The nanostructure of hydrogenated amorphous silicon, examined by means of thermal annealing and light soaking

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MASTER OF SCIENCE THESIS

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Cover photo: FTPS measurement of a solar cell being soaked with blue light.
Abstract

Photovoltaic energy is one of the key components of a sustainable energy future. While the market is currently dominated by crystalline silicon solar modules, thin-film silicon technology holds the promise of a cheap, resource-efficient and versatile alternative. The major drawback of thin-film silicon PV is its relatively low conversion efficiency, in part caused by the metastable defect phenomenon known as the Staebler-Wronski effect. To fully optimize the potential of thin-film silicon solar cells, a thorough understanding of hydrogenated amorphous silicon (a-Si:H) is required. To this end, an experiment is designed in which the effects of thermal annealing and light soaking on various material properties of a-Si:H are determined.

Sets of p-i-n solar cells are deposited on Asahi VU substrates and sets of intrinsic a-Si:H films are deposited on Corning Eagle XG glass and on n-type c-Si wafers. The intrinsic layer of the solar cells and the films are deposited using hydrogen-to-silane flow rate ratios of 0, 2.5, 5, 7.5 and 10. The solar cells and films are annealed in vacuum for one hour at a time at temperatures increasing from 25 °C to 500 °C. In between annealing steps, measurements are performed using the following techniques and methods: Fourier transform photocurrent spectroscopy (FTPS), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, reflectance/transmittance (RT), external quantum efficiency and solar cell external parameter determination. A separate set of solar cells and films is light soaked in a degradation chamber at 25 °C with a light intensity of 1 kW/m² and an AM1.5 spectrum. At 0, 1, 10, 100 and 1000 hours of cumulative light soaking time, the same measurements as during the annealing experiment are performed (excluding FTIR and Raman spectroscopy). Additionally, the solar cells are light soaked in-situ in the FTPS setup using blue and white light with an intensity of 1 kW/m². Light soaking times increase exponentially and range from 0.5 s to approximately 200 h. FTPS measurements are performed after each step.

Analysis of the FTIR results suggests that divacancies agglomerate into larger vacancies and nanosized voids during annealing, which is supported by the evolution of the bandgap obtained from RT measurements. Silicon-hydrogen bonds start breaking at around 300 °C, at which temperature FTPS data show that the subgap absorption starts to increase, suggesting that defects are created in the form of un- or underpassivated vacancies and nanosized voids. Analysis of the FTPS data also reveals that the subgap absorption coefficient spectrum con-
sists of at least 4 distributions, implying that the isolated dangling bond (which results in
two defect distributions) cannot be the sole type of defect in a-Si:H.

Analysis of the light soaking FTPS data reveals metastable defect creation with two distinct
regimes: a fast regime ($\text{defect creation } \propto t^{\beta}$ with $\beta = 0.4 - 0.9$) at timescales ranging from
several hours to several days, and a slow regime ($\beta = 0.1 - 0.2$) at timescales ranging from days
to weeks. This finding contradicts the commonly assumed single value of $\beta = \frac{1}{3}$, associated
with the isolated dangling bond as sole type of metastable defect.

The combined results strongly support a view of the nanostructure of a-Si:H, in which unpas-
sivated divacancies and nanosized voids contribute significantly to metastable defect creation.

Performance changes due to light soaking using different wavelengths of a-Si:H solar cells
with absorber layers deposited using different hydrogen-to-silane gas flow rate ratios have
been observed using FTPS. These observations are correlated to the external parameters
of the devices. It is suggested that the fitted subgap distributions are linked spatially or
energetically to particular defect entities. This highlights the potential of FTPS for monitoring
metastability effects in solar cells.
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Preface

This report marks the end of my Master’s thesis project conducted in the context of the Sustainable Energy Technology program at Delft University of Technology. I started it, convinced of the necessity of working towards a sustainable future and these last few years have only reinforced that conviction. My time in the SET program has been stimulating, hectic, interesting, varied and fun, with many new things learned and people met along the way. Whatever step I take next in my professional life, I will carry these experiences with me.

I would like to thank Prof. dr. Miro Zeman, for giving the lectures which prompted me to pursue PV research and for welcoming me into the Photovoltaic Materials and Devices group. Thanks also go to Dr. Arno Smets, my project supervisor, for the guidance and support. Our discussion and whiteboard sessions never failed to provide renewed insight, clarity and focus. I am grateful for all the technical support with lab equipment I received from Stefaan Heirman and Martijn Thijssen. Thanks also go to all members of the PVMD group for providing a stimulating work environment and for generally being a great bunch of people to be around.

I am especially indebted to Jimmy Melskens, my daily supervisor, who was very much involved with all aspects of my Master’s thesis project. His patient, thorough and meticulous supervision has made sure that the work I’ve done and the report you’re reading is something I’m proud of.

Finally, I’d like to thank my friends and family for their continued support, and above all my lovely girlfriend, whose patience and support border on the supernatural.

Marc Schouten, October 25, 2013
Nomenclature

List of symbols and abbreviations

\( \alpha \) Absorption coefficient [cm\(^{-1}\)]
\( \alpha_{Si-H} \) Polarizability of Si-H bond [Cm\(^2\)V\(^{-1}\)]
\( \alpha_{Si-Si} \) Polarizability of Si-Si bond [Cm\(^2\)V\(^{-1}\)]
\( \bar{\nu} \) Wavenumber [cm\(^{-1}\)]
\( \bar{\nu}_{max} \) Folding wavenumber [cm\(^{-1}\)]
\( \beta \) Time exponent of metastable defect creation during light soaking [-]
\( \delta \) Path difference [cm]
\( \eta \) Solar cell efficiency [%]
\( \gamma \) Time exponent of metastable defect removal during annealing [-]
\( \lambda \) Wavelength [cm]
\( \mu \) Hydrogenated microcrystalline silicon
\( \phi \) Photon flux density [s\(^{-1}\)m\(^{-2}\)]
\( \phi_0 \) Incident photon flux density [s\(^{-1}\)m\(^{-2}\)]
\( \sigma \) Electrical conductivity [S/cm]
\( A_{erf} \) Intensity parameter of error function fitted to absorption coefficient spectrum [cm\(^{-1}\)] or FTPS-EQE spectrum [-]
\( B(\bar{\nu}) \) Wavenumber-dependent corrected light beam intensity in spectroscopic experiment [Wm\(^{-2}\)]
\( c_H \) Atomic hydrogen content [at.\%]
\( d \) Layer thickness [nm]
\( D^{-/0/+} \) Negative/neural/positive charge state of dangling bond
\( E^{+/0} \) Transition energy from positive to neutral charge state of dangling bond [eV]
\( E^{0/-} \) Transition energy from neutral to negative charge state of dangling bond [eV]
\( E_c \) Conduction band energy [eV]
\( E_g \) Band gap energy [eV]
E_v  Valence band energy [eV]
E_{a1}  Bandgap energy at which absorption coefficient is $10^4$ cm$^{-1}$
E_{mob}  Mobility bandgap energy [eV]
E_{ph}  Photon energy [eV]
f_0  Modulation frequency [Hz]
$H(\bar{\nu})$  Wavelength-dependent experimental setup correction factor [-]
I  Intensity of light beam in spectroscopic experiment [Wm$^{-2}$]
i  Integrated absorption strength
$I_{SC}$  Short-circuit current [A]
$J_{SC}$  Short-circuit current density [Am$^{-2}$]
m_{Si}  Mass of Si-atom [g]
n  Refractive index [-]
n_{\infty}  Refractive index for $\lambda \to \infty$ [-]
$N_e$  Number of electrons collected from a solar cell
$N_{ph}$  Number of incident photons onto a solar cell
$P_{erf}$  Energy position of error function fitted to absorption coefficient of FTPS-EQE spectrum [eV]
$P_{in}$  Input power [W]
R  Hydrogen dilution defined as $\frac{[H_2]}{[SiH_4]}$ [-]
$R^*$  Nanostructure parameter defined as $\frac{r_{HSM}}{r_{LSM} + r_{HSM}}$ [-]
$R_s$  Series resistance [Ω]
$R_{sh}$  Shunt resistance [Ω]
t  Time [s]
t_a  Annealing time [s]
t_s  Light soaking time [s]
v  Mirror speed [cm/s]
(rf) PE-CVD  (Radio-frequency) plasma-enhanced chemical vapor deposition
a-Si:H  Hydrogenated amorphous silicon
c-Si  Crystalline silicon
CIGS  Copper indium gallium selenide
CPM  Constant photocurrent method
CRN  Continuous random network
DB  Dangling bond
DNHV  Disordered network with hydrogenated vacancies
DOS  Density of states
DPM  Defect-pool model
DTGS  Deuterated triglycerine sulphate
DV  Divacancy
EQE  External quantum efficiency [-]
ESR  Electron-spin resonance
<table>
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<th>Acronym</th>
<th>Definition</th>
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<td>FF</td>
<td>Fill factor</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared (spectroscopy)</td>
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<td>FTPS</td>
<td>Fourier transform photocurrent spectroscopy</td>
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<tr>
<td>FTPS-EQE</td>
<td>EQE spectrum connected to FTPS spectrum</td>
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<td>FWHM</td>
<td>Full width at half maximum</td>
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<td>HCM</td>
<td>Hydrogen collision model</td>
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<td>HSM</td>
<td>High stretching mode</td>
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<tr>
<td>HWM</td>
<td>High wagging mode</td>
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<tr>
<td>LED</td>
<td>Light-emitting diode</td>
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<tr>
<td>LSM</td>
<td>Low stretching mode</td>
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<tr>
<td>LWM</td>
<td>Low wagging mode</td>
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<tr>
<td>MP</td>
<td>Maximum power</td>
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<tr>
<td>NV</td>
<td>Nanosized void</td>
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<tr>
<td>PDF</td>
<td>Pair distribution function</td>
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<td>PDS</td>
<td>Photothermal deflection spectroscopy</td>
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<td>PV</td>
<td>Photovoltaics</td>
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<td>PVMD</td>
<td>Photovoltaic materials and devices</td>
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<tr>
<td>RT</td>
<td>Reflectance/transmittance</td>
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<tr>
<td>SJT</td>
<td>Stutzmann-Jackson-Tsai (model)</td>
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<tr>
<td>SM</td>
<td>Stretching mode</td>
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<td>SWE</td>
<td>Staebler-Wronski effect</td>
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<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
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<tr>
<td>TF-Si</td>
<td>Thin-film silicon</td>
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<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
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<tr>
<td>Voc</td>
<td>Open circuit voltage [V]</td>
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<tr>
<td>VHF</td>
<td>Very high frequency</td>
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<td>WM</td>
<td>Wagging mode</td>
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Chapter 1

Introduction

This work describes a study of hydrogenated amorphous silicon. In this introduction, the relevance of this research is illustrated by providing the context in which it takes place. Starting with a broad view, the focus is narrowed until it arrives at the subject of this Master’s thesis project: the nanostructure of hydrogenated amorphous silicon. At the end of this chapter, the research question is formulated.

1-1 The energy landscape

Over the past decades, energy has become one of the most hotly debated topics worldwide. Rapidly increasing demand, depleting fossil fuel sources, economic interests and climate change present a complex landscape with a multitude of players and interests. Although there is not always consensus about the state of this landscape and what is the proper course of action, there are compelling arguments in favor of developing and implementing sustainable energy technologies. These arguments are laid out in this section.

Fossil fuels

The concept of peak oil was introduced by M. King Hubbert in 1956. It states that the rate of petroleum production in any geographical region can be described by a bell curve. At the center of this distribution the maximum amount of oil production is reached, after which the rate declines [1].

Although this simple description must be adapted for newly discovered reserves, technological advances and economical circumstances, the core principle remains: at some point fossil fuel production will start to decline and at a later time it will become practically and/or economically unfeasible to extract. Any sufficiently long-term, global energy policy therefore cannot rely on fossil fuels, but must instead employ renewable sources.

This is also reflected in the seminal 1972 book “The Limits to growth”, commissioned by the Club of Rome [2]. Although wider in scope than just energy sources, the book shows that
continuous consumption of non-renewable natural resources in a ‘business-as-usual’ scenario leads to a collapse of the global system by mid-21st century. A 2008 paper by Graham Turner shows that 30 years of historical data supports the predictions about such a scenario [3]. These findings illustrate the necessity and urgency of changing to a more sustainable model.

Climate change

One of the main effects of the mass burning of fossil fuels since the beginning of the industrial revolution has been increasing global average temperatures as a result of the greenhouse effect, amplified by increased concentrations of CO$_2$ (and other greenhouse gases like methane and nitrous oxide) in the atmosphere. These increased concentrations result in a net positive radiative forcing$^1$, causing a rise in temperature. The projected temperature increase by 2100 ranges from +0.5 to +4 $^\circ$C[4] (see figure 1-2 (a) and (b)). A dramatic rise in temperature will have serious effects on sea levels, ecosystems and the availability of potable water and arable land.

Although often presented as a controversy in the media, the scientific community is all but convinced of the reality of climate change and its anthropogenic origin. Figure 1-3 shows the mismatch between the perception of the issue by the general public and by scientists actively involved with current research on the topic. A meta study involving almost 12000 peer-reviewed papers on climate change confirms that more than 97% of papers which take a stance on the issue do so in favor of anthropogenic climate change [5]. Figure 1-2 (c) shows the human contribution to temperature increase.

Geopolitics

Fossil fuel sources, by their nature, are localized. The availability of abundant and accessible energy has a great impact on a country’s wealth and on their position on the political world stage. Although often hard to isolate from other political developments, it is not hard to see that energy sources -directly or indirectly- influence geopolitics. For instance, it is often alleged that the US involvement in the Middle East is to secure continued access to oil. A more substantiated example of fossil fuels influencing political relations is the Russo-Ukrainian

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$^1$Radiative forcing is a measure of the influence that a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system [4].
Figure 1-2: (a) Concentration of CO$_2$ in the atmosphere and associated degree of radiative forcing associated with it. (b) Projected global average surface temperature increase in various emission scenarios. (c) Comparison of modeled and observed global average temperature change, supporting the claim of anthropogenic climate change. All figures from [4].

Figure 1-3: Response to the survey question “Do you think human activity is a significant contributing factor in changing mean global temperatures?” Adapted from [6].
gas dispute of 2009, in which a conflict between supplier Russia and buyer Ukraine resulted in terminated export of natural gas to Ukraine for two weeks. Because of Ukraine’s role as main corridor for gas pipelines from Russia to Europe, this resulted in serious practical and economical problems in several European countries [7]. Events like this illustrate the benefit of having decentralized and abundant energy sources.

**Economy and society**

The economic argument in favor of a transition to a sustainable energy supply is often not straightforward. The balance between benefits and negative consequences of an economic policy is difficult to predict. The topics described above, however, all have economic and societal aspects that are generally expected to improve with the transition to a sustainable (energy) economy. Negative externalities of fossil fuel use, such as pollution and health risks, can be reduced; the possibly very serious effects of climate change may be (partially) prevented or mitigated; economic dependency on foreign energy sources can be avoided.

In many individual situations it is already economically sensible to adopt sustainable energy technologies. For example, PV in the Netherlands is already a good investment with a payback period of well under 10 years [8] and a technical lifetime of more than 25 years. For society as a whole, a full switch to sustainable technologies like solar and wind energy presents additional challenges like grid stability and large scale energy storage. Recent papers show that it is entirely feasible to make the transition to a fully renewable global energy system by 2050 at similar or lower costs than that of the current system [9], [10].

### 1-2 Renewable energy technologies

The previous section highlighted the importance of replacing fossil fuels with renewable energy sources. A renewable energy source is one that replenishes at a faster rate than it is consumed. Examples of sources that fit this definition are solar energy, wind energy, (some) biomass, geothermal energy, hydro and ocean energy [11]. It is beyond the scope of this report to describe all these separately, but it is insightful to highlight some general aspects of these technologies and their relation to each other and to conventional energy sources and systems to illustrate the differences between conventional energy infrastructures and those employing renewable sources.

- **Reliability.** Solar and wind energy can only be used when sunlight and wind, respectively, are available. Both experience short-term (hourly, daily) and long-term (yearly) fluctuations. Unlike conventional, power plant based energy supply, large-scale implementation of solar and wind would therefore require provisions for load balancing, energy storage, grid stabilization.

- **Decentral vs. central.** Wind and solar energy are by their nature decentralized: they can supply energy wherever they are used. In the case of e.g. off-grid PV or solar heating, this can be a benefit, as reliance on existing infrastructure can be avoided. In the case of grid-connected PV or wind energy, however, problems with grid stability may occur. Sources like hydro, geothermal or tidal energy are not decentral, but they suffer from
geographical restrictions which impose additional infrastructural constraints. In general, large-scale incorporation of renewable energy technologies will require significant changes in existing infrastructure.

- **Supply and demand matching.** In a conventional system with central power plants, power is supplied by base load plants (e.g. coal or nuclear plants) with additional peak load plants to fulfill peak demand. This system is designed based on historical demand profiles and can be considered demand-driven. In a system with renewable sources like solar and wind, supply is limited by the availability of the sources, as mentioned above. To adapt to this limitation, a future energy infrastructure would have to be at least partially supply-driven. This would require changes on the demand side such as smart adaptation to supply by e.g. home appliances like washing machines. The incentive to do so already exists, as evidenced by the occasionally negative electricity spot prices in Germany during the summer [12].

- **Storage.** Related to the previous two points, large-scale storage of energy will become more important with increasing use of renewable energy sources. For heating and cooling, efficient techniques exist for both short-term (e.g. solar boilers) and long-term, seasonal (e.g. storage in underground aquifers) storage. Although limitations exist (e.g., the capacity of the aquifers), heat and cold storage is usually a cost-effective technique, especially for new buildings. For industry systems like phase change latent thermal storage are available [13]. Renewable energy for transport is possible using e.g. hydrogen created through electrolysis using electricity from renewable sources. Storage of hydrogen requires large-scale adaptation of the energy infrastructure, as well as advances in storage materials or containers [14]. Large-scale storage of electricity is currently challenging, because of the lack of a technology that is cheap, scalable and decentral. Pumped hydro, compressed air storage, batteries and fuel cells are relatively expensive and require additional materials and/or fuels. Inroads are made to remedy this problem, e.g. by electricity storage in electric vehicles and by the large-scale linking of electricity grids [15]. Presently, however, there is no single electrical energy storage system that can fulfill the storage demands imposed by the transition to a fully renewable energy infrastructure.

- **Cost.** The previous points all have their bearing on one of the most important aspects of designing the energy landscape of the future: cost. As already mentioned in the previous section, it is economically feasible to switch to a fully renewable energy system. When deciding which specific technologies to develop and prioritize, however, absolute and relative costs are often of critical importance.

Figure 1-4 shows the price ranges and price points for the most widely used applications for a wide range of technologies. Currently, the per-kWh price of most renewable energy sources is still higher than that of conventional sources. Notable exceptions are hydro and geothermal energy, which have comparable costs, and onshore wind, with costs approaching that of conventional sources.

Also significant is the large decrease in cost of photovoltaic technology. This year-on-year cost reduction fits in a decade-long trend of cost reducing with production capacity in which each doubling of production capacity has resulted in a price reduction of roughly 20% on average (see figure 1-5). Cumulative installed capacity has seen
exponential growth for more than a decade. If this trend continues, the cost of PV-generated electricity will rival that of conventionally generated electricity in the near future. In many situations where electricity prices and/or solar irradiance levels are high enough, this point has already been reached, like e.g. in Southern Europe or the Southwestern United States [16].

Figure 1-4: Levelized cost of energy in $/MWh for various renewable and conventional energy sources. Grey bars indicate ranges of costs for various applications; triangles indicate costs for the most widely used applications. Arrows emphasize the large relative decrease in cost of PV. Adapted from [17]; the reader is referred to this publication for details about the technologies.

The above is but a brief list of some of the factors that play a role in a transition to a sustainable energy infrastructure, but it underlines that there is no single technology that is a clear candidate to replace the current fossil fuel based energy landscape. Parallel paths of research and implementation are therefore crucial for an optimal transformation to a sustainable energy infrastructure. When it comes to deciding which technology to focus on, all of the already mentioned factors play roles of varying magnitude. Few factors, however, point in as clear a direction as potential. Figure 1-6 (a) shows how much larger the potential of (land-based) solar energy is compared to any other technology: one to three orders of magnitude. Advances in efficiency, cost reduction, production technology, therefore also have great potential impact, which makes research into solar energy particularly interesting.

This section has described the huge potential of solar energy as a renewable energy source. The next section details the most versatile and useful application of solar energy: electricity generation through photovoltaics. While other solar energy applications like solar heat and solar fuel generation are quite valuable, they are not discussed further in this thesis.
1-3 Photovoltaic technology

1-3-1 Operating principle: the photovoltaic effect

In solid-state physics, materials can be classified as insulators, conductors and semiconductors. An insulator has very low electrical conductivity ($\sigma < 10^{-8}\text{S/cm}$) and a metal very high conductivity ($\sigma > 10^3\text{ S/cm}$). Semiconductors have conductivities in between those of insulators and metals. The origin of this distinction can be found in quantum mechanics. Because of the Pauli exclusion principle, electrons which occupy the same quantum states in
Introduction

their respective isolated atoms cannot do so when the atoms are closely packed as they are in a solid. This gives rise to the splitting of quantum states to form densely populated bands of quantum states, separated by bands of forbidden energies [21].

Electrons which are bound to their atoms are in the valence band, while free electrons occupy the conduction band. The difference between the energy level at the bottom of the conduction band and the top of the valence band is called the band gap energy:

\[ E_g = E_c - E_v \]  

(1-1)

An electron in the valence band is bound to the atom, but can be freed from it if it gains enough energy to overcome the band gap energy and reach the conduction band, where it can contribute to an electric current. Metals typically have a very small or nonexistent band gap, which results in many free electrons and hence a high conductivity. Insulators have a very large band gap (typically \( E_g = 3.5-6 \) eV), which means nearly all electrons are in the valence band and hence the conductivity is very low. Semiconductors have band gaps of the order of 0.7-2 eV, which means that a moderate amount of energy is required to move an electron from the valence band into the conduction band [21]. Figure 1-7 shows the relative differences in the band structures of metals, semiconductors and insulators.

\[ \text{Metal} \quad E_g = 0 \text{ eV} \quad \text{Semiconductor} \quad E_g \sim 0.7-2 \text{ eV} \quad \text{Insulator} \quad E_g > 3.5 \text{ eV} \]

**Figure 1-7:** Schematic view of band structures of metals, semiconductors and insulators, showing the size of the bandgaps.

