (Aubonne, Switzerland). Prior to loading the substrates into the Neocera chamber, a rectangle of approximately 4 mm x 12 mm along one of the edges was coated with whiteout. After deposition, the whiteout was removed with acetone and in this area, the FTO remained uncovered by the film allowing it to be contacted with a wire (Section 3.4.3) such that the FTO served as a transparent back contact to the PLD deposited film.

The deposition process was very similar to that of the films for electrical characterization. However, the parameters were very different. For samples for PEC measurements, the laser also operated at a power of 300 mJ but at a repetition rate of only 5 Hz and most films were grown with only 30,000 pulses. The O$_2$ working pressure was set to 30 mTorr and the substrate temperature during deposition was 450°C. The base pressure, temperature ramp rates and preablation treatment were the same as above. The substrate to target distance was 7 cm. Again, the samples remained at the deposition temperature and working pressure for at least one hour after the deposition was completed. The thicknesses of the samples are listed in Table 3.4.
Table 3.4: Composition and thickness of films fabricated by PLD for PEC measurements.

<table>
<thead>
<tr>
<th>sample</th>
<th>composition</th>
<th>state(^2)</th>
<th>thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>(\text{Fe}_2\text{O}_3)</td>
<td>as-deposited</td>
<td>47 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>48 ± 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>50 ± 7</td>
</tr>
<tr>
<td>I2HSS</td>
<td>(\text{Fe}<em>{1.98}\text{Ti}</em>{0.02}\text{O}_3)</td>
<td>as-deposited</td>
<td>56 ± 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>58 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>58 ± 5</td>
</tr>
<tr>
<td>I33HSS</td>
<td>(\text{Fe}<em>{1.67}\text{Ti}</em>{0.33}\text{O}_3)</td>
<td>as-deposited</td>
<td>30 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>33 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>35 ± 2</td>
</tr>
<tr>
<td>I67HSS</td>
<td>(\text{Fe}<em>{1.33}\text{Ti}</em>{0.67}\text{O}_3)</td>
<td>as-deposited</td>
<td>32 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>32 ± 9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>32 ± 5</td>
</tr>
<tr>
<td>ilmenite</td>
<td>(\text{FeTiO}_3)</td>
<td>as-deposited</td>
<td>47 ± 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>41 ± 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>43 ± 5</td>
</tr>
<tr>
<td>H/I2(^3)</td>
<td>(\text{Fe}<em>2\text{O}<em>3/\text{Fe}</em>{1.98}\text{Ti}</em>{0.02}\text{O}_3)</td>
<td>as-deposited</td>
<td>45 ± 2</td>
</tr>
<tr>
<td>I2/H(^3)</td>
<td>(\text{Fe}<em>{1.98}\text{Ti}</em>{0.02}\text{O}_3/\text{Fe}_2\text{O}_3)</td>
<td>as-deposited</td>
<td>42 ± 2</td>
</tr>
</tbody>
</table>

3.2 Physical characterization

3.2.1 X-ray diffraction

X-ray diffractograms were collected at room temperature from both targets and pellets to identify their phase. In addition, the thin films on sapphire were subjected to XRD and high resolution XRD (HRXRD) measurements to confirm their epitaxial nature. For the former, a PANalytical X’pert PRO multipurpose diffractometer (Almelo, The Netherlands) was employed in conjunction with the Open Eulerian Cradle stage. For the latter, a Bruker D8 Discover (Billerica, MA) instrument was utilized.

\(^2\)The state refers to post-deposition processing as explained in Section 3.4.2.

\(^3\)Homojunctions of multiple materials, as is further explained in Section 5.4.3.
Phase identification

The X’pert PRO diffractometer operates in the Bragg-Brentano geometry and has a copper anode source emitting $K\alpha_1$ ($\lambda = 1.540598$ Å) and $K\alpha_2$ ($\lambda = 1.544426$ Å) spectral lines. A nickel filter is placed in front of the X’Celerator detector in order to filter out the Cu $K\beta$ lines. The tube power was set to a voltage of 45 kV and a current of 40 mA. Generally, incident beam optics were controlled by a 0.04 rad Soller slit, a 10 mm mask, a 2° anti-scatter slit and an automatic programmable divergence slit set to maintain the irradiated length on the sample at 6 mm. For smaller samples, a 5 mm mask and a 1° anti-scatter slit was used and the divergence slit was programmed to restrict the irradiated sample length to 2 mm. For the diffracted beam optics, the soller slit and the programmable divergence slit were matched with those of the incident beam.

Scans were collected using the X’pert Data Collector 2.2 software. In case of the bulk samples, a continuous scan would span $10 - 80 \ ^\circ 2\theta$ with a step size of 0.01671° at 50.165 sec/step. Scans for the thin films were limited to a range from $20 - 80 \ ^\circ 2\theta$ and measured using the same parameters as above.

The XRD patterns were matched to the Powder Diffraction File (PDF) database by the International Centre for Diffraction Data (ICDD) to establish phase identification using the High Score Plus 3.0e software. In this thesis, database files are referenced by their PDF number.

Epitaxy

High resolution X-ray diffractograms of thin films were collected using the Bruker D8 diffractometer operating at 40 kV and 40 mA. The incident beam configuration consisted of a Ge(002)x4 asymmetric monochromator emitting only the $K\alpha$ spectrum with a beam divergence of 25 arc-seconds, a 0.8 mm slit in the Gobel mirror slit, a 0.2 mm slit in the first monochromator slit to limit the beam height and a 1 mm slit in the second monochromator slit to limit the beam width. A Pathfinder detector system
with the receiving slit set to 0.2 mm was used on the diffracted beam side.

In order to confirm that a thin film grew epitaxially on its sapphire substrate, a coupled scan was collected for at least one symmetric peak and one asymmetric peak. The diffracted beam intensity was measured in 0.001° increments at 0.5 sec/step using the DIFFRAC plus XRD Commander 2.6.1 software, where the 2θ range was selected to encompass both the substrate and the film peaks. The asymmetric scan was collected at grazing incidence, which is more sensitive to surface layers and has higher intensity but can produce broader peaks compared to a grazing exit asymmetric scan. The XRD Wizard 2.9.0.22 software was used to calculate the correct ω tilt for the asymmetric peak.

Moreover, rocking curves of the film and substrate peaks were collected individually by fixing the detector so that it was in perfect alignment with each peak. To collect a scan, the sample tilt was gradually changed at 0.001° increments every 0.5 seconds such that the ω range would encompass the whole peak. Rocking curves provide qualitative information on the quality of the film, where a broader peak indicates a higher defect density in the film.

3.2.2 Optical absorption spectroscopy

Spectroscopy measurements were performed on thin film samples using an Aquila Instruments nkd-8000 spectrophotometer (Newport, Essex, UK). To determine a sample’s absorption, a monochromatic, P-polarized light beam incident at 30° irradiated the sample to simultaneously determine its transmission, T and reflection, R, over a wavelength range from 300 nm to 800 nm. Data was collected in 1 nm increments, making 50 readings at each step subject to a digital filter time constant of 50 ms. A reference spectrum was recorded prior to each measurement using a quartz reference. Due to instrument limitations, data below 350 nm was often noisy. In such cases, data analysis was restricted to wavelengths above the appearance of any such noise.
Absorption, $A$, was computed by the governing relationship

$$1 = T + R + A$$ \quad (3.1)

![Figure 3-2: Transmission, reflection and absorption of an FTO coated quartz substrate.](image)

In order to determine the true absorption of a thin film on an FTO coated quartz substrate, first the absorption of the substrate, primarily due to the FTO layer (Figure 3-2), was calculated after measuring the substrate’s transmission and reflection. Subsequently, the film’s absorption could be calculated as follows:

$$A_S = 1 - T_S - R_S$$ \quad (3.2)

$$A_T = 1 - T_T - R_T$$ \quad (3.3)

$$A_F = \frac{A_T - A_S}{1 - A_S}$$ \quad (3.4)

where subscripts $S$, $T$, $F$ denote parameters relating to the substrate, the sample (total) and the film, respectively.
Next, the absorption coefficient was determined using the Beer-Lambert law:

\[ I(z) = I_0 \exp(-\alpha z) \] (3.5)

where \( \alpha \) is the absorption coefficient and \( I \) is the intensity of transmitted light after propagating a distance \( z \), while \( I_0 \) is the incident intensity, i.e., the optical intensity at \( z = 0 \). When replacing \( z \) by the thickness, \( t \), of a thin film, \( I_0 \) now equals \((1 - R)\) and \( I(z) \) is equivalent to \( T \) and therefore

\[ \alpha = -\frac{1}{t} \ln \left( \frac{T}{1 - R} \right) \] (3.6)

The absorption coefficient can now be calculated and plotted as a function of the wavelength of the incident light. It is known that the absorption rate for a direct transition is proportional to the density of states at a given energy and thus exhibits the following behavior:

\[ \alpha h \nu = \begin{cases} 0 & \text{for } h \nu < E_g, \\ \propto (h \nu - E_g)^{\frac{1}{2}} & \text{for } h \nu \geq E_g. \end{cases} \] (3.7)

where \( h, \nu \) and \( E_g \) are Planck’s constant, frequency and the bandgap energy, respectively. In the case of an indirect bandgap, the relation takes the following form:

\[ \alpha h \nu \propto \left( h \nu - E_g \mp \frac{h}{2\pi} \Omega \right)^2 \] (3.8)

where \( \Omega \) is the phonon angular frequency of the phonon that is absorbed or emitted in conjunction with the absorbed photon in order to allow the indirect bandgap transition. As the dependency on frequency is different for a direct and an indirect transition, one can distinguish between the two. For a direct gap material, one plots \((\alpha h \nu)^2 \) vs. energy and the bandgap is determined by extrapolating the linear region to the principal axis. The x-intercept is equal to the value of \( E_g \). In the case of an indirect gap material, the linear extrapolation to the principal axis in a plot of \((\alpha h \nu)^{\frac{1}{2}} \) vs. energy reveals \( E_g \). Such plots are termed Tauc plots as J. Tauc was the first to
make use of such plots to extract optical bandgaps of silicon and germanium from absorption data [78,79]. The method described above was employed to calculate the bandgap values for several thin film samples reported in section 5.2.

3.2.3 Profilometry

Film thickness was measured with a KLA Tencor P-16+ profilometer (Milpitas, CA) or a Veeco Dektak 150 (Plainview, NY). Typically, the step height at the edge of a PLD deposited film was measured. The P-16+ operates with a stylus of 4 µm in diameter. Scans were performed using the Profiler v7.21 software at 50 µm/s with a sampling frequency of 200 Hz. The applied stylus force was set to 2.0 mg and the range (hills and valleys) to 13.5 µm. The Dektak, on the other hand, operates with a stylus of 25 µm/s in diameter. Scan parameters were programmed to 10 mg of stylus force, a scan rate of 35 µm/s with a sampling frequency of 300 Hz and a range (hills and valleys) of 6.5 µm using the Dektak Version 9.4 software.

![Figure 3-3: Dektak scan showing the step height of a hematite film on an FTO coated quartz substrate.](image)

Typical results from a profilometer scan are shown in Figure 3-3. The step height was determined by taking the difference between the average height of the range shaded in green and the average height of the range shaded in red. The measurement
was repeated in three to five different locations in order to calculate an average thickness.

3.3 Electrical characterization

3.3.1 Bulk samples

The DC conductivity of all bulk samples was measured simultaneously in a three zone tube furnace (Model STF55346C-1, Lindberg/Blue M, Asheville, NC) at temperatures ranging from 900°C to 1050°C and it is described in detail below. The partial pressure of oxygen (pO$_2$) in the furnace tube containing the samples was set by MKS (Andover, MA) mass flow controllers (MFC) controlled by a MKS Type 247 4 Channel Readout and monitored by an external pO$_2$ sensor.

![Figure 3-4: Schematic of a bulk sample with Pt contacts.](image)

**Figure 3-4:** Schematic of a bulk sample with Pt contacts.

Electrical contacts

The bulk samples described in section 3.1.1 were contacted with four platinum wires for four point DC measurements. Notches were cut into the specimen with a diamond saw in order to prevent the Pt wires from slipping. First, Pt paste (A4338A, Heraeus) was painted around the specimens at the notches to ensure good contact. The ends were also covered with Pt paste as part of contacts 1 and 4 (Figure 3-4). Then, Pt wire (0.25 mm diameter, Premion, 99.997% metals basis, Alfa Aesar) was wrapped around the specimen tightly at all painted notches to form contacts 1 through 4.
Table 3.5 lists relevant parameters for conductivity calculations. Cross sectional area and distance between contacts 2 and 3 are labeled as $A$ and $l$, respectively, in Figure 3-4.

<table>
<thead>
<tr>
<th>sample</th>
<th>$A$</th>
<th>$l$</th>
<th>$A/l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>0.071</td>
<td>0.405</td>
<td>0.175</td>
</tr>
<tr>
<td>I2HSS</td>
<td>0.088</td>
<td>0.410</td>
<td>0.215</td>
</tr>
<tr>
<td>I33HSS</td>
<td>0.255</td>
<td>0.448</td>
<td>0.166</td>
</tr>
<tr>
<td>I67HSS</td>
<td>0.112</td>
<td>0.440</td>
<td>0.254</td>
</tr>
<tr>
<td>ilmenite</td>
<td>0.171</td>
<td>0.413</td>
<td>0.414</td>
</tr>
</tbody>
</table>

**DC conductivity measurements**

The electrical conductivity of the bulk samples was measured with a modified setup previously described in reference [80]. The samples were mounted on alumina multi-bore tubes held in place by the same Pt wires that served as electrical contacts. The rods with the hematite, I2HSS and I33HSS samples (Figure 3-5) were mounted into the furnace with a custom fitting that also sealed the furnace tube at that end. Similarly, the I67HSS and ilmenite samples were mounted at the opposite end. The alumina multi-bore tubes served as feed throughs for all leads running to the samples. An S-type thermocouple, consisting of a Pt and a Pt / 10% Rh wire, also ran through each multi-bore tube to monitor the local temperature at each sample. A gas inlet and outlet emerging from the fittings allowed different gas mixtures to flow through the reaction tube. The $pO_2$ was set by MFCs regulating the flow of pure nitrogen and oxygen (Airgas). Conductivity measurements were performed at 900°C, 950°C, 1000°C and 1050°C. The heating and cooling rate was 5 °C/min. Each temperature and $pO_2$ was maintained until the conductivity of all samples had reached a steady value.

Current-voltage (IV) sweeps were performed using a Solartron Analytical (Ametek Inc., Berwyn, PA) Modulab system equipped with a Pstat 1MS/s (2087A) poten-
Figure 3-5: Bulk samples contacted with Pt wires mounted on alumina multi-bore tubes with thermocouples at each sample.

tiostat/galvanostat module and an FRA 1MHz (2055A) frequency response analyzer and the accompanying Modulab ecs 2.0 software package. The current was swept from 0 mA to 0.5 mA at a scan rate of 10 µA/s.

\[ V = IR \]  \hspace{1cm} \text{(3.9)}

\[ \sigma = \frac{1}{R} \left( \frac{l}{A} \right) \]  \hspace{1cm} \text{(3.10)}

Figure 3-6 displays typical results of such an IV sweep. Indeed all samples exhibited only ohmic behavior (Eq. 3.9) at the temperatures and pO$_2$'s examined. The conductivity, $\sigma$, was computed from the resistance, $R$, the slope of the IV curve, and the geometric factor, $A/l$ (Table 3.5 Equation 3.10).

**External pO$_2$ sensor**

The pO$_2$ of the gas flowing though the conductivity measurement chamber was continuously monitored by an external pO$_2$ sensor. The gas outlet of the three zone furnace was connected to another smaller Lindberg/Blue M furnace (Model TF55035A-1) containing a home-built zirconia oxygen sensor (Figure 3-7). The tip of a closed zirconia tube (0.25″ diameter) coated with Pt paste on the inside and outside as electrodes was held at 850 °C. The inside of the zirconia tube was exposed to room air and thus had a constant oxygen activity of 0.21. Additionally, a spring loaded
Figure 3-6: IV sweeps of a hematite bulk sample at different temperatures exhibiting ohmic behavior.

S-type thermocouple was placed inside the zirconia tube such that its tip was pushing against the Pt coated tip of the zirconia tube. Thus, the Pt wire of the thermocouple also served as a lead to the electrode inside the zirconia tube. An extra lead was fed through the fitting holding the zirconia tube in order to contact the electrode on the outside of the zirconia tube. The voltage difference between the two electrodes, equivalent to the electromotive force for this solid electrolyte (zirconia) concentration cell, was measured with a Hewlett Packard (Palo Alto, CA) 3478A multimeter and recorded using a LabView (National Instruments, Austin, TX) program. The pO₂ of the gas could then be calculated from the Nerst equation

\[ E = t_1 \left( \frac{kT}{4q} \right) \ln \left( \frac{pO_2}{pO_2^{(ref)}} \right) \]  

(3.11)

where \( t_1 \) is the ionic transference number (equal to 1 in the ideal case), \( k \) Boltzmann’s constant, \( T \) absolute temperature and \( q \) the charge of an electron. The reference pO₂ is 0.21 atm. The set temperature of 850 °C was chosen to ensure that \( t_1 \) would be very
near unity. Moreover, this ensures a proper operation of the pO$_2$ sensor, not limited by kinetics.

### 3.3.2 Thin films

The electrical conductivity of the thin films listed in Table 3.3 was measured by electrical impedance spectroscopy (EIS). An interdigitated electrode (IDE) was sputtered onto each film. Electrical contact was achieved by bonding Pt wires to the pads of the IDEs with Pt paste (Figure 3-8). The samples were then mounted on a custom-built holder providing two electrical leads to the sample and thermocouple. The electrical properties of the films were characterized in situ, at various temperatures and pO$_2$, in a Thermolyne 21100 tube furnace using a Novocontrol Technologies Model Alpha-A Impedance Analyzer (Hundsangen, Germany). The samples were heated to 800 °C at 10 °C/min and held at temperature for 24 hours at given pO$_2$. Subsequently, the temperature was decreased at 5 °C/min in 50 °C increments. At each increment, the temperature was held for 3 hours and EIS was measured. The pO$_2$ was established by flowing different pre-mixed gases (Airgas: UHP oxygen, compressed air, 1% oxygen in argon, 1000 ppm oxygen in nitrogen and 100 ppm oxygen in nitrogen) through the sample chamber.
Deposition of the interdigitated electrodes

The IDEs were deposited in a Kurt J. Lesker (Pittsburgh, PA) sputter system. First, the samples were mounted on a substrate holder and covered with a mask supplied by LaserTools Tecnologia (Sao Paulo, Brazil). The mask had 10 fingers per electrode each 5 mm long and 200 µm wide with a spacing of 100 µm (Figure 3-8(a)). Vacuum tape held both the sample and mask in place. After the 2” diameter Pt target (99.99% metals basis, Birmingham Metal) and substrate holder were mounted, the sputter chamber was pumped down to a base pressure of $1 \times 10^{-5}$ Torr. Deposition took place in pure argon (Airgas) at a working pressure of 5 mTorr. A DC power of 50 W was supplied to the Pt target to maintain a plasma during the deposition for 44 min including a 2 min pre-sputter of the target to remove surface contaminants. The samples were rotating during deposition for even coverage.

After deposition, the IDEs were examined under an optical microscope (Olympus BX51, Tokyo, Japan) for uniformity and continuity of the individual fingers (Figure 3-8(b)). Due to shadowing effects, the actual width of the fingers was 150 µm. Hence, the spacing became 150 µm as well.
Electrical impedance spectroscopy

AC impedance spectroscopy measures the real and imaginary impedance of a sample as a function of frequency. As different components of the total impedance have a different dependence on frequency, this technique enables the separation of these components, e.g., bulk, grain boundaries and interfaces. The bulk impedance is measured at high frequencies, whereas the impedance of interfaces is measured at low frequencies. Equivalent circuit models can be employed to fit the experimental data in order to extract resistance and capacitance values of the individual components.

In this study, EIS was measured over a frequency range of 0.01 Hz to 1 MHz with an integration time of 0.5 s or 1 cycle, whichever was longer. The oscillation amplitude was 500 mV and no additional DC bias was applied. Resulting spectra were analyzed with Scribner Associates’ ZView 3.3e software allowing to both model the equivalent circuit and fit the data. The conductivity, $\sigma$, was calculated from the resistance, $R$, determined from the EIS data and the relation

$$\sigma = \frac{1}{R(2N-1)l} \frac{d}{t}$$

where $d$ is the separation between the electrode fingers, $l$ the length of a finger and $t$ the thickness of the epitaxial film, respectively. $N$ is the number of fingers on one electrode.

3.4 Photoelectrochemical characterization

3.4.1 The PEC cell

Electrochemical measurements on thin films of various compositions of the IHSS system were performed in a three electrode PEC cell (Figure 3-9). The thin films functioned as the photoanode, i.e. the working electrode (WE), and were clamped down in the sample insert with a threaded ring, $R_2$. Another ring, $R_1$, then secured the
sample insert against the cell wall, sealed by an O-ring. Another O-ring was placed between the sample and sample insert to prevent any leakage of the electrolyte. The exposed area of the sample was 0.283 cm$^2$. In this case, the active area for measurements in the dark equaled that for measurements under illumination, compared to other cell configurations, where the photo-active area is determined by the size of the window through which the light enters. Here, front illumination occurred through a large quartz window, also sealed with an O-ring and fixed against the cell wall with threaded ring, $R_3$. Back illumination of the photoanode was also possible through $R_2$. The reference electrode (RE), Ag/AgCl (XR300, Radiometer analytical, Villeurbanne Cedex, France), was inserted through a feedthrough in the cell lid. Similarly, the counter electrode (CE), a Pt mesh at the end of a Pt wire, was also fixed in place by a feedthrough in the lid opposite to the RE (not shown in Figure 3-9).

