

Analysis of electronic transport in HIT solar cells

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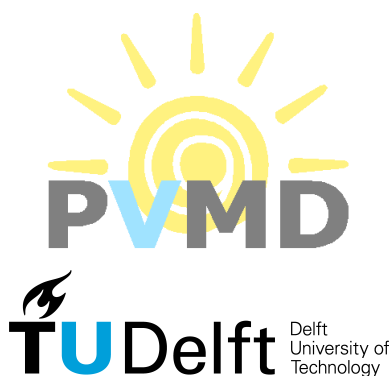
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Preface

This thesis comprises the work performed for the masters degree in Electrical Engineering at Delft University of Technology. I had the opportunity to work in the research group of Photovoltaic Materials and Devices (PVMD) under supervision of Dong Zhang and René van Swaaij. I have really enjoyed my time there and perhaps it can be prolonged for an additional four years.

Even though I have always been interested in many different fields of science, as reflected in my diverse choice of courses in my first year as a master student, I have felt a certain satisfaction to focus on only one. Additionally, I am proud that my research might contribute, even if it is just the tiniest bit, to the future of a sustainable society, where we are no longer dependent on the destruction of nature for our evergrowing thirst for energy.

Having said that, I would like to express my gratitude to the people who helped me get there. First of all, I would like to thank René van Swaaij for inviting not once, but twice to be in his group. I have enjoyed our weekly discussions and can honestly say those have made me learn to think as a researcher. Of course I want to thank Dong Zhang for being my supervisor and processing all those devices, I appreciate how much time and effort that required. Another word of thanks goes out to the other members of the HIT solar cell group: my fellow master student Ibadillah Digdaya and the PhD student Dimitris Deligiannis, who joined later but left an unerasable impression. I have enjoyed the time we spent during and outside our weekly meetings. Further I would like to thank the entire PVMD group for the good atmosphere, interesting research presentations and frequent instances of coffee++ :). Finally express my gratitude to my parents Otto and Petra, sister Lotte and brother Tomas for their unwavering support, confidence and love.

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Abstract

Heterojunction with intrinsic thin-film (HIT) solar cells combine the strengths of amorphous and crystalline silicon to create very efficient and stable devices. In fact, they have the potential to replace solar cells based on monocrystalline technology; the current solar cell market leader. The production can be done cheaper, at lower temperatures and with a potentially higher open circuit voltage V_{oc} . To advance the technology, much research is done in optimizing the performance of HIT devices.

For research purposes it is very valuable to completely understand the physics of HIT devices. A model that can adequately describe the behaviour of the device could be used to simulate the performance of different architectures, without going through the process of manufacturing, measuring and characterization. This would significantly speed up the optimization process.

Unfortunately, no such model exists and thus a lot of research is done to find one. To aid in this, the goal of this thesis is to find the dominant electronic transport mechanisms in HIT solar cells, because despite several previous studies on this, no consensus has been reached.

To characterize the current mechanisms that are present in the device, a number of measurements were performed, most importantly of which is the dark current-voltage (JV) measurement, where the temperature was varied. From this measurement, four current regions were distinguished: the reverse bias region ($-1.2 < V < 0$), the low forward bias region ($0 < V \lesssim 0.4$), the high forward bias region ($0.4 \lesssim V \lesssim 0.7$) and the current limited region ($0.7 \lesssim V < 0.9$).

For every dark JV measurement, each region was fitted with a fitting function. The information from these fittings can be found in the optimized fitting parameters and the choice of fitting function that could most accurately describe the current. From the optimized fitting parameters the activation energy of the saturation current E_{act} and exponential factor A was extracted. From A it is also possible to calculate the diode ideality factor n . These quantities are unique for a certain current mechanism and as such can be used to identify the dominant electronic transport.

It can be concluded that the dominant current in the low forward bias region is best described by the multitunneling capture-emission model, with an activation energy $E_{act,LFB} = 0.3 - 0.45$ eV and a logarithmic slope of $A = 3.5 - 4.5$ V⁻¹. The dominant electronic transport mechanism in the high forward bias region is still unclear. The combination of $E_{act,HFB} = 0.55 - 0.75$ eV and ideality factor $n = 1.25 - 1.4$ does not correspond to any known current mechanism. However,

an alternative method calculates the average ideality factor to be $\sim 1.8 - 1.9$, which would lead to the conclusion that the current is dominated by a recombination current. For very high bias, the current is limited by a space-charge limited current. A series resistance was not observed, probably due to the low area of the measured samples. The reverse bias is usually reported to be dominated by a reverse-bias generation current, but it is reasonable to assume that the actual dominant electronic transport is a combination of a parallel, ohmic resistance path and the reverse-bias characteristics of the tunneling current that dominates the low forward bias.