The energy required to move an electron from the valence band of a semiconductor into the conduction band can be provided by absorption of light. When a photon with energy greater than the band gap is absorbed by the material, an electron absorbs the energy of the photon, thereby gaining enough energy to move from the valence band into the conduction band. At its original position in the valence band, a hole remains which can be regarded as a charge carrier with opposite charge to the electron. Both electron and hole can diffuse freely. When an electron and a hole meet, they recombine, dropping the electron back into the valence band. This recombination can be radiative (emission of a photon) or non-radiative (Shockley-Read-Hall, or trap assisted recombination). A third possible process is Auger recombination, in
which the energy from the recombining charge carrier is transferred to another carrier which is excited to a higher energy state in the same band.

![Figure 1-8](image)

**Figure 1-8:** Generation (left) and (radiative) recombination (right) of an electron-hole pair. Adapted from [22].

In order to extract the charge carriers from the material and make use of them in the form of an electric current, this recombination has to be prevented. This is done by separating the charges with the help of an electric field. In crystalline silicon solar cells, this electric field is provided by the pn-junction. This junction consists of n-type silicon (silicon doped with e.g. phosphorus to provide excess electrons) brought into close contact with p-type silicon (doped with e.g. boron to provide excess holes). Electrons from the n-type material diffuse into the p-type where they recombine, leaving behind positively charged ions in the n-type and negatively charged ions in the p-type in what is called the *space charge region* or *depletion region*. Across this region, an electric field exists, which separates the diffusing electrons and holes. Once separated, the charge carriers can be collected at the terminals of the device, across which a voltage now exists. The presence of this voltage as a result of illumination of the material, and the corresponding current when an external load is connected, is known as the photovoltaic effect. The charge separation process is illustrated in figure 1-9.

![Figure 1-9](image)

**Figure 1-9:** Separation of electrons and holes across a pn-junction. Adapted from [22].

In amorphous silicon solar cells, the charge separation mechanism is slightly different. More on this in chapter 2.

**1-3-2 Types of PV technology and the role of thin-film amorphous silicon**

Although the principle of electric current generations is the same for all (charge carrier generation, separation and collection), many different PV technologies exist, each with their own strengths and weaknesses.
The current global PV market is dominated by crystalline silicon (c-Si) solar cells. This technology is mature, with well-established production methods and relatively high efficiencies of 15-20% for commercially available modules. Its applications range from the small scale (residential, recreational) to the very large scale (>100 MW power plants). In many situations, c-Si based solar cells are the best choice, especially since they have become much cheaper in recent years. Recent market developments have diminished the competitive edge of thin-film technologies. Part of the price decrease of c-Si has been artificial because of significant involvement by the Chinese government. Recently, this trend has shown signs of abating and with continuing advances in production technology and device quality, thin-film technologies may again gain the price advantage. However, because c-Si has reached the level of mass production and has become a commodity, continued dominance of the global PV market by c-Si is likely.

The downsides of c-Si solar cells are that they require relatively much base material, they are produced using an energy-intensive process and they are rigid, limiting their possibility of integration into buildings, vehicles, etc. There is also currently no expectation of significantly increasing efficiencies of single junction c-Si solar cells, as evidenced by decade old efficiency records [23]. These downsides are mostly absent from many thin-film technologies. The much higher absorption coefficients of the materials used allows the devices to be orders of magnitude thinner than c-Si solar cells. Thin-film solar cells therefore require much less base material. Their production methods are less energy-intensive, taking place at significantly lower temperatures. Because of their limited thickness, they can be deposited on both rigid and flexible substrates, allowing for more varied applications.

The three most mature thin-film solar cell technologies are copper indium gallium selenide (CIGS), cadmium telluride (CdTe) and thin film silicon (TF-Si). The former two have the higher (lab) efficiencies, at roughly 20%, versus 13% for TF-Si. Because TF-Si solar cells require fewer rare materials, however, the cost per watt, is roughly equal for all three, at around $0.80-0.90 [18]. Furthermore, TF-Si does not require the toxic cadmium, or the rare telluride or indium, which means fewer obstacles for large-scale implementation. Overall, thin-film silicon solar cells remain a very promising technology. To maximize their cost-to-performance ratio, several areas for improvement can be identified [24]:

- Increasing the conversion efficiency (e.g. through light management techniques, reduction of absorption losses, reduction of defect densities)
- Increasing the deposition rate (allowing for cheaper production because of reduced equipment overhead)
- The choice of mass production technology (one-chamber, multi-chamber, roll-to-roll, encapsulation)
- Lowering of material costs (substrate carrier, gas purity and utilization)
- Reduction or elimination of the Staebler-Wronski effect

Whereas the first four aspects in the above list have to do mainly with device and production design and optimization, the last one relies solely on the material properties of hydrogenated amorphous silicon (a-Si:H).
The Staebler-Wronski effect (SWE; described in detail in the next chapter) is the phenomenon that the conductivity of hydrogenated amorphous silicon decreases when exposed to light, an effect that is (partially) reversible by heating the material to temperatures above 150°C. The result of this effect is that during the first approximately 1000 hours of exposure to sunlight, a-Si solar cells lose up to 30% of their initial efficiency. After this initial degradation, the efficiency stabilizes.

Removing this decrease in efficiency, if at all possible, would significantly increase the usefulness of a-Si:H based solar cells. In order to achieve this, first an improved understanding of the SWE is required. However, in the 36 years since the discovery of the SWE, despite much research on the subject, its origins and workings have remained unclear, in particular the physical nature of the metastable defects that play a role in the SWE. The promise of potentially increasing stable efficiencies of thin-film amorphous silicon solar cells by up to 30% makes researching this topic particularly compelling.

1-4 Problem statement

As described in this chapter, a-Si:H can play an important role in the energy landscape of the future. When used in thin-film silicon solar cells, it has the potential of being a cheap and versatile energy source. A better understanding of its properties is necessary for fully optimizing this potential. This study aims to further that understanding by focusing on two areas: the nanostructure of the material and the kinetics of metastable defect creation. The two methods employed to reach this goal are light soaking and thermal annealing, the twin drivers behind the reversible metastable defect phenomenon, the Staebler-Wronski effect. This leads to the formulation of the following research question:

What can be learnt about the nanostructure of hydrogenated amorphous silicon and the kinetics of metastable defects under the effects of light soaking and thermal annealing?

To best answer this question, an experiment has been set up which tracks the effect of light soaking and thermal annealing on a wide range of parameters of both films and solar cells, deposited using varying degrees of hydrogen dilution of the silane gas used to deposit a-Si:H films and solar cells. The objective of this experiment is to build a body of data which allows drawing conclusions about the nanostructure of the material and its behavior under light soaking and thermal annealing.

The main measurement techniques used throughout this experiment are Fourier transform photocurrent spectroscopy (FTPS) and Fourier transform infrared (FTIR) spectroscopy which yield information about the absorption coefficient and/or subgap external quantum efficiency and the hydrogen content and nanostructure of the material respectively. Additionally, Raman spectroscopy, external quantum efficiency measurements, reflectance/transmittance measurements and external parameter measurements are performed.

1-5 Report outline

In chapter 2, the reader will be presented with an overview of the properties of a-Si:H and its application in solar cells. Chapter 3 will describe the measurement and data processing
techniques employed. Chapters 4 and 5 describe and discuss the annealing and light soaking experiments respectively. Finally, chapter 6 presents conclusions and recommendations.
Chapter 2

Hydrogenated amorphous silicon

Hydrogenated amorphous silicon is the material of interest in this Master’s thesis. It is a widely used semiconductor material with applications in many different areas. This chapter will give an overview of the material, its structural, optical and electrical properties and its application in photovoltaic devices.

2-1 History and applications

Hydrogenated amorphous silicon was first produced in the second half of the 1960s by Sterling and Swann, in the context of research into amorphous semiconductors [25]. Whereas previously sputtering and thermal evaporation were used for creating amorphous silicon, Stirling and Swann used a radio frequency discharge glow discharge method with silane as feedstock. Chittick et al. showed in 1969 that amorphous silicon produced using this method had notable photoconductive properties and implied that the material contained relatively few defects [26]. In the mid-1970s it was determined that the material was an alloy of silicon and hydrogen in which the hydrogen passivated the abundantly present dangling bonds (see section 2-3), resulting in much better electronic properties. Since then, it is called hydrogenated amorphous silicon (a-Si:H) [27].

Also in the mid-1970s, it was found that amorphous silicon could successfully be doped with phosphorus and boron to produce n-type and p-type material [28]. The combination of a low-defect, dopable material led to a surge of research activity as the possible applications became apparent. In 1976, Carlson and Wronski reported the first thin-film amorphous silicon solar cell with an efficiency of 2.4% [29]. Today, although its electronic properties are poorer than its crystalline counterpart, amorphous silicon is used in a multitude of applications, owing to the fact that it can be deposited cheaply, uniformly and over a large surface area. Solar cells, thin-film transistors (TFT) for use in e.g. computer monitors, copiers, scanners, light sensors, color detectors and position sensitive detectors are examples of applications which use amorphous silicon [30].
2-2  a-Si:H in solar cells

As described in section 1-3, one of the fundamental aspects of a solar cell is the separation of photogenerated electron-hole pairs so that they may be collected at the terminals and used as current in an external circuit. In a crystalline silicon solar cell, when charge carriers are generated, they start diffusing until the minority carrier reaches the pn-junction where the electric field causes it to move across.

Doped a-Si:H is so defect-rich that a pn-junction is not a viable separation device: carriers will simply recombine too soon. Instead, the absorber layer is a less defect-rich undoped (intrinsic) layer. Charge carriers generated in this layer will not recombine as swiftly. However, in the absence of an electric field, they will also not reach the terminals easily. The intrinsic layer is therefore sandwiched in between a p-doped and an n-doped layer. This results in an electric field across the entire intrinsic layer, which causes the electrons and holes to drift in opposite directions, allowing for collection. The band diagram shown in figure 2-1 illustrates this mechanism. Notice the difference with figure 1-9. Although drift is the dominant separation mechanism in a-Si:H solar cells, it is noted that diffusion has a nonzero contribution to the carrier separation.

The two basic configurations that are used are p-i-n and n-i-p, the names reflecting the order in which the p-doped, intrinsic and n-doped layers are deposited. A p-i-n device has a transparent substrate, usually glass, with a transparent conductive oxide (TCO) layer deposited on it. An n-i-p device has an opaque substrate and a TCO layer on top to allow connection to the external circuit. [24]

a-Si:H can also be used in multi-junction cells (usually a-Si:H/µc-Si:H or a-Si:H/µc-Si:H/µc-Si:H) or heterojunction cells. Those types of solar cells are not discussed further in this thesis.
2-3 Material properties

2-3-1 Atomic structure

As already mentioned in chapter 1, the silicon used in solar cells can have a crystalline and an amorphous phase. Crystalline silicon is a structured array of silicon atoms with long-range order. It can be described by a diamond structure unit cell. Amorphous silicon, on the other hand, lacks long-range order and cannot be described by a unit cell. The material does show short-range order, in that atoms mostly have four nearest neighbors and bond lengths and angles similar to that in c-Si. This is shown in the atomic pair distribution function (PDF; see figure 2-3). This function describes the probability of finding an atom at a distance R from another atom. In c-Si, because of the long-range regular atomic spacing, this function is a set of discrete values. In a-Si:H the distribution of bond lengths and angles gives rise to a PDF which is continuous. It shows a first few peaks which line up with the discrete values of the PDF of c-Si, but after several atomic distance lengths it loses structure, illustrating the short-range order and long-range disorder of a-Si [32]. Microcrystalline or nanocrystalline silicon is an intermediate phase in between a-Si:H and c-Si, in which amorphous silicon is interspersed with small crystallites (“grains”). This material is not discussed further in this thesis.

The structural model of amorphous silicon depicted in figure 2-4 is an example of a continuous random network (CRN), first proposed for a-Si:H by D.E. Polk [33]. In a-Si:H, many silicon atoms will be bonded to 4 neighbors, as in c-Si. Some, however, will be undercoordinated (bonded to only three other silicon atoms) while others will be overcoordinated (bonded to five silicon atoms). The former situation leaves one electron unpaired, which is referred to as a dangling bond. The latter is called a floating bond [24]. A more complex model of a-Si:H is discussed in section 2-4-2.
2-3-2 The role of hydrogen

As mentioned in section 2-1, the presence of hydrogen in a-Si:H is what makes the material so suitable for use in thin-film semiconductor applications. The way in which the hydrogen is incorporated into the material affects its properties.

In a macroscopic sense, it is useful to express the hydrogen content of a-Si:H as an atomic percentage. This percentage is an indicator for the suitability of the material for use in PV
cells. If the hydrogen content is too low, the defect density becomes too large because of poor passivation. If the hydrogen content is too high, more complex silicon-hydrogen structures are formed, which also increases the density of states [27]. Generally, depending on the deposition parameters, a hydrogen content of 7-12 at.% leads to ‘device quality’ a-Si:H.

In the microscopic sense, it is useful to look at the interaction between hydrogen and silicon. Silicon-hydrogen bonds can have different vibrational modes which can be associated with different configurations of silicon and hydrogen in the material. Various vibrational modes exist, but those of interest for this project are the so called wagging modes (WM), associated with a rotational oscillation of hydrogen about the Si-atom and the stretching modes (SM), a longitudinal oscillation of the Si-H bond [34]. These modes are illustrated in figure 2-5.

![Figure 2-5: Wagging (left) and stretching (right) modes of Si-H bonds.](image)

These modes can be expressed in terms of Gaussian distributions on an absorptance spectrum which can be obtained from an FTIR measurement (see figure 3-7). Both the WM and SM can be approximated by a superposition of two Gaussians [34]. These two are described by the terms ‘low’ and ‘high’ (prefix ‘L’ and ‘H’ respectively), denoting the wavenumber around which they are centered: for the wagging modes, $\tilde{\nu}_{LWM} \approx 610 \text{ cm}^{-1}$ and $\tilde{\nu}_{HWM} \approx 650 \text{ cm}^{-1}$ and for the stretching modes, $\tilde{\nu}_{LSM} \approx 2000 \text{ cm}^{-1}$ and $\tilde{\nu}_{HSM} \approx 2100 \text{ cm}^{-1}$ [35]. The ways in which absorption coefficient spectra and these distributions are obtained are described in detail in chapter 3.

The integrated absorption strengths of these distributions can be used to obtain useful microscopic and macroscopic quantities, which are listed below.

The hydrogen content ($c_H$ in at.%) can be calculated by multiplying the amplitudes of the low wagging mode (LWM) and high wagging mode (HWM) with a constant which is experimentally obtained [36]:

$$c_{H,WM} = 0.397 (i_{LWM} + i_{HWM}) \quad (2-1)$$

where $i_{LWM}$ and $i_{HWM}$ represent the integrated absorption strengths of the wagging modes.

Alternatively, it can be obtained from the low and high stretching modes (LSM and HSM) by multiplying with another experimentally determined constant [37]:

$$c_H = \text{const} \times (i_{LSM} + i_{HSM})$$

c_{H,SM} = 2.2 (i_{LSM} + i_{HSM}) \tag{2-2}

where $i_{LSM}$ and $i_{HSM}$ represent the integrated absorption strengths of the stretching modes. The density of the film (in g/cm$^3$) can be calculated using the Clausius-Mosotti equation [37]:

$$\rho_{a-Si:H} = \left( \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \right) \frac{3m_{Si}}{4\pi} \left[ \frac{2\alpha_{Si-Si}}{1-c_H} \left( \alpha_{Si-H} - \frac{1}{2}\alpha_{Si-Si} \right) \right]^{2-3}$$

In the above equation, $n_\infty$ is the refractive index of the a-Si:H layer (which can be obtained from an FTIR measurement, as described in section 3-3-1), $m_{Si}$ is the mass of the Si-atom, $c_H$ is the atomic hydrogen content as obtained above either from the WM or SM and the $\alpha$’s are the polarizabilities of the bonds indicated by the subscripts, which are constants (determined as described in [37]).

Finally, the nanostructure parameter $R^*$ can be obtained as follows:

$$R^* = \frac{i_{HSM}}{i_{LSM} + i_{HSM}} \tag{2-4}$$

The parameter $R^*$ describes the relative contributions of the LSM and HSM, which can be interpreted in terms of the nanostructure of a-Si:H. The LSM corresponds to monohydrides in vacancies, while the HSM corresponds with hydrides on the surface of nanosized voids. The relative intensities of these two modes therefore indicate whether the material is relatively dense and dominated by divacancies or relatively porous and dominated by nanosized voids [38].

### 2-4 Defects and the density of states

A semiconductor is defined by its electrical conductivity, which has values in between those of insulators and conductors. The origin of this property lies in the distribution of electronic quantum states. The Pauli exclusion principle, which states that two identical fermions cannot occupy the same quantum state, leads to a band structure in solids with quasi-continuous bands of allowed and continuous bands of forbidden energies [21]. This section deals with the band structure and its corresponding energy states.

#### 2-4-1 The density of states

In crystalline silicon, the band structure consists of a valence band with states corresponding to electrons bound to atoms and a conduction band with states corresponding to unbound electrons, separated by the range of forbidden energies — the band gap, $E_g$ — which has a well-defined value of 1.12 eV. The ensemble of available states is known as the density of states (DOS).

Because of the crystalline nature of the material, the band gap in c-Si is sharply defined. Amorphous silicon, however, lacking long-range order, has a different band structure. There are three notable differences.
Firstly, the variation in bond lengths and angles (causing the long-range disorder) leads to band edges that are ‘tilted’: the energy states of the valence and conduction bands — the extended states — spread into the bandgap and form tail states, which are associated with weak Si-Si bonds in a CRN view of a-Si:H [27], [32]. In a DNHV view (see section 2-4-2), the band tails are explained as a superposition of many different band gaps induced by vacancies in the material [31].

Secondly, deviations from a perfect crystal structure give rise to allowed energy states in the band gap which are called defect states (more on defects in the next section). These gap states, together with tail states, constitute the localized states.

Thirdly, the band gap energy is different. In fact, there is no longer a well-defined band gap energy. A term frequently used is mobility gap ($E_{\text{mob}}$), which is determined by the energy levels at which the extended states meet the tail states. It derives its name from the sharp drop in mobility in the localized states compared to the extended states [24]. Its value has to be experimentally determined and is typically found to be between 1.7 and 1.8 eV.

Other definitions of the band gap are also used, such as the Tauc gap [39] (obtained by extrapolating the exponential regime of the absorption coefficient spectrum to the abscissa [27]) or the $E_{04}$ gap (defined as the energy at which the absorption coefficient is $10^4 \text{ cm}^{-1}$). The schematic densities of state for c-Si and a-Si:H are depicted in figure 2-6.

![Figure 2-6: Schematic density of states distribution for c-Si (a) and a-Si:H (b).](image)

### 2-4-2 Defects in a-Si:H

Figure 2-6 schematically shows the defect states (the purple region). The actual shape of the defect density of states is more complex and is (implicitly) the subject of much of the work done during this master’s thesis project. Defects serve as efficient recombination centers through a process called Shockley-Read-Hall recombination. The amount of defects directly affects the recombination rate and hence the efficiency of the solar cell. This section discusses defects in a-Si:H in more detail.

In c-Si, the definition of a defect is straightforward: any deviation from the ideal crystal structure shown in figure 2-4. Examples of defects are interstitials or vacancies, point, line and plane defects. In a-Si:H, this definition does not apply, since there is no crystal structure from which to deviate. Instead, it is useful to think of defects in a-Si:H as departures from an
‘ideal amorphous network’, which can be thought of as a CRN with all bonds satisfied. This means that all Si atoms are four-fold coordinated and all H atoms one-fold [32]. A defect by this definition has to involve too few or too many electrons per atom locally (in other words: it is a coordination defect). This simple view, however, does not fully describe the material. Many different models have been proposed; two of these, which demonstrate different schools of thought, are discussed next.

The defect-pool model

The basic principle of the defect-pool model (DPM) is that isolated dangling bonds (DB) are the dominant type of defect, which are formed by the breaking of weak Si-Si bonds. The density of defects is determined by the constant forming and breaking of these bonds, which are in equilibrium. DBs can have 3 possible charges: positive ($D^+$), neutral ($D^0$) and negative ($D^-$). A DB functions as a defect when it can trap a charge carrier, which means a change in charge level. This means that the electronic density of states of DB-related defects consists of two Gaussian distributions associated with the transitions between the charge levels (denoted by $E^{+/0}$ and $E^{0/-}$ for the transition between the positive and neutral state and the neutral and negative state respectively). These two Gaussian distributions are assumed to be located on opposite sides of $E_g/2$ (the midgap energy) and are also known as “defect pools” [40].

![Figure 2-7: The standard model for density of states, showing the two defect pools centered around the midgap energy [24].](image)

Disordered network with hydrogenated vacancies (DNHV)

Smets et al. propose a more complex description of a-Si:H, in which other deviations from the perfect CRN than the dangling bond exist [37], [38], [41]. These deviations come in various configurations involving hydrides (see figure 2-8) and can roughly be divided into vacancies and voids. In this model, a defect is one of these entities when not fully passivated by hydrogen. This by itself does not imply defect distributions different from those associated with isolated dangling bonds. It can be argued (as has been done [32]) that a dangling bond
in a void (or vacancy) is hard to distinguish from one in bulk Si. Smets argues, however, that nearby dangling bonds in vacancies and voids can create new orbitals with different energy levels (as suggested in earlier work by Carlson [42]). This implies that more than the 2 defect distributions as suggested by the DPM can exist in the a-Si:H bandgap [43].

**General case**

Since the purpose of this project is to learn about the nanostructure of a-Si:H, a more general description of the subgap DOS is helpful. This description does not assume anything about the number, type and energy level of defects. The only thing that is assumed is that they can be approximated by Gaussian distributions, which is traditionally justified by the amorphous nature of a-Si:H and the distribution of bond lengths and angles this entails.

By obtaining the DOS and deconvoluting the subgap states into Gaussians, information about the amount and type of defects can in principle be gained. The problem is that measuring the DOS directly is not possible. To nonetheless obtain information about the defect states, a different tool is used: the absorption coefficient spectrum, which is discussed next.
2-5 Absorption coefficient spectrum

The absorption coefficient $\alpha$ (cm$^{-1}$) of a material is a measure for how far into a material light of a certain wavelength can penetrate before it is absorbed, or alternatively, how a photon flux density $\Phi$ decreases as a function of the incident photon flux $\Phi^0$ and the distance $x$ passed in the material:

$$\Phi(x, E_{ph}) = \Phi^0(0, E_{ph}) e^{-\alpha(E_{ph})x}$$

(2-5)

where $E_{ph}$ is the photon energy.

Equation 2-5 is known as the Lambert-Beer absorption formula [27]. The absorption coefficient is a function of photon energy. In general, the absorption coefficient is higher for higher energy photons. This means that red light gets absorbed deeper in the material than blue light. The relation between absorption coefficient and photon energy is known as the absorption coefficient spectrum of the material.