![Figure 3-9: Design of the PEC cell used for this study. Figure adopted from [82].](image)

The electrolyte

Unless otherwise noted, the electrolyte utilized for these measurements was a 1.0 M NaOH solution (pH 13.6) prepared with NaOH pellets ($\geq$99%, Carl Roth GmbH) and 18.2 MΩ cm water (Milli-Q synthesis, Millipore, Billerica, MA). A large bubble
often formed at the photoanode when the solution was first dispensed into the cell. Using a pipet to squirt in the direction of the working electrode removed this bubble. At certain occasions, the electrolyte consisted of a 1.0 M NaOH and 0.5 M H$_2$O$_2$ solution. The H$_2$O$_2$ was diluted from a stabilized 30% H$_2$O$_2$ stock solution (Carl Roth GmbH).

### 3.4.2 Annealing

Some of the photoanodes were annealed in either oxidizing or reducing conditions. The samples were placed into a 0.75” quartz tube positioned in a Lindberg/Blue M furnace (Model TF55035A-1) and capped with a gas inlet and outlet. Gas flow was controlled by a manual flowmeter (FM-1050, Matheson, Basking Ridge, NJ) located prior to the inlet and checked with a bubbler at the gas outlet. Pure O$_2$ (UHP oxygen, Airgas) was streamed for oxidation and 100 ppm O$_2$ in N$_2$ (Airgas) for reduction of the thin films. The samples were annealed at 580 °C for 36 hours and the heating and cooling rate was 5 °C/min.

### 3.4.3 Contacting

FTO served as a transparent back contact to the thin films fabricated by PLD (Section 3.1.2). During deposition, a small area of the FTO was masked such that it remained uncoated by the film. This area was then used to contact the sample. A LiY wire (0.42 mm diameter, Conrad Bauelemente) was fixed to the sample with electrically conductive adhesive silver tape (3M) (Figure 3-10(a)). The other end of the wire could now be easily contacted with an alligator clip.

### 3.4.4 Catalyst deposition

In order to enhance performance of the photoanodes, a cobalt phosphate (CoPi) water oxidation catalyst was electrodeposited onto some of the thin film samples. To
do so, the sample was placed into the cell described above with a 0.5 mM solution of Co(NO$_3$)$_2$ in a 0.1 M potassium phosphate (KPi) buffer (pH 7). The solution was prepared by dissolving appropriate amounts of cobalt(II) nitrate hexahydrate (Merck), monobasic potassium phosphate and dibasic potassium phosphate trihydrate (Sigma-Aldrich) in water (18.2 MΩ cm). A thin layer of the catalyst was electrodeposited at a constant potential of 1.7 V vs. RHE using a EG&G Princeton Applied Research 273A potentiostat (now Ametek Inc., Berwyn, PA) for 10 min.

### 3.4.5 Photocurrent density measurement

To characterize the performance of a photoanode, the current density as a function of potential in the dark and under illumination was measured for the PEC cell as illustrated in Figure 3-11. The assembled cell was placed in the light path of a Wacom Electric solar simulator. More information about the solar simulator and its spectral irradiance may be found in Appendix A. A shutter (CS35S3S1-NL-100, Vincent Associates Uniblitz Electronic, Rochester, NY) controlled by a VMM-T1 shutter driver/timer (also Uniblitz) could block the beam in front of the PEC cell to enable chopping of the light in order to observe transients in the photocurrent. The cell’s electrodes were connected to a PRA 273A potentiostat (Ametek Inc., Berwyn, PA).
Figure 3-10(b) shows a picture of the assembled cell including the N\textsubscript{2} purge, which maintains a constant O\textsubscript{2} activity in the electrolyte during the experiments.

![Figure 3-11: Schematic of the experimental setup to measure the performance of a PEC cell under simulated sunlight. Figure adapted from [82].](image)

Cyclic voltamograms (CVs) were performed on the cell and recorded with CorrWare 3.3d (Scribner Associates). Typically, the voltage was scanned between 0.5 V and 1.8 V vs. RHE for three cycles starting and ending at the open circuit potential at a scan rate of 50 mV/s. All cycles were recorded to ensure reproducibility. First, the measurement was undertaken in the dark, then under front illumination and finally under back illumination of the photoanode. Afterwards, a constant potential of 1.0 V, 1.1 V, 1.2 V, 1.3 V, 1.4 V and/or 1.5 V was applied to the photoanode for 2 min while the light was chopped in 10 s increments.

### 3.4.6 IPCE measurement

Another approach to measure the performance of a PEC cell or photoanode is to determine the photocurrent as a function of wavelength. A common figure of merit is the incident photon-to-current conversion efficiency (IPCE), which is equivalent to the external quantum efficiency. To determine the IPCE, the thin film samples were characterized in a setup as depicted in Figure 3-12. Similar to the setup for measurements under simulated sunlight, the electrodes of the PEC cell were connected
to a PRA 273A potentiostat (Ametek Inc., Berwyn, PA) in order to apply a bias and measure the current. However, here, the sample was illuminated by monochromatic light. A 300 W Xenon arc lamp from LOT-Oriel GmbH (Darmstadt, Germany) with a high UV and VIS output and a continuous spectrum from 200 nm to 700 nm served as the light source. A Princeton Instruments (Acton, MA) SP2150i monochromator with entrance and exit slits of 1.00 mm reduced the spectrum of the light to a narrow band around a wavelength of interest. Two long pass filters were inserted into the beam after the monochromator to remove higher orders of diffracted light. Above 610 nm, a OG590 filter was used. Between 340 nm and 610 nm, a WG320 filter was inserted. No filter was necessary below 340 nm. The filters were controlled by a motorized filter wheel assembly (FA2448, Princeton Instruments). Additionally, lenses focused the beam onto both the monochromometer and the sample. A shutter (LS6T2-NL, Vincent Associates, Rochester, NY) could block the sample’s exposure to the light and was controlled with the same driver as in the simulated sunlight measurements.

Figure 3-12: Illustration of the experimental setup to measure the external quantum efficiency of a photoanode. Figure adapted from [82].

In order to measure the power density as a function of wavelength, a Nova II power meter from Ophir Photonics (Jerusalem, Israel) was employed. Figure 3-13 shows resulting calibration curves measured on different days. The data was recorded with a LabView program scanning wavelength from 700 nm to 300 nm at a rate of
30.0 nm/min. As the curves fall on top of each other, the light source was stable over the measurement period. One notes two step changes: a small one at 610 nm and a larger one at 340 nm. These correspond to the exchange of the long pass filters.

IPCE was measured for thin film samples mounted in the PEC cell at applied potentials of 1.23 V and 1.5 V vs. RHE. The wavelength was scanned from 700 nm to 300 nm at a rate of 15.0 nm/min. The shutter operated at 10 s increments. Figure 3-14 displays the raw data of an IPCE measurement. The current spikes immediately after opening or closing the shutter are due to charge accumulation and recombination. In order to calculate the actual IPCE value, the following formula is applied:

\[
\text{IPCE}(\lambda) = \frac{hc}{q\lambda} \left( \frac{j_{\text{photo}}(\lambda)}{P(\lambda)} \right)
\]

(3.13)

where \(c\) is the speed of light and \(\lambda\) the wavelength. \(j_{\text{photo}}\) and \(P\) are the photocurrent density and the light power intensity at a given wavelength. The light power intensity is known from the calibration curve (Figure 3-13). During the IPCE measurement, the current is allowed to stabilize for 8 s before it is averaged for the remaining 2 s.
Figure 3-14: Raw data as collected with the IPCE setup: the current is recorded as the light is chopped at constant time intervals and the wavelength is scanned allowing for the determination of the photocurrent as a function of wavelength. The inset shows a magnification of a representative sample of the current spikes due to the chopping of the light beam.

while the shutter is open. Afterwards, the procedure is repeated when the shutter is closed and the difference between the two current densities is the photocurrent density.

In addition to the external quantum efficiency of the PEC cell, one can determine the internal quantum efficiency, which is more informative for the limitations due to the photoanode such as charge carrier recombination. The APCE or the absorbed photon-to-current conversion efficiency is calculated from the IPCE and the absorption of the thin film

$$\text{APCE}(\lambda) = \frac{\text{IPCE}(\lambda)}{A_F(\lambda)}$$  \hspace{1cm} (3.14)
3.4.7 Mott-Schottky measurement

Mott-Schottky measurements were performed in order to determine the charge carrier concentration, $N_D$, and the flatband potential, $\phi_{FB}$, of some thin film photoanodes. The measurements were conducted in the dark using a Zahner Messsysteme (Kronach, Germany) electrochemical workstation IM6 combining a potentiostat and a frequency response analyzer. The space charge capacitance, $C_{SC}$, was measured as a function of applied potential, $\phi_A$. The potential was scanned from 1.4 V vs. RHE down to a potential near the flatband potential, 0.2 V or 0.4 V depending on the sample. The scan rate was 5 mV/s. The measurements were repeated at four frequencies: 5 kHz, 10 kHz, 20 kHz and 50 kHz with an oscillation amplitude of 10 mV. Results were plotted as $1/C_{SC}^2$ vs. $\phi_A$ allowing the extrapolation of $N_D$ from the slope and $\phi_{FB}$ from the intercept with horizontal axis. This approach follows from the typical Mott-Schottky equation

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon_0 \epsilon_r q N_D A^2} \left( \phi_A - \phi_{FB} - \frac{kT}{q} \right)$$

where $\epsilon_0$ is the permittivity of free space and $\epsilon_r$ is the relative dielectric constant for the material of the photoanode. For hematite, $\epsilon_r$ is 80 [84–86]. $A$ is the cross sectional area exposed to the electrolyte of the photoanode and all other variables have been previously defined.

In order to determine the correct frequency at which to perform the voltage sweep and analyze the results, the impedance of the cell for each sample was measured prior to the Mott-Schottky measurement using the same equipment. The frequency ranged from 0.1 Hz to 100 kHz with an oscillation amplitude of 10 mV at a constant applied potential of 0.7 V vs. RHE. The equivalent circuit of the cell should consist of only two elements in series to apply Equation 3.15 i.e. a bulk resistance, $R_{bulk}$, and the space charge capacitance. In this case, the complex impedance, $Z^*$, looks as follows

$$Z^* = R_{bulk} - j \frac{1}{\omega C_{SC}}$$

where $j$ is the imaginary unit and $\omega$ the angular frequency. When plotting the real and
the imaginary component versus the frequency, the real component needs to remain constant with frequency and the imaginary component needs to exhibit a slope of minus one for the equivalent circuit to apply. This was indeed observed at frequencies above 5 kHz for the measured samples. Hence, the Mott-Schottky measurements were carried out at the four frequencies mentioned above.
Chapter 4

Defect Chemistry of Hematite

The charge carrier concentrations of different species such as electrons, holes, ionized vacancies, etc. determine several material properties including the conductivity and also influence the mobilities and lifetimes of these carriers. In conventional semiconductors such as Si, one can assume that the concentration of free electrons in the conduction band at room temperature will be equal to the concentration of shallow donors in solid solution. This is not the case, however, if the semiconductor is simultaneously co-doped with a large concentration of acceptor impurities that will serve to compensate the donor impurities. The former assumption is commonly applied to donor-doped hematite, and on this basis, for example, the mobility of electrons has been calculated \[87\]. Although it is possible that donors are fully compensated by electrons and therefore dictate the electron charge carrier density, the conductivity of metal oxides is generally dependent on an equilibrium between several charge carrier species established at high temperatures during fabrication of the material or a post-processing annealing treatment. In order to understand the relationship between donor compensation and change in annealing atmosphere, one must examine how an oxide semiconductor, exhibiting some degree of non-stoichiometry, $\delta$, defined by $\text{Fe}_2\text{O}_{3+\delta}$, equilibrates with the atmosphere at different elevated temperatures. For this purpose, a defect model is derived and explained in this chapter.
4.1 Kröger-Vink notation

The Kröger-Vink notation effectively conveys a species’ position in a crystal lattice and its associated charge relative to that lattice position. It is written in the form of \( X^Z_{Y} \), where \( X \) designates the atom, ion, or vacancy (\( V \)) sited at lattice site \( Y \) with relative charge \( Z \). A positive charge is indicated by a \( \cdot \), a negative charge by a \( ' \) and \( x \) indicates a neutral charge. For example, \( V_{Fe}^{'''} \) denotes an iron vacancy with a relative charge of negative three with respect to its lattice position. Similarly, \( V_{O}^{''} \) denotes an oxygen vacancy with an associated plus two charge.

4.2 Defect reactions

Defect reactions govern the charge carrier concentrations of a material at a given condition. They are subject to three main requirements: conservation of mass, conservation of charge and conservation of lattice site stoichiometry. Intrinsic point defects exist in any material and are controlled by the intrinsic electronic and ionic defect disorder relations. Impurities are governed by incorporation reactions, and oxidation and reduction reactions describe the materials’ interactions with the atmosphere.

The intrinsic electronic disorder is given by the familiar reaction

\[
nil \rightarrow e^' + h^*
\]  \hspace{1cm} (4.1)

describing the generation of an electron-hole pair. The \( np \) product and corresponding mass action relation look as follows

\[
np = K_i (T) = N_C N_V \exp \left( -\frac{E_g}{kT} \right)
\] \hspace{1cm} (4.2)

The \( np \) product relates the electron and hole concentrations, \( n \) and \( p \), respectively, to the effective density of states of the conduction band, \( N_C \), and the valence band, \( N_V \),
and to the bandgap, $E_g$. $K_i (T)$ is the temperature dependent equilibrium constant for the intrinsic electronic defect disorder.

In hematite, the intrinsic ionic disorder is believed to be dominated by the formation of Schottky defects [69], i.e. by the coupled formation of vacancies on the Fe and O sublattices as described by

$$nil \rightarrow 2V''_{\text{Fe}} + 3V'_{\text{O}}$$

(4.3)

which is shorthand for noting that ions at elevated temperatures move to the surface leaving behind corresponding numbers of charged Fe and O vacancies within the lattice. The concentration of these defects are related via the following mass action equation

$$[V''_{\text{Fe}}]^2 [V'_{\text{O}}]^3 = K_S (T) = K_S^0 \exp \left( - \frac{E_S}{kT} \right)$$

(4.4)

where square brackets indicate the concentration of a charge carrier species. The term on the right is the temperature dependent equilibrium constant, $K_S (T)$, with the pre-exponential factor, $K_S^0$, and $E_S$ is the Schottky formation energy for the coupled group of vacancies.

Next, the reactions between hematite and the gas phase are described. For example, under sufficiently reducing conditions, oxygen is released by the crystalline structure and accommodated by the formation of O vacancies and electrons as described in the following

$$O_O^e \rightarrow V'_{\text{O}} + 2e^' + \frac{1}{2} O_{2(g)}$$

(4.5)

The corresponding mass action relation for the reduction reaction can be written as follows

$$n^2 [V'_{\text{O}}]^{\frac{1}{2}} p_{O_2} = K_R (T) = K_R^0 \exp \left( - \frac{E_R}{kT} \right)$$

(4.6)

in which $E_R$ is the activation energy describing the reduction reaction with equilibrium constant $K_R (T)$. Under sufficiently oxidizing conditions, oxygen is incorporated into the lattice and accommodated by the formation of Fe vacancies and holes as fol-
The corresponding mass action relation for the reduction reaction can be written as

\[ p^6 \left[V_{Fe}^{''''}\right]^2 p_{O_2}^{-\frac{3}{2}} = K_{Ox} (T) = K_{Ox}^0 \exp \left( -\frac{E_{Ox}}{kT} \right) \]  

(4.8)
in which \( E_{Ox} \) is the activation energy describing the oxidation reaction with equilibrium constant \( K_{Ox} (T) \). One should note that the equilibrium constants of the aforementioned reactions are not independent of one another and Eq. 4.2, Eq. 4.4, Eq. 4.6 and Eq. 4.8 can be combined to arrive at

\[ K_S = \frac{K_R^3 K_{Ox}}{K_i^6} \]  

(4.9)
expressing \( K_S (T) \) in terms of \( K_1 (T), K_{Ox} (T) \) and \( K_R (T) \).

Doping hematite with titanium can be described by substitutional incorporation of the donor. Therefore, Ti incorporation can be expressed as

\[ \text{FeTiO}_3 \xrightarrow{\text{Fe}_3\text{O}_3} \text{Ti}_{Fe}^\bullet + e^\prime + \text{Fe}_{Fe}^x + 3\text{O}_x \]  

(4.10)
in which a Ti ion substitutes for a Fe ion with an effective charge of plus one. Each Ti donor is compensated by the creation of one electron but the charge carrier concentrations of all species are governed by the general neutrality condition that must always hold

\[ n + 3[V_{Fe}^{''''}] = p + [\text{Ti}_{Fe}^\bullet] + 2[V_O^{**}] \]  

(4.11)
4.3 Defect diagram

4.3.1 Brouwer approximation for hematite: intrinsic case

In the intrinsic case, the charge neutrality condition will reduce to

\[ n + 3 V^{'''}_{Fe} = p + 2 V^{**}_{O} \] (4.12)

Depending on the atmosphere and temperature, different charge carriers will dominate the two sides of the equality sign in Equation 4.12. For the most reducing atmosphere, electrons are compensated by oxygen vacancies (Regime I(i)), where “i” refers to the intrinsic case. Conversely, holes are compensated by iron vacancies in the most oxidizing case (Regime III(i)). At intermediate oxygen partial pressures, electrons and holes compensate each other (Regime II(i)). For each regime, the charge carrier concentrations for electrons, holes, iron and oxygen vacancies can readily be solved for Table 4.1:

<table>
<thead>
<tr>
<th>Regime</th>
<th>I(i)</th>
<th>II(i)</th>
<th>III(i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defect</td>
<td>( n = 2 V^{**}_{O} )</td>
<td>( n = p )</td>
<td>( 3 V^{'''}_{Fe} = p )</td>
</tr>
<tr>
<td>( n )</td>
<td>( (2K_R)^{\frac{1}{3}} p_{O_2}^{\frac{1}{6}} )</td>
<td>( K_i^{\frac{1}{2}} )</td>
<td>( \frac{K_i}{(9K_{Ox})^{\frac{2}{3}}} p_{O_2}^{\frac{1}{16}} )</td>
</tr>
<tr>
<td>( p )</td>
<td>( \frac{K_i}{(2K_R)^{\frac{1}{3}}} p_{O_2}^{\frac{1}{6}} )</td>
<td>( K_i^{\frac{1}{2}} )</td>
<td>( (9K_{Ox})^{\frac{1}{2}} p_{O_2}^{\frac{2}{16}} )</td>
</tr>
<tr>
<td>( V^{**}_{O} )</td>
<td>( \left( \frac{K_R}{4} \right)^{\frac{1}{3}} p_{O_2}^{\frac{1}{6}} )</td>
<td>( \frac{K_R}{K_i} p_{O_2}^{\frac{1}{6}} )</td>
<td>( (9K_{Ox})^{\frac{1}{4}} \frac{K_R}{K_i^2} p_{O_2}^{\frac{1}{6}} )</td>
</tr>
<tr>
<td>( V^{'''}_{Fe} )</td>
<td>( 2 \frac{K_{Ox}}{K_i^3} K_R^{\frac{1}{4}} p_{O_2}^{\frac{1}{6}} )</td>
<td>( \left( \frac{K_{Ox}}{K_i^3} \right)^{\frac{1}{3}} p_{O_2}^{\frac{3}{16}} )</td>
<td>( \left( \frac{K_{Ox}}{729} \right)^{\frac{8}{3}} p_{O_2}^{\frac{3}{16}} )</td>
</tr>
</tbody>
</table>
in terms of the equilibrium constants (Eq. 4.2, Eq. 4.6, Eq. 4.8) and pO\textsubscript{2}, the solutions for which are listed in Table 4.1. The charge neutrality approximation relevant for each regime is listed at the top of each column. In addition, the isothermal pO\textsubscript{2} dependence of all the defects is illustrated in Figure 4-1 in a typical Brouwer diagram in which log (defect concentration) is plotted versus log (pO\textsubscript{2}) for all three regimes. A dotted line indicating a donor dopant concentration is included to show that, in the case where the Ti donor concentration is below the electron and hole concentrations in Regime II(i), intrinsic electronic compensation is also possible in doped metal oxides.

### 4.3.2 Brouwer approximations for hematite with a donor dopant: extrinsic case

In the case of donor doped hematite, four defect regimes are considered based on Eq. 4.11. For the most reducing atmosphere, electrons are compensated by oxygen vacancies (Regime I). Conversely, holes are compensated by iron vacancies in the most oxidizing case (Regime IV). This is equivalent to the outermost regimes for the intrinsic case. Consequently, the charge carrier concentrations exhibit the same pO\textsubscript{2} dependencies as before in these regimes. In the intermediate regimes, the electronic (Regime II) and ionic compensation of the donor (Regime III) is considered. Table 4.2 summarizes the solutions for all charge carrier concentrations in the different regimes given the presence of a donor. Figure 4-2 depicts the isothermal pO\textsubscript{2} dependence of all the defects in the form of a Brouwer diagram. Of particular note is the dependence of the electron density, n. It is indeed equal to the Ti donor concentration in one defect regime. However, n depends instead on the cube root of the Ti concentration under the conditions in which Ti is compensated largely by Fe vacancies. Indeed, in this latter defect regime, n becomes exponentially dependent on temperature and dependent on pO\textsubscript{2} via a power law.
Table 4.2: Predicted charge carrier densities for each possible neutrality regime for the extrinsic case.