Additionally, the influence of the thickness and doping level of the amorphous emitter layer was investigated. However, possibly due to drift in the depositions and inaccurate thickness specifications, this has not yielded many results. The only trends that have been observed are that a decrease in the doping level of the emitter increases the passivation and V_{oc} and that the thickness of the emitter layer influences the activation energy of the low forward bias. However, these trends are quite weak and additional research needs to be done before anything can be concluded.

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1. Introduction

On 11 March 2011, the world quite literally shook when an earthquake with a magnitude of 9.0 on the Richter scale occurred 72 kilometers off the coast of Honshu; the main island of Japan. A tsunami caused by the earthquake destroyed much of what was built on the coastline, occasionally even several kilometers inland.

One of the structures that was hit was the nuclear power plant Fukushima. Despite having been shut down immediately after the earthquake, the plant suffered massive destruction. Most unfortunately, the tsunami destroyed the diesel backup power systems, responsible for powering the cooling system, which cools down the reactor core in order to stop the nuclear chain reaction. The inability to do so has led to several so-called meltdowns, a danger inherent to this type of power generation where the reaction chamber melts and releases large amounts of radiation. Subsequently, due to the radioactive contamination in the area around Fukushima, it might take decades before the 80,000 people who were evacuated following the meltdown can return to their homes [2].

Nuclear energy is a significant force in the struggle of finding alternatives to coal-, oil- and gas-based power plants, especially with diminishing fossil fuel reserves [3]. However, the Fukushima catastrophe has brought about a significant aversion to nuclear power. Most notably, the German government announced it will phase out its nuclear power plants by 2022. Its aim is to have renewable energy sources provide 35% of the energy demand in 2020 and reach 80% by 2050 [4].

1.1. Solar Energy

Several alternatives of renewable energy sources are available - best known are wind, geothermal, hydro, biomass and solar. Especially the last one is compelling, considering that solar power is the most abundant of the five. Every year the Earth receives roughly 10,000 times more energy from the sun than the current global energy consumption [5]. This supports why many experts believe that solar energy will be the main energy source in the future [6, 7].

Obviously, in order to achieve this, a substantial investment of capital is required. The speed of the implementation of solar energy depends to a large extent on the economics involved. A lower cost per kWh of solar energy compared to fossil energy could accelerate the acceptance of this type of renewable energy considerably. Since

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the cost of fossil energy keeps rising, due to both increasing demand and political instability in oil-producing countries, and the cost of solar energy continuously decreases, driven by advancing research and more large-scale implementations, the general consensus is that it will not be long before this happens [8].

1.2. Solar cell developments

In the history of photovoltaic research, three generations of solar cells can be distinguished, shown in Figure 1.1. Still the dominant technology of the solar cell market today is the first generation of solar cells. It is mainly characterized by the use of crystalline silicon wafers as a substrate and high temperature processing. The record efficiency of this type of solar cell is 25% for cells produced in laboratories and 22.9% for commercial solar panels under standard testing conditions [9]. A significant disadvantage is the high processing temperatures that are required in the production process. This requires vast amounts of energy, increasing the energy payback time and reducing the beneficial effect of photovoltaics on the environment.

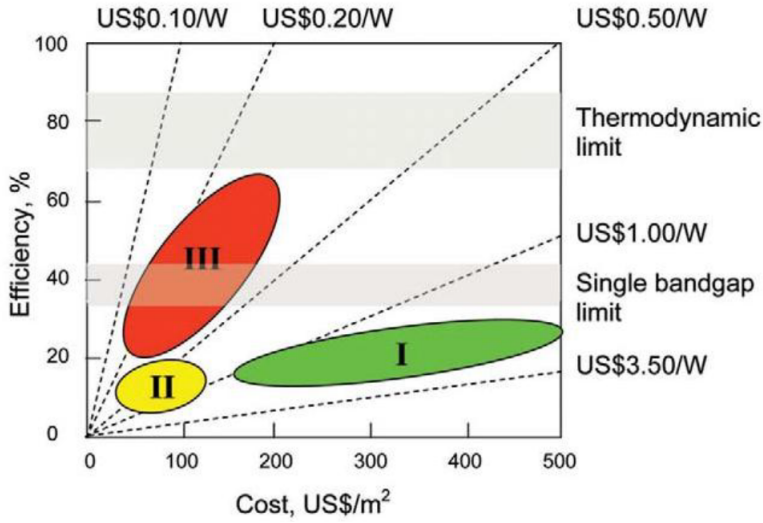


Figure 1.1.: Three generations of solar cell research [1].

The second generation of solar cells attempts to tackle these problems by using low temperature deposition methods and thin absorber layers to reduce material costs, typically in the order of 1 μm , as opposed to the 300 μm thick wafers used for first generation solar cells. Having such thin layers naturally increases the possibility of incident photons that are not absorbed, but instead escape the solar cell. To prevent this the absorber layer must have a high absorption coefficient.