2-5-1 Absorption of light in silicon

Figure 2-10 shows the absorption spectra for a-Si:H and c-Si. The figure shows that the absorption coefficient is much higher for a-Si:H in the visible range of the spectrum. This can be understood by realizing that c-Si is an indirect bandgap semiconductor. Conservation of electron momentum requires another particle (a phonon) to move the electron from the highest valence band energy to the lowest conduction band energy. Absorption is therefore not only dependent on the density of electron states, but also on the availability of phonons with the required energy. Only when a photon has an energy high enough to cause excitation across the direct bandgap (roughly 3.4 eV) a phonon is not needed. By contrast, because of its amorphous nature, a-Si:H does not have a well-defined band structure, and effectively behaves like a direct bandgap semiconductor for which absorption is only dependent on the density of electron states. This results in the already mentioned higher absorption coefficient for a-Si:H when compared to c-Si in the visible range of the spectrum [44], [45].

2-5-2 Relating defect states to the absorption coefficient spectrum

A photon absorbed in a-Si:H may transfer its energy to an electron, thereby causing a transition to a higher energy state. Figure 2-11 schematically shows three possible types of transitions: from the valence band to the conduction band (band-to-band transition), transitions through the tail states and through the defect states to the conduction band. Photons with energies larger than $E_{mob}$ will cause transition 1. This is the regular band-to-band excitation described in section 1-3. Slightly less energetic photons will cause transition 2. Experiments show that this transition results approximately in the following exponential relation:

$$\alpha = \alpha_0 e^{\frac{E_{ph}}{E_0}}$$

(2-6)

In this equation, $\alpha_0$ is a constant and $E_0$ is called the Urbach energy. Region 2 in the absorption spectrum is called the Urbach edge [24] and the Urbach energy can be obtained
Figure 2-10: Absorption coefficient spectra for c-Si and a-Si, showing the higher absorption for a-Si in much of the visible light range. Adapted from [31].

Figure 2-11: (a) Schematic representation of possible electron state transitions. (b) Absorption coefficient spectrum with ranges corresponding to these transitions indicated.

by fitting a straight line to the absorption spectrum (as plotted to a logarithmic y-axis) and determining its slope.

Transitions 3 are those caused by the least energetic photons and it is region 3 of the absorption
spectrum which can yield information about the defect density of states when one realizes
that the absorption spectrum can be considered as an integral over the density of states [46],
[47]. Photons with energies less than the energy of the defect will not excite an electron
into the conduction band and hence won’t contribute to the absorption spectrum. Those
with energies higher than that of the defect will. From low to high energy, the absorption
spectrum will therefore increase monotonically.
Assuming, as was justified in section 2-4-2, that the subgap density of states consists of a
certain number of Gaussian distributions, it can be represented mathematically:

\[ DOS_{subgap} = \sum_{i=1}^{N} A_i \cdot f_i(E_{ph}) \]  
(2-7)

with \( f_i(E_{ph}) \) being Gaussian functions given by:

\[ f_i(E_{ph}) = \frac{1}{W_i \sqrt{2\pi}} \exp \left( -\frac{(E_{ph} - P_i)^2}{2W_i^2} \right) \]  
(2-8)

In the above equations, \( N \) represents the number of defect distributions, \( A_i \) are scaling factors
representing the contributions of the individual distributions to the DOS, commonly known
as the cross section of the defect distributions, \( E_{ph} \) is the photon energy, \( P_i \) are the energies
around which the distributions are centered (named \( P \) because they indicate the position of
the distribution on the DOS spectrum) and \( W_i \) are the standard deviations of the distributions
(here named \( W \) because they are related to the full width at half maximum (FWHM) of the
distribution, according to FWHM=2\sqrt{2ln2W}).

The integral of a Gaussian is given by the error function:

\[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt \]  
(2-9)

Using the above, integrating \( DOS_{subgap} \) leads to the following mathematical representation
of the subgap absorption spectrum:

\[ \alpha_{subgap}(E_{ph}) = C_{int} \sum_{i=1}^{N} A_i \left[ \frac{1}{2} \left( 1 + \text{erf} \left( \frac{E_{ph} - P_i}{\sqrt{2W_i^2}} \right) \right) \right] \]  
(2-10)

with \( C_{int} \) a scaling constant introduced by the integration.

Equation 2-10 gives an expression for the subgap absorption, however, experiment yields only
the total absorption spectrum, including the Urbach edge (region 2 in figure 2-11) and the
band-to-band range (region 1). In this spectrum, the Urbach edge and the subgap absorption
overlap. To isolate the contribution of the subgap states to the total DOS, the Urbach edge
(equation 2-6) has to be subtracted from the absorption spectrum \( \alpha(E_{ph}) \), yielding:

\[ \alpha_{subgap}(E_{ph}) = C_{int} \sum_{i=1}^{N} A_i \left[ \frac{1}{2} \left( 1 + \text{erf} \left( \frac{E_{ph} - P_i}{\sqrt{2W_i^2}} \right) \right) \right] = \alpha(E_{ph}) - \alpha_0 \exp \left( \frac{E_{ph}}{E_0} \right) \]  
(2-11)
Equation 2-11 relates experimentally obtainable quantities (absorption spectrum, Urbach energy) to the parameters that define the subgap states and therefore constitutes a powerful tool for analyzing the properties of a-Si:H. Note that it is only valid for the range of energies spanning the subgap states. Subtracting the Urbach edge from the supergap absorption yields meaningless results.

2-5-3 Obtaining the absorption coefficient spectrum

Several methods exist to experimentally determine the absorption coefficient spectrum. A purely optical method utilizes reflectance-transmittance (RT) measurements. By using the complex refractive index obtained from an RT measurement, and by applying the Lambert-Beer equation, one can determine the wavelength-dependent absorption coefficient of a film above the bandgap. This method does not yield reliable subgap information, however, since a-Si:H is largely transparent to infrared light, resulting in an almost absorption-free signal (i.e. gap states are not optically detectable).

Subgap information can be obtained by employing opto-electrical techniques like the constant photocurrent method (CPM), dual beam photoconductivity (DBP), photothermal deflection spectroscopy (PDS) or Fourier transform photocurrent spectroscopy (FTPS). Without discussing the details of these techniques, it is mentioned that FTPS offers the highest dynamic range, which allows detection of the deepest gap states. It is therefore the technique of choice during this thesis project.

By connecting the photocurrent data from FTPS measurements to the absorption coefficient spectrum obtained from RT measurements, one obtains an absorption coefficient spectrum that spans the visible light range and the subgap infrared range of energies. These two techniques and the method by which the data are connected are described in sections 3-2 and 3-3.

2-6 Metastability: The Staebler-Wronski effect

In 1977, D.L. Staebler and C.R. Wronski reported a new photoelectronic effect that became known as the Staebler-Wronski effect (SWE). When a-Si:H is exposed to light for long periods of time (in the order of hours) its photoconductivity and dark conductivity decrease. The effect is lasting, but reversible by thermal annealing of the material at temperatures above 150 °C [48].

For photovoltaic applications, the decrease in photoconductivity is of utmost importance, since this directly impacts the efficiency and therefore the economic viability of PV systems based on a-Si:H. Because of this, the origin of the SWE has been the subject of extensive study but a satisfactory and widely applicable and accepted explanation is yet to be found.

2-6-1 Proposed explanations for the SWE

Early research by Elliott [49] and Staebler and Wronski [50] after the discovery of the SWE resulted in bond-breaking models, which ascribed the creation of defects to the breaking
of weak Si-Si bonds under illumination to create dangling bond defects. Another proposed explanation by Adler [51] stated that the dangling bond concentration was constant, and that it was the hybridization and charge state of the bonds that determined the observed reversible changes in the material. It was also suggested by e.g. Crandall that the defect creation depended on the presence of impurities [52].

An influential paper by Stutzmann, Jackson and Tsai in 1985 [53] showed that the SWE is a bulk effect, intrinsic to a-Si:H, that the SWE is largely independent of impurity concentration and that hydrogen stabilizes newly formed dangling bond pairs by “hopping” from a neighboring position to bind with one of the dangling bonds. This mechanism explains why broken Si-Si bonds do not simply reform after being broken. The paper also claimed a defect creation rate proportional to $t^{1/3}$, where $t$ is the illumination time. The SJT model, as it came to be known, supplanted the previous models at the time.

A problem with the SJT model was that it did not seem to correspond with electron-spin resonance (ESR) measurements. The local hopping of hydrogen near dangling bonds, or any other localized phenomenon, should leave a signature in the ESR measurements, but it did not. This led to the formulation of the hydrogen collision model (HCM) in 1999 by Branz [54]. Instead of ascribing the SWE to localized structural changes in the material, the HCM proposed the breaking of Si-H bonds by recombination of photogenerated carriers, resulting in mobile hydrogen atoms. When two such atoms collide, they form a metastable two-H complex, leaving behind two dangling bonds which by default also become metastable. The HCM is not a clear candidate for explaining the SWE either, particularly because the existence of the metastable two-H complex is statistically unlikely and has not been demonstrated experimentally. Several experiments confirm the model, but other practical and theoretical work conflicts with it (e.g., the assumption of a quasi-equilibrium between mobile H and dangling bonds may not be valid) [55].
Many other models have been presented (e.g. the floating bond model [56] and the proton motion model [42], but so far, the above models have in common that they all regard the dangling bond as the sole source of metastable defects and that they all fail to fully agree with experiment. More recent work indicates that the dangling bond may not be the only or even the dominant entity responsible for the SWE. Güneş [57] and Jiao [58] show that more than 2 defect states exist in the subgap, which they link to dangling bonds and divacancies. Smets et al. [41] propose a theoretical framework in which the (not fully hydrogenated) divacancy serves as an agent for the redistribution of bonded hydrogen and hence as a candidate for the source of the SWE. While this more recent work has made inroads into a better understanding of the SWE, a satisfactory explanation of this physical mechanism has not been found yet.

2-6-2 Degradation kinetics

As mentioned in the previous section, the SJT model states that the kinetic behavior of metastable defect creation follows a $t^{\frac{1}{3}}$ relation. This is concluded to be independent of illumination strength, which only affects the magnitude of the density of states, but not the time exponent [53]. The sublinear kinetics ($t < 1$), resulting in the stabilization of defect density, is attributed to the fact that recombination events which cause additional defects become relatively less frequent as the total number of defect increases. This relation is often quoted in literature and has long been seen as the de facto standard model.

More recent work, however, has suggested time constants different from $\frac{1}{3}$. It has been noted that isolating the recombination effects caused by just the metastable defects (and not the native ones) results in a higher time exponent [59], [60]. Additionally, “fast” and “slow” states have been identified in both the creation and annealing of defects [61]. These phenomena may occur under different conditions (e.g., fast states are suggested to be annealed at room temperature [62]), making it difficult to get a comprehensive description, let alone explanation. Wronski et al. have found different time constants for different defect distributions [63], complicating things further. Another complicating factor is that until now most studies towards the metastable sub gap defects that play a role in the SWE have been conducted on films and not on solar cell absorber layers. Due to the differences in carrier collection and properties of the light causing degradation in films and solar cell absorber layers, the degradation kinetics are likely to be different for films and solar cells. On this subject, like for the SWE as a whole, much is as yet uncertain.

2-6-3 Thermal annealing

As already mentioned, annealing a-Si:H reverses the creation of light-induced metastable defects. This happens at relatively low temperatures (~130-150 °C). Both the annealing temperature and duration affect the rate of recovery. This is illustrated in figure 2-13, which shows increasing magnitudes and rates of fill factor recovery for a-Si:H-based solar cells with annealing temperature [64].

Heating to higher temperatures also causes other changes in the material. The density of the material rises and the presence of molecular hydrogen increases. Increasing the temperature beyond roughly 350 °C results in the (staggered) effusion of hydrogen from the material [65]. At even higher temperatures (well over 500 °C) the material starts to crystallize [66].
In general, by tracking the properties of a-Si:H during annealing, information may be gained about the nanostructure of the material, which is exactly the reason behind the experiment described in chapter 4. An increased understanding of the nanostructure in the as-deposited state is particularly important when trying to comprehend the nature of stable and metastable defects in a-Si:H.
Chapter 3

Methodology

This chapter describes the deposition and measurement equipment used throughout this Master’s thesis project. The operating principles of the various techniques are explained, as well as experimental procedures and details and data processing routines.

3-1 Deposition methods

The samples investigated in this project have been created using two deposition tools: the Amigo cluster tool and the Provac physical vapor deposition tool.

3-1-1 Amigo

The Amigo is a multi-chamber cluster tool, built by Elettrorava, which can deposit intrinsic, p- and n-doped thin-film a-Si and μc-Si, Si alloys and ZnO:Al layers. It consists of 5 ultra-high vacuum (UHV) radio frequency/very high frequency plasma-enhanced chemical vapor deposition (rf/VHF PE-CVD) chambers, a sputtering chamber, a load lock and a UHV transport chamber containing a programmable robotic arm for transportation of the sample holders to and from the processing chambers and load lock. All PECVD deposition chambers are equipped with a showerhead electrode. The Amigo allows for manual or automated (based on programmable recipes) creation of single layers on for instance glass or c-Si substrates and solar cell devices.

One of the deposition parameters when depositing a-Si:H using PECVD is the presence and amount of hydrogen added to the silane flow. This is called hydrogen dilution and it can be used to manipulate various properties of a-Si:H. Hydrogen dilution is defined as:

\[ R = \frac{[H_2]}{[SiH_4]} \]  

(3-1)
Diluting the silane flow with hydrogen has several effects on the structure of a-Si:H. At moderate dilutions, it affects the density, hydrogen content and optical band gap [27]. It also increases the conductivity of the material and reduces the SWE: solar cells stabilize sooner and at a higher normalized efficiency than cells for which no hydrogen dilution is used in the deposition of the absorber layer[61]. Yang et al. suggest to link this to the suppression of “slow” defect states (see section 2-6-2) but state that the degradation kinetics are not easy to relate to structural properties.

At higher dilutions, microcrystalline silicon starts forming, first in the form of grains in a host a-Si:H material, later in full microcrystalline form. Figure 3-1 illustrates the relation between R and film thickness.

![Figure 3-1: The effect of hydrogen dilution (R) and layer thickness (d_b) on the material phase of a-Si:H deposited using PECVD [67].](image)

The hydrogen dilution by itself does not determine the material properties of the deposited a-Si:H; other deposition parameters such as substrate temperature, power and pressure also play a role. Hydrogen dilution typically results in a decreased deposition rate, which results in a lower defect density on one hand, but leads to an industrially undesirable longer deposition time on the other hand (see section 1-3-2).

Because the purpose of this project is to study a-Si:H, the samples used are all taken in the low to moderate dilution regime, meaning no microcrystalline material. All samples investigated have values of R between 0 and 10.

### 3-1-2 Provac

The Provac PRO500S, built by Provac (bankrupt in 2009) is a physical vapor deposition tool which uses an electron beam to evaporate aluminum, chrome, titanium or SiO\_2. Silver can be evaporated thermally by resistive heating. It was used in this project to deposit metal contacts on Si films or solar cells. Samples are placed in a rotating holder in a high vacuum chamber. Deposition takes place when the evaporated material reaches the sample through diffusion. Samples can be masked to block certain regions from deposition, allowing for different contact configurations.
3-2 Measurement techniques

In this section, descriptions are given of the measurement techniques used and their underlying principle. Because the two main techniques used in this project (FTIR spectroscopy and FTPS) share the same underlying principle - Fourier Transform spectroscopy -, this is discussed first.

3-2-1 Fourier transform spectroscopy

In a classical spectroscopic experiment, a spectrum (e.g. an absorption coefficient spectrum) is obtained by measuring the quantity of interest as a function of wavelength, which is varied through the use of a monochromator. By varying the wavelength in small steps, the spectrum is sampled directly [68]. Fourier transform spectroscopy, by contrast, is a method by which spectral information can be obtained quickly and simultaneously for different wavelengths using a specifically set up measurement. This setup is described next.

Experimental setup - the Michelson interferometer

In 1881, A.A. Michelson designed what came to be known as the Michelson interferometer. Although variations on the design have been made, the principle employed applies to all similar methods. The setup, schematically depicted in figure 3-4, consists of a light source, a beamsplitter, a fixed mirror, a movable mirror and a detector. First, monochromatic light with wavelength $\lambda (cm)$ and corresponding wavenumber $\bar{\nu} = \frac{1}{\lambda}(cm^{-1})$ is considered. A light beam emitted by the source is split into two halves at the beamsplitter (O). One half (dashed line in figure 3-4) is directed to the fixed mirror (F) and back; the other (dash-dotted line) to the movable mirror (M) and back. At the beamsplitter, each of the two beams is once again split into two halves. One of each of the halves is directed back towards the source and no longer of interest. The other two halves continue along the same path, causing interference.
The amount and sign of the interference are determined by the phase difference of the two beams, which is caused by a difference in path length. This path difference, or retardation, between the two interfering beams is given by:

\[ \delta = 2(OM - OF) \]  

(3-2)

As the retardation varies, interference ranges between constructive and destructive (both extremes shown in figure 3-5), and as a consequence, the intensity of the beam registered at the detector varies accordingly. As a function of \( \delta \), this measured intensity can be shown to be [70]:

\[ I(\delta) = 0.5I_{\text{source}}(\bar{\nu}) \left(1 + \cos \frac{2\pi \delta}{\lambda}\right) \]  

(3-3)

\[ = 0.5I_{\text{source}}(\bar{\nu}) (1 + \cos 2\pi \bar{\nu} \delta) \]  

(3-4)

Formula 3-4 describes a sinusoid with a constant (dc) and a modulated (ac) component. For spectroscopic analysis, only the ac component is of interest, and the dc component is dropped. This results in what is known as the interferogram of our monochromatic light source:

\[ I(\delta) = 0.5I_{\text{source}}(\bar{\nu}) \cos 2\pi \bar{\nu} \delta \]  

(3-5)

In the case of a constant mirror velocity \( v \), the retardation can be expressed as a function of time:
\[ \delta = 2vt \] (3-6)

which yields:

\[ I(t) = 0.5I_{\text{source}}(\tilde{\nu}) \cos 2\pi f_{\tilde{\nu}} t \] (3-7)

with \( f_{\tilde{\nu}} = 2\tilde{\nu}v \) the modulation frequency of the light. In a typical Fourier transform spectroscopic experiment, the variable is wavenumber, so this is used in the remainder of this section.

Moving from the ideal case example with a monochromatic light source to a real life situation, two things are noted. Firstly, any experimental setup will have non-ideal components, such as the beamsplitter, detector or amplifier, with wavenumber-dependent characteristics. This non-ideality is accounted for, by adding a wavenumber-dependent correction factor \( H(\tilde{\nu}) \) to equation 3-5:

\[ I(\delta) = 0.5H(\tilde{\nu})I_{\text{source}}(\tilde{\nu}) \cos 2\pi \tilde{\nu} \delta \] (3-8)

\[ = B(\tilde{\nu}) \cos 2\pi \tilde{\nu} \delta \] (3-9)

The parameter \( B(\tilde{\nu}) = 0.5H(\tilde{\nu})I_{\text{source}} \) now represents the intensity of the source, modified by the wavenumber-dependent characteristics of the experimental setup.

Secondly, the light source in an experiment is generally not monochromatic, but has a continuous spectrum. In such a case, the interferogram is not a single sinusoid, but an integral over all wavenumbers in the spectrum:

\[ I(\delta) = \int_{0}^{\infty} B(\tilde{\nu}) \cos 2\pi \tilde{\nu} \delta \cdot d\tilde{\nu} \] (3-10)

Equation 3-10 describes the interferogram of a polychromatic light source. The integral is a “summation” of interferograms of discrete wavelengths, as described by equation 3-4. Because
these interferograms are cosines with varying wavelengths, the only maximum they all share is at $\delta = 0$, which results in a combined interferogram with a distinct peak, as shown in figure 3-6.

The interferogram becomes an important part of Fourier transform spectroscopy when it is recognized that equation 3-10 is one half of a cosine Fourier transform pair, the other half being:

$$B(\bar{\nu}) = \int_{-\infty}^{\infty} I(\delta) \cos 2\pi \bar{\nu} \delta \cdot d\delta$$  \hspace{1cm} (3-11)

$$= 2 \int_{0}^{\infty} I(\delta) \cos 2\pi \bar{\nu} \delta \cdot d\delta$$  \hspace{1cm} (3-12)

Equations 3-11 and 3-12 are equivalent because $I(\delta)$ is an even function. Equations 3-11/3-12 represent the spectral characterization of the light source and the experimental setup. This characterization is used in Fourier transform infrared spectroscopy, which is described later in this chapter.

**Practical limitations and apodization**

The interferogram measured is a discrete signal with a sample distance $\Delta\delta$. According to the Nyquist sampling theorem, this means the maximum wavenumber (or folding wavenumber) that can be determined in its Fourier transform, without the effects of aliasing, is given by:

$$\bar{\nu}_{\text{max}} = \frac{1}{2\Delta\delta}$$  \hspace{1cm} (3-13)

where $\Delta\delta$ is the spacing of the sampled interferogram. Using
\[ \Delta \bar{\nu} = \frac{1}{N \Delta \delta} \]  
(3-14)

with \( \Delta \bar{\nu} \) the spacing of the resultant Fourier transform and \( N \) the number of samples, the maximum wavenumber can also be expressed as:

\[ \bar{\nu}_{\text{max}} = \frac{N \Delta \bar{\nu}}{2} \]  
(3-15)

The Fourier transformation of an interferogram into an ideal spectrum that contains all information about the interferogram is only mathematically possible if the interferogram is infinitely long, which would mean an infinitely long mirror path. This is obviously not possible in a practical measurement. Interferograms are therefore limited to a certain range of retardation. The interferogram as measured can be thought of as a multiplication of an ideal, infinitely long interferogram with a rectangular window function (a “boxcar” function) with amplitude 1 and width \( \delta \). Since the Fourier transform of a boxcar function is a sinc-function\(^1\), the calculated spectrum is the convolution of this sinc function with the spectrum of the (hypothetical) ideal interferogram. This convolution results in side lobes in the spectrum.

These side lobes can be suppressed by replacing the boxcar function with another, appropriately designed, window function. This process is called *apodization*. Many such functions exist. The two functions used throughout this project are the *Happ-Genzel* window and the *Blackman-Harris* window. The Happ-Genzel window offers adequate side lobe suppression at the cost of “band broadening”, i.e., the loss of fine detail in the spectrum. The Blackman-Harris window offers stronger side lobe suppression, but results in greater band broadening.

The more points are in a signal in the time domain, the higher the resolution in the frequency domain. To obtain a smooth spectrum, it is therefore useful to “pad” the signal with zeros. It is noted that this does not add information to the final spectrum, but it is an efficient way to create a smooth spectrum. Zero padding is also done to ensure that the time domain signal has a number of samples that is a power of 2, which allows for efficient calculation of the Fast Fourier Transform [71].

Zero padding the signal, however, may cause an abrupt transition from the signal to the zeros. Such an abrupt transition shows up in the spectrum as a periodic disturbance. There may also be external disturbances caused by equipment in the vicinity of the measurement setup. How strongly these effects are present in the spectrum depends on the choice of the window function. The previously mentioned Blackman-Harris window is better at suppressing high-frequency disturbances than the Happ-Genzel window.