<table>
<thead>
<tr>
<th>Regime</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n = 2 \left[ V_{O}^{\bullet\bullet} \right] )</td>
<td>( n = \left[ \text{Ti}_{\text{Fe}}^{\bullet} \right] )</td>
<td>( 3 \left[ V_{\text{Fe}}^{'''\prime} \right] = \left[ \text{Ti}_{\text{Fe}}^{\bullet} \right] )</td>
<td>( 3 \left[ V_{\text{Fe}}^{'''\prime} \right] = p )</td>
</tr>
<tr>
<td>Defect</td>
<td>( n )</td>
<td>( \left( 2K_{R} \right)^{\frac{1}{3}} p_{O_{2}}^{-\frac{1}{6}} )</td>
<td>( K_{i} ) ( \frac{\left[ \text{Ti}<em>{\text{Fe}}^{\bullet} \right]}{K</em>{Ox}^{\frac{1}{3}}} ) ( p_{O_{2}}^{-\frac{1}{4}} )</td>
<td>( K_{i} ) ( \frac{1}{\left( 9K_{Ox} \right)^{\frac{1}{3}}} p_{O_{2}}^{-\frac{1}{16}} )</td>
</tr>
<tr>
<td></td>
<td>( p )</td>
<td>( \frac{K_{i}}{(2K_{R})^{\frac{1}{3}}} p_{O_{2}}^{-\frac{1}{6}} )</td>
<td>( \frac{K_{i}}{\left[ \text{Ti}_{\text{Fe}}^{\bullet} \right]} )</td>
<td>( K_{Ox} \left( \frac{3}{\left[ \text{Ti}<em>{\text{Fe}}^{\bullet} \right]} \right)^{\frac{1}{3}} p</em>{O_{2}}^{-\frac{1}{4}} )</td>
</tr>
<tr>
<td></td>
<td>( \left[ V_{O}^{\bullet\bullet} \right] )</td>
<td>( \left( \frac{K_{R}}{4} \right)^{\frac{1}{3}} p_{O_{2}}^{-\frac{1}{6}} )</td>
<td>( \frac{K_{R}}{K_{i}^{2}} \left[ \text{Ti}<em>{\text{Fe}}^{\bullet} \right]^{2} p</em>{O_{2}}^{-\frac{1}{2}} )</td>
<td>( \frac{K_{R} K_{Ox}^{\frac{1}{3}}}{K_{i}^{2}} \left( \frac{3}{\left[ \text{Ti}_{\text{Fe}}^{\bullet} \right]} \right)^{\frac{2}{3}} )</td>
</tr>
<tr>
<td></td>
<td>( \left[ V_{\text{Fe}}^{'''\prime} \right] )</td>
<td>( 2 \frac{K_{Ox}^{\frac{1}{3}} K_{R}^{\frac{1}{3}}}{K_{i}^{\frac{1}{3}}} p_{O_{2}}^{\frac{1}{4}} )</td>
<td>( \frac{K_{Ox}^{\frac{1}{3}}}{K_{i}^{\frac{1}{3}}} \left[ \text{Ti}<em>{\text{Fe}}^{\bullet} \right]^{\frac{3}{4}} p</em>{O_{2}}^{\frac{3}{4}} )</td>
<td>( \frac{\left[ \text{Ti}_{\text{Fe}}^{\bullet} \right]}{3} )</td>
</tr>
</tbody>
</table>
Figure 4-1: Intrinsic case: Defect diagram depicting the pO$_2$ dependence of various charge carriers ($n$ - black, $p$ - blue, iron vacancies - red, oxygen vacancies - purple) in the different regimes. The regime at intermediate pO$_2$ is governed by intrinsic electronic compensation, which is also possible for doped hematite (dotted line indicates Ti donor concentration) as long as the electron and hole concentrations dominate.

Figure 4-2: Extrinsic case: Defect diagram depicting the pO$_2$ dependence of various charge carriers ($n$ - black, $p$ - blue, Ti donors - green, iron vacancies - red, oxygen vacancies - purple) in the different regimes.
Chapter 5

Results

This chapter contains the experimental results obtained in this study. Various compositions of the ilmenite hematite solid solution (IHSS) system were produced as both bulk samples and thin films. X-ray diffraction patterns of the bulk samples and thin films serve to establish phase identity and homogeneity. Additionally, high resolution X-ray diffractograms confirm the epitaxial growth of $(\text{FeTiO}_3)_{1-x}(\text{Fe}_2\text{O}_3)_x$ on the single crystal sapphire substrates utilized in this study. Optical absorption spectroscopy was used to determine the transmission, reflection and absorption of the thin films on sapphire as well as for the thin films on FTO coated quartz used for PEC measurements. From these data, the optical bandgaps for the samples of varying compositions were calculated.

Next, the chapter details the findings of the conductivity measurements for the bulk and thin film samples of the IHSS system. Finally, the PEC performance of these materials is presented before and after annealing treatments. This includes the Mott-Schottky analysis in order to determine the majority charge carrier density of the photoanodes following the oxidizing and reducing treatments.
5.1 X-ray diffraction

In this section, the XRD results for the bulk samples and thin films are discussed. Bulk samples were prepared to serve as PLD targets as well as for DC conductivity measurements (pellets) as explained in Section 3.1.1. Results show that the desired materials for both purposes were fabricated as expected. Then, XRD and high resolution XRD scans of the epitaxial films are shown. These show expected results as well. They also show that films with higher ilmenite concentrations are more strained.

5.1.1 Targets

Both hematite and ilmenite have a trigonal structure and belong to the $R-3c$ space group. Given that titanium ions replace half the iron ions in the ilmenite lattice and thereby form alternating titanium and iron layers between planes of oxygen, the XRD patterns for both materials are very similar. The diffraction peaks for ilmenite are nearly identical in intensity but shifted to slightly lower $2\theta$ values with respect to peaks of the hematite lattice. The shift is due to the difference in lattice parameters. Hematite’s lattice parameters are $a = 5.0356\ \text{Å}$ and $c = 13.7489\ \text{Å}$. The lattice parameters for ilmenite are $a = 5.0884\ \text{Å}$ and $c = 14.0930\ \text{Å}$.

Figure 5-1 displays the XRD patterns of the PLD targets synthesized for this study. Reference patterns for hematite and ilmenite are included in the form of symbols above the respective scan. A symbol is shown for peaks of 5% or greater in intensity and the height of the symbol indicates the relative intensity of that peak. The XRD patterns for all compositions show that only the desired phase is present; no secondary phases formed, nor did precipitation of ilmenite in a hematite matrix at intermediate concentrations occur. An exception is the $\text{Fe}_{1.33}\text{Ti}_{0.67}\text{O}_3$ target, which shows an erroneous peak at $27^\circ 2\theta$. This peak could only be matched to one other $\text{Fe}_2\text{O}_3$ phase with a monoclinic structure known as $\epsilon$-$\text{Fe}_2\text{O}_3$. A series of small peaks between $35^\circ$ and $40^\circ 2\theta$ also indicate the presence of secondary phases. These peaks match $\text{Ti}_2\text{O}_3$. 

88
Figure 5-1: X-ray diffraction patterns of the \((\text{FeTiO}_3)_{1-x}(\text{Fe}_2\text{O}_3)_x\) targets produced for PLD. Peak positions and their relative intensities for ilmenite (PDF 00-029-0733, black) and hematite (PDF 00-033-0664, red) are indicated by the symbols above the patterns of the respective solid solution end member.

and TiO, although their most intense peaks are not visible in the data of this sample. Generally, peaks at higher \(2\theta\) values become broader and exhibit a secondary peak. This phenomenon is due to K\(\alpha_2\) spectral lines exhibiting more dispersion at higher \(2\theta\) values. As the ilmenite content increases, all peaks systematically shift to lower \(2\theta\) values in accordance to an increase in lattice parameters.

5.1.2 Pellets

Diffraction patterns for the pellets used for bulk electrical characterization are similar to those of the targets. Figure 5-2 shows the scans in relation to each other as well as the reference patterns of the two end members of the IHSS system. Here, the
Figure 5-2: X-ray diffraction patterns of the \((\text{FeTiO}_3)_{1-x} (\text{Fe}_2\text{O}_3)_x\) pellets produced for electrical characterization. Peak positions and their relative intensities for ilmenite (PDF 00-029-0733, black) and hematite (PDF 00-033-0664, red) are indicated by the symbols above the patterns of the respective solid solution end member.

Pattern of the hematite pellet reveals the presence of secondary phases those being FeO and \(\text{Fe}_3\text{O}_4\). However, as hematite is the thermodynamically stable phase of iron oxide at high oxygen partial pressures and the pellets would be heated to very high temperatures during the DC conductivity measurements (Section 3.3.1), this was of little concern. The \(\text{Fe}_{1.33}\text{Ti}_{0.67}\text{O}_3\) pellet shows similar behavior to that of the target of the same material. Finally, the \(\text{Fe}_{1.98}\text{Ti}_{0.02}\text{O}_3\) pellet, although very brittle, did not break into pieces until an attempt was made to cut a small piece from it for DC conductivity measurements. The XRD pattern reveals that indeed the right phase was formed and no additional peaks are present.
5.1.3 Thin films

XRD patterns of the thin films grown on sapphire are presented in Figure 5-3. At the bottom, a scan of the bare C plane cut sapphire substrate is included. The main peak of the substrate, the 006 peak, corresponds to that expected for the <0001> orientation of the single crystal and is indicated by a grey triangle for all scans. A second, colored triangle indicates the corresponding 006 peak of the film for each composition. No other peaks besides those due to the substrate are visible in the scans for the films. This does not yet confirm epitaxy, but it is evidence for highly textured films. The 006 film peak loses intensity as the ilmenite concentration increases. Since the basal lattice parameter for sapphire is only 4.7587 Å, the mismatch for ilmenite is even greater than that for hematite. Therefore, higher strain and a higher density of

![Figure 5-3: X-ray diffraction patterns of the (FeTiO₃)₁₋ₓ(Fe₂O₃)ₓ thin films on sapphire substrates. The triangles indicates the 006 peak of the substrate and the that of the thin films.](image-url)
mismatch dislocations is expected for the ilmenite thin film compared to the hematite thin film, explaining the decrease in intensity of the 006 peak going from hematite to ilmenite.

**Epitaxy**

In order to confirm epitaxial growth of the thin films on sapphire, high resolution XRD was performed. Surface morphology of these films is documented in Appendix B.1. Figure 5-4(a) shows a coupled scan and rocking curves for the 006 symmetric peaks of hematite and sapphire. The thickness fringes of the film peak, visible in the coupled scan, allow confirmation of the film thickness already determined by profilometry. The sharp peak in the rocking curve, centered on hematite’s 006 peak, indicates low defect concentrations in the bulk of the film, while the tails of the peak suggest thread dislocations at the interface with the substrate due to film-substrate lattice mismatch. In addition to the 006 symmetric peak, the 1 0 10 asymmetric peak (Figure 5-4(b)) was observed for hematite and sapphire in both a coupled scan and rocking curves for each.

![Image of XRD scans](image)

(a) symmetric peaks  
(b) asymmetric peaks

**Figure 5-4:** High resolution XRD scans of the epitaxially grown hematite thin film on sapphire. The coupled scan (top) shows both the film and substrate peaks. Individual rocking curves of the film and substrate are depicted at the bottom.
Coupled scans and rocking curves were also collected for symmetric and asymmetric peaks of the IHSS films. Similar to pure hematite, the Fe$_{1.98}$Ti$_{0.02}$O$_3$ film exhibits clear peaks for both the symmetric 006 peak as well as for the asymmetric 1 0 10 peak (Figure 5-5), verifying that this film also grew epitaxially on the <0001> sapphire single crystal. In addition, the 018 asymmetric peak was also observed for this film with results similar to those shown in Figure 5-5(b). Therefore, there is also sufficient evidence that this film grew epitaxially on its substrate.
Again, the same observation was made for the Fe$_{1.33}$Ti$_{0.67}$O$_3$ thin film (Figure 5-6). Symmetric and asymmetric peaks for the film are both observed in the coupled scans taken when the instrument was aligned on the appropriate substrate peaks. The intensity is weaker for these film peaks compared to the previous two films, hence the data is exhibited on a log scale for better visibility. However, the mere existence of the film peaks confirm the epitaxial nature of the film. The broader peaks in the rocking curves indicate a higher defect density in the bulk.

Figure 5-7: High resolution XRD coupled scan of the highly textured Fe$_{1.33}$Ti$_{0.67}$O$_3$ thin film on sapphire showing both the film and substrate peaks.

Figure 5-8: High resolution XRD scans of the epitaxially grown FeTiO$_3$ thin film on sapphire. The coupled scan (top) shows both the film and substrate peaks. Individual rocking curves of the film and substrate are depicted at the bottom.

Figure 5-7 displays the coupled scan of the symmetric 006 peaks for the Fe$_{1.33}$Ti$_{0.67}$O$_3$ thin film. Even on a log scale, the evidence for an epitaxially grown film is not sufficient. No film peak can be identified in the coupled scan of the asymmetric 1 0 10 peak either. Therefore, this film, although being textured (Figure 5-3) did not grow fully epitaxially.

Conversely, the ilmenite thin film did grow epitaxially on sapphire as exhibited by
Figure 5-8. Both the film and substrate 006 peaks are clearly visible in the log scale coupled scan. Additionally, the rocking curve on the film peak is sharp and hence the concentration of bulk defects is low. The long tails of that same peak, however, indicate a large number of thread dislocations. This can be explained by the 6.9% misfit between ilmenite and sapphire inducing compressive strain in the film. This also explains why no film peak was identified in the coupled scan (not shown) of the 1010 asymmetric peak aligned on the substrate peak. High lattice strain shifts the film peak from its expected position, making it invisible in a scan centered on the substrate’s asymmetric peak.

5.2 Absorption spectroscopy

Prior to depositing the IDEs onto the thin films grown for electrical characterization, the optical properties of the films were determined and the bandgap for each composition was calculated as described in Section 3.2.2. This process was repeated for photoanodes of varying ilmenite and hematite compositions as well.

5.2.1 Thin films for electrical characterization

Figure 5-9 shows the results for this analysis for the epitaxially grown thin films on sapphire. The absorption spectra (Figure 5-9(a)) of hematite and 1% Ti doped hematite (Fe$_{1.98}$Ti$_{0.02}$O$_3$) exhibit a sharp step around the wavelength corresponding to the known direct bandgap of hematite [13,41]. This step becomes less sharp and shifts to lower wavelength for solid solutions with higher ilmenite content. Accordingly, the absorption coefficient, $\alpha$, decreases in magnitude and steepness in its profile with higher ilmenite content (Figure 5-9(b)) as well. This indicates an increase in bandgap with higher ilmenite content in the solid solutions as well as the presence of an indirect bandgap. Indeed, both Tauc plots exhibit linear regions.

Turning to the extrapolation of the direct bandgap (Figure 5-9(c)), the linear region
between 2.2 eV to 2.3 eV for hematite and doped hematite corresponds well to the steep step in their respective absorption spectrum yielding a direct gap of 2.2 eV. Samples with intermediate ilmenite content reveal two linear regions: between 2.2 eV to 2.4 eV and above 2.8 eV. This indicates that the band structure is such that two direct gaps are present, one with a low density of states at \( \sim 2.2 \text{ eV} \) and 2.3 eV for I33HSS and I67HSS, respectively, and another with a larger density of states at \( \sim 2.6 \text{ eV} \) for both. This is not believed to be caused by phase separation as both samples only exhibit one phase in their XRD patterns. Ilmenite, on the other hand, only exhibits one linear region above 3.1 eV and the extrapolation results in a direct bandgap of 3.0 eV. The values of the optical bandgaps are summarized in Table 96.
5.1

Extrapolations from the Tauc plot for the indirect bandgap (Figure 5-9(d)) are more complex. There exist linear regions for all samples, most notably between 2.1 eV to 2.3 eV for hematite, I2HSS and I33HSS and between 2.7 eV to 3.0 eV for I67HSS and ilmenite with that of ilmenite extending even further. Indirect bandgap were extrapolated from these regions and are also listed in Table 5.1. Presence of an indirect bandgap in these materials is reasonable, given that a weak onset of absorption is present at wavelength higher than those corresponding to the direct gap of the respective sample.

Table 5.1: Optical bandgaps of the epitaxially grown IHSS thin films on sapphire.

<table>
<thead>
<tr>
<th>sample</th>
<th>composition</th>
<th>Direct gap eV</th>
<th>Indirect gap eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>Fe$_2$O$_3$</td>
<td>2.19</td>
<td>2.05</td>
</tr>
<tr>
<td>I2HSS</td>
<td>Fe$<em>{1.98}$Ti$</em>{0.02}$O$_3$</td>
<td>2.17</td>
<td>2.03</td>
</tr>
<tr>
<td>I33HSS</td>
<td>Fe$<em>{1.67}$Ti$</em>{0.33}$O$_3$</td>
<td>2.58</td>
<td>1.76</td>
</tr>
<tr>
<td>I67HSS</td>
<td>Fe$<em>{1.33}$Ti$</em>{0.67}$O$_3$</td>
<td>2.63</td>
<td>1.99</td>
</tr>
<tr>
<td>ilmenite</td>
<td>FeTiO$_3$</td>
<td>2.98</td>
<td>2.19</td>
</tr>
</tbody>
</table>

5.2.2 Thin films for PEC measurements

Figure 5-10 shows the results of the optical spectroscopy measurements and analysis for the IHSS thin films later implemented as photoanodes. For each composition, three samples were characterized: as-deposited, annealed in 100 ppm O$_2$ (reduced) and annealed in 100 % O$_2$ (oxidized). As the results for one composition were nearly identical regardless of the post-fabrication anneal, Figure 5-10 only displays results for the oxidized samples. Table 5.2 then lists the direct bandgap for each sample characterized.

The polycrystalline thin films grown on FTO coated quartz substrates show similar behavior to their epitaxially grown counterparts on sapphire. The absorption spectra (Figure 5-10(a)) of undoped and doped hematite again show a steep step below
600 nm. As before, solid solutions with higher ilmenite concentrations exhibit a more gradual increase in absorption. The calculated absorption coefficients are shown in Figure 5-10(b). Direct bandgaps are extrapolated from the Tauc plot in Figure 5-10(c). The linear region fitted for undoped and doped hematite is visible just above the x-axis between 2.2 eV to 2.3 eV. Again, there are short linear regions visible for the I33HSS and I67HSS samples at lower energies indicating the presence of a direct gap with low density of states. The more substantial direct gap is extrapolated from the longer linear region at higher photon energies for each curve and reported in Table 5.2. It should be noted that literature reports the bandgap of ilmenite varying within a range of 2.5 eV to 3.6 eV [63,66,68].
A Tauc plot for extrapolation of indirect gaps is displayed in Figure 5-10(d). However, as there are no extensive linear regimes, no explicit fit was performed. The curves are similar again to those for the epitaxial films discussed above, but shifted to slightly higher values. This could be due to the light’s interaction with the thin film/FTO interface acting as another source of reflection, which is not captured by the spectrometer’s detectors and hence inflates the measured absorption. In fact, the absorption for all samples is slightly above zero (see Figure 5-10(a)). When compensating for this shift and extrapolating from the short linear regions around 2.2 eV for hematite, I2HSS, I33HSS and I67HSS and the longer linear region for ilmenite at higher energy, the values for an indirect gap for these compositions are similar to those listed in Table 5.1. In addition, the surface morphology of these thin films was investigated. Results are summarized in Appendix B.2.

### Table 5.2: Optical bandgaps of the IHSS thin films used as photoanodes.

<table>
<thead>
<tr>
<th>sample</th>
<th>composition</th>
<th>state</th>
<th>Direct gap eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>Fe₂O₃</td>
<td>as-deposited</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>2.17</td>
</tr>
<tr>
<td>I₂HSS</td>
<td>Fe₁.₉₈Ti₀.₀₂O₃</td>
<td>as-deposited</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>2.16</td>
</tr>
<tr>
<td>I₃₃HSS</td>
<td>Fe₁.₆₇Ti₀.₃₃O₃</td>
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<td>2.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>2.60</td>
</tr>
<tr>
<td>I₆₇HSS</td>
<td>Fe₁.₃₃Ti₀.₆₇O₃</td>
<td>as-deposited</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>2.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>2.66</td>
</tr>
<tr>
<td>ilmenite</td>
<td>FeTiO₃</td>
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</tr>
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<td></td>
<td></td>
<td>oxidized</td>
<td>2.86</td>
</tr>
</tbody>
</table>
5.3 Electrical conductivity

This section summarizes the results of the DC conductivity measurements of the bulk samples as well as the EIS results of the thin films. For the bulk samples, hematite and doped hematite exhibit no dependence on pO$_2$. This indicates that pure hematite is in the intrinsic regime and doped hematite in the extrinsic regime as this sample shows no temperature dependence within the range of characterization. The remaining samples with higher ilmenite concentrations all exhibit nonstoichiometry as their conductivity changes with pO$_2$. Decreasing conductivity with increasing pO$_2$ indicates n-type conductivity.