Several semiconductors have this property, such as cadmium-telluride (CdTe), copper indium gallium diselenide (CIGS) and hydrogenated amorphous silicon (a-Si:H), sometimes combined with hydrogenated microcrystalline silicon (μ c-Si:H). Solar cells based on these materials typically use only a small fraction of the material used by first generation solar cells. The drawback, however, are that they are either very rare and toxic (CdTe), mass production of solar cells has proven to be difficult (CIGS [10]) or the efficiency of the solar cells degrade due to light exposure (a-Si:H), an ironic disadvantage for a solar cell that will be further addressed in Section §2.4. Another drawback of the second generation solar cells is the conversion efficiency. Typical efficiencies of large scale second generation solar cell modules are 9-12%, whereas mass produced first generation modules reach efficiencies between 13-20% [1]. Figure 1.2(a) and (b) show an example of the structure of a first and second generation solar cell, respectively. The third generation solar cell is the next big step, where novel concepts are implemented to achieve high efficiency, thin-film solar cells.

1.3. Photovoltaic principle

Most solar cells are in essence a semiconductor p/n junction, or diode, that has been optimized for light absorption, of which three examples are shown in Figure 1.2. Three steps can be distinguished to be the basic processes behind the photovoltaic effect:

1. The generation of an electron-hole pair by absorption of a photon
2. The separation of the electron-hole pair by an electric field
3. The collection of the separated charge carriers at the opposite terminals of the device

Step 1 is a consequence of the band diagram that characterizes a semiconductor. The conduction and valence band are separated by the forbidden band gap. Free electrons are located on the conduction band, while valence band electrons are fixed in the material. When a photon with an energy of at least the band diagram transfers that energy to an electron in the valence band, it can be promoted to the conduction band. This leaves behind a positively charged hole particle, which is a way to conceptualize the interaction of electrons in the vicinity of an unfilled electron state.

For first generation, thick solar cells, the generation of the electron-hole pair occurs mainly in the thick p-type layer, as shown in Figure 1.2(a). The electron, the minority charge carrier in the p-type silicon, diffuses towards the depletion region, where it is accelerated by the electric field. Holes, the majority carrier in the p-type layer, are repulsed by the electric field, so the electron-hole pair is now separated.

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For thin film solar cells, the electric field usually permeates the entire device and the electron-hole pair is immediately separated after generation.

Finally, if the photogenerated charge carriers have not recombined in the process, they arrive at the terminals of the device, generating a potential difference across them.

1.4. Heterojunction with intrinsic thin-layer solar cell

In this thesis the Heterojunction with Intrinsic Thin-layer (HIT) solar cell is analyzed, of which a schematic is shown in Figure 1.2(c). Like the familiar first generation crystalline silicon solar cell, it is wafer-based. The most notable difference is the use of amorphous silicon (a-Si) as the emitter, passivation and back surface field layer.

Amorphous/crystalline silicon interfaces had been investigated before [11, 12], but for solar cell application the breakthrough came in 1992 when Tanaka et. al. published a paper which showed that a thin intrinsic amorphous silicon layer between the doped amorphous layer and the wafer very efficiently passivates the defect-rich interface, significantly increasing the V_{oc} . Since 1992, a lot of research has been done in this field [13, 14, 15], leading to a current record cell efficiency of 23% for a solar cell with an area of 100 cm² [16].

The HIT solar cell takes advantage of the maturity of the wafer-based industry and the promise of amorphous silicon. After wafer production, no high-temperature process steps are required for the junction formation. High temperature steps can deteriorate material properties and have a substantial negative effect on the energy payback time, so should be avoided as much as possible. In a HIT cell the amorphous layers can be deposited on the wafer using plasma enhanced chemical vapour deposition (PECVD), a relatively low temperature deposition method. PECVD will be discussed in more detail in Section §5.1.

1.5. Solar cell model

It is necessary to understand how a solar cell is modeled electrically to understand which currents exist and how they affect the solar cell. This is useful for later in this study, most notably Chapter 4. The basic electrical model of a solar cell is shown in Figure 1.3. The various components will be explained and justified.

Current source Under illumination, a photogenerated current J_{photo} is present in the solar cell, which is in the basic model assumed to be a function of only the