### 3-2-2 Fourier transform infrared spectroscopy

In a Fourier transform infrared (FTIR) spectroscopic measurement, the setup of figure 3-4 is modified by placing a sample of interest between the beamsplitter and the detector, which distorts the signal measured at the detector. This distortion is incorporated in the quantity \( B(\bar{\nu}) \), which means that applying equation 3-11 can yield spectral information about the sample, i.e., the absorptance of the sample as measured in transmittance mode.

\(^1\text{sinc}(x) = \frac{\sin(x)}{x}\)
The light source produces infrared light, which either passes through, or is absorbed by the sample. Absorption produces peaks in the measured absorption spectrum, which is given by equation 3-12. The positions and heights of these peaks are indicative of chemical properties of the sample, i.e., the presence and quantity of chemical elements, and of the vibrational modes of the atomic bonds associated with the absorption [72].

The FTIR spectrometer used in this experiment was a Thermo Scientific Nicolet 5700 which outputs via USB to a PC running the Omnic software package to process the data. The light source is an infrared lamp. The spectrometer contains a KBr beamsplitter and a HeNe laser with a wavelength of 632 nm which is used for tracking the position of the moving mirror. The spectral range was set to 400-4000 cm\(^{-1}\).

The samples used are films of a-Si:H deposited on a c-Si wafer by rf-PECVD. To correct for the spectrum of the lamp and other optics in the spectrometer, a measurement consists of two parts: one measurement of the sample and one of a piece of the same wafer without a layer of a-Si:H. These measurements were done consecutively, using the movable sample stage inside the Nicolet, after having purged the device with nitrogen for at least 15 minutes to remove contaminants such as water vapor. The two measurements are combined by the Omnic software, which yields the FTIR transmittance spectrum of the a-Si:H film. A typical result is shown in figure 3-7. The most noteworthy features of the spectrum are the interference pattern (the background “wave”), caused by internal reflection in the film, and two pronounced absorptance peaks associated with the wagging and stretching modes of silicon-hydrogen bonds. These peaks contain useful information, the extraction of which is described in section 3-3-1.

![Figure 3-7: A typical FTIR spectrum of an a-Si:H film](image)

3-2-3 Fourier transform photocurrent spectroscopy

Fourier transform photocurrent spectroscopy (FTPS) is a modification of FTIR spectroscopy first used by Vanecek and Poruba [73]. Instead of placing a sample between the Michelson in-
The sample can be either a photoresistor or a photovoltaic device. In the former case, an external voltage is applied to the terminals of the sample to extract the light-induced free carriers; in the latter case, the current flows due to the intrinsic electric field and no external voltage is needed to extract the carriers. The photocurrent is amplified by an external current amplifier, fed through an A/D converter and back into the FTIR spectrometer, which outputs to a PC for data processing. Figure 3-8 shows the schematic setup and a photograph of the actual setup used.

Figure 3-8: (a) Schematic setup. Taken from [73]. (b) Setup as used. FTIR spectrometer (A), current amplifier (B), A/D converter (C), PC (D), voltage source (E; not visible), sample box (F).

The dynamic range of a photocurrent spectrum is quite large, spanning several orders of magnitude. As a result, any signal below a certain wavenumber (typically below 12000 cm\(^{-1}\)) will be obscured due to the much weaker absorption in a-Si:H of infrared light in comparison to visible light. To resolve the photocurrent induced by the absorption of infrared light more accurately, a set of optical filters is used. The filters are denoted: RG645, RG695, FGL780, RG850 and Si. The numbers indicate the cutoff wavelengths. The Si filter is a piece of c-Si wafer; its bandgap of 1.12 eV corresponds to a cutoff wavelength of 1107 nm, or wavenumber of 9033 cm\(^{-1}\).

The photocurrent spectrum is measured multiple times, using filters with progressively low cut-off wavenumbers. Doing this allows for a progressively higher amplification of the photocurrent signal extracted from the sample, resulting in a better signal-to-noise ratio on the interferogram and hence on the photocurrent spectrum. Put differently, using filters allows “zooming in” on the low amplitude portion of the signal. This process is illustrated in figure 3-9. A linear plot of the measurements (subfigure (a)) shows that the base measurement with the RG645 filter results in a relatively low photocurrent spectrum. Measurements using filters RG695 through RG850 were done at one order of magnitude higher amplification, resulting in a significantly stronger signal in the range covered by those filters. The measurement with the c-Si filter was done at one order of magnitude higher amplification still, which gives a stronger signal in the low wavenumbers. Plotted on a logarithmic scale, the same higher signal strengths show. It can also be seen that the signal-to-noise ratio is improved for the lower cutoff filters. This is most notable in the 7000-9000 cm\(^{-1}\) range, where the silicon filter
signal is much smoother than the other measurements.

![Graph of FTPS measurements](image)

**Figure 3-9**: FTPS measurements taken under identical conditions using different optical filters, plotted against a linear (a) and logarithmic (b) axis. Dashed lines indicate the cutoff wavenumbers of the filters.

To correct for the spectral dependence of the signal on the light source and various optics in the system, the signal is normalized using a background measurement done on a spectrally calibrated detector (in this case: a built-in deuterated triglycerine sulphate (DTGS) detector). To obtain the same high dynamic range in the background measurement, the same approach using filters is taken.

The frequency response of the sample is different from that of the DTGS detector and neither are constant (as evidenced by different signals at different mirror speeds). To determine and correct for these responses, extra background and sample measurements have to be taken at different scanning velocities. By changing the scanning velocity, the modulation frequency is changed. Taking measurements at different scanning velocities therefore yields the spectral response of the detector. This correction is described further in section 3-3-2.

The spectrometer used throughout this project is a Thermo Scientific Nicolet 8700. It has
several light sources, but only the white lamp has been used in this project. Two filter wheels are fitted inside which hold the filters mentioned above, as well as a screen wheel (neutral density filter). A movable mirror allows for switching the light beam between the background detector and the external sample compartment.

The spectrometer is controlled by the Omnic software package. At the highest resolution available, the spacing in the wavenumber domain is 15.428 cm$^{-1}$. At 2048 samples per scan, this allows for obtaining spectra with a maximum wavenumber of 15798 cm$^{-1}$ (see equation 3-15. This is just short of the wavenumber of the laser, which is 15822 cm$^{-1}$ (corresponding to 632 nm). To make sure that the laser signal does not affect the measurement, the maximum wavenumber is set slightly lower than this, to 15700 cm$^{-1}$.

The external compartment consists of an aluminum box used to shield the sample from electromagnetic disturbances. Inside the box are a horizontal sample stage, a parabolic off-axis mirror to direct the beam toward the sample and an array of changeable LEDs.

The sample stage is temperature controlled, allowing active cooling and heating up to roughly 180°C. The LED array consists of 4 blocks of 16 LEDs each. These blocks can be switched out for a different color. During this project, white LEDs with a wavelength range of 400-800 nm and blue LEDs with a wavelength of 475 nm are used. The LEDs are controlled by a Tektronix AFG3101 function generator which allows for turning on the LEDs for a specified time and with specified intensity. Calibration of the LEDs’ intensity was done with an Avantes spectrometer. The temperature controlled stage and water cooling are controlled by a custom control system. A Keithley 428 current amplifier is used to amplify the signal as described above.

3-2-4 External Quantum Efficiency

The external quantum efficiency (EQE) is defined as the ratio of the number of electrons extracted ($N_e$) from a solar cell to the number of incident photons ($N_{ph}$) as a function of wavelength of the incident light:

$$\text{EQE}(\lambda) = \frac{N_e}{N_{ph}}$$  \hspace{1cm} (3-16)

The EQE is determined by shining light onto a device and measuring its output current. The polychromatic light is led through a monochromator (a set of rotating gratings) in steps of 10 nm. The output current as a function of wavelength is normalized by a calibration measurement done on a photodiode with a known response, resulting in the EQE of the sample.

3-2-5 External Parameters

The main external parameters of interest of a solar cell are its open circuit voltage ($V_{OC}$), its short circuit current ($I_{SC}$) or current density ($J_{SC}$), its fill factor ($FF$) and its efficiency ($\eta$). The FF is defined as:
In the above equation, MP stands for maximum power. Visually, the FF is a measure of the “squareness” of a JV-curve. This squareness is affected by two other parameters: the series resistance ($R_s$) and shunt resistance ($R_{sh}$). These two resistances are part of the equivalent circuit of a solar cell, shown in figure 3-11.

The efficiency is defined as the ratio of output power to input power. If operating at MP, using the definition of FF, this results in:

\[
\eta = \frac{V_{MP}I_{MP}}{P_{in}} = \frac{V_{OC}I_{SC}FF}{P_{in}}
\]  

(3-18)

All of the above are obtained by combining the model of figure 3-11 with a measured JV-curve. This curve is measured using the PASAN setup shown in figure 3-12. A voltage is swept across the terminals of a solar cell while measuring the current under illumination. The
illumination is provided by a flash and the measurement is calibrated using a photodiode with a known response.

**Figure 3-12:** PASAN setup, showing the box containing the flash (A), the sample stage (B) and the back contact probe control mechanism (C).

### 3-2-6 Reflection/transmission

Reflection/transmission (RT) measurements are done using a setup named Mini RT, manufactured by Eta-optik. The setup consists of a sample stage with a hole allowing for illumination by light from an aligned halogen lamp. Two silicon diode arrays on either side of the sample register the reflected and transmitted components of the light. The transmittance and reflectance signals are calibrated by taking a dark measurement and measurement on a piece of c-Si respectively.

The Scout software package allows fitting the data using a model which takes into account the layers (air, a-Si:H, glass), their thicknesses and properties and internal reflection. Applying the Fresnel equations to this model results in estimates of the film’s thickness, the bandgap of the a-Si:H, the Urbach energy and the $n$ and $k$ data (the wavelength dependent real and imaginary components of the complex refractive index respectively).

The absorption coefficient $\alpha$ as a function of photon energy $E_{ph}$ is then calculated from the $k$ data using [27]:
3-2-7 Raman spectroscopy

Raman spectroscopy is a measurement technique based on the scattering of monochromatic light. When a photon hits a material, it may induce an oscillating dipole caused by the deformation of the electron cloud around an atom under the influence of the electromagnetic field of the incident radiation. This oscillation can change the polarizability (i.e.: the deformability) of the electron cloud, which causes an amplitude modulation of the oscillation. It is this modulation which contains information about the structural properties of the material.

The interaction between the photon and the material can be described as a momentary absorption by a transition from the ground energy state into a “virtual state”. Relaxation from this state results in the emission of a photon and possibly a phonon. When only a photon is emitted (which is in the majority of cases), it is called elastic or Rayleigh scattering. When both a photon and a phonon are emitted, the phonon is associated with the change in vibrational mode which is reflected in the above mentioned modulation. The emitted photon will have an energy that is slightly lower (“Stokes”) or higher (“anti-Stokes”) than the incident photon and the difference can be measured. This type of scattering is called Raman scattering and the energy (or frequency or, most commonly, wavenumber) shift associated with it (i.e., the difference in energy between the incident and emitted photon) is called the Raman shift, given by equation 3-20 [74], [75].

\[
(\Delta \bar{\nu})_{\text{Raman}} = \bar{\nu}_{\text{incident}} - \bar{\nu}_{\text{emitted}}
\]  

(3-20)
A Raman spectroscopic experiment consists of shining monochromatic (laser) light onto the material of interest and measuring the intensity of the scattered light as a function of wavenumber, filtering out the Rayleigh scattering to improve the signal quality. From the peaks in the resulting Raman spectrum, one can infer information about the structural properties of the material.

Because the photon has very low momentum compared to that of a Si-atom, only the optical phonon, associated with opposite phase (and hence momentum-neutral) oscillation of neighboring atoms, will cause a Raman shift for crystalline silicon. This results in a very sharp peak at 520 cm\(^{-1}\) in the Raman spectrum. In amorphous silicon, the variation in bond lengths and angles allow for the transfer of momentum of the photon, which results in a broader Raman peak centered at 480 cm\(^{-1}\) [76]. This peak contains information about transverse and longitudinal optical and acoustic modes, which some claim contain information about medium/short range order [77]. Typical spectra for both materials are shown in figure 3-14.

![Raman spectra of a-Si and c-Si](image)

**Figure 3-14:** Raman spectra of a-Si and c-Si, showing the different Raman peak shapes and positions.

The measurements were performed with a Renishaw inVia Raman microscope (see figure 3-15. The sample was illuminated with a green Argon laser with a wavelength of 514 nm.

### 3-3 Data processing and manipulation

Before measurement results can be interpreted, it is often necessary to process them and transform them into meaningful quantities. How this is done for data obtained through the various measurement techniques is described in this chapter.

#### 3-3-1 FTIR

An FTIR spectrum such as the one shown in figure 3-7 contains information about the refractive index \(n_\infty\), nanostructure and hydrogen content of a-Si:H and of the layer thickness,
as discussed in section 2-3-2. This information is contained in the wagging and stretching modes. In order to extract this information, Gaussian distributions are fitted to the absorption peaks.

To fit the background signal, an optical fit model is used (see appendix B for this and the WM and SM fit functions) with four fit parameters: the layer thickness $d$, the refractive index $n$ and two scaling factors $c_1$ and $c_2$. To fit the background properly, the peaks are cut from the signal (see figure 3-16). The fit gives only a rough estimation, indicating that the fit function does not perfectly describe the physical system. The value of the fitted thickness should be similar to the one obtained through an RT measurement, assuming the same a-Si:H film was co-deposited on a glass substrate (see section 3-2-6).

To fit the wagging modes, only the peak data are used. The values for $n$ and $d$ found during the background fit are used and the values for $c_1$ and $c_2$ are adjusted to ensure the background connects well with the boundaries of the peak (see figure 3-17 (a)). With the background properly set, two Gaussians for the LWM and HWM are fitted to the peak with free fit parameters $i$, $f$ and $s$ representing the amplitude, position and width of the Gaussians respectively. The end result is shown in figure 3-17 (b). Also shown is the composition of the final fit by the LWM and HWM (c).

The background fit for the stretching modes is more complicated than that for the wagging modes. Fitting a background through the data points next to the SM is problematic without adding two additional Gaussians with opposite signs and similar amplitudes to the background. This may have to do with the fact that the c-Si reference wafer has not been exposed to a plasma, while the c-Si wafer on which the film under investigation is deposited has. This may have had etching and hydrogenation effects which could have introduced nanostructural differences with the reference wafer.

Care is taken to ensure these distributions do not significantly overlap with the stretching
**Figure 3-16:** Determining the background fit of an FTIR spectrum.

**Figure 3-17:** Determining the WM from an FTIR measurement. Fitting the background (a) and fitting the WM (b). End result of fit after subtraction of background and flipping sign. Total fit is shown as sum of LWM and HWM (c).
Figure 3-18: Determining the SM from an FTIR measurement. (a) Fitting the initial background on data points somewhat removed from the SM position. (b) Adding two Gaussians to the background to account for the deviation of the data from the background closer to the SM. (c) Fitting the LSM and HSM to the SM data. The gap in the FTIR data around 2350 cm\(^{-1}\) is due to noise removed to improve the background fit.
Data processing and manipulation

modes themselves. See table 3-1 for an overview of the data ranges used for all fits. It is sometimes necessary to also use $n$ and $d$ as free fit parameters to improve the quality of the fit. Since the area of interest is the evolution of local modes, and because the values for $n$ and $d$ do not change very significantly, this is deemed acceptable. Once a proper background has been created, the two Gaussians for the LSM and HSM are fitted to the peak, each again with the three fit parameters already mentioned. The process is illustrated in figure 3-18.

<table>
<thead>
<tr>
<th>Fit</th>
<th>Wavenumber ranges [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td>1200-1700 / 2400-4000</td>
</tr>
<tr>
<td>WM</td>
<td>530-790</td>
</tr>
<tr>
<td>SM background</td>
<td>1500-1750 / 2375-2600</td>
</tr>
<tr>
<td>SM improved background</td>
<td>1500-1850 / 2150-300</td>
</tr>
<tr>
<td>SM</td>
<td>1800-2200</td>
</tr>
</tbody>
</table>

Table 3-1: Wavenumber fitting ranges for WM, SM and backgrounds.

3-3-2 FTPS

Processing the photocurrent data

As discussed previously, one FTPS measurement consists of 5 measurements with different filters, and 2 additional measurements for frequency correction. Each measured spectrum is stored as wavenumber-intensity pairs in a comma-separated value file. To obtain a usable spectrum, several steps need to be taken.

As mentioned in section 3-2-3, both the background and sample measurements need to be corrected for the frequency response of the DTGS detector and the sample itself respectively. The sample measurements also need to be corrected for the non-linear transfer characteristic of the current amplifier. This latter correction is done by simply dividing every individual measurement by the normalized frequency characteristic of the appropriate amplification factor/filter rise time setting of the amplifier. These characteristics were separately obtained for this purpose and they can be found in appendix E.

For the detector frequency correction, a method described elsewhere [78] has been refined. To find the frequency response of the DTGS detector, three measurements each are taken at different mirror speeds and hence different modulation frequencies (see section 3-2-1). These measurements are then grouped into sets of three: one of each speed at every measured wavenumber value. Because the actual amplitude of the FTPS signal at any particular wavelength is a function of the light source and the optics of the system, the individual components of the frequency characteristic have to be normalized to each other. This is done by scaling each set of 3 using the values of the obtained exponential fits at a chosen wavelength. The result is a dataset that corresponds to a normalized frequency response of the detector and an exponential is fit to obtain the final characteristic. This process is illustrated in figure 3-19.

The frequency response of the sample is obtained in almost exactly the same manner. The only change that is made to the procedure is that groups of three which are taken in regions where the signal to noise ratio is poor are discarded, to ensure a faithful fit of the true
Figure 3-19: Obtaining the frequency response of FTPS background measurements. Measurements are taken at three different mirror speeds (a). They are converted to modulation frequency by multiplying by the mirror speed and an exponential is fit to each set of 3 points with the same wavenumber (dashed lines)(b). The signal is normalized and the exponential frequency response (dashed blue line) of the detector is fitted (c).
Figure 3-20: Obtaining the frequency response of FTPS sample measurements. Measurements are taken at three different mirror speeds (a). They are converted to modulation frequency by multiplying by the mirror speed and an exponential is fit to each set of 3 points with the same wavenumber (dashed lines)(b). The data within 97% of the maximum value are normalized and the exponential frequency response (dashed blue line) of the detector is fitted (c).
Table 3-2: Energy ranges used for the various filtered measurements.

<table>
<thead>
<tr>
<th>Filter</th>
<th>energy range (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RG645</td>
<td>&gt;1.75</td>
</tr>
<tr>
<td>RG695</td>
<td>1.58-1.75</td>
</tr>
<tr>
<td>FGL780</td>
<td>1.40-1.58</td>
</tr>
<tr>
<td>RG850</td>
<td>1.00-1.40</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;1.00</td>
</tr>
</tbody>
</table>

classical. This is done by taking only those data points that are within 97% of the maximum value. The procedure is illustrated in figure 3-20.

After dividing every measurement by the frequency correction functions in the appropriate range, the separate measurements have to be combined into a single photocurrent spectrum. To do this, each set of measurement data has to be cropped to its relevant range (i.e., from roughly the cutoff wavenumber of its own filter to that of the next). Before cropping, however, some or all of the measurements require smoothing to remove noise. Without this smoothing the connection cannot be made reliably, as there might appear discontinuities in the combined spectrum due to the connection of two measurements at a noise peak. Smoothing is done by applying one or multiple passes of Savitzky-Golay smoothing. Typical amounts of passes are 0 or 1 for the RG645 and RG695 filters, 1 to 3 for the FGL780 and RG850 filters and 5-30 passes for the Si filter. Care is taken to apply an amount of smoothing passes that removes all or most of the noise, but leaves intact all apparent characteristics of the signal (i.e., the smoothed signal should cross noise fluctuations, but not significantly deviate from the signal).

After the smoothed signal for each filter is compared to the unsmoothed to ensure the two overlap in the relevant wavenumber range, they are connected into one smoothed photocurrent spectrum. These connections are done by selecting connection energies slightly lower than the cutoff energy, and scaling the “lower” spectrum linearly to the “higher” one. The default energy ranges used for each filter are shown in table 3-2. This smoothing and connecting of individual filter measurements is illustrated in figure 3-21.

**Connecting the photocurrent spectrum to RT/EQE**

The resultant connected and frequency corrected photocurrent spectrum then has to be normalized. This is done in one of two ways. When the FTPS measurement is taken of a film on glass, it is useful to connect to an absorption coefficient spectrum, to obtain a wide-range absorption coefficient spectrum. A band-to-band absorption coefficient spectrum can be obtained from an RT measurement, as described in section 3-2-6. By matching the slope of the FTPS spectrum with that of the absorption spectrum in a predefined energy range (1.60-1.68 eV by default, but this may need to be adjusted slightly, depending on the measurement), the two data sets can be connected smoothly.

Because the substrate is flat, however, there will be significant interference fringes present in the signal. An optical model [79] is used to remove these fringes. Care is taken to verify that the calculated thickness that the model yields corresponds to the thickness determined using the RT measurement, confirming that the interference has been adequately removed. The process is illustrated in figure 3-22.
Figure 3-21: Smoothing of FTPS measurements using RG645 (a), RG695 (b), FGL780 (c), RG850 (d) and Si (e) filters with energy ranges used in connected FTPS spectrum shown in magenta. (f) Final connected and smoothed FTPS spectrum.
Figure 3-22: Connection of FTPS signal of varying thickness films on glass to absorption spectra (indicated by RT) and removal of interference fringes [80]. (a) FTPS and RT data before processing and connection. (b) Final absorption spectra. The thicknesses are indicated by $d_{RT}$ (fitted using RT measurement; see section 3-2-6) and $d_{FTPS}$ (fitted using the optical model mentioned earlier in this section [79]).
When the FTPS measurement is of a solar cell, connection to an absorption coefficient spectrum is not possible. A reliable RT measurement cannot be taken because of the opaque back contact of the cell and the complex configuration of a solar cell, which introduces interface effects and does not allow for reliable determination of the nk-data of the intrinsic layer. As an alternative, the FTPS data can be connected to an EQE measurement taken of the same sample, since both represent the wavelength dependent conversion efficiency from incident photons to collected charge carriers. Although an EQE measurement decays rapidly towards the lower energies close to the band gap, there is a region where the two sets overlap. Again, by matching the slopes a smooth connection can be made, resulting in a “wide-range” EQE, which will be denoted as FTPS-EQE henceforth. Although this exercise results in a quantity that is less directly related to defect densities of state (which is normally done by integration of an absorption coefficient spectrum), it is nonetheless useful to track relative changes in subgap states.