Results for the thin films show again that the conductivity of pure hematite is not dependent on pO$_2$. However, the conductivity at room temperature of 1% Ti doped hematite is highly dependent on the pO$_2$ in which it was annealed and can be up to nine orders of magnitude greater than that of pure hematite. The conductivity of thin films containing a higher concentration of ilmenite are also dependent on the annealing conditions but do not reach absolute conductivities as high as that of the Ti doped film.

5.3.1 DC conductivity of bulk samples

The conductivity of the bulk samples was determined by fitting IV curves as described in Section 3.3.1. Figure 5-11 displays the conductivity of hematite as a function of pO$_2$ at 900°C, 950°C, 1000°C and 1050°C. It becomes immediately obvious that this material exhibits very little nonstoichiometry, i.e. its conductivity exhibits no dependence on pO$_2$. This is in good agreement with Dieckmann’s thermogravimetric analysis, which concludes that the deviation from stoichiometry, ε in Fe$_2$O$_{3-ε}$, is only around $10^{-4}$, even at temperatures as high as 1100°C within a pO$_2$ range from $10^{-4}$ atm to 1 atm O$_2$. The conductivity increases with increasing temperature as is typical for a semiconductor.
Figure 5-11: DC conductivity of $\alpha$-Fe$_2$O$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1050°C.

Figure 5-12 displays the conductivity of 1% Ti doped hematite or I2HSS at temperatures from 900°C to 1050°C. This sample exhibits no dependence on the partial pressure of oxygen, as well as no clear dependence on the temperature. This indicates that it is in the extrinsic regime, which is only attainable by a doped material. In this regime, the charge carrier density is solely determined by the donor concentration, which is independent of both the pO$_2$ and the temperature (see Regime II in Table 4.2 and Figure 4-2). The average conductivity is $(6.28 \pm 0.26)$ S/cm. Being in the extrinsic regime, one can calculate the electron mobility as discussed in detail in Section 6.1.1.

In contrast to the I2HSS sample, the I33HSS sample exhibits both a dependence on the pO$_2$ and temperature (Figure 5-13). The conductivity is defined as

$$ \sigma = nq\mu_n + pq\mu_p $$

(5.1)

where $\mu_n$ and $\mu_p$ are the electron and hole mobilities, respectively. In Figure 5-13...
the conductivity decreases with increasing pO$_2$, which is a typical signature of an n-type semiconductor. Therefore, the electron contribution to the total conductivity dominates and the second term in Eq. 5.1 related to holes may be neglected. Hence, the conductivity is now directly proportional to the electron concentration and the pO$_2$ dependence of the conductivity is equivalent to that of the electron density. Figure 5-13 shows that the conductivity indeed follows a power law dependence on pO$_2$ as predicted by the defect model. A $-3/16$ slope and a $-1/4$ slope are included in Figure 5-13 for comparison. The smaller sloped corresponds to the power law dependence for the intrinsic case given a negligible hole mobility (see Table 4.1 and Figure 4-1). The larger slope is in accordance with expectations of the extrinsic case (see Table 4.2 and Figure 4-2). From data in this regime, one can derive the activation energies of the reaction constants, as explained in Section 6.1.2. Towards lower oxygen partial pressures, the power law dependence on the pO$_2$ weakens for the I33HSS sample, indicating that here, the material transitions into Regime II(i).

The trend for the I67HSS sample is similar to that described for the I33HSS sample, however the data is noisier. The $-3/16$ power dependence on pO$_2$ is observed at 1000°C and 1030°C (Figure 5-14). At lower temperatures, the slope becomes even less steep. The temperature distribution in the triple zone furnace was not perfect and the set point of 1050°C could not be attained for the I67HSS and ilmenite samples. The I67HSS sample also had to be replaced early on, as it had become very brittle at these high temperatures and high pO$_2$’s. Additionally, there are indicators that iron segregates to the surface of these bulk materials, as discussed in Section 6.1.3.

Figure 5-15 displays the conductivity results for the ilmenite bulk sample. As for the I33HSS and I67HSS samples, one observes a power dependence on pO$_2$ at partial pressures above 0.05 atm. This regime extends to even lower pO$_2$’s for higher temperatures. Eventually, the conductivity levels off at lower partial pressures. As observed for all samples (with exception of the fully electronically compensated I2HSS sample), the conductivity increases with increasing temperature as is typical for metal oxide semiconductors.
Figure 5-12: DC conductivity of Fe$_{1.98}$Ti$_{0.02}$O$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1050°C.

Figure 5-13: DC conductivity of Fe$_{1.67}$Ti$_{0.33}$O$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1050°C.
Figure 5-14: DC conductivity of Fe$_{1.33}$Ti$_{0.67}$O$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1030°C.

Figure 5-15: DC conductivity of FeTiO$_3$ as a function of partial pressure of oxygen at temperatures between 900°C to 1030°C.
5.3.2 ElS results for thin films

The conductivity of thin films was determined by measuring the EIS of each film as a function of temperature and $\text{pO}_2$ and fitting the data to extract the resistance at a given condition. The resistance was then converted to conductivity for the given thin film as described in Section 5.3.3. Typical complex impedance spectra for the hematite and the Fe$_{1.98}$Ti$_{0.02}$O$_3$ thin films are plotted in Figure 5-16. The spectra fit a simple equivalent circuit composed of a resistor and constant phase element (CPE) in parallel (see inset of Figure 5-16(a)). The factor characterizing the deviation from ideal capacitance, $n_q$, indicates a negligible depression of the semi-circle with $n_q = 0.992 \pm 0.003$, meaning that the CPE can be replaced by an ideal capacitor. As expected for a semiconductor, the diameter of the impedance spectra, equal to the resistance, decreases with increasing temperature (5-16(a)). Also, the Fe$_{1.98}$Ti$_{0.02}$O$_3$ film shows a decrease in impedance with a decrease in $\text{pO}_2$ during the anneal (Figure 5-16(b)), as is typical for an n-type semiconductor. These two Nyquist plots are representative for the EIS spectra measured for the other thin films as well.

5.3.3 Conductivity of thin films

The electrical conductivity results for hematite and the Fe$_{1.98}$Ti$_{0.02}$O$_3$ epitaxial thin films derived from the EIS data, performed as a function of temperature and $\text{pO}_2$, are summarized in Figure 5-17. The conductivity of the hematite film falls to extremely low values upon cooling, reaching conductivities below $10^{-10}$ S/cm at room temperature. The hematite thin film shows nearly no sensitivity to the $\text{pO}_2$ in which it was annealed at elevated temperature; i.e. there is no change in room temperature conductivity after annealing the pure hematite sample in simulated air or in 100% $\text{O}_2$. The negligible $\text{pO}_2$ sensitivity agrees with the findings of Dieckmann for bulk hematite [69]. Similarly, the data agrees well with an extrapolation of the bulk intrinsic conductivity of hematite determined between 650°C to 1000°C by Warnes et al. [87]. The small deviation from intrinsic conductivity down to temperatures as low
as 200°C indicates a pinning of the Fermi energy near mid gap in the hematite film. The activation energy, derived from the data collected for hematite between 600°C to 800°C, is (1.06 ± 0.04) eV. This value is in good correspondence with half the optical bandgap ∼ 1.09 eV.

Doping hematite with 1% Ti, equivalent to the 2% ilmenite 98% hematite solid solution (I2HSS), results in an increase of more than seven orders of magnitude in the room temperature conductivity when annealed in simulated air. Furthermore, the donor-doped material now exhibits significant sensitivity to changes in pO$_2$, i.e. annealing the doped film in lower pO$_2$ results in an increased conductivity. Indeed, as illustrated in Figure 5-17, it is possible to tune the room temperature conductivity of the donor-doped hematite thin film by as much as five orders of magnitude by varying the annealing pO$_2$ between 10$^{-4}$ atm to 1 atm O$_2$. This observation has important implications, since it demonstrates that the electron density is not fixed by the donor
dopant density, but can differ from it by orders of magnitude. This observation is further discussed in Section 6.2.1.

Solid solutions with higher ilmenite concentrations show similar results to those for the I2HSS thin film. Figure 5-18 displays the large sensitivity to annealing atmosphere exhibited by the Fe$_{1.67}$Ti$_{0.33}$O$_3$ or I33HSS sample. Annealing in a pO$_2$ between $10^{-4}$ atm to 1 atm O$_2$ enables one to tune the conductivity by up to six orders of magnitude. The room temperature conductivity of I33HSS annealed in simulated air is more than four orders of magnitude larger compared to that of pure hematite.

Turning to the Fe$_{1.33}$Ti$_{0.67}$O$_3$ (I67HSS) thin film (Figure 5-19), the spread in attainable conductivities for the same range of pO$_2$ as above decreases to four orders of magnitude. The conductivity of the I67HSS sample remains constant when annealed in $10^{-4}$ atm and $10^{-3}$ atm O$_2$. In general, the magnitude of the conductivity decreases compared to that of the I2HSS and I33HSS samples; it still remains one and a half orders of magnitude higher than that of pure hematite at room temperature when annealed in 21% O$_2$.

**Figure 5-17:** Conductivity of the Fe$_{1.98}$Ti$_{0.02}$O$_3$ and hematite thin films as a function of temperature at different partial pressures of oxygen.

![Graph showing conductivity as a function of temperature for different partial pressures of oxygen.](image)
Figure 5-18: Conductivity of the Fe$_{1.67}$Ti$_{0.33}$O$_3$ and hematite thin films as a function of temperature at different partial pressures of oxygen.

Figure 5-19: Conductivity of the Fe$_{1.33}$Ti$_{0.67}$O$_3$ and hematite thin films as a function of temperature at different partial pressures of oxygen.
Figure 5-20: Conductivity of the FeTiO$_3$ and hematite thin films as a function of temperature at different partial pressures of oxygen.

Ilmenite, the other end-member of the IHSS system, displays a conductivity similar in magnitude to that of hematite as a function of temperature when annealed in simulated air (Figure 5-20). Unlike hematite, the ilmenite thin film does exhibit a pO$_2$ dependence allowing the room temperature conductivity to vary by up to four orders of magnitude when annealed in a pO$_2$ ranging from $10^{-4}$ atm to 1 atm. Overall, the highest room temperature was achieved by the 2% IHSS, which is equivalent to doping hematite with 1 atom% titanium. The greatest tunability in room temperature conductivity was observed for the I33HSS thin film within the pO$_2$ range examined in this study. Its absolute conductivity is only one to two orders of magnitude lower than that of the I2HSS thin film. With increasing ilmenite content, the conductivity further decreases until it is comparable again with that of hematite.
5.4 PEC performance

This section documents the achieved photocurrent densities and quantum efficiencies of the thin film photoanodes of varying compositions of the IHSS system. Current densities, with the presence of a hole scavenger and a water oxidation catalyst, are also included. The charge carrier densities of the different photoanodes are derived from Mott-Schottky analysis. Finally, the performance of a hematite homojunction with a built-in electric field is presented. Measurement techniques applied to attain these results are detailed in Section 3.4. Throughout this section, all biases are listed with respect to the reversible hydrogen electrode (RHE), unless otherwise noted.

5.4.1 Hematite ilmenite solid solutions

The photocurrent density for hematite as a function of applied potential is shown in Figure 5-21. Solid lines indicate illumination of the photoanode by simulated sunlight (AM1.5). Dashed lines serve as a reference of the performance in the dark. The photoanode was illuminated either from the front through the electrolyte or from the back by reversing the orientation of the PEC cell in the light beam. The result for three hematite anodes are displayed: as-deposited, reduced (red.) and oxidized (ox.). The anneal treatments are detailed in Section 3.4.2. Performance is very reproducible for these samples as all cyclic voltammograms (CVs) include three complete loops that fall exactly on top of each other for a given sample.

The photocurrent density of pure hematite is on the order of 100 µA/cm² in 1.0 M NaOH (Figure 5-21(a)) with an onset voltage of approximately 1.2 V. The photocurrent density of the as-deposited and the reduced sample is one order of magnitude lower than that reported for the best hematite nanostructures in the literature [41, 49, 50]. Lower photocurrent density is expected as these are dense thin films deposited by PLD. Nanostructures benefit from a much greater surface area, and thereby have a larger active area participating in the water oxidation reaction. Besides, nanostructures can also enhance light absorption by scattering [88].
Figure 5-21: PEC performance of as-deposited and annealed undoped hematite thin films.

(a) in 1.0 M NaOH

(b) in 1.0 M NaOH with 0.5 M H₂O₂

Figure 5-22: Quantum efficiencies and absorption of the as-deposited and annealed hematite thin films.

(a) IPCE at 1.23 V vs. RHE

(b) IPCE at 1.5 V vs. RHE

(c) Absorption

(d) APCE at 1.23 V and 1.5 V vs. RHE
Front and back illumination provide insights on the limiting charge carrier. Under front illumination, most electron-hole pairs are generated at the semiconductor/electrolyte interface and hence the electron has a longer path to the back contact, whereas the hole only has to travel a short distance to the semiconductor/electrolyte interface. The reverse is true for back illumination. Therefore, if the photocurrent density under front illumination is higher, the photoanode’s performance is limited by hole transport, whereas higher photocurrent under back illumination suggests that transport is electron limited. From the EIS results of the hematite thin film (Section 5.3.3) it is known that pure hematite acts as an insulator. Thus, its PEC performance should be greater under back illumination. This is indeed the case for the as-deposited and the oxidized hematite photoanodes (Figure 5-21(a)). It is not so apparent for the reduced sample. One should note, however, that these are very thin films (∼ 50 nm, Table 3.4) and so absorption occurs over a large fraction of the film and not just near the interfaces with the electrolyte or the back contact depending on the orientation of the film.

The performance of the reduced and the as-deposited samples is similar, while that of the oxidized sample is lower. This is unexpected as the hematite thin film exhibited little nonstoichiometry change, i.e. its conductivity was independent of the pO₂ it had been annealed in. Assuming the conductivity is equal for both films, reduced and oxidized, a cause of the change in performance could be due to a change in the surface chemistry resulting from the different anneals.

The performance of all samples was again tested under the same conditions with the addition of a hole scavenger, H₂O₂. Hydrogen peroxide serves as a sacrificial reagent, capturing all holes that have reached the semiconductor/electrolyte interface, thereby eliminating the kinetic overpotential required for water oxidation. Figure 5-21(b) reveals the performance of the hematite photoanodes with the addition of such a hole scavenger. The onset potential for all samples now shifted to 0.65 V, indicating that the overpotential for the oxidation reaction was about 550 mV. The photocurrent density for the reduced sample is still better than that of the oxidized sample. The
as-deposited sample performs best here. However, one should note that this sample was exchanged with another where the new film was only $\sim 30$ nm thick, because the original sample had been destroyed during a previous measurement. Performance of these films is thickness dependent and the performance of the 30 nm film was higher than that of the 50 nm film in 1.0 M NaOH without the hole scavenger as well (not shown here). Regardless of thickness and post-deposition annealing treatment, the back illumination resulted in a better performance. This is not necessarily an indication of electron limited transport as $\text{H}_2\text{O}_2$ photolytically decomposes \cite{92}. The decomposition results in the formation of small bubbles throughout the electrolyte and thus significant light scattering occurs, reducing the power density of the simulated sunlight when the PEC cell is illuminated from the front.

Figure 5-22 exhibits the quantum efficiencies for the hematite samples. Figure 5-22(a) and Figure 5-22(b) show the external quantum efficiency or IPCE, at an applied bias of 1.23 V and 1.5 V, respectively. As the onset potential is around 1.2 V for these samples, the IPCE at 1.23 V is expected to be low. Indeed, its maximum is less than one percent for the as-deposited and reduced hematite samples. As the performance of the oxidized sample was even lower, its IPCE was not measured at this applied bias. At shorter wavelengths, the IPCE increases to single digit percentage values for all three samples at an applied potential of 1.5 V. The IPCE values begin to increase above $\sim 570$ nm, matching the direct optical bandgap of hematite of 2.2 eV. The increase is gradual as the density of states at higher energies is larger, allowing more electron-hole pairs to be generated at shorter wavelengths.

In order to determine the internal quantum efficiency or APCE, it is necessary to know how many photons of the incident light were actually absorbed by the photoanode. The absorption of the hematite thin films is displayed in Figure 5-22(c). The absorption was determined for the entire sample and was then corrected for the absorption due to the FTO, which served as the transparent back electrode (see Section 3.2.2). As there is nearly no photocurrent at 1.23 V, the APCE values are also near zero, even at short wavelengths. At an applied potential of 1.5 V, the APCE rises to
4.9%, 2.8% and 1.3% for reduced, as-deposited and oxidized hematite, respectively. The increase and scatter in the APCE values above 570 nm for the oxidized and reduced samples is due to the correction for the FTO layer. The increase in the APCE at these wavelengths is not real.

The CoPi water oxidation catalyst was deposited on the as-deposited hematite thin film as described in Section 3.4.4 and the PEC performance tested. Results are plotted in Figure 5-23 in comparison to the PEC performance of uncatalyzed hematite in 1.0 M NaOH with and without the presence of a hole scavenger. Performance is significantly enhanced with application of the catalyst. With the catalyst, the onset potential shifts to 0.65 V and the photocurrent density increases at a given potential by up to 200 μA/cm². In the presence of a hole scavenger, an even higher photocurrent density is attained. Noticeable is, however, that the onset potential for the catalyzed film is nearly as low as that for the uncatalyzed film in the presence of H₂O₂. Both effectively reduce the kinetic overpotential due to water oxidation. The CoPi deposition was not perfected in terms of the amount of charge passed during
electrodeposition or thickness of the resulting catalytic film and its light absorption. Performance may be further improved when considering these parameters.

The PEC performance of the 1% Ti doped hematite thin films, or I2HSS samples, is displayed in Figure 5.24. In 1.0 M NaOH, the as-deposited I2HSS thin film outperforms undoped hematite by one order of magnitude. The annealed films exhibit a lower onset potential by approximately 300 mV compared to the as-deposited I2HSS thin film, but also a lower photocurrent density at higher applied potentials. The performance of the reduced film, and therefore the more conductive film based on the thin film EIS results (see Section 5.3.3), is better by $\sim 150 \mu A/cm^2$ above 1.3 V. For the as-deposited and the reduced films, front illumination produces a slightly higher photocurrent than back illumination does indicating that hole transport is limiting in the doped films contrary to the undoped films. The doped films are more conductive by several orders of magnitude and hence the reversal of the limiting charge carrier was expected and has also been previously observed in the literature [93]. In the case of the oxidized thin film, the results overlap for the different orientations. When a hole scavenger is added to the electrolyte (Figure 5.24(b)), the onset potential shifts to a much lower value as observed for the pure hematite thin films. Here, the onset is between 0.55 V and 0.65 V depending on the post-processing anneal of the I2HSS thin films. Again, performance is better under back illumination due to light scattering at bubbles occurring under front illumination, which reduces the overall light intensity reaching the photoanode.

Quantum efficiencies further characterize the performance of a photoanode and provide more insights into its limiting factors. IPCE values already reach 1% and 5% at 1.23 V applied bias for reduced and oxidized I2HSS, respectively (Figure 5-25(a)). As the onset potential of the as-deposited film is greater than 1.23 V, the IPCE for this film is zero at this applied potential. At 1.5 V, the IPCE values increase to 14% and 13% for the reduced and oxidized samples and to 3% for the as-deposited sample (Figure 5-25(b)). At this applied bias, however, the photocurrent density of the as-deposited film becomes comparable to that of the reduced sample, and is already
greater than that of the oxidized sample, yet its IPCE value is much lower than both
the annealed samples. This indicates that current density does not scale linearly with
the intensity of the light source and that the charge carrier recombination rate is
much higher in the as-deposited sample. This phenomenon is discussed in detail in
Section 6.3.2. Figures 5-25(c) and 5-25(d) show the corresponding absorption spectra
and APCEs for the I2HSS thin film photoanodes.

The PEC performance of the I33HSS thin films is summarized in Figures 5-26 and 5-
27. The photocurrent densities of the annealed films are similar to that of the I2HSS
annealed films. The performance for the as-deposited I33HSS is slightly lower. Again,
a shift of the onset potential to a lower bias is observed after annealing in either
oxidizing or reducing atmosphere. For all three films, back illumination results in
better performance. Photocurrent densities for the reduced thin film, in presence of a
hole scavenger, are also presented. Here, the onset potential shifts to 0.65 V, similarly
to the doped and undoped hematite films. Quantum efficiencies for the reduced
and oxidized I33HSS thin films overlap as expected from their similar photocurrent
densities. As the onset potential of the as-deposited sample is around 1.1 V, its IPCE
at 1.23 V is already above zero. At 1.5 V, the reduced and oxidized samples reach
IPCE values of 17% to 18%, while the as-deposited sample reaches an IPCE of 15%
at 300 nm. The IPCE only begins to increase slowly below ~ 570 nm and more rapidly
below ~ 500 nm, in accordance with the direct gaps observed for this material (see
Figure 5-10(c) and Table 5.2). As there is a slight absorption for the I33HSS films at
longer wavelengths due to an indirect bandgap, the APCE is inflated above 550 nm.
Overall, this material displays better quantum efficiencies than the 1 % Ti doped thin
films.