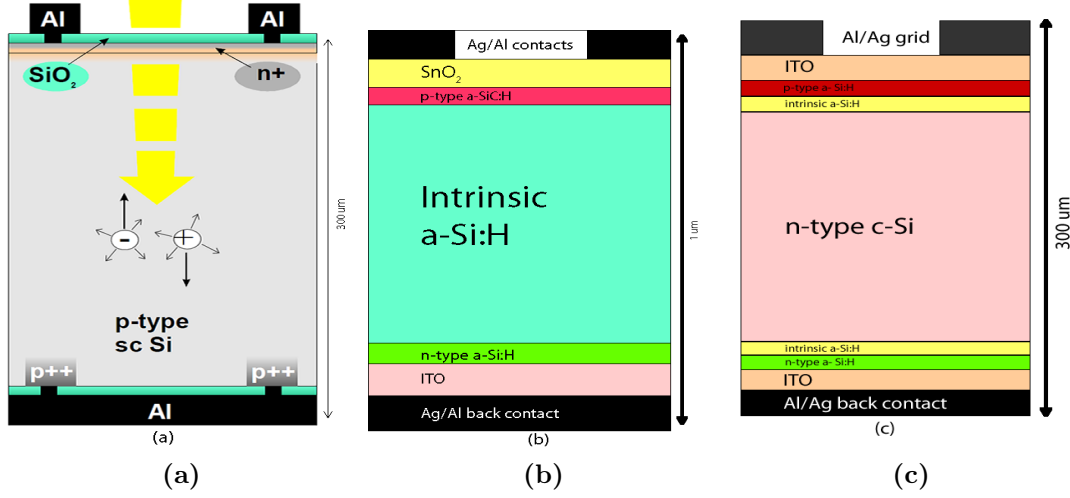


Figure 1.2.: Three solar cell architectures. 1.2(a) shows a first generation homojunction wafer-based cell, 1.2(b) shows a second generation thin-film solar cell and the figure on the right depicts a heterojunction (HIT) cell. [1]

light intensity. With a constant light intensity, it can be modeled using a constant current source. Under dark circumstances, such as during a dark current-voltage measurement, no photogenerated current is present and the current source modeled as an open connection.

Diode Various current mechanisms with an exponential voltage dependence that can exist in a solar cell can be modeled by a diode, such as diffusion, generation-recombination and tunneling. As will be explained in Chapter 4, current mechanisms with exponential voltage dependence can be described with the generic junction rectification equation:

$$J_{diode} = J_0[\exp(AV_a) - 1]. \quad (1.1)$$

The different current mechanisms will also be elaborated upon in Chapter 4. With only a current source and diode present, the model yields the ideal voltage-current relationship. Under illuminated conditions:

$$J_{out} = J_0[\exp(AV_a) - 1] - J_{photo}, \quad (1.2)$$

where V_a is the voltage across the diode, which in this case is equal to V_{out} . This is shown in Figure 1.4(b).

Parallel resistance The parallel (shunt) resistance models an additional current path parallel to the p/n junction. The current-voltage relation is assumed to be

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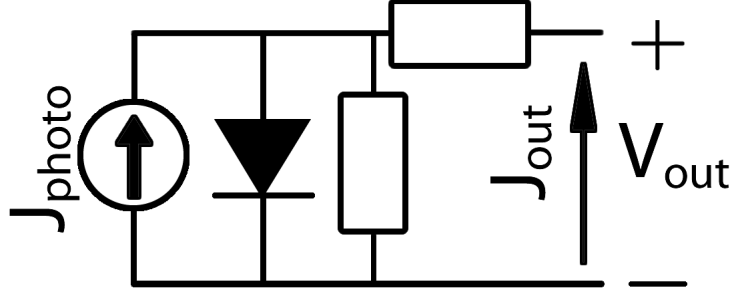


Figure 1.3.: The basic electrical model of a solar cell. A current source models the photogenerated current, a diode models the p/n junction and the two resistors model the shunt and series resistance.

ohmic and can therefore be described by Ohm's law:

$$J_{rp} = \frac{V_a}{R_p}, \quad (1.3)$$

with R_p as the parallel resistance. Ideally, the parallel resistance is very large and can be ignored, but sometimes faulty processing causes a shunt that is low enough to be significant. The possible origin(s) of additional ohmic current paths will be described in Section §4.5. The total current including the parallel path becomes

$$J_{out} = J_0[\exp(AV_a) - 1] + \frac{V_a}{R_p} - J_{photo}. \quad (1.4)$$

The effect of R_p on the illuminated IV-curve is shown in Figure 1.4(d)

Series resistance Voltage drops across the conductive oxide, metal and bulk are modeled as a series resistance. This potential difference decreases the voltage across the diode, making it unequal to the output voltage, i.e. $V_a < V_{out}$. The voltage drop depends on the output current; $\Delta V_{Rs} = J_{out}R_s$, leading to $V_a = V_{out} - J_{out}R_s$. This changes the ideal current-voltage relation of Eq. (1.2) to

$$J_{out} = J_0[\exp(A(V_{out} - J_{out}R_s)) - 1] - J_{photo}. \quad (1.5)$$

The addition of a series resistance makes Eq.(1.5) an implicit equation and it can therefore no longer be analyzed analytically. Instead, to determine how R_s affects the current-voltage relation, Eq.(1.5) needs to be solved numerically. The effect of different values of R_s on the illumined IV-curve is shown in Figure 1.4(f).