In a solar cell, too, interference plays a role. The effect is expected to be much smaller than for a film on glass, however. Because of the textured substrate (Asahi VU) and consequently, the various textured interfaces, the light reaching the i-layer is much less coherent than that hitting an i-layer on glass. A reliable model for this interference is currently lacking, but recently a correction method (inspired on [81]) has been developed at the PVMD group which attempts to remove the effects of interference from an FTPS spectrum [80]. Figure 3-23 demonstrates this correction and shows that the measured and corrected signals converge for thinner i-layers. Both the magnitude and the frequency of the interference fringes diminish with i-layer thickness. The correction routine depends on accurately determining the inflection points of the uncorrected signal (which becomes more difficult to do for thinner i-layers). The measured and corrected signals are already quite similar for an i-layer of 364 nm thickness and are expected to be even more closely matched for cells with an i-layer of 250 nm, which were used throughout this project. For this reason, the correction method was not deemed necessary in this case and was not used to correct the spectra obtained. However, when interpreting results from FTPS measurements, one is reminded that interference may still play a role.

After removing the interference from the FTPS signal, it is connected to an EQE signal obtained from the same sample (see figure 3-24). This is done again by matching the slopes of the signals in an appropriate energy range (around 1.7 eV by default).

**Fitting the defect distributions**

After having obtained an absorption coefficient spectrum, information about the makeup of the subgap signal is extracted by applying equation 2-11. First, the Urbach line is fitted to the exponential part of the spectrum using a least squares approach (figure 3-25). This line is then subtracted from the signal, after which a variable number of error functions is fitted. This is illustrated in figure 3-26. Also shown in that figure are the derivatives of the data and defect distributions, to illustrate the mathematical relation between the Gaussians associated with defect distributions and their integrals (see section 2-5). In the remainder of this report, whenever error function fitting occurs, the reader is reminded of this link.

The procedures for obtaining absorption coefficient spectra and FTPS-EQE spectra are mathematically identical. The quantities involved are different, but for the purpose of qualitative
Figure 3-23: Photocurrent spectra of solar cells with i-layers of varying thickness (indicated by $d_{Si}$ with and without interference [80].
Figure 3-24: Connecting the FTPS signal obtained to an EQE signal for solar cells with i-layers of varying thickness (indicated by $d_{Si}$)[80].

(a) FTPS and EQE data before processing and connecting. (b) Final FTPS-EQE spectra.
3-3-3 Raman spectroscopy

A common data processing technique for Raman spectra is to extract information about the crystallinity of an a-Si:H/µc-Si:H film. This involves determining the relative contributions of the amorphous and silicon peaks around 500 cm\(^{-1}\) to the Raman spectrum. As this technique has not revealed many significantly new insights in the a-Si:H nanostructure (see chapter 4), it is not explained further and the interested reader is referred to [76].

Almost entirely analogous to extracting information about the stretching mode from an FTIR spectrum, fitting Gaussians to the 2000-2100 cm\(^{-1}\) mode of a Raman spectrum can give information about the SM. Because the signal to noise ratio of a Raman spectrum is decidedly worse than that of an FTIR spectrum, however, no attempt is made to fit a HSM and LSM separately, as this would not yield any meaningful information about the ratio between them. Instead, a single Gaussian is fit to the mode, to be able to make a qualitative comparison of the evolution of the mode between the Raman data and e.g. the hydrogen content as given in equation 2-2 (in which the contributions of the LSM and HSM are summed).

Because the absolute magnitude of a Raman spectrum depends both on the alignment of the laser on the sample and the number of measurement scans, all spectra were normalized to their (well-defined) maximum peak value. Next, again analogous to the FTIR fitting procedure, the SM peak was cut from the signal and a (linear) background baseline fit is done on the

![Figure 3-25: Determining the Urbach line. The remainder of the signal after subtraction of this line is indicated by the shaded area.](image)
Figure 3-26: Fit of subgap FTPS-EQE and deconvolution of fit into variable number (in this case 4) of error functions (a) and derivatives of the same (b).
neighboring data. This baseline was subtracted from the signal and a Gaussian is fitted to the resulting (net) SM peak. This process is illustrated in figure 3-27.

Figure 3-27: Example of processing the SM of a Raman spectrum. Normalized Raman SM (a), linear baseline fit (b), net normalized SM (c) and Gaussian fit of SM (d)
This chapter describes a thermal annealing study of a-Si:H. Its purpose is to track various properties while exposing it to incrementally higher temperatures, in order to deduce information about the material. Note that parts of this work have been published [35].

4-1 Experiment

4-1-1 Samples

The samples used in this experiment consist of films of a-Si:H on glass, films on c-Si and solar cells. The films on c-Si are made for the purpose of doing FTIR measurements. By comparing an FTIR measurement of a film on c-Si to a baseline measurement of the bare wafer, the absorptance spectrum of just the a-Si:H film can be obtained. This is not possible if the measurement is done on a film on glass, since glass absorbs infrared light very effectively.

The films on glass and on c-Si are deposited during the same run in the Amigo cluster tool described in section 3-1, to ensure comparable properties. Five sets of films are created with hydrogen dilutions of R=0, 2.5, 5, 7.5 and 10. The glass is Corning Eagle XG. Coplanar rectangular aluminium contacts 300 nm thick were deposited 0.5 mm apart. The c-Si substrate was cut from a <100> n-type c-Si wafer with a thickness of 500-550 µm. A piece of the same wafer was cut to serve as reference in FTIR measurements.

The solar cells are deposited on an Asahi VU substrate, which is a textured float glass with a SnO$_2$:F-based transparent conductive oxide (TCO) layer [82]. On each strip of Asahi, 30 p-i-n solar cells (“dots”) are deposited. The p-layer consists of an a-Si:H layer with a µc-Si:H top layer. This extra µc-Si:H is added to allow comparison with cells on flat aluminum zinc oxide substrates, which require such a layer to prevent damage to the transparent conductive oxide layer. The a-Si:H p-layer undergoes a H-plasma treatment to improve the electrical contact at the p-i interface. In between the a-Si:H p- and i-layers, a SiC buffer layer is deposited to help increase the $V_{OC}$ of the device.
Solar cells with hydrogen dilutions of R=0, 2.5, 5 and 7.5 are created. The front contacts consist of 300 nm aluminum; the back contacts consist of layers of silver (100 nm), chromium (30 nm) and aluminum (300 nm). The silver has high reflectance and the aluminum acts as a stable measuring electrode. The chromium is added as a diffusion barrier between silver and aluminum. Prior to the start of the experiment, all samples are annealed for 30 minutes at 130 °C. Note that this does not imply that all metastable defects are removed from the films/cells (as illustrated in figure 2-13). However, annealing at higher temperatures might lower the solar cell efficiency through undesired boron diffusion from the p-layer into the i-layer. The annealing temperature of 130 °C is therefore chosen as a good compromise.

All deposition parameters are given in tables A-1 through A-5 in appendix A.

4-1-2 Experiment design

The experiment consists of a repeating cycle of measurements and annealing. Below is an overview of the measurements done and the sample type on which it was done. See chapter 3 for descriptions of all the measurement techniques used.

- FTIR (films on c-Si)
- RT (films on glass)
- External parameters (solar cells)
- EQE (solar cells)
- FTPS (films on glass and solar cells)
- Raman (films on glass)

Annealing is done after each measurement cycle. Deposition chambers of the Amigo are used in order to anneal at UHV conditions. This is done to avoid the influence of contaminants and oxidation effects during the annealing process. Heater temperatures are set such that calibrated substrate holder temperatures are at the desired annealing temperatures. Annealing is done for one hour in a pre-heated chamber. After annealing, the samples are returned to the Amigo load lock where they are left to cool in vacuum. Since vacuum cooling is generally slow (radiative only), care is taken to allow for enough time to let the samples cool to room temperature. For the higher temperature annealing steps, samples are left in the load lock overnight for this purpose. Annealing starts at 50 °C and increases in 50 °C steps up to 500 °C.

After each annealing step, new Al contacts are deposited on the films on glass (using the Provac), to avoid any negative side-effects (e.g. diffusion of the Al into the silicon) of the annealing on the contact or the contact-layer interface. Contacts are placed close to the old contacts, to minimize the effect of possible inhomogeneity of the film.

EQE and FTPS measurements are done on the solar cell with the highest efficiency after each annealing step.
In addition to the above experiment, the in-situ annealing capability of the FTPS setup is tested. To this end, a solar cell (R=10 absorber layer, simple p-i-n structure; see section 5-1) degraded through light soaking is annealed at 130 °C during exponentially increasing periods. Before, after and in between these periods, FTPS measurements are performed. To ensure similar conditions during each measurement, the sample is cooled to 25 °C after each annealing period. After the FTPS measurement, the stage is heated up again. Because of the ramp-up and ramp-down times of heating and cooling respectively, the time period is measured between the moment that the stage temperature reaches 120 °C during heat-up and the moment that it reaches 35 °C during cooldown. External parameters of the solar cells are measured before and after the experiment.

4-2 Results and discussion

4-2-1 FTIR spectroscopy

The FTIR spectra of the films obtained during the annealing experiment are processed as described in section 3-3-1, yielding the intensities, positions and widths of the lower and higher wagging and stretching modes. The intensities are then used in equations 2-1 and 2-2 to obtain the more physically meaningful hydrogen content. The results, plotted for all hydrogen dilutions are given in figure 4-1.

![Figure 4-1: Hydrogen content calculated from the WM (a) and SM (b)](image)

The hydrogen contents calculated from the WM and SM show roughly the same characteristic, as is to be expected (see section 2-3-2).
In both cases \( c_H \) shows a plateau for \( T_a < 300 \, ^\circ\text{C} \), after which it declines sharply. At 500 \( ^\circ\text{C} \) \( c_H \) approaches zero, which means there are almost no Si-H bonds left in the material. This is consistent with the hydrogen effusion that takes place at temperatures greater than 300 \( ^\circ\text{C} \) (see section 2-6-3).

As given by equation 2-2, \( c_{H,SM} \) consists of contributions by the LSM and the HSM. Figure 4-2 shows these separate contributions.

The contribution from the LSM shows largely the same trend as that of \( c_{H,SM} \) as a whole, which makes sense as the LSM has a much larger intensity than the HSM. The contribution from the HSM shows a decidedly different trend. Like the LSM, it starts out at a plateau, but unlike the HSM, there is a distinct peak at 300 \( ^\circ\text{C} \). As described in section 2-3-2, the LSM is associated with Si-H bonds in divacancies and the HSM is related to bonds at the surface of nanosized voids. An increase in \( c_{H,HSM} \) therefore means an increase in the number of these voids.

This result can be interpreted as the agglomeration of some of the divacancies into nanosized voids. As the temperature rises, the vacancies in the material become mobile. When divacancies encounter other divacancies, they seem to agglomerate [83]. Since \( c_{H,LSM} \) does not change significantly, the amount of voids has to be relatively modest compared to the amount of divacancies. This is in line with the finding in [37] that material with \( c_H < 14\% \) contains predominantly divacancies, rather than nanosized voids.

Note that \( c_{H,LSM} \) still increases slightly from \( T_a = 250 \) to 300 \( ^\circ\text{C} \), even though the divacancies

**Figure 4-2: Contributions of the LSM (a) and HSM (b) to \( c_H \). Nanostructure parameter \( R^* \) (c)**
already appear to have started agglomerating. It could be that H\textsubscript{2} is accumulating inside divacancies, changing the Si-H bond oscillation strength and affecting the FTIR measurement. Alternatively, H\textsubscript{2} buildup inside divacancies might cause a temporary increase of Si-H bonds.

At 350 °C, both \(c_{H,LSM}\) and \(c_{H,HSM}\) drop off rapidly, but \(c_{H,LSM}\) drops off more quickly. This means that, although the total amount of Si-H bonds is decreasing, the relative contribution of the HSM increases, meaning relatively more nanosized voids. This is reflected in the nanostructure parameter \(R^*\), also shown in figure 4-2, which keeps increasing until 350 °C. This can be interpreted as a combination of continued vacancy agglomeration and hydrogen effusion.

From 400 °C to 500 °C, both \(c_{H,LSM}\) and \(c_{H,HSM}\) rapidly approach zero, which can be associated with the complete effusion of bonded hydrogen from the remaining divacancies and voids.

Summarizing, 4 stages can be identified: 1) little activity below 250 °C, 2) vacancy agglomeration around 300, 3) combined agglomeration/effusion and 4) complete effusion. These stages show up clearly in a “phase plot” of \(c_{H,HSM}\) vs \(c_{H,LSM}\) (figure 4-3). A recent annealing study using positron annihilation shows that already in stage 1 vacancy agglomeration occurs and stages 1 and 2 could therefore be combined into one stage with vacancy agglomeration without hydrogen effusion [35].

![Figure 4-3](image-url)

\textbf{Figure 4-3:} Contributions to the hydrogen content by the HSM vs that by the LSM for varying R. Regions indicated as described in text.

The above interpretation is supported by the evolution of the density of the film, as calculated using equation 2-3 and shown in figure 4-5. Hydrogen accumulation in vacancies causes a pressure increase in the material, which is reflected in the density peak. Note that the density at this point is higher than that of c-Si. This pressure is subsequently released when
the hydrogen effusion from the vacancies starts at $T_a > 300^\circ C$, causing a decrease in the density of the material.

Figure 4-4 shows the positions of the LSM and HSM as function of annealing temperature. Disregarding the data for $T_a=450^\circ C$ (at which temperature fitting the HSM to the FTIR spectrum has become difficult), it is clearly seen that the HSM has a larger shift to lower wavenumbers than the LSM. Literature shows that the shift in wavenumber is proportional to the reciprocal effective volume of a monohydride in the a-Si:H network [38]. A larger shift for the HSM than for the LSM therefore means that the effective volume available to monohydrides in nanosized voids decreases more than the effective volume available to monohydrides in divacancies. This suggests that the hydrogen which is effusing from the material is accumulating in the nanosized voids. The largest wavenumber drop happens between 300 and 350 $^\circ C$. This is in line with the previously identified stages: in stage 3, both agglomeration and effusion take place. When divacancies with trapped effused hydrogen agglomerate, the effective volume available to the hydrogen increases, releasing the pressure on the matrix and lowering the density. At the same time, the effective volume available to monohydrides in nanosized voids decreases because of the hydrogen added to the voids from the agglomerating divacancies (in addition to ongoing effusion from the surface of the voids), resulting in a decrease in wavenumber of the HSM.

Figure 4-4: Positions of the fitted LSM and HSM as function of annealing temperature for varying $R$. 
The role of hydrogen dilution

Figure 4-1 shows differences between the plots for different hydrogen dilutions. For values greater than 0, there is a positive correlation between $R$ and $c_H$: adding more H$_2$ to the silane flow during deposition increases the hydrogen content in the a-Si:H. This can be explained when one realizes that adding more hydrogen to the material allows for the passivation of more dangling bonds and hence more Si-H bonds. The data for $R=0$ do not fit in this trend, which might be explained by the different deposition pressure used (see appendix A).

A closer look at the transition from plateau to decline shows that the transition becomes more gradual with increasing $R$. In other words: for the more hydrogen-rich material, Si-H bonds start breaking sooner, but it takes longer for all of them to break, because there is more H available.

Looking at $c_{H,SM}$ in figure 4-2, it is noted that for $R>0$, the increase happens abruptly from
250 to 300 °C, whereas the increase is more gradual for the R=0 material, in other words, the formation of voids starts at lower temperatures for R=0. The reason for this is that vacancy mobility is reduced for increasing R: unpassivated DVs, of which there are more for lower R, agglomerate more easily [83].

4-2-2 FTPS

All FTPS measurements, both for films and solar cells, are processed as described in section 3-3-2, yielding absorption coefficient and FTPS-EQE spectra respectively, as well as defect density distribution parameters as a function of annealing temperature. These findings are discussed in this section.

It is noted that at the time of the experiment, the effect of different windows, described in section 3-2-1 had not yet been considered. The default Happ-Genzel window has therefore been used for all measurements. Disturbances in the signal due to external influences therefore had to be smoothed out after the Fourier transform from interferogram to photocurrent spectrum, rather than beforehand through the use of the Blackman-Harris window. The former method results in greater error than the latter.

Films on glass

Figure 4-6 shows the absorption coefficient spectra obtained for the film with R=0. The spectra for the higher dilutions are shown in appendix D; the reader is encouraged to confirm that they show generally the same characteristics.

**Figure 4-6:** Absorption coefficient spectra at different annealing temperatures for R=0 film on glass.

Four ranges can be distinguished in the spectra in figure 4-6. At low energies, up to roughly $E_{ph} = 0.6$, the spectra consist of noise. The range from 0.6 to roughly 1.4 contains the subgap
absorption information. From 1.4 to 1.7, the Urbach edge can be identified and above 1.7 we see supergap absorption.

Across the entire range, it can be noted that the spectra roughly overlap up to 250 °C. The spectrum for 300 °C already exhibits notably higher absorption when compared to the spectra for T_a<300 °C and the spectra for the two highest temperatures are raised even further. There is no spectrum available for 500 °C, because after that annealing step there was no longer a meaningful FTPS signal to be measured. For the higher dilutions, this was already the case at 450 °C, which means spectra are only available up to 400 °C.

Some deviations from the main trends can be observed. A significant dip appears in the spectrum for T=250 °C at 1.1 eV. This can be attributed to a failed RG850 filter measurement. For T=450 °C, the spectrum is much less regular. This can be attributed to the smoothing of a very noisy signal at that temperature.

Looking at the region around 1.8 eV, it is clear that the bandgap decreases with increasing temperature: using the E_{04} gap definition (i.e., the energy at which \( \alpha = 10^4 \text{cm}^{-1} \)), a clear shift to the lower energies can be observed for increasing T_a.

Figure 4-7 shows this more clearly and for all dilutions. A more or less constant bandgap energy of 1.87-1.92 eV is observed for T_a< 300 °C, after which it quickly drops to below 1.75 eV at temperatures above 400 °C. Comparing this result to the results from the FTIR analysis in the previous section, the similarities are immediately apparent: the decrease of the bandgap is mirrored by that of the hydrogen content. Figure 4-8 illustrates this trend, which is in line with recent research showing this dependence [84]. More specifically, the large decrease in E_{04} above 300 °C supports the idea that stress is released from the film at this stage.

![Figure 4-7: E_{04} bandgap as function of annealing temperature for varying R.](image-url)
Figure 4-8: \( E_{04} \) bandgap as function of hydrogen content obtained from the SM for varying \( R \).

Figure 4-9 combines the information presented in figures 4-3 and 4-7 and shows the bandgap energy as a function of both \( c_{H,LSM} \) and \( c_{H,HSM} \).
The subgap range is investigated by fitting defect distributions to the low energy part of the absorption coefficient spectrum, as described in section 3-3-2. It is found that to properly fit the spectra, at least four distributions are needed. This is illustrated in figure 4-10, which shows that the goodness of fit, expressed here as 1-R^2, is an order of magnitude smaller for four distributions than it is for three\(^1\). Using five distributions rather than four does not noticeably improve the goodness of fit. In fact, adding a fifth distribution often makes it harder to produce a high quality fit, since there are no obvious initial values for it. The added degrees of freedom makes it difficult to fit properly without adding constraints to the parameters. Moreover, doing this does not produce consistent fit results in terms of distribution intensity or position, like it does when using four distributions.

\[ 1-R^2 = \frac{SS_{\text{res}}}{SS_{\text{tot}}} \]

\(^{1}R^2\) is defined as 1-SS\(_{\text{res}}\)/SS\(_{\text{tot}}\), with SS\(_{\text{res}}\) the residual sum of squares and SS\(_{\text{tot}}\) the total sum of squares. Since in absolute terms, the subgap absorption coefficients are very small numbers, that nonetheless span several orders of magnitude, SS\(_{\text{res}}\) will always be orders of magnitude smaller than SS\(_{\text{tot}}\), resulting in a value for R^2 which is very close to 1. By plotting 1-R^2 on a logarithmic scale, the difference between using 3 and 4 distributions becomes apparent.

![Figure 4-10: Goodness of fit of absorption coefficient spectrum using three and four distributions. Obtained from random sample of measurements of films and solar cells.](image-url)
A clear trend for different values of R cannot be distinguished. It appears that hydrogen dilution does not significantly affect the defect intensities or creation kinetics. To be able to make a quantitative comparison between the distributions, the intensities for each value of R are therefore averaged. The result is shown in figure 4-12.

It can be seen that all four distributions increase at roughly the same rate: the slopes of the increase are largely parallel. This is confirmed by a linear fit between T=300 °C and T=400 °C, which shows that all slopes are within $10^{-1.79}$ and $10^{-1.94}$ [(cm °C)$^{-1}$].

It is tentatively observed that the energy distributions located closer to the conduction band edge appear to start increasing at lower temperatures. Distributions X and A show significant increase from T=200 °C, B shows significant increase from T=250 °C and C from 300 °C. This would imply that those defects closer to the conduction band become mobile sooner than those closer to the valence band. This might mean that the defects closer to the conduction
band are softer and most easily changed. As there is significant scatter on the characteristics, however, conclusions must be drawn with caution and further study is deemed necessary.

Figure 4-13 shows the positions of the 4 distributions. Although the characteristics are fairly noisy, the positions are quite stable, as evidenced by the almost flat linear fits (dashed lines). This tells us that if these distributions are linked to different defect configurations, the configurations do not change in such a way that the energy required to free a charge carrier from them changes significantly. In other words, these findings do not suggest a change of defect configuration under the influence of thermal annealing. However, it is known from FTIR spectroscopy and positron annihilation measurements discussed earlier (see section 4-2-1) that divacancies agglomerate into larger vacancies and many Si-H bonds are broken when \( T_a > 300^\circ \text{C} \). Since large nanostructural changes are taking place in the material and defect configurations, which is not reflected in the positions of the distributions, it is therefore unlikely, based on these measurements, that any of the fitted subgap distributions corresponds directly to one specific defect configuration with a certain geometry. The number of defects corresponding to each distribution, however, changes differently as a function of annealing temperature, as shown in figure 4-12 (the increase in error function intensity is different for the X and A, for the B and for the C distributions). This is an indication that certain defect configurations become less favorable when the material is heated and Si-H bonds are being broken.

### Solar cells

FTPS measurements are also done on solar cells, which have an absorber layer deposited under the same conditions as the films on glass discussed in the previous subsection. Data are not available for the full temperature range, however, as the cells stopped functioning at around
250-300 °C. This is due to diffusion of dopants from the p-layer at higher temperatures. The signal quality is already very poor at 250 °C and indistinguishable from noise at 300 °C. The signal quality is also more variable for solar cells than it is for the films, which results in often unusable measurements for the lower wavenumber filters (RG850 and Si, and sometimes even FGL780). This results in noisier spectra at lower energies, making it difficult to conduct a meaningful distribution fit in these ranges. Throughout the experiment, different solar cells from the same sample are also used, as solar cells sometimes stop working, requiring using the next best solar cell. Because of the above, conclusions drawn from the information about the error function amplitudes and positions during annealing should be tentative.