Figure 5-28 shows the photocurrent densities as a function of applied potential for the
I67HSS thin film photoanodes. The as-deposited film exhibits the lowest photocur-
rents and highest onset potential at 1.05 V among this set of samples. The onset
for both annealed samples occurs at 0.9 V, but the reduced sample outperforms the
oxidized sample by ~ 100 µA/cm². In all three cases, the photoanodes boast better
current densities in the case of back illumination. The reduced I67HSS shows the best performance for this composition. Compared to the I33HSS thin film, its photocurrent density is $\sim 300 \, \mu\text{A/cm}^2$ lower. With the addition of a hole scavenger, the onset potential of the reduced I67HSS thin film shifts to 0.6 V.

Corresponding quantum efficiencies are displayed in Figure 5-29. IPCE values of up to 7.5% are reached for the annealed samples at 1.23 V. The as-deposited film reaches nearly 3% at this bias. At the higher potential of 1.5 V the IPCE of the reduced, oxidized and as-deposited film is 17%, 14% and 12%, respectively, at 300 nm. For this composition, the IPCE only slowly increases below 580 nm and more steeply below 500 nm. The shift to lower wavelengths is expected due to the increase in bandgap with increasing ilmenite content in the solid solution. Due to the low absorption of this film, the internal quantum efficiency is quite high.

The photocurrent densities achieved by the ilmenite thin films (Figure 5-30) are comparable with those of the hematite thin films (Figure 5-21). However, for ilmenite the onset potentials are lower at 0.95 V and 0.9 V for as-deposited and annealed ilmenite films, respectively. Also, the as-deposited film exhibits the lowest photocurrent densities, the oxidized film performs better and the reduced ilmenite film performs best for this composition. Again, back illumination results in higher current densities. Photocurrent densities, even in the presence of a hole scavenger, are quite low and therefore it is difficult to observe an exact onset voltage in Figure 5-30(b). The onset voltage does shift to lower values between 0.6 V and 0.7 V compared to the results without the hole scavenger present.

Figure 5-31 shows the quantum efficiencies for ilmenite. At 1.23 V, the IPCE reaches 9.5% for reduced ilmenite and 4.5% for both oxidized and as-deposited ilmenite thin films. At 1.5 V, the reduced film again has the highest IPCE at 15%, while the oxidized and as-deposited films show similar IPCE values reaching up to 9%. IPCE values begin to significantly increase below 450 nm. The APCE shows low percentage values even between 500 nm and 600 nm due to a tail in the absorption at those wavelengths.
Figure 5-24: PEC performance of as-deposited and annealed 1% Ti doped hematite thin films.

(a) in 1.0 M NaOH
(b) in 1.0 M NaOH with 0.5 M H₂O₂

Figure 5-25: Quantum efficiencies and absorption of the as-deposited and annealed 1% Ti doped hematite thin films.
Figure 5-26: PEC performance of as-deposited and annealed Fe$_{1.67}$Ti$_{0.33}$O$_3$ thin films.

(a) in 1.0 M NaOH

(b) in 1.0 M NaOH with 0.5 M H$_2$O$_2$

Figure 5-27: Quantum efficiencies and absorption of the as-deposited and annealed Fe$_{1.67}$Ti$_{0.33}$O$_3$ thin films.

(a) IPCE at 1.23 V vs. RHE

(b) IPCE at 1.5 V vs. RHE

(c) Absorption

(d) APCE at 1.23 V and 1.5 V vs. RHE
(a) in 1.0 M NaOH

(b) in 1.0 M NaOH with 0.5 M H₂O₂

Figure 5-28: PEC performance of as-deposited and annealed Fe₁.₃₃Ti₀.₆₇O₃ thin films.

(a) IPCE at 1.23 V vs. RHE

(b) IPCE at 1.5 V vs. RHE

(c) Absorption

(d) APCE at 1.23 V and 1.5 V vs. RHE

Figure 5-29: Quantum efficiencies and absorption of the as-deposited and annealed Fe₁.₃₃Ti₀.₆₇O₃ thin films.
(a) in 1.0 M NaOH with 0.5 M H$_2$O$_2$

Figure 5-30: PEC performance of as-deposited and annealed ilmenite thin films.

(a) IPCE at 1.23 V vs. RHE
(b) IPCE at 1.5 V vs. RHE

(c) Absorption
(d) APCE at 1.23 V and 1.5 V vs. RHE

Figure 5-31: Quantum efficiencies and absorption of the as-deposited and annealed ilmenite thin films.
5.4.2 Mott-Schottky analysis

A Mott-Schottky analysis was performed for the 1% Ti doped and undoped hematite thin films. The procedure is explained in detail in Section 3.4.7. Figure 5-32 shows the results. The data is plotted as \((A/C)^2\) vs. applied bias, where \(C\) is the space charge capacitance and \(A\) is the area of the photoanode. Based on Eq. 3.15, one can extract the charge carrier density, \(N_D\), from the slope and the flatband potential, \(\phi_{FB}\), from the intercept with the x-axis. The flatband potential for all undoped hematite films is \(\sim 0.2\) V and that for the doped films \(\sim 0.4\) V, similar to those observed in other studies. Early studies by Kennedy et al. report a flatband potential of 300 mV for polycrystalline hematite [84]. Later, Benko et al. reported a slightly lower flatband potential of \((200 \pm 50)\) mV for both amorphous and polycrystalline hematite [85]. More recently, the flatband potential was reported near 400 mV by Grätzel and coworkers for nanostructured silicon doped hematite photoanodes [16, 86].

![Mott-Schottky plots](image)

(a) undoped hematite  
(b) 1% Ti doped hematite

**Figure 5-32:** Mott-Schottky plots of undoped and doped hematite thin films measured after different annealing treatments.

The charge carrier densities for hematite can be extracted from Figure 5-32(a) between 0.2 V and 0.4 V. At higher potentials, the slope changes indicate a change in charge carrier density. This is further discussed in Section 6.3.3. The charge carrier densities for all films are summarized in Table 5.3. For the oxidized and reduced hematite thin films, the charge carrier densities are of the same order of magnitude, as the
corresponding slopes are very similar. The EIS measurements (see Section 5.3.3) revealed that the conductivity did not depend on pO\textsubscript{2} for pure hematite. Hence, their charge carrier density was expected to be the same. The charge carrier density of the as-deposited hematite thin film is an order of magnitude higher than that of the annealed samples, indicating that the sample did not reach equilibrium during the PLD deposition.

For the doped hematite samples (I2HSS thin films), only the oxidized thin film exhibits the same behavior as described above with a change in slope at 0.6 V. Its charge carrier density is also comparable with that of the oxidized undoped hematite thin film. On the other hand, the reduced doped film shows no change of slope and its slope is much less steep, revealing a charge carrier density of more than one order of magnitude larger than that of the oxidized film. The charge carrier density of the as-deposited sample is even higher, as the slope is so flat that it is barely visible at the scale of Figure 5-32(b). This strengthens the hypothesis that the samples are more oxygen deficient after PLD than assumed. Furthermore, it indicates that even for the I2HSS sample, the photocurrent density increases with greater conductivity as the as-deposited sample showed the largest photocurrent density and has the highest charge carrier density. The \( N_D \) values for these samples are also reported in Table 5.3.

### Table 5.3: Charge carrier densities of the hematite and I2HSS thin film photoanodes.

<table>
<thead>
<tr>
<th>sample</th>
<th>composition</th>
<th>state</th>
<th>( N_D ) cm(^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>Fe(_2)O(_3)</td>
<td>as-deposited</td>
<td>6.6( \times )10(^{18} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>8.1( \times )10(^{17} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>6.1( \times )10(^{17} )</td>
</tr>
<tr>
<td>I2HSS</td>
<td>Fe(<em>{1.98})Ti(</em>{0.02})O(_3)</td>
<td>as-deposited</td>
<td>2.3( \times )10(^{20} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reduced</td>
<td>1.8( \times )10(^{19} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>oxidized</td>
<td>5.6( \times )10(^{17} )</td>
</tr>
</tbody>
</table>
5.4.3 Homojunctions

Recently, Abdi et al. have shown that PEC performance can be enhanced by creating a homojunction of doped and undoped BiVO$_4$ where a layer of the doped material is sandwiched between the back contact and the undoped material forming the semiconductor/electrolyte interface \[37\]. When the Fermi levels of the doped and undoped layer equilibrate, additional band bending results, beneficial to electron and hole separation (Figure 5-33). In this study, this principle was applied to the hematite photoanode. Two samples were prepared: H/I$_2$ and I$_2$/H. For the former, H/I$_2$, first a layer of 1% Ti doped $\alpha$-Fe$_2$O$_3$ was-deposited on a FTO coated quartz substrate, followed by a layer of undoped hematite. This resulted in the preferential band bending as depicted in Figure 5-33 for BiVO$_4$. The latter, I$_2$/H, was fabricated as a reference where first hematite was-deposited, and then the doped material, resulting in band bending unfavorable for charge separation in the case of a photoanode. Both samples were prepared using the same conditions recorded in Section 3.1.2 but for each material only 15k laser pulses were used for a total of 30k pulses per sample. Resulting thicknesses were 42 nm and 45 nm for H/I$_2$ and I$_2$/H, respectively, and are also listed in Table 3.4.

![Figure 5-33: Energy band schematic of a BiVO$_4$ and 1% W doped BiVO$_4$ homojunction adopted from 37.](image)

The PEC performance of these samples is shown in Figure 5-33. The photocurrent densities of the as-deposited doped and undoped hematite thin films are included as a reference. In fact, both homojunctions, regardless of direction of the electric field
due to the band bending, show similar photocurrent densities at a given potential. Both homojunctions perform better than pure hematite but not nearly as well as the as-deposited 1% Ti doped α-Fe₂O₃ thin film. In case of the H/I₂ sample, hole transport is limiting, whereas electron transport is limiting for the I₂/H sample. In the latter case, the undoped material, which is less conductive, presents a barrier to electron transport to the back contact. This is not the case for the H/I₂ sample.

![Figure 5-34: PEC performance of the 1% Ti doped Fe₂O₃ homojunctions compared to that of the doped and undoped hematite thin films.](image)

The PEC results of the homojunctions suggest that there is significant charge carrier recombination even in areas where the carrier transport is controlled by drift and not by diffusion. The H/I₂ sample has a conductive material (doped hematite) between its back contact and the less conductive undoped hematite that also forms the interface with the electrolyte. At the applied potentials where a photocurrent is present, the depletion width spans the undoped region due to its low carrier density. Therefore, all charge carriers created in the hematite layer should be swept to either the electrolyte interface (holes) or into the doped hematite layer (electrons) by the electric field present from the space charge region further enhanced by the band bending from
the Fermi level equilibration. In I2HSS, electron transport is not limiting based on the PEC performance of the I2HSS thin film. In addition, I2HSS achieved a photocurrent density over 1 mA/cm$^2$, such that performance of the H/I2 homojunction sample should be higher than that of the I2HSS sample if no recombination occurred in an area where an electric field is present.

Figure 5-35 shows the quantum efficiencies for the homojunction samples. Generally, the IPCE as well as the APCE are comparable with the efficiencies recorded for the simple thin films of either doped or undoped hematite. The homojunction samples were also annealed in reducing atmosphere, however, their performance (not shown) did not improve significantly and still fell between that of hematite and doped hematite.

![Figure 5-35: Quantum efficiencies and absorption of the 1% Ti doped Fe$_2$O$_3$ homojunctions.](image-url)
Chapter 6

Discussion

This chapter investigates some of the key findings from the previous chapter in much greater detail, drawing attention to links between the bulk and thin film analyses as well as the characterization of the photoanodes. The bulk sample conductivity data allow the determination of the electron mobility in polycrystalline hematite in addition to the derivation of key thermodynamic parameters such as the enthalpy of Schottky defect formation and the enthalpy of reduction. The electron mobility can also be determined for the thin films. Additional room temperature conductivity measurements of the I2HSS thin film annealed at only 580°C reveal that at this temperature, kinetics are limiting and the sample is no longer able to achieve a difference of 5 orders of magnitude of conductivity when annealed in different pO₂. This explains why the range of charge carrier densities of the annealed I2HSS photoanodes is smaller than expected based on the thin films annealed at temperatures up to 800°C. The last section of this chapter relates the PEC performance to the different compositions of the IHSS photoanodes and identifies additional benefits of the annealing procedure besides the tuning of the magnitude of the conductivity. Finally, the change in slope of the Mott-Schottky plots is discussed and evidence of a deep trap in hematite presented.
6.1 Electrical characterization of the bulk samples

Section [5.3.1] presented the results of the DC conductivity measurements for bulk samples of the IHSS system. The conductivity of undoped hematite was dependent only on temperature, as the data exhibited no oxygen partial pressure dependence. The 1% Ti doped hematite or I2HSS sample was neither dependent on temperature nor pO$_2$ for the conditions examined. The remaining three samples, I33HSS, I67HSS and ilmenite all decreased in conductivity with decreasing temperatures and increasing pO$_2$. From these findings, certain parameters of this system will be derived, as discussed in the following sections.

6.1.1 Electron mobility in polycrystalline bulk hematite

As the conductivity of I2HSS is pO$_2$ independent between $10^{-4}$ atm and 1 atm O$_2$, the material is within Regime II of the defect diagram (Figure 4-2). This means that the donor dopants, 1% Ti, are fully electronically compensated and therefore

\[ n = N_D \] (6.1)

Eq. 4.10 explains the incorporation of Ti into the hematite lattice when forming a IHSS. One Ti ion substitutes on an Fe site per FeTiO$_3$. Therefore, the donor concentration in hematite for a solid solution of 2% ilmenite and 98% hematite can be calculated based on the formula units per unit cell of ilmenite and the unit cell volume of hematite (see Section 2.4).

\[ N_D = 0.02 \times \frac{6}{302.72 \text{ Å}^3} \times \left( \frac{10^8 \text{Å}}{1 \text{ cm}} \right)^3 = 3.96 \times 10^{20} \text{ cm}^{-3} \] (6.2)

As this material is in Regime II for the given conditions and the electrons dominate as charge carrier species, the conductivity can be expressed as

\[ \sigma = nq\mu_n \] (6.3)
In addition, the conductivity of the I2HSS bulk sample does not exhibit any temperature dependence between 900°C and 1050°C, so the electron mobility is temperature independent as well. From the measurements, the average conductivity was determined to be \((6.28 \pm 0.26)\) S/cm (see Section 5.3.1). Combining Eq. 6.1 and Eq. 6.3 yields an electron mobility of \((0.099 \pm 0.004)\) cm²/Vs. The first report of the electrical properties of polycrystalline hematite was presented by Morin with an electron mobility of \(10^{-2}\) cm²/Vs at 1000 K with an activation energy 0.1 eV \([94]\). Later on, Warnes et. al. also reported an activated electron mobility but of higher magnitude \([87]\). At 1000 K, they calculated a mobility of 0.3 cm²/Vs with an activation energy of 0.17 eV. On the other hand, others report a non-activated mobility on the order of \(\sim 0.1\) cm²/Vs for single crystal Zr doped \(\alpha\)-Fe₂O₃ \([95]\) as well as for polycrystalline \(\alpha\)-Fe₂O₃ doped with Zr, Ti or Nb between 960 K and 1500 K \([96,97]\). The latter studies are in very good agreement with findings in this investigation and also, a mobility of 0.1 cm²/Vs is generally accepted in the PEC literature \([38]\).

### 6.1.2 Thermodynamic parameters derived from the application of the defect chemical model

The defect model derived in Chapter 4 in conjunction with the experimental results for the bulk conductivity of the IHSS system, allow the determination of key thermodynamic parameters. Generally, the equilibrium constant of a certain reaction can be related to the Gibbs free energy of that reaction, \(\Delta G^\circ\), as follows

\[
\Delta G^\circ (T) = -kT \ln [K (T)] \tag{6.4}
\]

The Gibbs free energy, in turn, is related to the enthalpy, \(\Delta H^\circ\), and the entropy, \(\Delta S^\circ\), of the reaction as given by the following relation \([99]\)

\[
\Delta G^\circ (T) = \Delta H^\circ - T\Delta S^\circ \tag{6.5}
\]
When combining Eq. 6.4 and Eq. 6.5, one arrives at

$$K(T) = K_0 \exp \left( -\frac{\Delta H^\circ}{kT} \right)$$

(6.6)

where the entropy term has been absorbed into the pre-exponential factor, $K_0$. Consequently, the activation energies $E_S$, $E_R$ and $E_{Ox}$ are equivalent to the standard enthalpies $\Delta H^\circ_S$, $\Delta H^\circ_R$ and $\Delta H^\circ_{Ox}$ for the Schottky defect formation, the oxidation reaction and the reduction reaction, respectively (see Eq. 4.4, Eq. 4.6 and Eq. 4.8).

$K_i$ and $K_R$ of polycrystalline hematite

First, attention is drawn to the conductivity of bulk hematite, replotted as a function of temperature in Figure 6-1. As pure hematite shows no dependence on $pO_2$, no reaction constants pertaining to the Schottky defect formation, the reduction reaction or the oxidation reaction can be derived directly. However, at these temperatures, metal oxides, including $\alpha$-$Fe_2O_3$, are dominated by intrinsic electronic disorder, i.e. their electron and hole concentrations are equal ($n \approx p$) [70]. When this is the case, Eq. 4.2 can be rewritten as

$$n = \sqrt{N_C N_V} \exp \left( -\frac{E_g}{2kT} \right)$$

(6.7)

Since the mobility is now known (see Section 6.1.1) and the conductivity behaves as

$$\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)$$

(6.8)

one can calculate $E_g$ and the $\sqrt{N_C N_V}$ factor (assuming that $\mu_n \gg \mu_p$ as discussed below) by combining Eq. 6.3, Eq. 6.7 and Eq. 6.8. The pre-exponential factor $\sigma_0$ was determined as $(3264 \pm 73) \text{S/cm}$ from a best fit to the data in Figure 6-1. So,

$$\sqrt{N_C N_V} = \frac{\sigma_0}{q\mu_n} = (1.92 \pm 0.06) \times 10^{23} \text{ cm}^{-3}$$

(6.9)
The activation energy of $(0.98 \pm 0.02)$ eV resulting from the same fit corresponds to $1/2 \ E_g$. In other words, the bandgap determined by the bulk electrical conductivity measurements as part of this study is $(1.96 \pm 0.04)$ eV. This calculation is only valid if the mobility is not temperature activated, as observed in Figure 5-12 and calculated above. Optical spectroscopy of the hematite thin film resulted in an indirect and direct bandgap of 2.05 eV and 2.19 eV, respectively, which is in good agreement with the bandgap determined here. Mochizuki et al. also report a thermal energy gap of 2.0 eV based on microwave conductivity measurements [100]. Combining these two results yields a solution for the intrinsic equilibrium constant describing electron-hole generation

$$K_i(T) = (3.69 \pm 0.16) \times 10^{46} \ \text{cm}^{-6} \ \exp \left( -\frac{(1.96 \pm 0.04) \text{ eV}}{kT} \right) \quad (6.10)$$

Based on his thermogravimetric analysis on polycrystalline hematite, Dieckmann es-
established that oxygen vacancies are the majority ionic defect in the regime of electronic compensation (Regime II(i)) \cite{69}. His findings were reviewed in greater detail in Section 2.4. He was able to determine an expression for the equilibrium constant for the formation of anion vacancies, $K_V$, given that $n \approx p$

$$K_V(T) = \left[V_O^{\bullet\bullet}\right]P_{O_2}^{\frac{1}{2}} = 2.065 \times 10^7 \exp\left(-\frac{39380 K}{T}\right)$$  \hspace{1cm} (6.11)

resulting in an activation energy for vacancy generation, $E_V$, of 3.393 eV. The pre-exponential factor is expressed in terms of $\epsilon$, the deviation from stoichiometry in Fe$_2$O$_{3-\epsilon}$ related to the vacancy concentration. Based on the formula units per unit cell and unit cell dimensions (see Section 2.4)

$$\left[V_O^{\bullet\bullet}\right] = \epsilon \times 1.982 \times 10^{22} \text{ cm}^{-3}$$  \hspace{1cm} (6.12)

Therefore, rewriting Dieckmann’s expression for $K_V$ in terms of units consistent with this work, one arrives at

$$K_V(T) = 4.093 \times 10^{29} \text{ cm}^{-3} \exp\left(-\frac{3.393 \text{ eV}}{kT}\right)$$  \hspace{1cm} (6.13)

Since this expression for $K_V$ is only valid in Regime II(i), $n \approx p$ and hence, $K_i = n^2$. Substituting this condition into Eq. 4.6 and combining it with Eq. 6.11 results in

$$K_R(T) = K_i \left[V_O^{\bullet\bullet}\right]P_{O_2}^{\frac{1}{2}} = K_i K_V$$  \hspace{1cm} (6.14)

and $K_R$ can now be determined as

$$K_R(T) = (1.51 \pm 0.07) \times 10^{76} \text{ cm}^{-9} \exp\left(-\frac{(5.35 \pm 0.04) \text{ eV}}{kT}\right)$$  \hspace{1cm} (6.15)

$K_i$, $K_{\text{Ox}}$ and $\mu_n$ for different IHSS

As the conductivity of the I2HSS bulk sample exhibited no P$O_2$ dependence, the data allowed the determination of the electron mobility (see Section 6.1.1) for bulk
hematite; but it does not enable the calculation of the enthalpy of oxidation or reduction. However, the I33HSS bulk sample containing 15 at.% Ti exhibits a pO\textsubscript{2} dependence at high partial pressures of oxygen, as predicted by the defect model. The conductivity for this sample is replotted in Figure 6-2 as a function of inverse temperature. Best fits to these data in simulated air and 100 % O\textsubscript{2} atmosphere result in activation energies, $E_a$, of $(0.81 \pm 0.05)$ eV and $(0.83 \pm 0.05)$ eV, respectively. Similar behavior is observed for the I67HSS and ilmenite samples. Figure 6-3 shows the conductivity as a function of inverse temperature for I67HSS. A best fit results in an activation energy of $(0.54 \pm 0.10)$ eV in both simulated air and 100 % O\textsubscript{2}. For ilmenite, the activation energy was determined as $(1.23 \pm 0.20)$ eV in simulated air and as $(1.37 \pm 17.00)$ eV in an 100 % O\textsubscript{2} atmosphere (see Figure 6-4).