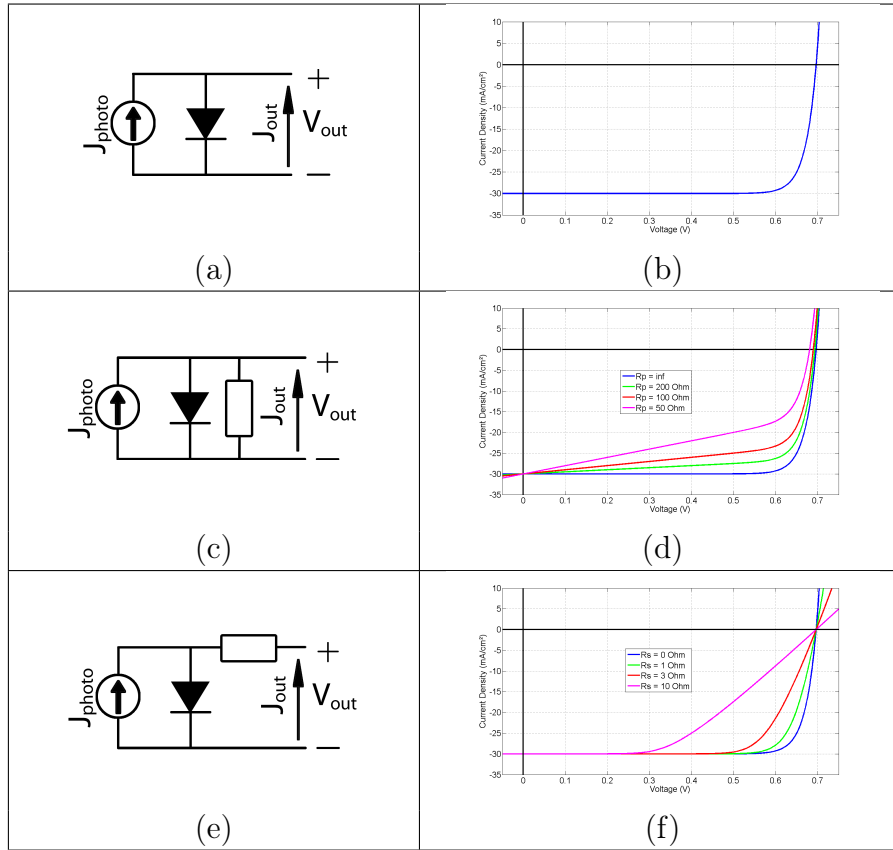


Figure 1.4.: The current-voltage relation under illuminated conditions with the effect of the parallel resistance in (D) and series resistance in (F).

1.6. Thesis motivation and outline

To become more competitive in the solar cell market, HIT solar cell technology is constantly improved upon by research groups worldwide. The research done in our PVMD group of the Technical University of Delft to contribute to this progress is relatively young and there is ample opportunity for improvement. Also, the in-house developed semiconductor simulation software ASA is not yet able to accurately predict the solar parameters, because the available models do not include HIT cell-specific physics. A model that can adequately describe the behaviour of a HIT device could be used to simulate the performance of different architectures, without going through the process of manufacturing, measuring and characterization. This would significantly speed up the process of optimizing the HIT solar cell.

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Unfortunately, not such model exists and thus a lot of research is done to find one. To aid in this, the goal of this thesis is to find the dominant electronic transport mechanisms in HIT solar cells, because despite several previous studies on this, no consensus has been reached. To that purpose, HIT solar cells with different layer characteristics were made and analyzed with a set of measurements, the most important of which is the dark current-voltage measurement. From this measurement a great deal of information about the solar cell can be extracted.

Several authors have already studied and published on the dark current characteristics of their HIT cells. However, those were usually aimed at finding the dynamics of a single solar cell or the effect of different architectures. The reported results are useful to put our results in perspective, so will be referenced frequently.

To extract information from the dark current measurements, the data was fitted to a number of fitting functions, including a two-diode model. The danger of a fitting is that if the model assumptions are incorrect, the resultant fit yields no information or can even be misleading. However, various authors agree that in this case it is a valid approach and can be a useful tool.

This thesis is divided into three parts. To understand this work, the basics of semiconductor physics and electrical transport mechanisms are discussed in the first part of this thesis, Fundamentals which is comprised of Chapter 2, where the nature of amorphous silicon is examined, Chapter 3, which details the different dominant recombination mechanisms and Chapter 4, where the physics and characteristics of several electrical transport mechanisms are explored. The second part, Experimental, details the experimental methods that have been employed. Chapter 5 briefly describes the deposition techniques for manufacturing HIT solar cells. Chapter 6 summarizes the characterization methods that have been employed in characterization of both the individual solar cell layers as well as that of a finished device. An important section of this chapter explains the fitting procedure, which is crucial for interpreting the results. Chapter 7 lists how the deposition and characterization methods of Chapter 5 and 6 are employed in practice. The final part of this thesis, Results and Discussion, shows in Chapter 8 the measurement and fitting results of every current region and attempts to find which of the mechanisms mentioned in Chapter 4 characterizes the electronic transport best. Finally, in Chapter 9, the results will be discussed and explained how the results can be improved upon with future research.

Part I.