Figure 4-14 again shows the spectra of the R=0 sample (higher R-values are shown in appendix D). The same four ranges as for the films on glass can again be identified, although it is noted that the supergap range now consists of an EQE spectrum. Like for the films, the spectra of the solar cells are mostly bundled together. Since there are no data available for $T_a > 300$ °C, nothing can be said about a potential significant increase at these temperature, similar to

![Figure 4-13: Error function positions for each of the 4 fitted distributions as function of annealing temperature for varying R. Linear fits of the combined data are indicated by the dashed lines.](image-url)
that of the films. In fact, it seems that the subgap FTPS-EQE spectra are decreasing slightly with increasing $T_a$, which could mean that the defect density in the i-layer is decreasing. This is in line with the changes in external parameters, shown in figure 4-21, which show slightly increasing $V_{OC}$ and FF with $T_a$. The dip observed in the $T=250 \degree C$ spectrum is attributed to the already very poor signal quality at that temperature.

![Figure 4-14: FTPS-EQE spectra at different annealing temperatures for solar cell with R=0 absorber layer.](image)

Figure 4-15 shows the error function amplitudes. They are plotted on the same scale (although with a shifted y-axis) as those of the films, to facilitate comparison. Some notable features are apparent. The peaks on the plot for X appear to be scatter. This is not unexpected, since the signal to noise ratio in the range at which X appears is typically quite poor. For all 4 distributions, an initial slight downward trend is visible. This may be attributed to the fact that some defects at the interface in the solar cell and bulk of the i-layer are removed under the influence of low energy annealing. Metastable defects that might have formed during deposition are annealed out in the temperature range typically associated with the removal of SWE-defects.

At higher temperatures, this trend seems to stop, or perhaps even reverse slightly, which would indicate renewed defect creation. Since no data is available at $T>250 \degree C$ and the data at $T=250 \degree C$ is of poor quality, it is hard to judge whether this is the start of a trend or simple scatter. When considering the sharp decrease of the solar cell performance for $T_a > 250 \degree C$ however, it is likely that boron diffusion from the p-layer into the i-layer, in combination with the increase of $A_{erf,XABC}$ as shown for the films, causes the solar cells to stop working at this point.

Comparing figure 4-14 with figure 4-6, the most striking impression is that they both show more or less a plateau in the 25-250 °C region. This would imply that the defects present in a solar cell are dominated by those in the intrinsic layer and not in the doped- or buffer layers or interface regions.

Figure 4-16 shows the positions of the distributions, again on the same scale as those of the
films on glass. Indicated on the figure are outliers for which it is readily apparent by inspecting the spectra that their values are severely influenced by the poor quality of said spectra. The reader is encouraged to verify this by inspecting the spectra given in appendix D.

Disregarding these outliers, and the unreliable data for $T=250 \, ^{\circ}C$, the positions, like those of the film distributions, are relatively constant. The dashed lines are constants fitted to the remaining data$^2$. The similarity with the data for the films is again apparent and the same conclusions therefore hold.

It is insightful to compare the positions and intensities of the distributions of the films and of the solar cells. This comparison is made in figure 4-17. The values for the positions are obtained from the linear fits shown in figures 4-13 and 4-16, excluding the mentioned outliers, and the values for the intensities are taken as averages over $R$ in the 25-250 $^{\circ}C$ temperature range.

$^2$In this case, a linear fit was not done, because of uneven weighing caused by the missing outliers.
It is seen that although the distributions do not overlap perfectly, they are quite close together. The intensity of X is of course the same for films and solar cells because of normalization, but the value for the position is also almost identical. Distributions A and B are somewhat separated, but as the error bars indicate, they still correlate quite well. Distributions C match up almost perfectly. This result implies two things. First, for the purpose of tracking changes in defect distributions during annealing, both solar cells and films can be used. Secondly, any effect of interference that might still be present in the signal after interference removal (see section 3-3-2) is likely minimal. The reason for this is that the films on glass have a thickness greater than 400 nm, while the i-layers in the cells are 250 nm thick and the entire silicon stack is 280 nm thick. These different thicknesses would result in interference fringe patterns...
Figure 4-17: Comparison of averaged error function intensities vs. positions for films and solar cell absorber layers. Solar cell absorber layer distribution intensities have been normalized to those of distribution X of the films.

with differently spaced peaks, as illustrated in figure 3-22 and 3-23. These differently spaced fringes would force the distributions into certain positions. The fact that their positions are similar indicates that this is not happening.

For both intensities of the distributions and their positions, there appear to be no trends as a function of hydrogen dilution. This means that the different DV passivation degree cannot be directly identified from the subgap absorption measured with FTPS. Moreover, since the energy positions of the fitted error functions to the subgap absorption coefficient spectrum/FTPS-EQE spectrum in both films on glass and solar cell absorber layers seem to be equal, it is likely that distributions X, A, B and C are illustrating the same kind of bulk defects.

4-2-3 Raman spectroscopy

Raman measurements were taken of the films on glass after each annealing step. As described in section 3-2-7, information about the crystallinity of the material can be extracted from the phonon mode peaks around 500 cm$^{-1}$. For R=0, the normalized Raman spectra around this value are shown for all annealing temperatures in figure 4-18. As can clearly be seen, there is no change in the character of the peak. The dashed line indicates the position where the crystalline peak would appear. This shows that no crystallization happens at temperatures up to 500 °C. Graphs for the other dilutions are given in appendix D and show the same trends. Suggested sensitivity for medium range order that have been reported earlier [77] are thus not observed here.

As is the case with FTIR spectroscopy, the peak around 2000-2100 cm$^{-1}$ contains information about the Si-H stretching modes. Figure 4-19 shows this peak (smoothed and corrected for background as described in section 3-3-3) for increasing temperatures and R=0. It can be
seen that the peak height fluctuates somewhat and starts declining around 300 °C. This is better visualized in figure 4-20, which shows the relative intensities of Gaussians fitted to these peaks for all dilutions.

Figure 4-20 shows a generally similar trend to that in the result from FTIR spectroscopy (figure 4-1: a plateau at lower temperatures and a drop to zero at higher temperatures). It can also be seen that the same R-dependence holds for the plateau: the higher dilutions have higher values for the intensity of the mode, with R=0 somewhere in the middle. The most notable difference is that the first significant decline happens from 250 to 300 °C, whereas the same decrease occurs from 300 to 350 °C in the FTIR analysis. This difference could be due to different growth of a-Si:H on glass and on c-Si or, more likely, to the lower accuracy of SM fitting on Raman data in comparison to FTIR data. The Raman signal is much noisier than the FTIR signal. For the most exact analysis of the SM, FTIR spectroscopy therefore remains the technique of choice.

4-2-4 External parameters, EQE and RT

Figure 4-21 shows the external parameters of the solar cells used, up to a temperature of 250 °C. All solar cells stopped functioning after the next annealing step at 300 °C.

Looking at the $V_{OC}$ and FF, a small but noticeable increase can be seen. This can be related to the FTPS results, i.e. the slight decrease in defect state intensities discussed in section
Figure 4-19: Raman spectrum SM peaks for increasing annealing temperature, normalized and background corrected (see section 3-3-3).

Figure 4-20: Relative intensities of Gaussians fitted to the SM peaks of Raman spectra of films on glass for increasing annealing temperatures and varying R.

4-2-2. The $J_{SC}$ shows more irregular behavior. Significant variation in its values can be seen between annealing steps. An explanation for this behavior is hard to give, but a suggested
explanation is irregular p-i interface and bulk i-layer degradation between the different solar cells.

Figure 4-21: External parameters of solar cells with absorber layers with varying R for increasing annealing temperature. (a) $V_{OC}$, (b) $J_{SC}$, (c) FF, (d) $\eta$.

Figure 4-22 shows the EQE spectra for all temperature steps and all R. The spectra for $T_a=250 \, ^\circ C$ all lie below the others, which is understood as the start of the cells breaking down (also seen in the external parameters). The other spectra, when examined carefully, follow the $J_{SC}$ trend: the peak heights correspond to the pattern in the $J_{SC}$ characteristics. It is interesting to note that the EQE degradation is most pronounced in the blue region of the spectrum. This supports the idea that the boron diffusion from the p-layer into the i-layer is significantly contributing to the breakdown of all solar cells at $T_a=300 \, ^\circ C$.

Figure 4-23 shows the bandgap energy and thickness of the films as obtained from fitting the RT measurement data.

The thickness trend shows an irregular pattern with overall slight decline. The decline can be seen to be correlated with the increase in density shown in figure 4-5: the roughly 2% increase in density corresponds with a roughly 2% decrease in thickness. The absence of a spike in thickness, like there is in density, at 300 °C can be understood when it is realized that the density is that of the film without empty space. This density spikes under the influence of pressure buildup inside (as discussed in section 4-2-1), but this does not have an effect on the macroscopic thickness of the film.

The bandgap energy follows the same trend as the one calculated from the absorption coefficient spectrum. The only difference is its absolute value, which is roughly 0.1 eV lower. The
reason for this difference is the two different definitions used for bandgap energy ($E_0$ from the absorption coefficient spectrum and $E_{Tauc}$ from the RT measurement fit). For comparison, both are shown in figure 4-24.

4-2-5 In-situ annealing

Figure 4-25 shows the subgap region of the FTPS-EQE spectra obtained during the in-situ annealing experiment described in section 4-1-2. The initial spectrum has the highest amplitude, caused by the high defect density associated with the initial degraded state. The amplitude shows a downward trend with increasing annealing time, which is recognized as the recovery half of the SWE. This is confirmed by comparing the FF and efficiency before and after the experiment: the FF increases from 0.608 to 0.684 and the efficiency from 6.48% to 8.00%.

As evidenced by the continuous downward trend, stabilization of defect density has not set in after the last step. As stabilization normally sets in after several hours of annealing at most, this is an unexpected result. The reason might be found in the fact that annealing is done by heating the sample stage, which is only in contact with the Asahi substrate, rather than the entire sample environment as would be the case in an oven.

Figure 4-26 shows the fit parameters of the error functions fitted to the subgap data of the FTPS-EQE spectra. The intensity parameters $A_{erf}$ show a steadily declining trend for...
all distributions, which is in line with the downward trend of the spectra. The scatter on the intensities, positions and widths are quite small, much more so than during the ex-situ annealing experiment. This is likely due to the fact that the sample and the contacts stay in the exact same position during the entire experiment, showing the added value of using the in-situ annealing setup over an ex-situ setup.

As can be seen in figure 4-26, the error function intensity shows a linear decline throughout most of the experiment. A straight line on a double logarithmic scale equates to a time dependence given by $t^{\gamma}$, with $\gamma$ a constant. By fitting a straight line to the error function intensities, this exponent is obtained. This is shown in figure 4-27.

Note that the time exponent is a measure for the decrease of the total defect density, and not of only the metastable defects. Although a value for $\gamma$ can be obtained and used in comparative analysis, its absolute value has no apparent physical meaning, because of the lack of a standardized environment for annealing. Nonetheless, this setup offers a controlled environment in which to further investigate annealing kinetics and as such, this first test can be considered a success.

### 4-2-6 Conclusions

The FTIR analysis strongly suggests that divacancies and nanosized voids play a role in an accurate description of the a-Si:H nanostructure. Following the temperature increase,
the changes in hydrogen content, LSM and HSM, and density all support the view that divacancies agglomerate into larger vacancies and voids and that hydrogen effuses from these configurations. This is further supported by the change in bandgap observed from the FTPS measurements.

Comparing the FTIR and FTPS results, it is immediately obvious that a large change in the material occurs at roughly 300 °C. At this temperature, Si-H bonds are breaking and hydrogen effusion is suggested to take place, mainly from divacancies (significant decrease in $c_{H,LSM}$). At the same temperature, the defect distribution intensities start increasing. This leads to the conclusion that the breaking of Si-H bonds in vacancies is the likely cause of this increase and hence that un- or underpassivated vacancies and voids are the types of defects being observed by the FTPS measurements.

The fact that 4 defect distributions are required to properly fit the absorption or FTPS-EQE spectra has implications for the nature of those defects. A dangling bond has three charge states and hence two associated transitions between them, which show up as distributions in the density of states spectrum. Having 4 distributions in the a-Si:H bandgap means that the single, unpassivated DB is unlikely to be the sole type of defect in the material. Other types of defects must be present in the material, and based on the above, the unpassivated DV seems a likely candidate.

No significant differences in sensitivity of any particular defect type to changes in temperature have been observed. All distributions appear to start increasing at roughly the same temperature and at roughly the same rate. There may be a weak correlation between the temperature at which defect distribution intensities start increasing and their energy position in the spectrum: defects closer to the conduction band edge seem to start increasing

Figure 4-24: Comparison of Tauc bandgap of films with varying R, obtained from RT measurements and $E_{04}$ bandgap obtained from absorption coefficient spectra.
slightly earlier. There is no apparent shift in the energy positions of the distributions during annealing. This implies that changes that take place in the defects as a function of annealing temperature can not be linked to certain specific distributions labeled X, A, B or C in the subgap absorption coefficient or FTPS-EQE spectrum.

Hydrogen dilution appears to have no significant effect on the evolution of defect states during annealing.

A practical conclusion is that both films and solar cells can be used to obtain information about defect distributions in a-Si:H. This allows for flexibility in experiment design, as the type of sample most suitable for a particular technique or circumstance can be used. For example, solar cells are not suitable for high temperature annealing experiments and the FTPS signal is generally of lower quality for films on glass in comparison to solar cells.

The in-situ annealing FTPS setup offers a controlled environment in which to study annealing kinetics. Preliminary experimental results show much less scatter on measured quantities than on those obtained using an ex-situ setup.

**Figure 4-25:** FTPS-EQE spectra of solar cell with R=10 absorber layer during in situ annealing.
Figure 4-26: Parameters of error function distributions fitted to subgap data of FTPS-EQE spectra of solar cell with R=10 absorber layer during in situ annealing.
Figure 4-27: Obtaining time exponent $\gamma$ of annealing kinetics for each of the subgap error function distributions fitted to FTPS-EQE spectra.
This chapter describes a light soaking study of a-Si:H. Its purpose is to track various material properties while exposing it to light for incrementally longer periods, in order to deduce information about the material, and especially the defects therein that play a role in the SWE.

5-1 Experiment

5-1-1 Samples

The samples used in this experiment consist of both solar cells and films on glass.

A set of solar cells with the same structure as those used in the annealing study has been deposited. Hydrogen dilutions of 0, 5 and 10 are used for the deposition of the absorber layer and two samples are deposited for each condition, to allow for in-situ light soaking with light of different wavelengths using the FTPS setup.

Another set of solar cells with a simple p-i-n structure is also deposited with hydrogen dilutions of 0, 2.5, 5, 7.5 and 10 for the absorber layer, for the purpose of ex-situ light soaking.

The films on glass are deposited such that they have the same thickness as the i-layers in the solar cells.

All deposition parameters are given in appendix A.

5-1-2 Experiment design

The first part of this experiment consists of in-situ light soaking with the FTPS setup. Solar cells with three different values of R are exposed to light of two different wavelengths each, which makes for a total of 6 light soaking runs. Each run consists of the following steps:
• Annealing of the sample for 30 minutes at 130 °C in a Thermo Scientific Heratherm benchtop oven (see figure 5-1)

• Determination of the highest efficiency solar cell through measurements of the external parameters using the PASAN setup

• Measurement of an EQE spectrum of said best solar cell

• Alternating FTPS measurements and in situ light soaking periods in the FTPS setup

• Measurement of the external parameters of the light soaked solar cell

• Measurement of the EQE of the light soaked solar cell

Figure 5-1: Thermo Scientific Heratherm benchtop oven (closed and open) used for annealing films on glass and solar cells.

The above allows tracking of the properties of defect distributions during light soaking and linking the results to pre and post light soaking states.

Light soaking was done for increasing periods of time, such that the cumulative soaking times were roughly logarithmically equidistant with 2 points per decade, starting at 0.5 s$^1$. The reason for this is that literature shows a sublinear time dependence of defect creation (see section 2-6-2). This means that the more a sample is soaked, the more additional time is needed to create a similar amount of defects. In order to track both the short-term and long-term kinetics of defect creation, such a design of the experiment is therefore useful. The light soaking was done with two wavelengths of light (white and blue light, produced by LEDs; see section 3-2-3). The idea behind this is that the white light is expected to generate defects throughout the cell, whereas the (higher energy) blue light does not penetrate as deep and is therefore expected to generate defects closer to the p-i interface (assuming that the generation

$^1$The cumulative light soaking times were, subsequently, 0.5, 1.5, 5, 15, 49, 147, 490, 1470, 4899, 14695, 48981 and 146940 seconds. After this last step, for practical reasons, intervals were not fixed.
and recombination profile are spatially correlated). This introduces a spatial component to the defect generation kinetics, which might express itself in the measurement data.

The intensities for both the white and blue light are calibrated at 1000 W/m$^2$ using an Avantes spectrometer. It is noted that the spectrum of the white LEDs is not the same as AM1.5, so the kinetics tracked are not exactly the same as those under natural illumination conditions or standard test conditions. Nevertheless, the spectral differences between the LEDs are significant and are thus useful in studying the spatial creation of metastable defects in the i-layer.

The second part of the experiment consists of ex-situ light soaking. Solar cells and films on glass with 5 different values of R are exposed to white light in a degradation chamber (see figure 5-2). This chamber contains metal halide lamps with a spectrum approximating AM1.5, again calibrated at 1000 W/m$^2$. The samples are initially annealed for 30 minutes at 130 °C. Before light soaking and after each soaking period, the following measurements are done:

- Measuring the external parameters of the solar cells using the PASAN setup
- Measurement of an EQE spectrum of the solar cell under investigation
- RT measurement of the films
- FTPS measurements of the films and the solar cells

![Figure 5-2: Degradation setup for ex-situ light soaking.](image)

The solar cell that shows the highest efficiency on each substrate is used throughout the experiment. On one occasion (for the R=2.5 sample), the best solar cell had stopped functioning
after the first light soaking step. The next best solar cell was used for the remainder of the light soaking experiment.

## 5-2 Results and discussion

### 5-2-1 FTPS

**In-situ light soaking**

FTPS-EQE spectra are composed from the FTPS and EQE measurements like described in section 3-3-2. An example of the results for all light soaking time steps is shown in figure 5-3.

![FTPS-EQE spectra for all white light soaking steps performed on solar cell with an R=0 absorber layer.](image)

**Figure 5-3:** FTPS-EQE spectra for all white light soaking steps performed on solar cell with an R=0 absorber layer.

From left to right, the following regions can be identified (separated by dashed lines): noise up to roughly 0.6 eV, subgap FTPS-EQE up to roughly 1.4 eV, the Urbach tail up to roughly 1.7 eV and the EQE spectrum above 1.7 eV. By necessity, the FTPS spectra are connected to the pre-soaking EQE data, so any changes in the spectrum during light soaking appear only in the subgap region. This region is shown for both blue and white light soaking and all R values in figure 5-4.

All six plots show generally the same trend: spectra are roughly stationary up to light soaking times around 5000 seconds. After that, they all show increases. To better analyze these
Figure 5-4: Subgap portions of FTPS-EQE spectra for solar cells with absorber layers with varying R under the influence of white and blue light soaking.
increases, it is useful to perform the defect distribution fitting described in section 3-3-2 and plot the calculated defect distribution intensities versus light soaking time. The results are given in figure 5-5.

![Figure 5-5: Intensities of error functions fitted to FTPS-EQE spectra of solar cells with absorber layers with varying R under the influence of white and blue light soaking.](image)

There are some striking features of the graphs in figure 5-5 to discuss. The amplitudes of the fitted error functions all start off at constant values, with the exception of \( A_{erf,A} \), blue, R=0 (more on this below). They remain constant until roughly \( 10^3 \) to \( 10^4 \) s, at which point they start increasing. For blue, R=5 and white, R=0, the increase seems to slow down at roughly \( 10^5 \) s. This appears to be the switch from the “fast” to the “slow” states mentioned in section 2-6-2.

Between the simple p-i-n structures (R=10) and the complex ones (R=0 and R=5), two differences are readily apparent. Firstly, the data for the X distributions, and to a lesser extent the A distributions, are much smoother for the simple structures. The reason for this can be found in the transition from the noise floor to the FTPS signal. Careful inspection of figure 5-4 shows that this transition is more regular for the R=10 data. This implies that the simple structures have a better signal to noise ratio in the deep subgap range, which might be attributed to less influence of the p-layer or to buffer layer degradation. The smoother curves shown in figure 5-5 allow for more accurate determinations of the metastable defect creation rate (see figure 5-8).

Secondly, the relative intensities of the distributions are different for the simple solar cell structures than for the complex ones. It seems that the difference in structure results in a
differently shaped FTPS-EQE spectrum (as can be seen in figure 5-4), which could be related to a different occupation of the gap states.

Figure 5-6: Positions of error functions fitted to FTPS-EQE spectra of solar cells with absorber layers with varying R under the influence of white and blue light soaking

Figure 5-6 shows the positions of the fitted distributions. Here again, the complex structures (R=0 and R=5) show more irregular data than that of the simple structures (R=10). As in the annealing experiment, the positions are stationary, implying that the fitted error functions reflect entities that do not change during light soaking, such as the approximate energy position of a defect in the bandgap. The positions of the distributions in the simple solar cells are shifted to higher energies by roughly 0.1 eV (except, perhaps, the blue, R=0 X distribution, which has roughly the same energy). The reason for this shift might be found in the different structures, which lead to different occupation of gap states. Figure 5-7 shows the positions of the 4 distributions, averaged over R. As can be observed, the distributions are quite distinct, non-overlapping. The difference between blue and white light soaking is almost nonexistent.

Several issues with the experiment need to be mentioned. Firstly, the R=10 samples used were simple p-i-n structures. The original samples, with the more complex layer structures described in section 5-1-1, had very poor external parameters (η<5%). For this reason, a new set of solar cells was deposited. At the time, it was thought that the layer structure would not make a significant difference. As it turned out, it did, as evidenced by the different results for both positions (see figure 5-6) and intensities of the defect distributions for these samples. Secondly, there was a problem with the cooling system of the LED array during the white
light, R=5 light soaking experiment. A poor contact with the heat sink caused the feedback system to shut down the LEDs and power them up again when they had cooled. This on-off cycle caused the irradiation during the last two steps to be significantly less than intended. A correction of the time scale, based on the measured ratio between on and off times has been performed, but the results of the last two steps should not be taken as completely reliable.

Thirdly, on two occasions (blue R=0 and white R=10), the light soaking experiment had to be aborted and restarted due to a breakdown of the solar cell, both times after approximately 14 cumulative hours of light soaking. To reset the state of the samples, they were annealed again for 30 minutes at 130 °C. It is possible, however, that they were not in the exact same state as the other samples, which had only received one annealing treatment.