The conductivity data of the bulk samples (see Section 5.3.1) shows that the I33HSS, the I67HSS and the ilmenite samples are transitioning from one Brouwer regime to another. At high oxygen partial pressures, a power law dependence on pO\textsubscript{2} becomes

![Figure 6-2: Conductivity dependence of bulk Fe\textsubscript{1.67}Ti\textsubscript{0.33}O\textsubscript{3} on temperature. A best fit results in an activation energy of $(0.81 \pm 0.05)$ eV in simulated air and $(0.83 \pm 0.05)$ eV in 100 % O\textsubscript{2}.]
**Figure 6-3:** Conductivity dependence of bulk Fe\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{3} on temperature. A best fit results in an activation energy of (0.54 ± 0.09) eV in simulated air and (0.54 ± 0.10) eV in 100 % O\textsubscript{2}.

**Figure 6-4:** Conductivity dependence of bulk FeTiO\textsubscript{3} on temperature. A best fit results in an activation energy of (1.23 ± 0.20) eV in simulated air and (1.36 ± 0.17) eV in 100 % O\textsubscript{2}.
evident and the previous paragraph presented the activation energies for all three samples in this regime. As the data approaches a pO$_2$ of $10^{-4}$ atm, the partial pressure dependence for these three samples diminishes. Therefore, a solution for the electron density in this transition regime is required in order to determine the equilibrium constants for the different compositions of the solid solutions. Derivations of the electron density in such a transition regime is presented in Appendix C for three different cases: the extrinsic case, the intrinsic case and their combination.

First, the extrinsic case is considered. As the activation energies at 21% and 100% O$_2$ are comparable for each of the three solid solutions discussed here, it follows that the conductivity data at these partial pressures fall within Regime III. From the expression for the electron concentration in this regime (see Table 4.2),

$$E_a = E_g - \frac{1}{6} E_{Ox} + E_\mu$$  \hspace{1cm} (6.16)

where $E_\mu$ is the hopping energy of a thermally activated mobility. Including this restriction in the solution for the electron concentration derived in Appendix C.1 results in a fit to the data for each solid solution (not shown).

From Figures 5-13, 5-14 and 5-15 (data are replotted in Figures 6-5, 6-6 and 6-7), it is evident that the conductivity does not converge for all temperatures at low pO$_2$ for any sample discussed here, as expected in the extrinsic case with a non-activated mobility and contrary to the I2HSS sample (Figure 5-12, replotted in Figure 6-8). Therefore, the conductivity must be thermally activated in Regime II for the solid solutions with higher ilmenite content, if the extrinsic case applies. Extrapolating the fit to lower partial pressures of oxygen enables calculating the activation energy in Regime II for each composition. As the electron density is set by the titanium concentration in this regime, it is independent of temperature. Hence, the activation energy is equivalent to $E_\mu$ in this regime. Results yield hopping energies of 0.92 eV, 0.84 eV and 1.7 eV for I33HSS, I67HSS and ilmenite, respectively. Generally, hopping energies for metal oxides are of the order of a few hundred meV. Hence, it appears that the application of the extrinsic case is not valid here.
As more ilmenite is added to the solid solution, the band structure changes. Especially
the conduction band will be influenced as a Ti3d band forms with higher Ti content.
If there is limited overlap with the Fe3d band, some electrons may become trapped
in the lower Fe3d band and the effective electron concentration due to the Ti is
much smaller than the Ti content in the solid solution. In this case, the material
may actually exhibit intrinsic behavior at the temperatures observed in this study.
As discussed above, the electron concentration is independent of pO2 in this case
but exponentially dependent on temperature as given by Eq. [6.7]. Considering the
definition of conductivity (Eq. [5.1]), one arrives at
\[
E_a = \frac{E_g}{2} + E_{\mu_n}
\]
for Regime II(i). This assumes that the hole mobility is negligible in comparison to the
electron mobility. This must be the case as at higher pO2 values, the conductivity
decreases with increasing pO2 in accordance with n-type behavior of metal oxide
semiconductors. However, in Regime III(i), the hole concentration dominates the
electron concentration (see Figure [4-1]) and therefore, conductivity should increase
with increasing pO2, unless hole mobility is much lower than that of electrons.
Since the data reveals that conductivity is still controlled by electrons in Regime III(i),
one can determine the relation between the thermal activation energy, the bandgap
and the enthalpy of the oxidation reaction based on the electron density in this regime
\[
E_a = E_g - \frac{1}{8} E_{Ox} + E_{\mu}
\]
Based on the experimental values for \(E_a\) in Regime III(i) and the bandgap from
the optical measurements for the different solid solutions and the solution for the
electron density in the transition region between Regime II(i) and Regime III(i) (see
Appendix [C.2]), fits have been generated for the conductivity of bulk I33HSS, I67HSS
and ilmenite. These are displayed in Figures [6-5], [6-6] and [6-7]. From the fits, one can
now extract the different energies. These are listed in Table [6.1] along with the pre-
exponential factors used to generate the fits to the data for each solid solution.

One should note that the solution for the electron density in the transition regime (Appendix C) dictates the shape of the fit only. Where the transition occurs (change from no $pO_2$ dependence to the $-3/16$ power law dependence for the intrinsic case) is dependent on the relative magnitudes of the pre-exponential factors of $K_i$ and $K_{Ox}$, which can be determined from the data. The absolute magnitude of the conductivity is determined by the pre-exponential factors of $K_i$ and the mobility in Regime II(i). The absolute conductivity in this regime is known from the extrapolation of the fit to lower $pO_2$ values, but this alone does not allow the determination of the correct pre-exponentials for both $K_i$ and mobility. Therefore, the values of the pre-exponential factors in Table 6.1 represent those used for the fits in Figures 6-5, 6-6 and 6-7 and are in the correct relation to each other, but are not the absolute values. The extraction of the activation energies is exact, as there is sufficient experimental evidence for their determination.

Table 6.1: Thermodynamic parameters controlling the charge carrier concentrations based on fits to the bulk conductivity data.

<table>
<thead>
<tr>
<th></th>
<th>Equilibrium constant or mobility</th>
<th>Pre-exponential</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I33HSS (Fe$<em>{1.67}$Ti$</em>{0.33}$O$_3$)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intrinsic disorder</td>
<td>$K_i$</td>
<td>$5 \times 10^{16}$ cm$^{-6}$</td>
<td>2.0 eV</td>
</tr>
<tr>
<td>Oxidation</td>
<td>$K_{Ox}$</td>
<td>$5 \times 10^{19}$ cm$^{-24}$</td>
<td>9.4 eV</td>
</tr>
<tr>
<td>Mobility</td>
<td>$\mu$</td>
<td>1.7 cm$^2$/Vs</td>
<td>0</td>
</tr>
<tr>
<td><strong>I67HSS (Fe$<em>{1.33}$Ti$</em>{0.67}$O$_3$)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intrinsic disorder</td>
<td>$K_i$</td>
<td>$8 \times 10^{14}$ cm$^{-6}$</td>
<td>2.0 eV</td>
</tr>
<tr>
<td>Oxidation</td>
<td>$K_{Ox}$</td>
<td>$3 \times 10^{19}$ cm$^{-24}$</td>
<td>12.1 eV</td>
</tr>
<tr>
<td>Mobility</td>
<td>$\mu$</td>
<td>1.1 cm$^2$/Vs</td>
<td>0.05 eV</td>
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<tr>
<td><strong>Ilmenite (FeTiO$_3$)</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Intrinsic disorder</td>
<td>$K_i$</td>
<td>$6 \times 10^{16}$ cm$^{-6}$</td>
<td>2.2 eV</td>
</tr>
<tr>
<td>Oxidation</td>
<td>$K_{Ox}$</td>
<td>$5 \times 10^{19}$ cm$^{-24}$</td>
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</tr>
<tr>
<td>Mobility</td>
<td>$\mu$</td>
<td>12 cm$^2$/Vs</td>
<td>0.3 eV</td>
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</tbody>
</table>
Figure 6-5: Conductivity of bulk Fe$_{1.67}$Ti$_{0.33}$O$_3$ as a function of pO$_2$ including fits based on the transition between Regime II(i) and Regime III(i).

Figure 6-6: Conductivity of bulk Fe$_{1.33}$Ti$_{0.67}$O$_3$ as a function of pO$_2$ including fits based on the transition between Regime II(i) and Regime III(i).
Figure 6-7: Conductivity of bulk FeTiO$_3$ as a function of pO$_2$ including fits based on the transition between Regime II(i) and Regime III(i).

An approximation of the Schottky formation energy in $\alpha$-Fe$_2$O$_3$

Based on the relation between the intrinsic, the reduction, the oxidation and the Schottky equilibrium constants (Eq. 4.9), the relation of their activation energies can be determined as

$$E_S = 3E_R + E_{Ox} - 6E_g$$  \hspace{1cm} (6.19)

Using $E_{Ox}$ of the I33HSS as a first order approximation for the enthalpy of oxidation for 1% Ti doped hematite, the Schottky formation energy, $E_S$, for this material can be calculated as 13.4 eV. This represents the activation energy of the formation of two iron vacancies and three oxygen vacancies and is therefore expected to be quite large. Normalizing this activation energy for the formation of one defect results in a Schottky formation energy of 2.7 eV per defect.

When using the $K_{Ox}$ from the I33HSS bulk conductivity fit in conjunction with $K_i$
and the mobility determined for the Ti doped hematite, one can generate a model for the intrinsic conductivity for the doped sample. Results are displayed in Figure 6-8. The modeled conductivity falls far below the conductivity data for this sample. That agrees with the donor dopants dominating and therefore the extrinsic case applies for 1% Ti doped hematite.

6.1.3 Phase stability

In earlier studies of the IHSS system characterizing its magnetic properties, Ishikawa et al. report that solid solutions with higher ilmenite content were not stable in air above 800 K and exhibited porosities between 10% and 20% [63, 101]. Also, in the atmosphere containing less oxygen, $\alpha$-Fe$_2$O$_3$ tends to transition to Fe$_3$O$_4$ or magnetite [69]. Some samples examined in this study, specifically the I33HSS, I67HSS and ilmenite compositions, show some noise in their bulk conductivity data (see Figure 6-8).
Figures 5-13 through 5-15. In order to ensure that the phase of these samples was indeed stable throughout the DC conductivity measurements, all bulk samples were annealed at 1000°C for 24 h in UHP N₂ (Airgas, Berwyn, PA) resulting in a pO₂ of the order of 10⁻⁴ atm, corresponding to the lowest partial pressure for the conductivities reported in Section 5.3.1.

Figure 6-9 shows the diffractograms of the samples after they were annealed. As samples for the DC conductivity measurements had already been cut from the pellets, only small scraps remained for the annealing treatment. Hence, there was a trade-off between intensity and irradiated area of the samples when performing the XRD measurements. Consequently, the diffractograms are a superposition of the peaks due

![X-ray diffraction patterns of the \((\text{FeTiO}_3)_{1-x}(\text{Fe}_2\text{O}_3)_x\) pellets after an anneal at 1000°C. Peak positions and their relative intensities for ilmenite (PDF 00-029-0733, black) and hematite (PDF 00-033-0664, red) are indicated by the symbols above the patterns of the respective solid solution end member.](image-url)
to the sample and those of the XRD sample holder offset by ∼3 mm, as that was the average pellet height. For better comparison, a XRD scan of the sample holder by itself is included at the bottom of Figure 6-9. Even though it was corrected for the 3 mm offset, each sample has a different height (see Table 3.2) and therefore, the peaks due to the holder do not align perfectly with the holder reference scan. Looking at the scans for the solid solutions, the peaks matching the hematite phase are present for all samples although they are not very obviously for the ilmenite sample. Absent is the shift towards lower 2θ values with increasing ilmenite content, suggesting that at least the surface of these sample is primarily hematite.

Segregation of the larger metal cation has been observed in other metal oxide electrodes dependent on operating conditions [102]. In SrTi$_{1-x}$Fe$_x$O$_3$, the Sr cation is the largest among the metal constituents and segregates to the surface with increasing iron content [103]. In the ilmenite lattice, both metal cations sit in octahedral sites and are sixfold coordinated [104, 105]. The ionic radius for Ti$^{4+}$ at such a site is 0.605 Å [106]. In comparison, Fe$^{2+}$ has an ionic radius of 0.78 Å and Fe$^{3+}$ in hematite has an ionic radius of 0.65 Å [106]. Therefore, it is reasonable to assume that Fe$^{2+}$ ions in the solid solutions with greater ilmenite content will segregate to the surface.

Figure 6-10: X-ray diffraction patterns of the annealed (FeTiO$_3$)$_{0.33}$(Fe$_2$O$_3$)$_{0.67}$ pellet before (green) and after (blue) polishing. Peak positions and their relative intensities for ilmenite (PDF 00-029-0733, black) and hematite (PDF 00-033-0664, red) are indicated by the symbols above the patterns.
Figure 6-11: X-ray diffraction patterns of the annealed \((\text{FeTiO}_3)_{0.67}(\text{Fe}_2\text{O}_3)_{0.33}\) pellet before (green) and after (blue) polishing. Peak positions and their relative intensities for ilmenite (PDF 00-029-0733, black) and hematite (PDF 00-033-0664, red) are indicated by the symbols above the patterns.

In order to test this hypothesis, the I33HSS, I67HSS and ilmenite samples were polished to remove a few surface layers and subsequently their XRD patterns were collected again. Results for the I33HSS specimen are displayed in Figure 6-10. The excerpt shows clearly that the peaks of the sample shift towards lower 2\(\theta\) values, away from the reference lines of the hematite diffraction pattern, after polishing. Similar results are presented for the I67HSS sample in Figure 6-11. In this case, the
shift of the peaks towards the ilmenite reference pattern is further compared to the I33HSS sample, as is expected of a solid solution with higher ilmenite content. The most dramatic shift is visible for the ilmenite sample itself (Figure 6-12). Based on the XRD results, one can conclude that, indeed, Fe ions segregate to the surface when the material is held at elevated temperatures for extended periods of time. XPS measurements on the I67HSS sample also confirm this iron segregation to the surface (see Appendix D for more details). On the other hand, the phase of these solid solutions is stable at partial pressures as low as $10^{-4}$ atm $O_2$ at these temperatures.

6.2 Electrical characterization of thin film specimens

The EIS results characterizing the epitaxially grown thin films of the IHSS system are in good agreement with the derived defect model. They also follow the trends established by the bulk samples. Pure hematite again exhibits very little nonstoichiometry between a $pO_2$ of $10^{-4}$ atm and 1 atm and its activation energy is equivalent to $1/2 E_g$, even down to temperatures as low as 250°C. Contrary to bulk results, the I2HSS thin film does exhibit a change in conductivity with $pO_2$ when annealed in an atmosphere with more than $10^{-3}$ atm $O_2$. Below this value, its conductivity again is $pO_2$ independent and a value for the mobility can be derived (see Section 6.2.1).

Generally, all solid solutions containing some ilmenite start to exhibit intrinsic behavior above 600°C where the activation energy of their respective conductivities changes and approaches that of hematite. The extrinsic region is confined between 600°C to 400°C, below which a second slope change occurs and the conductivity becomes dependent on the ionization of ions or defects. The conductivity is highest for the 1% Ti doped or I2HSS thin film and decreases successively with increasing ilmenite content.
6.2.1 Electron mobility in epitaxial thin films of hematite

Within the extrinsic regime, the range of $pO_2$ where the I2HSS sample shows no dependence on the partial pressure of oxygen, the electron mobility can be determined as above for the bulk samples. As the sample possesses the same composition, the calculation for its charge carrier density is equivalent and amounts to $3.96 \times 10^{20}$ cm$^{-3}$ as before. The conductivity between 400°C and 600°C is $(0.640 \pm 0.025)$ S/cm. A more careful fitting results in an activation energy of only 0.026 eV and it is unclear if this small temperature dependence may simply be due to the incomplete transition from the intrinsic to the extrinsic regime below 600°C. Applying Eq. 6.3 results in an electron mobility of $(0.0101 \pm 0.0004)$ cm$^2$/Vs. Since the conductivity was determined by EIS with IDEs deposited on top of the epitaxial film, both the conductivity and the calculated electron mobility are the in-plane quantities and describe the electrical properties of the basal lattice plane for these thin films. The mobility calculated for the thin films is an order of magnitude lower than that for the bulk samples but still agrees with some of the lower mobilities reported in the literature for hematite [94, 95, 107]. Again, the mobility was determined to be temperature independent, as was the case for that determined for the bulk samples.

6.2.2 Thin film conductivity after an anneal at 580°C

Based on the thin film conductivity, a difference of five orders of magnitude in electron concentration was expected after annealing a film in 100% $O_2$ versus in a $pO_2$ of less than $10^{-3}$ atm. However, the Mott-Schottky analysis of the I2HSS thin films used as photoanodes revealed that the charge carrier density only differed by an order and a half in magnitude (see Table 5.3). Moreover, the as-deposited sample had a charge carrier density larger than that of the sample annealed in $10^{-4}$ atm $O_2$. The latter indicates that the samples fabricated by PLD do not attain equilibrium conditions and are likely oxygen deficient. This also agrees with Mott-Schottky results for the hematite photoanodes. The as-deposited hematite film exhibited a charge carrier
Figure 6-13: Conductivity of the Fe_{1.98}Ti_{0.02}O₃ and hematite thin films as a function of temperature at different partial pressures of oxygen, in comparison to room temperature conductivity after an anneal at only 580°C.

In order to investigate the limited spread of charge carrier density and hence conductivity of the I2HSS photoanodes, the EIS measurements were repeated on the epitaxially grown I2HSS film, but with annealing conditions matching those of the photoanodes (see Section 3.4.2). After a highly conductive I2HSS was held at 580°C in 100% O₂ and subsequently cooled to room temperature, its conductivity was two orders of magnitude higher than if it had been annealed at 800°C. Taking this same film to 580°C again but in 0.1% O₂ resulted in a subsequent room temperature conductivity two orders of magnitude lower than when the sample was previously annealed at 800°C in the same atmosphere. Figure 6-13 shows a comparison of the room temperature conductivities after the anneals at the different temperatures. These findings indicate that the thin films do not attain equilibrium when annealed only at 580°C. Sluggish kinetics would require a higher annealing temperature in order to better
tune the conductivity. In this study, the annealing temperature of the photoanodes was limited by the maximum temperature sustainable by the FTO [108] needed to maintain a conductive transparent back electrode.

6.3 Photoelectrochemical performance

6.3.1 Change in performance due to composition

One of the drawbacks of hematite as a photoanode is the position of its conduction band. It sits 300 mV to 400 mV below the redox potential for hydrogen evolution [38,84,109,110]. The aim of creating a solid solution with a larger bandgap material (ilmenite) was to increase the bandgap of hematite, thereby pushing the conduction band closer to or even above the H⁺/H₂ redox potential. Indeed, optical spectroscopy results (see Section 5.2.2) reveal a larger direct bandgap for ilmenite at 2.8 eV to 3.0 eV, compared to that of hematite at 2.2 eV. However, evidence for both materials also indicates an indirect gap between 2.0 eV to 2.2 eV. This is observed for the solid solutions of various compositions as well. The direct gap, on the other hand, increases with increasing ilmenite content.

The onset potential observed in a typical cyclic voltammetry (CV) curve to test PEC performance is equivalent to the sum of the flatband potential, the overpotential due to charge carrier separation and the overpotential due to slow water oxidation kinetics [82,90]. Therefore, an increase in bandgap that also pushes the conduction band edge to a higher potential results in a lower flatband potential and thus, a lower onset potential. Figure 6-14 replots the CVs for the reduced IHSS photoanodes in one graph. There is a clear shift in onset potential between the hematite sample and the other samples containing ilmenite. However, there is no successive shift to lower onset potentials for increasing ilmenite content. On that account, the shift in onset potential is most likely due to less charge carrier recombination with the addition of ilmenite and not a shift in the conduction band edge. The fact that the photocurrent
density decreases with increasing ilmenite content does suggest that the total bandgap increases. A larger bandgap requires higher energy photons for the generation of an electron-hole pair. So the larger the bandgap, the fewer photons present in the solar spectrum are capable of exciting an electron. Hence, the photocurrent density is expected to decrease with larger bandgap anodes. Of course, a lower conductivity can also cause a lower photocurrent density.