Fundamentals

2. Amorphous Silicon

As mentioned in Section §1.4, the HIT solar cells that will be investigated in this study incorporate amorphous silicon (a-Si) as passivating, emitter and back surface field layers, and as such are very important. Amorphous silicon has been of particular interest to the electronics industry since 1965, when Sterling et al. reported the deposition of amorphous silicon onto a substrate [17]. The main advantage of amorphous silicon for the wafer-based HIT solar cell are the passivating properties and the fact that deposition can be done using PECVD; a low temperature, large area deposition technique. For thin film silicon solar cells an additional advantage is the a high absorption coefficient, allowing for a very thin device that can use low-cost and flexible substrates.

Because it is so important for HIT solar cells, it is useful to understand how amorphous silicon is modeled using semiconductor device physics. To this end, this chapter introduces a basic overview of the physics regarding amorphous silicon.

2.1. Material structure

The distinguishing property of amorphous silicon in contrast to the crystalline form is the absence of long range order in the atomic structure. Whereas in crystalline silicon the atoms are arranged in a regular lattice, the atoms in amorphous silicon are distributed randomly, as illustrated schematically in Figure 2.1. For silicon atoms, it is thermodynamically most favorable to have four bonds with other silicon atoms. However, due to the highly irregular and disordered state of atoms in amorphous silicon, this is not always possible. As a consequence, some valence electrons are unbound, which are referred to as dangling bonds. Dangling bonds are very efficient recombination centers and their properties will be described in more detail in Chapter 3. To decrease the density of dangling bonds, hydrogen is introduced in the material. Hydrogen atoms can bond with silicon atoms, passivating the dangling bonds. A significant amount of defects will remain, though.

2.2. Density of states

Amorphous semiconductors are not completely irregular. Even though no long range order is present, the short range order is comparable to that of crystalline silicon.

2. Amorphous Silicon

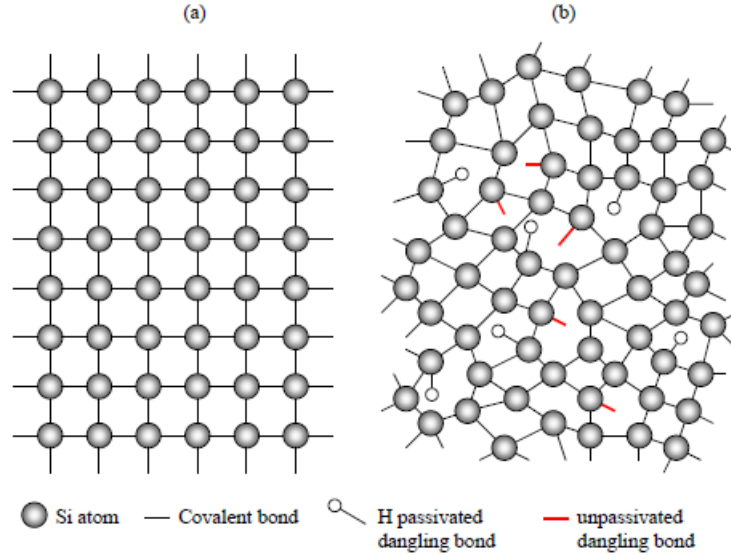


Figure 2.1.: The schematic representation of the crystal lattice of (a) crystalline silicon and (b) hydrogenated amorphous silicon [1]

The bonds between the atoms are similar to those in crystalline silicon in that the average number of neighbours and bond lengths and angles are the same. Therefore, the density of states distribution of amorphous silicon is similar to that of its crystalline counterpart. However, the irregular structure does reflect in the density of states distribution. The bonding disorder gives rise to localized band tails and the structural defects such as dangling bonds cause electronic defect states in the band gap [18]. The density of states distribution for crystalline and amorphous silicon is shown in Figure 2.2(a) and (b), respectively.

The classical concepts of conduction and valence band, in Figure 2.2(a) and (b) indicated as the extended states, are continuous throughout the material. Free charge carriers, i.e. holes in the valence band and electrons in the conduction band can freely move through the material to adjacent states with comparable energies. The tail and defect states, however, are localized. Adjacent states do not necessarily have similar energies, so charge carriers in these states are immobile and are essentially trapped. Trapped charge carriers can be emitted to their respective band or recombine with a carrier from the other band. Due to the non-zero local density of states distribution between the extended states, it is not possible to define a classical forbidden energy band gap. However, the sharp decrease in mobility in the localized tail and defect states allow to define a mobility gap. The mobility gap of amorphous silicon is larger than the band gap of crystalline silicon, typically estimated at 1.8-1.9 eV [19, 20].