To gain insight into the degradation kinetics, the increases in defect distribution intensities have to be isolated. To do this, a baseline is fitted to the initial plateau of each data set and subtracted from it. This leaves just the increase which is a measure for the generation rate of metastable defects. By fitting a straight line to the remaining data, the time exponent $\beta$ mentioned in section 2-6-2 is obtained. This process is illustrated in figure 5-8.

This procedure is performed for blue and white light soaking and for all dilutions (graphs in appendix D). An overview of the time exponents is given in figure 5-9.

Several things are noted about these time exponents. The results for the X distribution for R=0 and R=5 are highly unreliable. As can clearly be seen in figure 5-5, the scatter on these characteristics is significant and fitting a straight line through the last several points is not very accurate.

The $\beta$ value of the A distribution for blue, R=0 is quite low. It can be seen in figure 5-5 that, unlike the evolution of the A state in the other 5 light soaking experiments, the A state for blue, R=0 has much less of a plateau and more of a steady incline, starting after a few seconds. This results in an overall shallower slope and hence lower time exponent. A

![Figure 5-7: Positions of error functions fitted to FTPS-EQE spectra of solar cells, averaged over R.](image-url)
possible reason for this different light soaking behavior of the A state might be a combination of the following. Firstly, the blue light does not penetrate deeply into the material, but only reaches that part of the i-layer near the p-i interface. Secondly, in R=0 material, the degree of defect/DV passivation is lower than it is for higher dilutions. It might be that this combination of circumstances exposes a particular type of defect close to the p-i interface, which is only visible in the material with the highest unpassivated dangling bond density. Although the link is not conclusively proven, it seems worthwhile to explore this possible relation further.

Except for these three data points, all values of $\beta$ lie between 0.4 and 0.9, which is significantly higher than the often reported value in literature of $\beta=1/3$. Distributions further away from the conduction band edge seem to have higher $\beta$ values. Other than this, there appear to be no trends in the values of the time exponent relative to the distribution type, hydrogen dilution or light color.

Ex-situ light soaking

The FTPS measurements taken on solar cells and films during the ex-situ light soaking experiment are processed into FTPS-EQE and absorption coefficient spectra respectively, which can be found in appendix D. As before, error functions are fitted to the subgap data. The results of these fittings are shown in figure 5-10.
Looking at the results for the solar cells, the distributions all show an initially fast defect generation rate, which slows down later. This is in line with the idea of fast and slow states and it seems that doing measurements on this timescale yields useful information about the slow state. The positions vary only somewhat.

The films show a somewhat less consistent situation. The R=0 and R=2.5 plots show still increasing distributions up to 1000h. For R=5 and up, however, it appears that stabilization has set in. It thus seems that the higher hydrogen dilution (and hence content; see chapter 4) causes the material to stabilize sooner.

The positions of the fitted error functions appear largely constant in the case of films on glass. The averaged positions for both the films and the solar cells are plotted side by side in figure 5-11. The positions of the distributions for the solar cells are noticeably higher than those for the films, which could be related to the fact that surface states play a role in the films (the current flows close to the surface in between the coplanar contacts). All positions are again well-defined.

The degradation kinetics are again obtained through a linear fit, this time of the three rightmost data points of each plot. This means that for some cases, stabilization may have already set in (i.e.: for the higher dilution films). To maintain a consistent approach, this was deemed acceptable.

**Figure 5-9:** Time exponents grouped by distribution for in situ blue and white light soaking and varying R. Error bars indicate fit errors. Dashed line indicates the often reported value of $\beta=1/3$ (see section 2-6-2).
Figure 5-10: Error function intensities and positions for solar cells (top two rows) and films on glass (bottom two rows) for varying R (columns).
Figure 5-11: Positions of fitted error functions during ex-situ light soaking for solar cells and films, averaged over R.

All individual time exponents for the solar cells and films can be found in appendix D. Figure 5-12 shows the values of the time exponent $\beta$ averaged over R. As can clearly be seen, their values are much lower than those for the in-situ experiment, demonstrating the presence of slow and fast states. The error bars represent standard deviation and show that the values of $\beta$ for X and A of the films are less well defined than the values for B and C. The values of $\beta$ for B and C appear slightly lower for films than for solar cells, although the difference is marginal. It could be that the values for the films are slightly underestimated, because of the stabilization that has already set in, or it could be that the longer light path in the solar cells due to scattering slightly increases the metastable defect creation rate.

Comparison in-situ and ex-situ

Figure 5-13 shows a comparison between the positions of the distributions obtained in the in-situ and ex-situ experiments. The positions obtained during the annealing experiment (shown in figure 4-17) are also added for comparison. Although the ranges of positions and error margins do overlap partially for the X and A positions, it is safe to say that this is again good evidence in support of the presence of four distributions.

Figure 5-14 shows the different time constants obtained from the in-situ and ex-situ experiments (both averaged over R), clearly demonstrating the distinction between the slow and fast states.

The conclusion that can be drawn from this experiment with respect to the degradation kinetics, is that in-situ measurements can yield information about the fast state degradation kinetics. Long timescale ex-situ light soaking can qualitatively demonstrate the slow state degradation and a rough indication of its time exponent can be given. For a proper characterization of the long timescale defect creation kinetics, however, a higher resolution is needed. The moving of the samples from degradation chamber to measurement setups and back also
introduces some uncertainty, although with proper planning this can be minimized. As such an in-situ experiment is to be preferred, also for the long timescale.
5-2-2 External parameters, EQE and RT results

In-situ light soaking

Figure 5-15 shows the values of $V_{OC}$, $J_{SC}$, FF and $\eta$ before and after the in-situ light soaking experiment for both colors and all dilutions. Because of the variation in initial conditions, it is useful to compare the relative changes, which are given in figure 5-16.

For the white light, it can be seen that the higher the hydrogen dilution, the more stable the solar cell. The relative change in efficiency goes down with increasing R and the absolute efficiency for R=0 is lowest after light soaking, while it was highest initially. The same is found for the FF.

For the blue light, the degradation of the different solar cells is less different. The relative changes in efficiency are similar and the $J_{SC}$ shows a reversed trend to that for the white light: higher R means greater decrease. The reason for this lack of trend may be found in the level of stabilization at the end of the experiment. Recall from figure 5-5 that the blue, R=5 defect state intensities appear to show notable stabilization, which is not the case for the R=0 and R=10 cells.

More interesting to note is the overall smaller FF degradation for blue light vs. white light. An interpretation that fits these results is that the higher DV passivation degree is present mostly in the bulk. White light penetrates deeply into the bulk, causing the creation of metastable defects, while blue light creates defects mostly near the (already relatively defect-rich) p-i interface and not as much in the bulk, therefore causing smaller absolute and relative degradation.
Further, it seems that for blue light, only R=10 shows enhanced stability of the FF, while R=0 and R=5 degrade more similarly. This would imply that for R=10, most defects are near the p-i interface, which explains the relatively low $V_{OC}$. Apparently, having a high value for R is beneficial for bulk stability, but detrimental for p-i interface stability. This means that it would be beneficial to vary the silane/hydrogen ratio during deposition (i.e., silane profiling).

The findings from the external parameters are mirrored in the EQEs, given in figure 5-17. The white light characteristics show notably less decline with increasing R. This is not as clear for the blue light. In all cases, the most significant decline is in the blue region; the light color does not seem to change this. This is a hint that degradation with both white and blue light takes place in the same spatial region of the i-layer (near the p-i interface). It could also mean that electron collection is degrading mostly, and not the hole collection.

**Ex-situ light soaking**

Figure 5-18 shows the $V_{OC}$, $J_{SC}$, FF and efficiency for the ex-situ experiment for all light soaking steps and dilutions. It illustrates the previously mentioned varying quality of the solar cells: the fill factors and efficiencies of the solar cells with R=2.5 and R=5 are significantly worse than those of R=7.5 and R=10, with R=0 in between. The FF appears to be the main contributor to the loss of efficiency, given the similarities between the characteristics.

It is noted that the solar cells which are worse at the start do not degrade as much as the initially better ones: the FF and efficiency converge, hinting at a final stabilized efficiency of
roughly 6%. This is a relative loss of around 30% for the R=7.5 cell.

Figure 5-19 shows all EQE spectra obtained throughout the ex-situ light soaking experiment. The bottom right panel confirms that the solar cells were not of comparable quality at the start of the experiment: the solar cells with R=2.5 and R=5 had clearly the worst EQE; R=0 was slightly better and R=7.5 and R=10 were significantly better.

All solar cells show significant loss of EQE in the blue region. The loss is greatest for the solar cells with the highest initial EQE, again mirroring the findings from the external parameters. The solar cells with the worst initial EQE (R=2.5 and R=5) show virtually no decline for wavelengths larger than ~500 nm, whereas the others do. This suggests that those two poor solar cells are initially in a state where the most metastable defect states (i.e., the fast states) are already created and do not degrade further when exposed to light. In other words: fast states may be linked to the red response of a solar cell.

Looking closely at the error function amplitudes for these solar cells in figure 5-10, this finding seems correlated with the relative intensities of the B and C distributions. For the two best solar cells (R=7.5 and R=10), the B distribution intensity has a significantly higher value throughout than that of the C distribution. This difference is smaller for the R=0 solar cell and smaller still for the R=2.5 and R=5 solar cells. It is therefore suggested that the relative intensities of the B and C distributions (in other words, the shape of the subgap FTPS-EQE spectrum in the range of 1.0-1.4 eV) can be indicators of fast state defects.

Figure 5-20 shows the bandgap energy and film thickness of the films on glass as fitted from the RT measurements. The film thickness appears largely constant, implying that light soaking does not macroscopically affect the material properties. Any variation that is apparent is likely
Figure 5-17: EQE spectra of solar cells before and after in-situ blue and white light soaking for varying R. Note: several data points are missing from the white, R=10, before measurement due to a temporary malfunction.

due to small changes in homogeneity of the film, while the much larger changes in electrical properties (photoconductivity and defect density) do not result in a different bandgap or thickness.

5-2-3 Conclusions

Like in the annealing experiment, four error functions were required to fit the subgap absorption and FTPS-EQE spectra. The same conclusion regarding dangling bonds and more complex defect configurations can therefore be drawn: the single, unpassivated DB is unlikely to be the sole type of defect in the material.

The effect of light color on the light soaking kinetics appears to be limited. Two findings hint at changes in the material caused by different light color.

Firstly, the A distribution for the R=0 solar cell appears to start increasing under the influence of blue light significantly sooner than any of the other combinations of color and dilution. This suggests that this distribution is related to a type of defect close to the p-i interface (i.e., near the surface and hence sensitive to blue light), which is only detectable in the material with the highest unpassivated defect/DV concentration (i.e., R=0 material). This seems to
Figure 5-18: External parameters of solar cells with absorber layers with varying R during ex-situ light soaking. (a) $V_{OC}$, (b) $J_{SC}$, (c) FF, (d) $\eta$.

contradict the reasoning followed in section 5-2-2, where it was argued that the R=10 material has the highest defect density near the p-i interface. However, it should be noted that in the case of the fast increasing A distribution, only one error function distribution shows deviating behavior, whereas the finding for R=10 in section 5-2-2 is based on external parameters and therefore entails all defect distributions in the material.

Secondly, there appears to be a link between the red response of solar cells and the B or C distributions in cells. The red response decrease appears to be something typically only visible in high efficiency solar cells. Both of these findings warrant further research.

It has been shown that both the solar cells and the films exhibit fast and slow degradation kinetics. The time exponents associated with these kinetics are not constant, but vary depending on the energetic position in the bandgap and are decidedly higher (0.4-0.9) than the often reported 1/3 for the fast states and lower (0.1-0.2) for the slow states.
The effect of hydrogen dilution is not readily apparent in the absorption coefficient and FTPS-EQE spectra. With respect to the external parameters of the solar cells, however, the hydrogen dilution results in generally more stable solar cells.

For light soaking experiments, both solar cells and films on glass can be used. For solar cells, the better results are obtained using simple p-i-n structures, rather than the more complex structure with buffer layers and double p-layers.
Figure 5-20: Bandgap energy and thickness of films on glass during ex-situ light soaking for varying R.
In this chapter, the main results and analysis presented in chapters 4 and 5 are summarized. Recommendations for future research based on these findings are given.

6-1 Conclusions

Fundamental conclusions

Analysis of the FTIR data obtained during the annealing study strongly suggests that divacancies and nanosized voids are required for an accurate description of the nanostructure of a-Si:H. The evolution of hydrogen content, density and relative contributions of the LSM and HSM to the FTIR spectra under the influence of increasing annealing temperatures indicate agglomeration of divacancies into larger vacancies and voids. This view is supported by the change in bandgap observed from RT and FTPS measurements and is in line with recent positron annihilation and hydrogen effusion studies.

In addition, it is found that to properly fit the subgap data of absorption coefficient and FTPS-EQE spectra, at least four error function distributions are required. This is another indication that the nanostructure of a-Si:H is more complex than a model in which the isolated dangling bond is the dominant type of defect, since such a defect has only three charge levels, allowing for two defect distributions. Moreover, the main changes observed in both FTPS and FTIR measurements happen at the same temperature (300 °C). The breaking of Si-H bonds observed in FTIR measurements is mirrored by the increase in subgap absorption seen in FTPS measurements, suggesting that the defects observed are un- or underpassivated vacancies and voids.

The kinetics of defects created under the influence of light soaking, expressed in terms of $t^\beta$, show two distinct regimes: a fast regime with time exponent $\beta$ ranging from 0.4-0.9, and a slow regime with $\beta$ ranging from 0.1-0.2. This finding contradicts the often reported single time constant of 1/3 and is another indication that the nanostructure of a-Si:H should be described using more than only the unpassivated dangling bond as source of defects.
Light soaking with different color light overall appears to have limited effect on the defect creation kinetics as observed using FTPS measurements. For the solar cell with an R=0 absorber layer, however, light soaking with blue light causes a deviating trend: the A distribution increases sooner than other distributions, hinting at a possible link between this distribution and a particular type of defect. Additionally, the external parameters show that the relative degradation of the solar cells is smaller using blue light, suggesting a sensitivity to defects near the p-i interface. These findings do not allow drawing strong conclusions, but they do hint at the possibility that the fitted distributions represent different defect entities, the spatial and energetic properties of which might be obtained through further study. Varying the hydrogen dilution appears to expose spatial differences in defect densities under light soaking with different wavelengths, notably near the p-i interface. This, too, warrants further study.

**Practical conclusions**

A fitting routine has been developed that allows precise fitting of subgap absorption coefficient and FTPS-EQE spectra with a variable number of error functions. The effects of interference can be removed effectively from absorption coefficient and FTPS-EQE spectra, however, a universal and flexible removal procedure is currently lacking.

Both films on glass and solar cells can be used to study defects, with similar results. This allows for flexibility of experiment design, choosing the most suitable of the two depending on the circumstances. Solar cells with a simple p-i-n structure give better results than more complex structures with extra layers.

FTPS measurements on samples annealed in situ are a feasible method to study recovery kinetics of solar cells and films on glass.

**6-2 Recommendations**

To further substantiate the findings given in the previous section, the body of data needs to be expanded. Two main topics of investigation seem opportune: the energetic and the spatial distributions of defects in a-Si:H. To study this, it is recommended that the measurements performed during this project be repeated with several additional variables: i-layer thickness, sample temperature, light soaking color (e.g. red), deposition power and pressure. Red light soaking is particularly interesting, because the lower energy light will result in a homogeneous generation profile and because red light is spectrally very different from white and blue light.

To better study the fast and slow regimes of metastable defect creation during light soaking, and the transition from one to the other, it is recommended that the measurements be performed either all in situ, or all ex situ. In-situ measurements have the benefit of allowing for more detailed investigation of the subgap absorption coefficient and FTPS-EQE spectra and hence the possible linking of fitted subgap distributions to distinct defect types. They do have the practical objection that the measurement system would be occupied for several months. Ex-situ measurements allow for determining external parameter, EQE, RT and other measurements throughout the experiment, at the cost of a lower time resolution FTPS series.
To be able to monitor annealing kinetics more closely, it is recommended that in-situ annealing in the FTPS setup be further investigated. Several aspects deserve attention. To avoid the disturbances introduced by the warmup and cooldown of the heating stage, it is worthwhile to evaluate the usefulness of performing FTPS measurements while annealing, or while cooling to a higher temperature. Alternatively (or additionally), the measurement time could be kept as short as possible by using fewer filter measurements, or by using a filter with a sloped transfer characteristic. It should be carefully evaluated, however, whether this does not negatively affect the accuracy with which the fitted distribution parameters can be determined.

Optimization and automization of the FTPS measurement process would lead to faster and more reliable measurements. In an ideal situation, switching filters and mirror speeds, starting measurements and saving files are automated, requiring only manual control of the amount of scans required for a sufficient quality signal and the current amplifier settings.

The interference fringe removal process used has been adequate for the purposes of this project. When solar cells with thicker i-layers are used, however, the effects of interference become more pronounced and require laborious manual processing to remove. It is recommended that the removal process be further investigated and improved where possible.
## Appendix A

### Deposition parameters

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**Table A-1:** Deposition parameters of films on glass and on c-Si (deposited in the same run) used in annealing experiment.

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**Table A-2:** Deposition parameters of films on glass used in light soaking experiment.
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</tbody>
</table>

Table A-5: Deposition parameters of solar cells with complex structure used in light soaking experiment.
Appendix B

Fit functions used in FTIR data processing

Background fit

The function below is used to fit the refractive index (n), layer thickness (d) and scaling constants (c1 and c2). Fixed variables are the refractive index of air (n0=1) and that of c-Si (nc=3.42). Variable x is the wavenumber in the applicable fit range.

\[
0.5 \times (1 + (c1 + c2 \times x + 10^{(-4)})^2) \times ((4 \times (n^2 + (10^{-(-3)})^2) / ((n+n0)^2 + (10^{-(-3)})^2)) \times (4 \times nc^2 / ((n+nc)^2 + (10^{-(-3)})^2)) / (4 \times nc^2 / ((n+nc0)^2)) / (exp(-2 \times (-2pi \times (10^{-(-3)}) \times d \times 10^{-(-7)}) \times x + (c1 + c2 \times x + 10^{-(-4)}) \times 2 \times (n0-n-2 \times 10^{-(-3)})^{-2}) / ((n0+n)^2 + (10^{-(-3)})^{-2})) \times exp(2 \times (n0-2 \times n-2 \times 10^{-(-3)})^{-2}) / ((n0+n)^2 + (10^{-(-3)})^{-2})) \times sin(2 \times (2pi \times n \times d \times 10^{-(-7)}) \times x)
\]

Mode fit

The function below is used to fit two Gaussian modes to the signal. The parameters n, d, c1, c2, n0 and nc are defined as above. Parameters i, s and f are the intensity, width and position respectively for each of the Gaussians with numbers 1 and 2 indicating which Gaussian.

\[
0.5 \times (1 + (c1 + c2 \times x + 10^{(-4)})^2) \times ((4 \times (n^2 + (10^{-(-3)})^2) / ((n+n0)^2 + (10^{-(-3)})^2)) \times (4 \times nc^2 / ((n+nc)^2 + (10^{-(-3)})^2)) / (4 \times nc^2 / ((n+nc0)^2)) / (exp(-2 \times (-2pi \times (10^{-(-3)}) \times d \times 10^{-(-7)}) \times x + (c1 + c2 \times x + 10^{-(-4)}) \times 2 \times (n0-n-2 \times 10^{-(-3)})^{-2}) / ((n0+n)^2 + (10^{-(-3)})^{-2})) \times exp(-0.5 \times ((x-f1)/s1)^2)) \times exp(-0.5 \times ((x-f2)/s2)^2)) / ((n0+n)^2 + (10^{-(-3)})^{-2})) \times exp(-0.5 \times ((x-f1)/s1)^2) \times exp(-0.5 \times ((x-f2)/s2)^2)) \times 2 \times (n0-n-2 \times 10^{-(-3)})^{-2}) / ((n0+n)^2 + (10^{-(-3)})^{-2})) \times sin(2 \times (2pi \times n \times d \times 10^{-(-7)}) \times x)
\]
Shown below is the Matlab script used to perform the fitting of subgap absorption coefficient or FTPS-EQE spectra with a variable number of error functions. This script is based on the approach first developed by Robin Quax [85].

```matlab
% Attempts to fit an absorption spectrum or photocurrent spectrum resulting
% from an FTPS measurement using a fit function consisting of a
% superposition of a variable number of error functions.

% Version 1.0
% March 13, 2013
% Marc Schouten
% marcschouten@gmail.com

% Version 1.1
% June 7, 2013
% Marc Schouten
% Many small corrections and improvements.
% * Fixed problem with CIs
% * Output commented
% * Automatic determination of Urbach edge
% * graph color settings

% Working assumption is that the sub gap absorption spectrum or photocurrent
% spectrum can be modeled as a superposition of error functions (erf).
This
% script attempts to fit a variable number of error functions to the
% signal.
%
% Input:
% Expected input is a text file with two columns: energy and photocurrent
% or energy and absorption coefficient.
```
% A fitting range is given and fit bounds and initial values for the chosen
% number of distributions are set. Optional fixed parameter values can be % given.
% % Output:
% All fit parameters with confidence intervals and figures of the signal % and fit. Also some additional parameters.
% % Supporting information in the plot:
% * Individual error functions are shown
% * The positions of the ERFs are indicated by vertical lines
% * The widths of the ERFs are indicated by small horizontal lines at the % top of the plot
% * If any of the parameters is at or close to its bound, the respective % indicator will show red (number for amplitude, vertical line for % position, horizontal line for width). If this is the case, loosen % parameters until all are well within bounds after fit.
% % Tip: Set bounds very loose for amplitude parameters. Can be orders of % magnitude higher or lower than actual value; fit routine will find proper % value. For position, try to have non-overlapping intervals. For width: % recommended to keep values between -0.01 and -0.2. Loosen only if bounds % are hit.

%% Initialize
clear all;
close all;
clc;

%% SET VARIABLES %

% === data file ===
samplepath='_'output/ex_situ_layers/1.52_1.60-using_EQE_t0/';
 samplename='M3822-1000h';
samplefileextension='relative.ftps.dbp.abs';
filename=[samplepath samplename samplefileextension];

% === Urbach tail ===
minusUrbach=1; % Set to 0 to fit original spectrum (and to determine the % position of the Urbach edge)
 % Set to 1 to determine spectrum minus Urbach edge

option=1;
 % Option 1: automatic detection of position of Urbach tail. Set range in % which to look for maximum slope. Recommended: 1.3-2.0
 urbach_search_min=1.3;
 urbach_search_max=2;
 show_help_plot=1; % Show determination of maximum of derivative.
Recommended value: 1
% Option 2: manual selection of position of Urbach tail.
xUrbachMiddle = 1.544;

% If you want to use the Urbach tail of another data set, enter the path
% below and set the flag to 1
useOtherUrbach = 1;
otherUrbachFile = '_output/ex_situ_layers/1.52_1.60-using_EQE_t0/M3822-
AA_relative.ftps.dbp.abs';

% number of points around which the linear fit of the Urbach line is
taken:
urbachRange = 20; % recommended to leave as is.