6.3.2 Change in performance due to annealing

In literature, the performance of hematite photoanodes has been shown to improve with the addition of donor dopants, which increase the charge carrier density \[43,50,52,93,111,112\]. The thin film conductivity analysis in this study revealed that all IHSS compositions allow tuning of their conductivities through an anneal treatment with the exception of pure hematite. Indeed, the charge carrier densities calculated from the Mott-Schottky data are approximately equal for oxidized and reduced hematite and vary by an order and a half in magnitude for oxidized and reduced I2HSS (see
Table 5.3. The conductivity data suggested that the difference in charge carrier density should be up to five orders in magnitude for the I2HSS sample. However, sluggish kinetics limit the charge carrier densities to a smaller range, as uncovered by the anneals at 580°C with subsequent conductivity measurements (see Section 6.2.2). So by annealing the photoanodes in oxidizing conditions, their charge carrier densities are decreased. Annealing the photoanodes in reducing conditions increases the charge carrier densities and thereby enhances conductivity.

Turning to the PEC performance of these samples, the photocurrent density is indeed greater for the reduced than for the oxidized films of the I2HSS, I67HSS and the ilmenite compositions. This trend is also reflected in the quantum efficiencies at 1.5 V applied bias. As these films did not fully equilibrate during their depositions, there is no reference point for the as-deposited films in order to relate their charge carrier densities to those of the annealed films, unless they were explicitly determined. Mott-Schottky results showed that the charge carrier density of the as-deposited I2HSS photoanode is in fact even greater than that of the reduced film by an order of magnitude. The photocurrent density reached by this film is also the highest amongst the three I2HSS samples. The I33HSS photoanodes do not follow the trend and exhibit about the same photocurrent densities if reduced or oxidized. In the case of pure hematite, the reduced and oxidized photoanodes possess the same charge carrier density as apparent from Mott-Schottky results and predicted by the thin film conductivity results. However, the photocurrent density is lower for the oxidized sample. This is not well understood. The difference may be due to a difference in surface chemistry following the different annealing treatments.

Another effect of the anneals, regardless if in oxidizing or reducing atmospheres, is the shift to a lower onset potential for all compositions containing at least some ilmenite. There is evidence that this shift is due to a decrease in the charge carrier recombinations, at least for the I2HSS composition. Most likely, this is also true for the other compositions but they were not investigated in as great detail as the I2HSS samples. The IPCE can serve as an indicator of the expected photocurrent density.
at a given applied bias of a sample under simulated sunlight \[21\]

\[ J_{\text{solar}} = \int \text{IPCE}(\lambda) \times \Phi(\lambda) \times q \, d\lambda \quad (6.20) \]

where \( J_{\text{solar}} \) is the expected solar photocurrent density, \( \Phi \) the photon flux determined from the irradiation spectrum of the solar simulator (see Appendix A), and \( \lambda \) is the wavelength. The intensity of the monochromatic light of the IPCE setup is about two orders of magnitude lower than that of the solar simulator. Eq. \[6.20\] accounts for this change in intensity. Consequently, it is assumed that the photocurrent increases linearly with the irradiation intensity.

Figure 6-15: Current densities for 1% Ti doped hematite as a function of wavelength at a constant applied bias of 1.5 V vs. RHE calculated from the IPCE values of each sample and normalized to match the spectral irradiance of the solar simulator.

Figure 6-15 displays the expected solar photocurrent as a function of wavelength for the as-deposited, reduced and oxidized I2HSS samples. Integrating these curves between 300 nm and 650 nm results in the expected solar photocurrent density. The resulting values are listed in Table 6.2, along with the measured photocurrent densities.
Table 6.2: Current density at a constant applied bias of 1.5 V vs. RHE for 1% Ti doped hematite.

<table>
<thead>
<tr>
<th>sample</th>
<th>based on IPCE mA/cm²</th>
<th>actual from CV mA/cm²</th>
<th>percentage %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I2HSS</td>
<td>0.077</td>
<td>0.696</td>
<td>11.1</td>
</tr>
<tr>
<td>reduced I2HSS</td>
<td>0.418</td>
<td>0.638</td>
<td>65.5</td>
</tr>
<tr>
<td>oxidized I2HSS</td>
<td>0.363</td>
<td>0.521</td>
<td>69.7</td>
</tr>
</tbody>
</table>

under AM1.5 irradiation. A percentage of the expected/actual photocurrent density is provided for easier comparison.

The actual photocurrent density is much higher than the expected values based on the IPCE at 1.5 V applied bias, especially in the case of the as-deposited I2HSS photoanode (Table 6.2). Therefore, the increase in photocurrent density with the irradiance is not linear, but superlinear. Such behavior is typical when the photoanode performance is limited primarily by charge carrier recombination at low light intensities [21][113]. Either the photoanode's performance suffers from surface or interface traps that must first be filled prior to charges being separated and contributing to the water electrolysis reaction, or from charge build-up due to slow transport or transfer across an interface causing accumulation of carriers and hence, recombination.

As the expected photocurrent density is only 11% of the actual value at 1.5 V, the charge carrier recombination in the as-deposited sample is much greater than in the annealed samples with comparable values of 66% and 70%. The charge carrier density and therefore the position of the Fermi level and also the band bending at the liquid interface in the oxidized and reduced samples are different, but both show a similar decrease in charge carrier recombination after annealing. This suggests that the recombination eliminated by the anneal may be due to improvements at the interface between the I2HSS film and the back contact. Indeed, photoanodes with a monolayer of SiO₂ or a 5 nm SnO₂ interfacial layer between the FTO back contact and hematite have demonstrated better performance, implying limitations due to the FTO/hematite interface [13][44][114][115]. Also, rapid thermal anneals improve the contact between the FTO back contact and hematite [116][117]. In this study, a de-
crease in charge carrier recombination at low light intensities was observed for the I2HSS samples after an annealing treatment, regardless if in oxidizing or reducing atmosphere.

Figure 6-16: Normalized current densities for doped hematite thin films at a constant applied bias of 1.3 V vs. RHE and chopped AM1.5 illumination. The schematic shows expected behavior when significant charge carrier recombination occurs.

Another, qualitative, indication of a reduction in charge carrier recombination by either annealing treatment is presented in Figure 6-16. Photocurrent transients are a sign of charge carrier accumulation and recombination. The typical case is depicted in Figure 6-16(a). The current attains its peak value, $i_t$, instantaneously when the photoanode is illuminated. Then, as generated photocarriers recombine, the current decays to its steady state value, $i_s$. The dark current is denoted by $i_d$. Data for the I2HSS samples show that there is a large transient for the as-deposited sample but no noticeable transients for the reduced or oxidized samples. This again demonstrated that there is a significant decrease in charge carrier recombination with either annealing treatment.

### 6.3.3 Deep traps in hematite

Mott-Schottky plots in Section 3.4.7 exhibit a change in slope, indicating a change in charge carrier density, at $\sim 0.55$ V and $\sim 0.75$ V vs. RHE for undoped hematite and
1% Ti doped hematite, respectively. In case of pure hematite, all three samples (as-deposited, reduced and oxidized) show this behavior. On the contrary, this behavior is only observed for the oxidized doped film, which possesses a charge carrier density similar to that of the oxidized and reduced undoped films and is about an order and a half lower in magnitude than the charge carrier density of the reduced I2HSS photoanode (see Table 5.3). There are two explanations for this behavior.

The first possibility is a change in charge carrier density due to the extension of the depletion width, $W$, through the hematite film at a voltage drop between 350 mV or greater across the space charge (SC). The voltage drop across SC, $V_{SC}$, is the difference between the applied potential, $\phi_A$, and the flatband potential, $\phi_{FB}$. The voltage drop where the change of slope occurs is equal for the undoped films as well as for the oxidized doped film (see Figure 5-32). The depletion width can be calculated from the following relation [21]

$$ W = \sqrt{\frac{2\epsilon_0\epsilon_r}{qN_D}} \left(\frac{\phi_{SC} - kT}{q}\right) $$  \hspace{1cm} (6.21)

There is a clear dependence of the depletion width, also known as the space charge region, on the free charge carrier concentration, in this case simply designated as the donor density, $N_D$. This relationship is depicted visually in Figure 6-17.

This phenomenon, where the depletion width extends through the film resulting in a change of slope in the Mott-Schottky plot, has previously been observed for TiO$_2$ photoanodes [118]. Figure 6-18 shows the results of this study. From the extrapolation of the two lines making up each Mott-Schottky curve, their intercept allowed one to determine the capacitance of the space charge region when the films were fully depleted. Using the equation for capacitance

$$ C = \epsilon_0\epsilon_r \frac{A}{d} $$  \hspace{1cm} (6.22)

where $A$ and $d$ are the cross sectional area of the electrode surface and the thickness of the film, respectively, one can determine the dielectric constant for thin films. This
value is expected to be constant regardless of thickness, if the depletion width extends through the semiconductor film. Indeed, an average value of 55 was determined as the dielectric constant for these thin films of anatase in this example study.

Returning to the investigation at hand, the depletion width for a 50 nm film is expected to extend through the entire film at a voltage drop of 50 mV for a charge carrier concentration of $10^{17}$ cm$^{-3}$, or at a voltage drop of 300 mV when the charge carrier concentration is $10^{18}$ cm$^{-3}$ (see Figure 6-17). At this voltage drop in the Mott-Schottky plot, a change of slope is expected and the slope at higher voltages should correspond to the charge carrier density of the back contact. The change in slope observed in this study occurs over a range of 150 mV to 350 mV in voltage drop across SC. The dielectric constant of FTO is 3 \cite{119, 120}. Based on Eq. 3.15 and the slope of the Mott-Schottky curves at higher potentials, the FTO charge carrier density can be calculated assuming that the depletion width indeed extends through the entire hematite film causing the change in slope. The results are tabulated in

**Figure 6-17:** Extension of the depletion width as a function of the voltage drop across the space charge for different charge carrier concentrations.
Table 6.3 along with the charge carrier densities determined for the films at low potentials, corresponding to the carrier concentration in the actual photoanode material. These were previously determined and copied from Table 5.3 for convenience. The calculated charge carrier concentration of FTO is in reasonable agreement with the expected charge carrier density for FTO of $4 \times 10^{20}$ cm$^{-3}$ [121,122] for all samples with the exception of the as-deposited hematite sample. No carrier density of FTO could be determined using the as-deposited and reduced I2HSS samples, as the carrier density of those films is so high that the depletion width never fully extends through these films within the range of applied bias.

Applying Eq. 6.22, one can calculate the dielectric constant for the doped and undoped hematite films using the approach as described for the TiO$_2$ example. Results are listed in Table 6.4. Only two of the four samples yield the expected result of $\epsilon_r = 80$ within error. Neither these calculations, nor those of the charge carrier densities for the FTO back contact fully support the assumption that the depletion width extends fully throughout the doped or undoped hematite films.

1The original $\sim 50$ nm as-deposited film was damaged during one of the earlier experiments and replaced with a slightly thinner as-deposited hematite film produced using the same conditions during PLD.
**Table 6.3:** Charge carrier densities of the hematite and I2HSS thin films on FTO coated quartz substrates as observed at low and high applied potentials.

<table>
<thead>
<tr>
<th>sample</th>
<th>state</th>
<th>(N_D) (low V) (\text{cm}^{-3})</th>
<th>(N_D) (high V) (\text{cm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>as-deposited</td>
<td>6.6(\times)10^{18}</td>
<td>2.3(\times)10^{21}</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>8.1(\times)10^{17}</td>
<td>5.0(\times)10^{20}</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>6.1(\times)10^{17}</td>
<td>4.4(\times)10^{20}</td>
</tr>
<tr>
<td>I2HSS</td>
<td>as-deposited</td>
<td>2.3(\times)10^{20}</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>1.8(\times)10^{19}</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>5.6(\times)10^{17}</td>
<td>5.6(\times)10^{20}</td>
</tr>
</tbody>
</table>

**Table 6.4:** Dielectric constant of hematite calculated from the Mott-Schottky data and the measured thickness of the thin films.

<table>
<thead>
<tr>
<th>sample</th>
<th>state</th>
<th>((A/C)^2) (F^{-2}\text{cm}^4)</th>
<th>thickness (\text{nm})</th>
<th>(\epsilon_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite</td>
<td>as-deposited</td>
<td>9.0(\times)10^{10}</td>
<td>29 ± 4</td>
<td>109 ± 15</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>4.9(\times)10^{11}</td>
<td>48 ± 10</td>
<td>77 ± 16</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>7.3(\times)10^{11}</td>
<td>50 ± 7</td>
<td>66 ± 9</td>
</tr>
<tr>
<td>I2HSS</td>
<td>as-deposited</td>
<td>NA</td>
<td>57 ± 10</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>NA</td>
<td>58 ± 4</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>7.8(\times)10^{11}</td>
<td>58 ± 5</td>
<td>74 ± 6</td>
</tr>
</tbody>
</table>

A second explanation for the change in slope in the Mott-Schottky plots is the presence of deep levels in the bandgap of hematite, in addition to the donor levels. Schematics to help understand the band bending in the semiconductor are presented in Figure 6-19. In the simple case, where no deep states are present, the band bending increases with higher applied potentials and the depletion width extends further into the semiconductor, as dictated by Eq. 6.21 (Figure 6-19(a) and 6-19(b)). When deep states are present, the picture becomes more complicated. As long as the applied bias is small enough and the Fermi energy remains above the deep states, the material behaves as before (Figure 6-19(c)). However, as soon as the applied bias is high enough to push the Fermi energy below the deep levels at the semiconductor/electrolyte interface, the deep states will also become depleted and their charge will contribute to the space charge (Figure 6-19(d)). Consequently, the band bending will be steeper and the depletion width shorter compared to the case where no deep levels are present.
Figure 6-19: Schematics of the band bending in the semiconducting photoanode at the liquid interface with and without the presence of deep trap states at low and high applied potentials.

When scenario 6-19(d) applies, the empty deep levels serve as traps for electrons, which results in charge carrier recombination within the space charge region. Normally, due to the electric field, charges are effectively separated in this region. It is already known that enhanced preferential band bending in the semiconductor did not improve PEC performance based on the experimental results of the homojunction photoanodes (see Section 5.4.3). Indeed, early literature also ascribes the change in slope in Mott-Schottky results for bulk hematite doped with titanium, niobium, or zirconium to a deep level in the hematite bandgap. These studies con-
clude a deep level 0.4 V to 0.7 V below the conduction band of hematite. In addition, Goossens developed a model explaining a change in slope in the Mott-Schottky plot based on the presence of deep donors in the semiconductor [126].

Figure 6-20: In-situ optical transmission of the oxidized hematite thin film as a function of applied bias measured in the PEC cell.

In order to validate the existence of deep levels, an in-situ optical transmission experiment was devised in which the transmission through the PEC cell was monitored as a function of applied potential. The expectation was that a change of absorption would indicate when the applied bias was large enough to push the Fermi energy below the deep levels pinned at the semiconductor/liquid interface. As the Fermi energy moves through the deep states, they become unoccupied allowing the excitation of electrons from the valence band into these levels. A detailed description of the experimental setup can be found in Appendix E.

Figure 6-20 shows the results for the oxidized hematite sample. Transmission is displayed as a function of wavelength and applied potential vs. RHE. The reference was taken as the transmission at open circuit potential. There is a clear absorption edge at $\sim 550 \text{ mV}$, corresponding to the voltage at which the change in slope is observed.
in the Mott-Schottky data for this sample. Below 560 nm, absorption corresponds to excitation of an electron into the conduction band of hematite with a direct bandgap of 2.2 eV. Above that, absorption must be due to a sub-bandgap excitation into a deep level only possible at an applied bias of 0.55 V or greater. A small absorption peak appears around 800 nm, which corresponds to a transition requiring 1.55 eV in energy. Therefore, this data suggests that the deep levels sit 0.65 V below the conduction band of hematite as depicted in Figure 6-21. Further investigation is required into the nature and lifetime of these deep levels in order to characterize them further and understand their origin.

**Figure 6-21:** Schematic of the energy levels of the oxidized hematite photoanode.
Chapter 7

Summary and Future Work

7.1 Summary

This study was comprised of four components:

1. The fabrication of bulk and thin film samples of the ilmenite hematite solid solution system and their physical characterization.

2. Establishing the defect chemistry of doped hematite bulk samples in order to control charge carrier density dictating the conductivity.

3. Characterization of the thin film conductivity of epitaxially grown films serving as a model system.

4. Fabrication and testing of ilmenite hematite solid solution photoanodes with tuned conductivities for better photoelectrochemical performance.
Using traditional ceramic processing, bulk samples of the ilmenite hematite solid solution (IHSS) system were fabricated. X-ray diffraction confirmed that resulting targets and pellets were homogeneous mixtures of their constituents. The targets were used to deposit thin films by pulse laser deposition onto two substrates: C-plane cut single crystal sapphire and fluorine doped tin oxide coated quartz slides. In both cases optical spectroscopy revealed that the direct bandgap increases from 2.2 eV for pure hematite to 3.0 eV for pure ilmenite with increasing ilmenite concentrations. On the other hand, there remained evidence of an indirect bandgap for all compositions between 2.0 eV and 2.2 eV. The conduction band of ilmenite is comprised of both iron and titanium 3d levels. As the direct gap for ilmenite is greater than that for hematite, the 3d levels of titanium presumably lie above those of iron. While the density of states of the iron level is smaller in ilmenite than in hematite, iron levels are present and provide the lowest energy level for electrons in the conduction band. This is in line with a nominal change in the indirect gap as well as the Fe$^{2+}$ and Ti$^{4+}$ oxidation states in ilmenite.

A defect chemical model was derived considering donor dopants as well as oxygen and iron vacancies as lattice defects. The model predicts the charge carrier densities in addition to the electron and hole concentrations as a function of oxygen partial pressure at a given temperature. DC conductivity measurements on bulk samples of various compositions of the IHSS system confirmed the predicted behavior by the model and enabled establishing key thermodynamic parameters characterizing this system. For hematite, the enthalpy of reduction was determined as 5.4 eV and that of the Schottky defect formation as 13.4 eV by a first order approximation. The activation energy in the intrinsic regime was determined as 1.0 eV corresponding to an energy bandgap of 2.0 eV as is widely accepted for hematite. In addition, the electron mobility in hematite was calculated as 0.10 cm$^2$/Vs and it did not exhibit a temperature dependence.

Impedance spectroscopy allowed the electrical characterization of the IHSS thin films. Similarly to the bulk samples, pure hematite exhibited no measurable non-stoichiometry,
i.e. its conductivity remained unchanged even when annealing the film in different oxygen partial pressures, while doped hematite and samples with higher ilmenite concentrations exhibited a conductivity greatly dependent on the atmospheric oxygen content during annealing. In fact, hematite’s room temperature conductivity could be increased by as much as nine orders of magnitude by doping with a donor such as Ti. Furthermore, controlling the non-stoichiometry of Ti-doped hematite by annealing the film in different atmospheres enabled tuning donor doped hematite’s conductivity by up to five orders of magnitude. The extrinsic regime of the epitaxial thin film occurred between 600°C and 400°C. From the 1% Ti doped hematite film, the electron mobility was determined as 0.01 cm²/Vs in this case.

Finally, the photoelectrochemical performance of the various compositions of the IHSS system was characterized by measurement of photocurrent density as a function of applied potential as well as by quantum efficiency. Performance of the hematite photoanode improved five-fold with the addition of titanium as a donor. The sample containing 33% ilmenite performed nearly as well. A Mott-Schottky analysis revealed that the charge carrier density is indeed changed by anneals in different oxygen partial pressures for all samples except hematite and generally, those samples with higher conductivity exhibit higher photocurrents. Pure hematite as well as doped hematite annealed in oxidizing conditions show evidence of a deep trap state 0.65 V below the conduction band presumably providing recombination sites within the space charge region. An optical signature of these traps became visible through an in-situ UV-vis transmission experiment.

### 7.2 Future work

**Near term**

Bulk sample conductivities followed the trends expected based on the derived defect chemical model, thereby validating the model. They allowed the determination of
several activation energies and revealed that the hole mobility is negligible compared to the electron mobility for the samples and temperatures studied. In order to determine the equilibrium constants fully, i.e. establishing the exact values of their pre-exponential factors, either the charge carrier concentration or the mobility must be measured in situ, e.g. by high temperature thermopower measurements. This will allow the explicit determination of $K_i$ in the Regime II(i) for solid solutions with higher ilmenite content and the other equilibrium constant pre-exponentials will follow from the conductivity data.

For the doped hematite sample, I2HSS, the mobility is known and the exact values of the $K_{Ox}$ pre-exponential and activation energy could be determined by allowing the system to equilibrate at lower temperatures. Kinetics are too slow to observe this process for the bulk materials, but nanomaterials enable access to this information. By measuring the conductivity of the thin films at intermediate temperatures as a function of oxygen partial pressure, one should observe a decreasing conductivity with increasing $pO_2$. With the derivation for the electron density in the transition region between electronic and ionic compensation of the donors (see Appendix C.1), one can then explicitly determine the equilibrium constants for doped hematite.

Mott-Schottky analysis revealed the charge carrier densities for various samples after different anneal treatments. The as-deposited I2HSS sample exhibited the highest photocurrent density of all samples tested and had the highest charge carrier density. Annealing in oxidizing and reducing conditions resulted in a reduced overpotential, but the charge carrier density was decreased in both cases and so was the photocurrent density. One should anneal this composition at even more reducing conditions to increase the charge carrier concentration or at least maintain the concentration after PLD deposition. Then, testing this sample could show the lower onset potential as well as the higher photocurrent density.