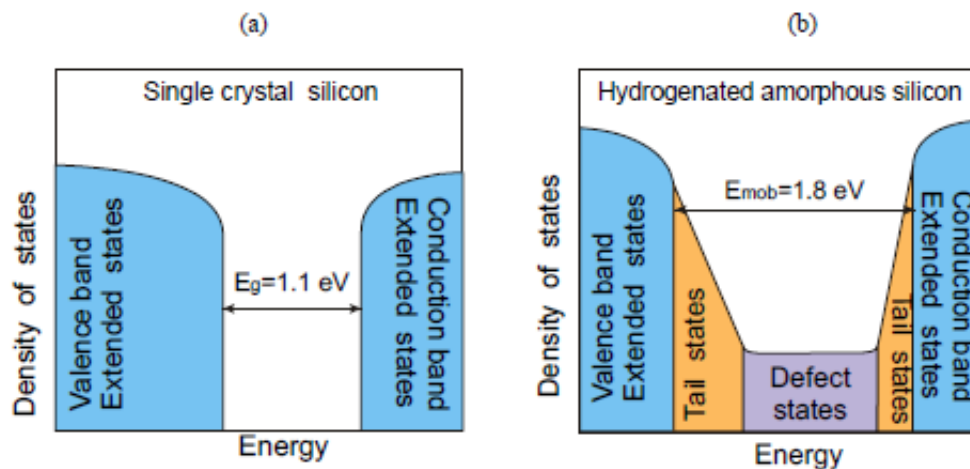


Figure 2.2.: The density of states distribution for (a) crystalline silicon and (b) hydrogenated amorphous silicon [1].

2.3. Doping

For the p-type emitter and the n-type back surface field, the amorphous silicon has to be doped with impurities. This is relatively simple and efficient for crystalline silicon due to the strong regularity of the lattice. Group III or V impurities that take the place of a silicon atom are forced into the crystalline structure, donating a hole or electron, respectively.

However, for amorphous silicon the irregular crystal structure is detrimental for the doping capabilities. This is due to an effect called the 8-N rule, introduced by Mott in 1967 [21]. It states that the natural coordination; the optimal number of covalent bonds Z , of an atom in a continuous random network is determined by the number of valence electrons N :

$$\begin{aligned} Z &= 8 - N & \text{for } N \geq 4 \\ Z &= N & \text{for } N < 4 \end{aligned}$$

This means that for the n-type dopant phosphorus with valence electrons $N = 5$, the coordination $Z = 3$ and for the p-type dopant boron with $N = 3$ the optimum number of covalent bonds $Z = 3$. Substitutional doping like in crystalline silicon relies on the impurity atoms to have four bonds and the 8-N rule predicts that that will not happen. Therefore, it was long thought that doping of amorphous silicon was impossible.

Consequently, the demonstration of doping of amorphous silicon in 1975 by Spear and LeComber was an important breakthrough [22]. They reported the ability to control the electrical conductivity of amorphous silicon over many orders of magnitude by doping with substitutional impurities, albeit with a much lower doping

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efficiency compared to doping of crystalline silicon. Apparently, a small percentage of the impurity atoms are incorporated in the lattice in a donor- or acceptor-like state. How this is possible was explained by Street in 1982 by the autocompensation model [23]. The details of this model are outside the scope of this introduction, but there are two important consequences. The first is that doping of an amorphous semiconductor inevitably leads to an increasing number of defects, which has a significant, negative effect on the lifetime of charge carriers in a doped amorphous semiconductor. The other consequence is due to the self-inhibiting nature of doping of amorphous silicon. This implies that the maximum doping is limited, i.e. the activation energy can not be pushed lower than 0.2 eV for doped n-type and 0.3 eV for doped p-type amorphous silicon.

2.4. Staebler-Wronski effect

The first full amorphous silicon solar cell was created by Wronski and Carlson in 1976 [24]. In 1977, Staebler and Wronski observed that the conversion efficiency of their device decreased over time. Prolonged exposure to light decreased both the photoconductivity and the dark conductivity, indicating that a structural change had occurred [25]. This effect is since called the *Staebler-Wronski effect*. It describes the metastable creation of defects in the amorphous silicon due to the exposure to light. These defects will act as recombination centers and degrade the quality of the material. The defects are metastable in the sense that an annealing of the sample for several minutes at sufficiently high temperature reverses the change in conductivity to the original value.

The effect is mostly affecting thin-film solar cells, where the largest part of the device is amorphous silicon. Therefore, a lot of research has been done and is still done, since the definite cause has not been pinpointed to date [26, 27, 28, 29, 30].

3. Recombination

When an electron in the conduction band, i.e. a 'free' electron, crosses the band gap, takes the place of a hole in the valence band and releases the difference in energy, it is said to have recombined. The limit on the lifetime of free charge carriers imposed by the rate of recombination is an important device characteristic for many semiconductor devices, including solar cells, because when two photogenerated charge carriers recombine, the excess energy is usually thermalized in the lattice and can not contribute to the energy production of the solar cell.