% === Fitting range ===
eVfrom = 0.642;
eVto = 1.347;

% === Fit parameters === each row is one distribution. Comment/uncomment
% to remove/add distributions. Dims of ivm,lbm,ubm and fp must be the
% same.
ivm = [ % A P W % Initial values (amplitude, position, width)
        2e-2 .63 0.01;
        1e-1  .82 0.05;
        6e-2  .92  .075;
        1.3e-1 1.38 0.03;
        ];

lbm = [ % A P W % lower bounds (amplitude, position, width)
        1e-7 0.5 0.005;
        1e-6 0.65 0.01;
        1e-6 .85  0.02;
        1e-6 1.05 0.02;
        ];

ubm = [ % A P W % upper bounds (amplitude, position, width)
        3.3e3 0.75 0.2;
        1e3  .85  0.2;
        1e3 1.25 0.2;
        5e3 1.65 0.3;
        ];

fp = [ % if set as 0, use as free fit parameter. If set to numerical
% value, use that value as fixed.
        0 0 0;
        0 0 0;
        0 0 0;]
0 0 0;
% 0 0 0;
% 0 0 0;
];

% === Plot options ===
xmin=.2;
xmax=2;
ymin=le-4;
ymax=le3;
fit_range_color=[1 1 .5];
urbach_line_color='c';
data_color='r';
fit_color='b';
positive_dist_color=[0 1 1]; % color of individual positive distribs
negative_dist_color=[.6 1 .6]; % color of individual negative distribs
help_line_color_default=[.8 .8 .8]; % color of help lines when parameters are safe
help_line_color_alarm=[1 .27 0]; % color of help lines when parameters push against fit limit
set(0, 'DefaultFigurePosition', [100 100 1200 800]); % determine default position for graph windows. Useful when you have two monitors.

% === Other variables ===
stepsize=0.001; % Step size of final fit result
x=0:stepsize:xmax; % x range of final fit result
confidence_interval=0.95; % confidence interval for fit coefficients
raisedecades=0;

%% Determine parameter names based on fit matrices
n=length(ivm);
if(length(lbm)~=n || length(ubm)~=n || length(fp)~=n)
    error('IV, LB, UB and FP matrices do not have the same number of rows ');
end

prefix=['A' 'P' 'W']; % used for generation of parameter names
paramnames=cell.empty; % all (possible) parameter names (A1,P1,W1...
An, Pn, Wn)
fitparamnames=cell.empty; % names of all free fit parameter names (those fixed in fp are excluded)
iv=double.empty; % vector with initial values of free fit parameters for input into fit
lb=double.empty; % vector with lower bound values of free fit parameters for input into fit
ub=double.empty; % vector with upper bound values of free fit parameters for input into fit

for t=1:3
    for u=1:n
        paramnames(u+(t-1)*n)=strcat(prefix(t),num2str(u)); % fill paramnames
if(fp(u,t)==0)
  fitparamnames(u+(t-1)*n)={strcat(prefix(t),num2str(u))};  % fill freeparamnames
  iv=[iv ivm(u,t)];  % generate corresponding initial values
  lb=[lb lbm(u,t)];  % generate corresponding lower bounds in
  a vector
  ub=[ub ubm(u,t)];  % generate corresponding upper bounds in
  a vector
end
end
fitparamnames=fitparamnames(~cellfun('isempty',fitparamnames));  % remove
empty elements from fitparamnames

%% Data selection

% import data:
data=importdata(filename);
if data(length(data),1)<data(1,1)  % check to see if the data is in
  ascending eV values.
  data=flipud(data);  % This is done because the output
  files of our FTPS data have descending eV values, while Robin's files
  are ascending.
end

if(useOtherUrbach==1)  % check if other Urbach line is to be used
  urbachData=importdata(otherUrbachFile);
  if urbachData(length(urbachData),2)<urbachData(1,2)  % check to see
    if the data is in ascending eV values.
      urbachData=flipud(urbachData);  % This is done
      because the output files of our FTPS data have descending eV values,
      while Robin's files are ascending.
    end
  else
    urbachData=data;
  end
end

if(option==1)  % Automatic detection of position of Urbach line
  % Calculate derivative of spectrum; determine maximum for position
  of Urbach
  % line:
  for i=1:length(urbachData(:,1))-1
    dy(i)=log10(urbachData(i+1,2))-log10(urbachData(i,2));
    dx(i)=urbachData(i+1,1)-urbachData(i,1);
    dx_pos(i)=urbachData(i,1);  % take position of derivative as
    % midpoint between x values
    % dx_pos(i)=urbachData(i,1)+dx(i)/2;  % take position of
    % derivative as midpoint between x values
  end
  dydx=[dx_pos' (dy./dx) ']:
urbachRangeX = urbachData(find(dx_pos > urbach_search_min & dx_pos < urbach_search_max), 1); % Determine x values of subrange to search for maximum slope
urbachRangeY = urbachData(find(dx_pos > urbach_search_min & dx_pos < urbach_search_max), 2); % Determine y values of subrange to search for maximum slope
dyx_urbachmaxrange = [dydx(find(dyx(:,1) > urbach_search_min & dyx(:,1) < urbach_search_max), 1) dydx(find(dyx(:,1) > urbach_search_min & dyx(:,1) < urbach_search_max), 2)]; % create subrange matrix
maxval maxind = max(dyx_urbachmaxrange); % Look for values and indices of maximum values in subrange
xUrbachMiddle = dydx_urbachmaxrange(maxind(2)); % Determine x value at maximum y of subrange (= position where log(slope) is steepest)

urbachFitData = [urbachData(min(find(urbachData(:,1) > xUrbachMiddle)) : urbachRange/2 : min(find(urbachData(:,1) > xUrbachMiddle)) + urbachRange/2, 1) urbachData(min(find(urbachData(:,1) > xUrbachMiddle)) : urbachRange/2 : min(find(urbachData(:,1) > xUrbachMiddle)) + urbachRange/2, 2)]; % calculate urbach line:
urbachLine = [data(:,1), exp(p(2) + p(1)*data(:,1))]; % Define Urbach line
dataMinusUrbach = [data(:,1) data(:,2) - urbachLine(:,2)]; % Subtract Urbach line from data
if (minusUrbach == 1)
data = dataMinusUrbach;
end

% define data to fit
selecteddata = data(min(find(data(:,1) >= eVfrom)) : min(find(data(:,1) >= eVto)), :);

% Fitting

% definition of fit function below.
% the log10 is taken, because we are going to fit the log10 of our data, to
% avoid having to weigh the data.
% Construct fit function string for fit input, based on number of
% distributions used and possible fixed parameters:
allparams = cell.empty;
for t = 1:n % fill cell with all parameter names or fixed values
    for u = 1:3
        if (fp(t, u) == 0) % If a fixed value is not set, use parameter name
            allparams(t + (u - 1)*n) = strcat(prefix(u), num2str(t));
        else % otherwise, use fixed value
            allparams(t + (u - 1)*n) = fp(t, u);
        end
    end
end
funcpartstring = {' *(1+erf((x-')/(sqrt(2*','^2))))'};  % parts of function string following A, P and W respectively

funcstring = 'log10(';  % start of function string
for t=1:n
    funcstring = strcat(funcstring, '+0.5*');
    for u=1:3
        % add either variable name or fixed parameter value to funcstring, followed by "in between" parts of the function
        funcstring = strcat(funcstring, num2str(cell2mat(allparams(t+(u-1)*n ))), funcpartstring(u));
    end
end
funcstring = strcat(funcstring, ')');  % end of function string
funcstring = char(funcstring(:));  % convert from cell to string

% define fittype and options:
fit_function = fittype(funcstring, 'Coefficients', fitparamnames);
options = fitoptions('Method', 'NonlinearLeastSquares', 'StartPoint', iv, 'Lower', lb, 'Upper', ub);

% define log10 of data for input into fit
logdata = [data(:,1) log10(data(:,2))];
logselecteddata = [selecteddata(:,1) log10(selecteddata(:,2))];

% fit:
[defects_fit_object, gof] = fit(selecteddata(:,1), logselecteddata(:,2), fit_function, options);

% fit results:
parameter_values = coeffvalues(defects_fit_object);
parameter_names = coeffnames(defects_fit_object);

% Put confidence interval in allCIs:
% (This is needed, because the fit routine only outputs CIs for free fit parameters, which means that if a parameter is fixed, the matrix size becomes smaller and elements get mismatched. e.g.: if A1 is fixed, the first element of CI is that of A2. Values of 0 are inserted for those parameters that are fixed.)
CIs = confint(defects_fit_object, confidence_interval);
v = 1;
allCIs = zeros(12,2);
for t=1:3  % set CI to 0 if parameter is fixed
    for u=1:n
if(fp(u,t)==0)
    allCIs(u+(t-1)*n,:) = CI s(:,v)';
    v = v+1;
else
    allCIs(u+(t-1)*n,:) = [0 0];
end
end
end

% calculation of error (if 95% conf. int. used: this is 2*sigma):
allerrors = ((allCIs(:,2)-allCIs(:,1))/2);

% Plot results
f=figure(1);
set(gca, 'yscale', 'log')
title(strrep(samplename, '_net', ''));
hold on
% indicate fitting range:
rectangle('Position',[eVfrom, ymin, eVto-eVfrom, ymax-ymin], 'FaceColor',
fit_range_color, 'LineStyle', 'none');
axis([xmin xmax ymin ymax]);
% plot urbach line , if applicable:
if(minusUrbach~=-1)
    semilogy(data(:,1), exp(p(2)+p(1)*data(:,1)), 'Color',
urbanb_line_color);
end
% plot spectrum:
semilogy(data(:,1), data(:,2), strcat('-', data_color));

% plot fit result:
for t=1:n
    for u=1:3
        if(cell2mat(allparams(t+(u-1)*n))===strcat(prefix(u), num2str(t ))))  % if a parameter is free
            % find the value in parameter_values corresponding to the
            % variable name by looking up the index of the variable in parameter_names
            fittedparams(t+(u-1)*n)=parameter_values(find(~cellfun('isempty',
            strfind(parameter_names, strcat(prefix(u), num2str(t)) ))));
        else
            fittedparams(t+(u-1)*n)=fp(t,u);  % use the fixed value
        end
    end
end
finalfit = zeros(1, length(x));
fitresult = zeros(n, length(x));
for t=1:n
    fitresult(t,:) = +0.5 * fittedparams(t) * (1 + erf((x - fittedparams(t+n))
/(sqrt(2*fittedparams(t+n+2)^2))));
    finalfit = finalfit + fitresult(t,:);
end
semilogy(x, finalfit, strcat('--', fit_color));
%semilogy(x, (0.5* parameter_values(1)*(1+erf((x-parameter_values(6))/
sqrt(2*parameter_values(11)^2)))+0.5* parameter_values(2)*(1+erf((x-
parameter_values(7))/sqrt(2*parameter_values(12)^2)))+0.5* parameter_values(3)*(1+erf((x-
parameter_values(8))/sqrt(2*parameter_values(13)^2)))+0.5* parameter_values(4)*(1+erf((x-
parameter_values(9))/sqrt(2*parameter_values(14)^2)))+0.5* parameter_values(5)*(1+erf((x-
parameter_values(10))/sqrt(2*parameter_values(15)^2))));

% plot individual erf contributions:
for t=1:n
    % if contribution is negative, flip and plot in purple, otherwise
    % in green
    if(fittedparams(t)<0)  % negative distributions
        semilogy(x, -fitresult(t,:), '-.', 'Color', negative_dist_color);
        plot purple dashed-dotted line
    else
        c=[0 0 0];
    end
    text(max(x) - 1, -fittedparams(t), num2str(t), 'Color', c);  % plot
    number of erf near right edge of plot
    if(x(find(-fitresult(t,:)>ymin,1)))  % don’t attempt to
        % plot number if it’s below the edge of the plot window
        text(x(find(-fitresult(t,:)>ymin,1)), ymin+2, num2str(t),'
BackgroundColor', [1 1 1]);  % plot number of erf near bottom edge of plot
    end
else  % positive distributions
    semilogy(x, fitresult(t,:), ':', 'Color', positive_dist_color);
    %plot green dotted line
    if(abs(fittedparams(t)/lbm(t,1)-1)<1e-2 || abs(fittedparams(t)
/ubm(t,1)-1)<1e-2)
        c=help_line_color_alarm;
    else
        c=[0 0 0];
    end
    text(max(x) - 1, fittedparams(t), num2str(t), 'Color', c);  % plot
    number of erf near right edge of plot
    if(x(find(fitresult(t,:)>ymin,1)))  % don’t attempt to
        % plot number if it’s below the edge of the plot window
        text(x(find(fitresult(t,:)>ymin,1)), ymin+2, num2str(t),'
BackgroundColor', [1 1 1]);  % plot number of erf near bottom edge of plot
end
text(x(find(fitresult(t,:)>ymin,1)),ymin+2,num2str(t),'Color',c,'BackgroundColor',[1 1 1]); % plot number of erf near bottom edge of plot
end

% plot vertical lines indicating positions of distributions:
if(abs(fittedparams(t+n)/lbm(t,2)-1)<1e-2 || abs(fittedparams(t+n)/ubm(t,2)-1)<1e-2) % change help line color to orange to indicate parameter is near upper or lower bound
  c=help_line_color_alarm;
else
  c=help_line_color_default;
end
line([fittedparams(t+n) fittedparams(t+n)],[ymin ymax],'Color',c);

text(fittedparams(t+n),ymax*.3,num2str(t),'BackgroundColor',[1 1 1]); % plot number of erf near top of plot

% set help line color to orange when parameter is less than 1% from the upper or lower bound
if(abs(fittedparams(t+2*n)/lbm(t,3)-1)<1e-2 || abs(fittedparams(t+2*n)/ubm(t,3)-1)<1e-2)
  c=help_line_color_alarm;
else
  c=help_line_color_default;
end

% plot horizontal lines indicating widths of distributions:
line([fittedparams(t+n)-fittedparams(t+2*n)/2 fittedparams(t+n)+fittedparams(t+2*n)/2],[ymax*.5 ymax*.5],'Color',c);

end
xlabel('Energy (eV)');
ylabel('Absorption (1/cm) or normalized photocurrent (-)');
hold off

% add some info to plot

text(xmin+(xmax-xmin)/20,ymax/10,strcat('fitting range: ',num2str(eVfrom),' - ',num2str(eVto),' eV'),'BackgroundColor',[1 1 1]);
text(xmin+(xmax-xmin)/20,ymax/20,strcat('Position of Urbach edge: ',num2str(xUrbachMiddle),' eV'),'BackgroundColor',[1 1 1]);
text(xmin+(xmax-xmin)/20,ymax/40,strcat('R-squared: ',num2str(gof.rsquare)),'BackgroundColor',[1 1 1]);

if(minusUrbach==0 & option==1 & show_help_plot==1) % Plot determination of Urbach tail to assess correctness
  hold on;
  figure(9);
  semilogy(dx_pos',dydx(:,2),data(:,1),data(:,2),strcat('r-','data_color'));
end
line([xUrbachMiddle xUrbachMiddle],[1e-10 1e3]);
line([urbach_search_min urbach_search_min],[1e-10 1e3], 'LineStyle ', '--', 'Color','g');
line([urbach_search_max urbach_search_max],[1e-10 1e3], 'LineStyle ', '--', 'Color','g');
text(xUrbachMiddle+.05,ymax/5,strcat('Position Urbach tail: ', num2str(xUrbachMiddle)));
hold off;
end

%% Output fitted parameters to console
format 'longE';
for t=1:n
    allparameters_grouped(t,:)=[fittedparams(t) fittedparams(t+n)
fittedparams(t+n*2)];
    allerrors_grouped(t,:)=[allerrors(t) allerrors(t+n) allerrors(t+n*2)];
end
allparameters_grouped
allerrors_grouped

%% Output results to files
% subpath='';
% if(minusUrbach==0)
%    samplename=strcat(strrep(strrep(filename,samplepath,''),'_FTPS_EQE_combined.ftps',''),'_urbach'); %extracts sample name from filename; adds '_urbach'
% else
%    samplename=strcat(strrep(strrep(filename,samplepath,''),'_FTPS_EQE_combined.ftps',''),'_net'); %extracts sample name from filename; adds '_net'
% end

for t=1:3+n % put all parame
    paramsanderrors(2*t-1,1)=fittedparams(t);
    paramsanderrors(2*t,1)=allerrors(t);
end
p1=p(1);
p2=p(2);
rsq=gof.rsquare;
arsq=gof.adjrsquare;

saveas(f,[samplepath samplename], 'fig');
saveas(f,[samplepath samplename], 'png');
if(minusUrbach==1)
save([samplepath samplename], 'paramsanderrors', 'p',
defects_fit_object', 'ivm', 'lbm', 'ubm', 'fp', 'rsq', 'arsq'); % save as .mat file
save([samplepath samplename '_custom_output_Origin.txt'],
paramsanderrors', 'p1', 'p2', 'eVfrom', 'eVto', 'rsq', 'arsq', '-ASCII');

f=fopen([samplepath samplename '_all_output' '.txt'], 'wt');
fprintf(f, '%s
', '% Parameter names. Format:');
fprintf(f, '%s
', '% parameter name, value, CI_lower_bound, CI_upper_bound, error');
for i=1:length(fittedparams)
    fprintf(f, '%s
', num2str(paramnames{i}, ', num2str(fittedparams(i), ',
    num2str(allCIs(i,1), ', num2str(allCIs(i,2), ', num2str(allerrors(i))));
end
fprintf(f, '%s
', '% Other parameters:');
fprintf(f, '%s
', '% Linear fit of Urbach line:');
fprintf(f, '%s
', '[p1 (=b in a+bx), num2str(p1)];
fprintf(f, '%s
', '[p2 (=a in a+bx), num2str(p2)];
fprintf(f, '%s
', 'Fitting range:');
fprintf(f, '%s
', 'eVfrom, num2str(eVfrom));
fprintf(f, '%s
', 'eVto, num2str(eVto));
fprintf(f, '%s
', 'Goodness of fit:');
fprintf(f, '%s
', 'R-squared, num2str(rsq));
fprintf(f, '%s
', 'Adjusted R-squared, num2str(arsq));
fclose(''all'');

% message to console:
disp(strcat('Parameters, confidence intervals, errors, urbach params, eV range and goodness of fit written to '', samplename, '_all_output.txt.'));
disp('All fit matrices and output also saved in .mat file.');
disp('Figures saved as .png and matlab .fig file');
disp(strcat('Custom output written to '', samplename, '_custom_output_Origin.txt" for easy copy-pasting into Origin'));
disp('Format is: A1, error, A2, ... P1, error, P2, ... W1, error, W2, ... p(1), p(2), eVfrom, eVto, r-squared, adj.r-squared.');
end
Appendix D

Data not shown in main text

D-1 Annealing study

D-1-1 Spectra of layers on glass

Figure D-1: Absorption coefficient spectra at different annealing temperatures for R=2.5 film on glass.
Figure D-2: Absorption coefficient spectra at different annealing temperatures for R=5 film on glass.

Figure D-3: Absorption coefficient spectra at different annealing temperatures for R=7.5 film on glass.
Figure D-4: Absorption coefficient spectra at different annealing temperatures for R=10 film on glass.
D-1-2 FTPS-EQE spectra of solar cells

**Figure D-5:** FTPS-EQE spectra at different annealing temperatures for R=2.5 absorber layer solar cell.

**Figure D-6:** FTPS-EQE spectra at different annealing temperatures for R=5 absorber layer solar cell. Spectrum missing for $T_a=200\,^\circ\text{C}$, because of failed measurement.
Figure D-7: FTPS-EQE spectra at different annealing temperatures for R=7.5 absorber layer solar cell.
D-1-3 Raman spectra phonon modes

Figure D-8: Normalized Raman spectra of layer on glass with $R=2.5$ at increasing annealing temperature. Dashed line indicates the wavenumber at which a crystalline peak appears.

Figure D-9: Normalized Raman spectra of layer on glass with $R=5$ at increasing annealing temperature. Dashed line indicates the wavenumber at which a crystalline peak appears.
Figure D-10: Normalized Raman spectra of layer on glass with $R=7.5$ at increasing annealing temperature. Dashed line indicates the wavenumber at which a crystalline peak appears.

Figure D-11: Normalized Raman spectra of layer on glass with $R=10$ at increasing annealing temperature. Dashed line indicates the wavenumber at which a crystalline peak appears.
D-2 Light soaking study

D-2-1 In-situ light soaking

Figure D-12: Linear fits of relative increase of error function intensities for all distributions X, A, B, C for R=0 (a), R=5 (b) and R=10 (c), white light soaking.

Figure D-13: Linear fits of relative increase of error function intensities for all distributions X, A, B, C for R=0 (a), R=5 (b) and R=10 (c), blue light soaking.
Figure D-14: Width of error functions fitted to FTPS-EQE spectra of solar cells under blue light soaking for (a) R=0, (b) R=5, (c) R=10. Width of error functions fitted to FTPS-EQE spectra of solar cells under white light soaking for (d) R=0, (e) R=5 and (f) R=10.
D-2-2  Ex-situ light soaking
Figure D-15: Spectra obtained during ex-situ light soaking experiment. FTPS-EQE spectra of solar cells for (a) $R=0$, (b) $R=2.5$, (c) $R=5$, (d) $R=7.5$ and (e) $R=10$. Absorption coefficient spectra of films on glass for (f) $R=0$, (g) $R=2.5$, (h) $R=5$, (i) $R=7.5$ and (j) $R=10$. 
Figure D-16: Width of error functions fitted to FTPS-EQE spectra of solar cells for (a) R=0, (b) R=2.5, (c) R=5, (d) R=7.5 and (e) R=10. Width of error functions fitted to absorption coefficient spectra of films on glass for (f) R=0, (g) R=2.5, (h) R=5, (i) R=7.5 and (j) R=10.
Figure D-17: Time exponents of metastable defect creation during ex situ light soaking for solar cells.

Figure D-18: Time exponents of metastable defect creation during ex situ light soaking for films. Note the large spread with some negative values for the X and A distributions (and to a lesser extent B and C), indicating the poor consistency of the absorption coefficient spectra.
Appendix E

Transfer characteristics of Keithley current amplifier

Figure E-1 shows the transfer characteristics of the Keithley 428 current amplifier used in FTPS measurements.

Figure E-1: Keithley 428 current amplifier transfer characteristics as a function of frequency for varying amplification factors and at filter rise time settings of 30 µs (a) and 100 µs (b).
Appendix F

List of works

The work conducted during this Master’s programme contributed to the following publications and presentations.

Journal publications


Presentations


Silicon Films and Solar Cells”, 25th International Conference on Amorphous and Nanocrystalline Semiconductors, Toronto, Canada, 18-23 August 2013.

Posters