In addition, Mott-Schottky analysis of the pure hematite films and the oxidized IHSS film showed a change of charge carrier density at a certain applied potential. This phenomenon was attributed to the existence of trap states in the bandgap of hematite.
In order to confirm this hypothesis, this analysis should be repeated with films of the same material but of varying thickness. If this behavior is independent of thickness, the existence of traps is validated. Thickness dependence would indicate depletion of the entire film at the point of the slope change (Section 6.3.3 presents a more detailed explanation).

XRD and XPS of the annealed bulk samples with higher ilmenite concentration show that iron segregates to the surface after extended exposures to high temperatures, at least in reducing environments. It would be interesting to investigate if this also occurs in the thin films used as photoanodes. For this, the film thickness will have to be increased. Before and after annealing, one can perform XPS on these samples to observe any changes in surface chemistry. Also, absorption spectroscopy is relevant as the absorption spectrum of iron varies with changes in oxidation states. Then, one can etch the surface after the annealing treatment to remove the iron-rich layer, observing the PEC performance before and after as well as the absorption post etch again.

**Long term**

Other continuations of this study that require longer time periods are the preparation of single crystal photoanodes and the development of a more stable transparent conductive oxide (TCO) enabling higher temperature anneals of the photoanodes with this material as a back contact. The former is of interest as hematite possesses a hexagonal structure and single crystals would allow observation of the effect of anisotropy on conductivity as well as reaction rates on different surfaces. In addition, a truly smooth surface could be fabricated in order to determine the true benefit of nanostructures and/or the detrimental effect of high-angle grain boundaries. Presumably, there is a trade-off between a perfect structure and a larger active area. The latter undertaking would be a revolution in itself. Moreover, a high temperature sustaining TCO would enable annealing the thin films at temperatures well above 580°C without introducing an extraneous series resistance by damaging the back contact.
This would enhance kinetics exponentially allowing for higher charge carrier densities in these films.
Appendix A

Irradiance of the solar simulator

![Power density spectra of the simulated sunlight reaching the photoanode in the PEC cell compared to the AM1.5G standard.](image)

**Figure A-1:** Power density spectra of the simulated sunlight reaching the photoanode in the PEC cell compared to the AM1.5G standard.

To properly measure the performance of a PEC device or a photoanode, it is necessary to measure its properties under sunlight. As that is difficult inside a laboratory, one resorts to a solar simulator. The simulator used in this study, a Super solar simulator from Wacom Electric Co., Ltd. (Otone, Saitama, Japan) with Xenon lamps, has a
spectral irradiance matching the AM1.5G spectrum. For the AM1.5G standard published by the American Society for Testing and Materials (ASTM-G173-03) the total integrated intensity is 1000 W/m² and matches the irradiance of direct and indirect sunlight that has passed through 1.5 times the thickness of the earth’s atmosphere and is incident on a 37° tilted, south facing surface averaged over the area of the United States of America over one year [127].

Figure A-2: Integrated spectral irradiance of the AM1.5G standard between 300 nm and 600 nm.

The power density spectrum of the light reaching a photoanode sample in the PEC cell (as described in section 3.4) was measured with an Ocean Optics (Dunedin, FL) USB2000+ Fiber Optic Spectrometer. The cell was placed in front of the spectrometer and both orientations, front and back illumination, were measured and compared to the AM1.5G standard (Figure A-1). The spectra match very well below 600 nm, where absorption of hematite or other compositions of the IHSS system becomes relevant. When integrated between 300 nm and 600 nm, the intensity of the AM1.5G irradiance is 337 W/m² (Figure A-2). The values achieved for front and back illumination of the PEC cell were 337 W/m² and 315 W/m², respectively. The slight decrease in intensity
for the back illumination may be due to light scattering in the R_2 ring (Figure 3-9), which could not be further improved.
Appendix B

Surface morphology characterization

B.1 Undoped and 1% Ti doped hematite thin films grown epitaxially on single crystalline sapphire

Figure B-1 presents images of the surfaces of undoped and 1% Ti doped films grown for electrical characterization. High resolution XRD patterns provided evidence that these films grew epitaxially on the sapphire substrates (see Section 5.1.3). Scanning electron microscopy (SEM) reveals that the surfaces of these films are not perfectly flat, but exhibit some morphology. The low magnification image of the undoped hematite film (Figure B-1(a)) shows a smooth surface with pores of typically hundreds of nm in diameter, as also confirmed in the image at higher magnification shown in Figure B-1(b) as well as some debris. Atomic force microscopy (AFM) confirmed that these near surface pores lead to height variations of approximately 10 nm (Figure B-2(a)). These features can be due to droplets of material that did not fully coalesce on the surface during PLD. Figures B-1(c) and B-1(d) show SEM images for the 1% Ti doped hematite (I2HSS) film at low and high magnification, respectively. In this case, the surface layer appears to be more coalesced than in the case of the undoped.
material but otherwise, the observations are similar. In case of the doped film, AFM revealed that the height variations along a cross-section are twice as large as in the case for the undoped film (Figure B-2(b)). However, the doped film is also 50 nm thicker.

Figure B-3(a) presents an AFM image of the surface of the epitaxial, undoped hematite thin film based on phase angle data. Non-coalesced droplets in the outermost surface layer of approximately 100 nm are visible. Figure B-3(b) shows the AFM data for the surface of the Ti doped hematite film grown epitaxially. The features are similar to those of the undoped film, but roughly twice as large again. Analysis of the AFM data for roughness resulted in root mean square values of 2.19 nm and 7.08 nm for the undoped and the doped film, respectively.
Figure B-2: Cross-sectional profiles of epitaxial $\alpha$-Fe$_2$O$_3$ thin films on single crystalline sapphire.

![Cross-sectional profiles of epitaxial $\alpha$-Fe$_2$O$_3$ thin films on single crystalline sapphire.](image)

(a) undoped  
(b) 1at.% Ti doped

Figure B-3: AFM phase angle images depicting the surface morphologies of epitaxial $\alpha$-Fe$_2$O$_3$ thin films on single crystalline sapphire.

![AFM phase angle images depicting the surface morphologies of epitaxial $\alpha$-Fe$_2$O$_3$ thin films on single crystalline sapphire.](image)

(a) undoped  
(b) 1at.% Ti doped
B.2 Undoped and 1% Ti doped hematite thin film photoanodes grown on FTO

The surface morphology of the films grown for PEC testing were also subjected to AFM analysis. Table B.1 lists the results. Roughness values are higher than expected. This can be explained by the surface morphology of the substrates. In fact, the FTO does not form a smooth layer on the quartz but exhibits a morphology as depicted in Figure B-4. The root mean square of the roughness for this survey area is 22.15 nm. The roughness determined for the undoped hematite thin films are in close agreement with that of the FTO coating suggesting uniform, conformal coverage by the hematite film. Annealing these films did not cause a significant change in roughness. On the other hand, the doped material, even though deposited under the same conditions, is nearly perfectly flat with a roughness of 0.56 nm. After annealing in either reducing or oxidizing conditions, the roughness increases significantly.

Figure B-5 shows the surface profile of 1 µm × 1 µm survey areas for the different films. The results include data for undoped and doped hematite thin films as they were deposited, after oxidation and after reduction. In line with the roughness analysis, all hematite films, regardless of post-deposition treatment, exhibit similar surface morphologies as the FTO and further support conformal coverage. On the other hand, the doped material appears to be blanketing the FTO (Figure B-5(b)) during

<table>
<thead>
<tr>
<th>sample</th>
<th>state</th>
<th>roughness nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO</td>
<td>as received</td>
<td>22.15</td>
</tr>
<tr>
<td>hematite</td>
<td>as deposited</td>
<td>23.82</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>22.12</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>22.30</td>
</tr>
<tr>
<td>I2HSS</td>
<td>as deposited</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>11.44</td>
</tr>
<tr>
<td></td>
<td>oxidized</td>
<td>15.76</td>
</tr>
</tbody>
</table>
PLD deposition, resulting in a very smooth surface. Annealing then results in better conformation of the film material to the substrate. This is in agreement with a lower onset potential for the annealed films of the doped material due to a better contact with the FTO (see Section 6.3.2). While not perfectly flat, these films clearly do not exhibit a morphology with a surface area anywhere as large as that of purposefully nanostructured photoanodes such as the cauliflower structures grown by Grätzel et al. [49].
Figure B-5: AFM images depicting the surface morphologies of $\alpha$-Fe$_2$O$_3$ thin films deposited by PLD onto FTO coated quartz.
Appendix C

Solutions for the electron density in transition regions between adjacent Brouwer regimes

C.1 Electron concentration as a function of $T$, $pO_2$ in the transition region between Regime II and III: extrinsic case

In a reducing atmosphere, the Ti donor is electronically compensated. Therefore the electron concentration, $n$, is not temperature or $pO_2$ dependent (Regime II, see Table 4.2 and Figure 4.2). At higher oxygen partial pressures, the donor is compensated ionically by iron vacancies. As a consequence, the electron concentration becomes dependent on $pO_2$ and temperature (Regime III). The Brouwer approximations, $n = \left[ Ti^*_{Fe} \right]$ for Regime II and $3\left[ V''_{Fe} \right] = \left[ Ti^*_{Fe} \right]$ for Regime III, result in an abrupt transition at the $pO_2$ boundary between these regimes. However, this transition is not abrupt in reality and in order to fit data in this transition region, it is necessary to solve for the electron concentration as a function of $K_i$, $K_{Ox}$, Ti content and $pO_2$ governed by
the neutrality condition

\[ n + 3[V_{Fe}'''] = [T_{iFe}] \]  \hspace{1cm} (C.1)

Using the mass action relation of the oxidation reaction (Eq. 4.8), the \( np \) product (Eq. 4.2) and the neutrality condition for the transition regime, one arrives at the following expression

\[ An^3 + n - [T_{iFe}] = 0 \]  \hspace{1cm} (C.2)

where

\[ A = 3\sqrt{K_{Ox}} \frac{3}{K_i^3} p_2^{3/2} \]  \hspace{1cm} (C.3)

Solving this equation for \( n \) results in the solution for the electron concentration in the transition region for the extrinsic case

\[ n = \frac{1}{6} \left( \frac{12^{1/3} \left( 9[T_{iFe}'] \sqrt{A} + \sqrt{3} \sqrt{27A[T_{iFe}']^2 + 4} \right)^{2/3} - 12^{1/3}}{\sqrt{A} \left( 9[T_{iFe}'] \sqrt{A} + \sqrt{3} \sqrt{27A[T_{iFe}']^2 + 4} \right)^{1/3}} \right) \]  \hspace{1cm} (C.4)

This solution is depicted graphically in Figure C-1(a). In the limit, \( n \) approaches \([T_{iFe}']\), \( 4.0 \times 10^{20} \text{ cm}^{-3} \), for low pO\(_2\) as expected for a complete transition into Regime II. The limit for high pO\(_2\) approaches the solution for \( n \) in Regime III as listed in Table 4.2.

**C.2 Electron concentration as a function of T, pO\(_2\) in the transition region between Regime II(i) and III(i): intrinsic case**

One can also solve for the electron concentration in the transition region between Regime II(i) and Regime III(i) for the intrinsic case. Here, the electron and hole concentrations are equal in reducing pO\(_2\). They are pO\(_2\) independent but exponentially
dependent on temperature as dictated by the \( np \) product (Eq. 4.2). In oxidizing conditions, the electron concentration decreases with increasing \( pO_2 \) and is dependent on temperature again. Proceeding as for the extrinsic case, one can adjust the neutrality condition to reflect the transition region for the intrinsic case

\[
n + 3 \left[ V_{Fe}''' \right] = p \tag{C.5}
\]

Substituting for \( \left[ V_{Fe}''' \right] \) using the oxidation mass action law (Eq. 4.8) and for \( p \) using the \( np \) product (Eq. 4.2), one arrives at

\[
An^4 + n^2 - K_i = 0 \tag{C.6}
\]

where \( A \) is the same as above (Eq. C.3). Solving for \( n \) results in a solution for the electron concentration in the transition regime of

\[
n = \frac{1}{2} \frac{\sqrt{2\sqrt{-1 + \sqrt{4AK_i + 1}}} - 1}{\sqrt{A}} \tag{C.7}
\]

Substituting for \( A \) results in

\[
n = \frac{1}{6} \sqrt{6K_i \sqrt{-K_i + \sqrt{12\sqrt{K_{Ox}P_{O_2}^{3/8}} + K_i^2}}} \frac{K_i}{K_{Ox}^{1/4}P_{O_2}^{3/8}} \tag{C.8}
\]

This solution for \( n \) for the intrinsic case is depicted graphically in Figure C-1(b). In the limit of low \( pO_2 \), the solution approaches a constant as expected for Regime II(i). In the limit of high \( pO_2 \), the solution exhibits a \(-3/16\) power law in accordance with the electron concentration in Regime III(i).
C.3 Electron concentration as a function of $T$, $pO_2$
in a transition region when the donor concentration is of the order of intrinsic compensation

In this case, the transition region still describes the case for which the electron concentration remains independent of $pO_2$ at low partial pressures but exhibits a power law dependence on $pO_2$ at high partial pressures. However, here, the donor concentration of the material is of the same order as the electron and hole concentration for the intrinsic case and therefore, the compensation mechanisms rival each other. Thus, the complete neutrality equation includes four terms for this scenario

$$n + 3\left[V_{Fe}''\right] = p + \left[T_{Fe}^*\right]$$

(C.9)

Figure C-1: Solutions for the electron concentration. (a) Extrinsic case (violet). A $-1/4$ power law dependence on $pO_2$ is indicated (black). (b) Intrinsic case (blue) and the case where intrinsic and extrinsic compensation rival each other (red). A $-3/16$ power law dependence on $pO_2$ is indicated (green).
As before, one substitutes for \([V^\prime\prime\prime_{Fe}]\) and \(p\) using the oxidation mass action law (Eq. 4.8) and the \(np\) product (Eq. 4.2) in order to arrive at an equation in terms of \(K_i\), \(K_{Ox}\), \([Ti_{Fe}^\ast]\) and \(pO_2\), where \(n\) is the only unknown

\[
An^4 + n^2 - [Ti_{Fe}^\ast] n - K_i = 0 \tag{C.10}
\]

\(A\) is the same as above and given by Eq. C.3. The solution to this equation is too complex for it to be included here, but it can be determined analytically by mathematical software such as Maple 18 (Maplesoft, Waterloo Maple Inc.). The result is plotted in Figure C-1(b) along with the solution for the purely intrinsic case. Again, the limits behave as expected based on the adjacent regimes.
In Section 6.1.3, the phase stability of all IHSS samples after a heat treatment in N\textsubscript{2} atmosphere was confirmed. X-ray diffraction scans on the samples provided evidence of the expected phase, but also indicated the segregation of iron to the surface of these bulk samples. In order to test this hypothesis, X-ray photoelectron spectroscopy (XPS), using a PHI VersaProbe II Scanning XPS Microprobe (Physical Electronics, 

Figure D-1: Two pieces of the Fe\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{3} pellet on the XPS sample mount. The top piece is as-fabricated. The bottom piece had been annealed at 1000 °C for 24 h in pure N\textsubscript{2}. Positions 1, 2 and 3 indicate where XPS spectra were measured.
Inc., Chanhassen, MN), was performed to analyze the surface composition of the I67HSS (Fe<sub>1.33</sub>Ti<sub>0.67</sub>O<sub>3</sub>) bulk sample before and after the heat treatment. Figure D-1 shows the two pieces of the I67HSS pellet that were examined. The surface appears uniform for the untouched sample. During the heat treatment, the sample had changed in color and the surface is no longer uniform. An XPS spectrum was taken at two different locations for the treated sample.

![Figure D-2: XPS survey scans for the as-fabricated (1) and the annealed (2 and 3) samples. Peaks are labeled with their corresponding element and orbital.](image)

Figure D-2 shows the XPS spectrum for the as-fabricated sample and two spectra for the annealed I67HSS sample. Expected peaks for iron, titanium and oxygen are all present in the scan for the as-fabricated sample. In addition, the spectra reveals a large amount of carbon contamination on the surface as well as traces of sodium, calcium, nitrogen, silicon and phosphorus. The two spectra of the annealed sample show a significant reduction in the carbon contamination. Also, the intensity of the titanium peak decreases significantly. Especially at position 2, the titanium peak is no longer visible at this scale. Table D.1 lists the relative amounts of iron and titanium at the surface based on the data displayed in Figure D-2. Based on the composition of the I67HSS sample, Fe<sub>1.33</sub>Ti<sub>0.67</sub>O<sub>3</sub>, a ratio of 2:1 Fe:Ti is expected at the surface if...
Table D.1: Atomic concentration ratios based on survey spectra on the Fe$_{1.33}$Ti$_{0.67}$O$_3$ samples

<table>
<thead>
<tr>
<th>sample</th>
<th>position</th>
<th>Fe2p3</th>
<th>Ti2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>expected</td>
<td></td>
<td>67</td>
<td>33</td>
</tr>
<tr>
<td>as-fabricated</td>
<td>1</td>
<td>57.46</td>
<td>42.54</td>
</tr>
<tr>
<td>post N$_2$ anneal</td>
<td>2</td>
<td>95.15</td>
<td>4.85</td>
</tr>
<tr>
<td>post N$_2$ anneal</td>
<td>3</td>
<td>74.80</td>
<td>25.20</td>
</tr>
</tbody>
</table>

Iron and titanium are distributed evenly throughout the sample. The as-fabricated exhibits an Fe:Ti ratio near the expected values, whereas the annealed samples show a much higher iron content at the surface. This iron surface enrichment is not uniform as indicated by the two survey locations for the annealed sample.

High resolution scans of the carbon, oxygen, iron and titanium peaks were performed for both samples at positions 1 and 2. Figure D-3 displays the results. The peak intensities have been normalized, such that they are no longer an indicator for the concentration of the different elements. The results were analyzed for relative concen-

Figure D-3: High resolution XPS data of the C1s, O1s, Fe2p3 and Ti2p peaks of the untreated (red) and annealed (blue, Position 2) Fe$_{1.33}$Ti$_{0.67}$O$_3$ samples.
trations and these are presented in Table D.2. As significant carbon contamination is present on the surface of both samples and the carbon peak position is well established, the results were charge corrected to shift the C1s peak to 284.8 eV. The shapes of the Fe2p and the Ti2p peaks are nearly identical for both samples. There is a shift for the titanium peak of the annealed sample with respect to the as-fabricated sample, which remains unexplained. The data is also much noisier due to the smaller titanium content at the surface of the annealed sample. The very similar shape of those peaks suggests that the chemical environment is nearly the same around the iron and the titanium ions between the as-fabricated and the annealed sample. This makes sense, considering that the metal cations both sit in the octahedral sites of closed packed oxygen planes and therefore, are surrounded by oxygen ions. A difference in peak shape is observed for the O1s peak, indicating that its chemical environment is different between the two samples. This is in agreement with the change in carbon concentration and the change in iron to titanium ratio at the surface.

Table D.2: Atomic concentration ratios based on high resolution data of the Fe$_{1.33}$Ti$_{0.67}$O$_3$ samples

<table>
<thead>
<tr>
<th>sample</th>
<th>position</th>
<th>C1s (%)</th>
<th>O1s (%)</th>
<th>Fe2p (%)</th>
<th>Ti2p (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-fabricated</td>
<td>1</td>
<td>46.37</td>
<td>41.50</td>
<td>8.33</td>
<td>3.80</td>
</tr>
<tr>
<td>post N$_2$ anneal</td>
<td>2</td>
<td>30.21</td>
<td>55.57</td>
<td>13.65</td>
<td>0.58</td>
</tr>
<tr>
<td>expected</td>
<td></td>
<td>67</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-fabricated</td>
<td>1</td>
<td>68.66</td>
<td>31.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>post N$_2$ anneal</td>
<td>2</td>
<td>95.95</td>
<td>4.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table D.2 lists the atomic ratios for the four species for the as-fabricated and the annealed sample (at position 2). Considering only the ratio between the iron and titanium concentration at the surface, the results are in good agreement with the expected 2:1 ratio for the untreated sample. However, after heating the sample at 1000°C for 24 h in N$_2$, a significant increase in iron is noted at the surface. Therefore, iron clearly segregates to the surface of IHSS bulk samples when held at elevated temperatures, at least in reducing conditions, for extended periods of time.
Appendix E

In-situ electrochemical UV-Vis spectroscopy

Figure E-1: Illustration of the experimental setup to measure the optical transmission through the PEC cell while applying a bias (Courtesy of Fatwa Abdi).

Bias dependent absorption of the photoanode was determined by in-situ electrochemical UV-Vis spectroscopy as shown in Figure E-1. A Mikropack (Ostfildern, Germany) DH-2000-BAL halogen lamp served as the light source and an Ocean Optics (Dunedin, FL) 200 µm SR fiber split the beam in order to create a reference. A Mikropack fiber optic FOS-2x2-TTL dual switch allowed toggling the signal between the cell and the
reference and an Ocean Optics Maya 2000 pro spectrometer measured the spectra continuously, while the PEC cell was connected to the 273A potentiostat and operated by computer as already explained in detail above.

The spectrum of the beam passing through the cell was measured between 500 nm to 900 nm with an integration time of 100 ms at a constant applied bias. Immediately after, the reference spectrum was measured over the same wavelength range with an integration time of only 13 ms as its intensity was much greater. This procedure was repeated three times for a given potential. The applied bias was increased by 50 mV between the flatband potential (typically between 0.2 V to 0.4 V) for the given photoanode and 1.4 V.
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