The recombination rate R [$\text{cm}^{-3}\text{s}^{-1}$] is related to the lifetime τ [s] by the following definition:

$$R \equiv \frac{\Delta n}{\tau}, \quad (3.1)$$

where Δn is the excess carrier density [cm^{-3}]. When multiple recombination processes are present simultaneously, the total recombination rate is the sum of the contributions of the individual processes. The result of a lifetime measurement as described in Section §6.1 is always the effective lifetime τ_{eff} :

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \dots \quad (3.2)$$

In the case of a HIT cell, at the interface between the amorphous and crystal layer an abrupt discontinuity in the lattice structure is present. This is the source of a high concentration of dangling bonds, which are very efficient recombination centers and therefore much research is done on improving the interface by passivating these dangling bonds [31, 32, 33]. Due to the two-dimensional structure of the interface, recombination there is referred to as surface recombination. The definition of the surface recombination rate is very similar, although the formulation is in terms of recombination per unit surface rather than unit volume. The surface recombination rate U [$\text{cm}^{-2}\text{s}^{-1}$] is defined as

$$U \equiv S \cdot \Delta n_s, \quad (3.3)$$

where Δn_s is the excess carrier concentration density at the surface [cm^{-3}] and S is the surface recombination velocity [$\text{cm}\cdot\text{s}^{-1}$]. To qualify the surface recombination, determined by the interface passivation quality, usually the surface recombination velocity S is used instead of the surface recombination rate U . This is because it is injection level independent and therefore a fundamental property of the material.

3. Recombination

Surface recombination does not occur throughout the sample. Therefore, to determine the limit on the lifetime of excess carriers in the bulk due to the recombination at the surface, the wafer thickness W is needed:

$$\tau_s = \frac{W}{S}. \quad (3.4)$$

In a HIT cell, the crystalline wafer is sandwiched between two amorphous layers, creating two interfaces with high surface recombination. Assuming the recombination velocity is the equal at the front and the back, the effective lifetime τ_{eff} in a HIT solar cell including all the recombination process that will be discussed in this section becomes [34]

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S}{W}, \quad (3.5)$$

where τ_{bulk} is found as

$$\frac{1}{\tau_{bulk}} = \frac{1}{\tau_{aug}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{srh,bulk}}. \quad (3.6)$$

For this study it is important to note that certain dark current mechanisms are based on recombination. For example, as will be explained in Section §4.1, diffusion is due to recombination of minority charge carriers in the quasi-neutral region of the pn-junction. In order to understand the current mechanisms, it is necessary to comprehend the recombination that is responsible.

In this chapter the distinction is made between direct band-to-band recombination and recombination via defects in the band gap. Direct band-to-band recombination is inherent to the fundamental properties of the semiconductor and can not be reduced by improving the quality of the material and will occur even in perfect, defect-free semiconductor materials. When defects are present, however, an electron can travel from the conduction band to the valence band via defect states with an corresponding energy that lies in the forbidden band gap.

3.1. Direct band-to-band recombination

Radiative recombination Radiative recombination is when an electron falls back from the conduction to the valence band, recombining with a hole, releasing the energy equal to the band gap in the form of a photon [35], as depicted in Figure 3.1. This principle is exploited for light emitting diodes (LEDs) [36]. Most LEDs consist of direct band gap semiconductors, such as GaAs. This is because in case of an indirect band gap an additional particle, a phonon, is necessary to correct for the change in impulse. This make the process in an indirect band gap semiconductor a

3.1. Direct band-to-band recombination

four-particle process, which is much less likely to occur.

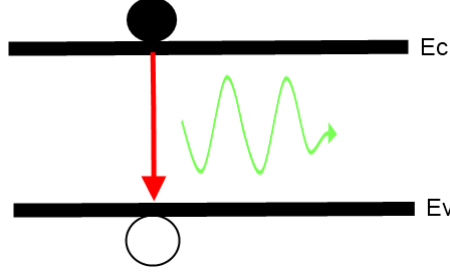


Figure 3.1.: A schematic representation of the radiative recombination process.

The efficiency of radiative recombination is proportional to the excess carrier density. The recombination rate R_{rad} for crystalline silicon, an indirect band gap semiconductor, is given by [37]

$$R_{rad} = 9.5 \times 10^{-15} np. \quad (3.7)$$

The recombination coefficient $B = 9.5 \times 10^{-15}$ is several orders of magnitude low for a semiconductor with an indirect band gap than for one with a direct band gap. For instance, GaAs, a semiconductor that is widely used for LEDs, has a recombination coefficient of $B_{rad} = 7.2 \times 10^{-10}$. In general, the radiative recombination in crystalline silicon is negligible small compared to the other recombination processes discussed after this. An additional effect which might decrease the influence of radiative recombination in silicon is photon recycling, where the emitted photon is reabsorbed somewhere else in the solar cell. Therefore, this recombination mechanism is generally neglected in further analysis.

Auger recombination The Auger recombination process is shown in Figure 3.2. It is a three-particle interaction where an electron recombines with a hole, with the excess energy transferred to a third electron or hole [38]. The eeh process is when the excess energy is transferred to a second electron. Likewise, the ehh process is when the excess energy is transferred to a hole [39]. The excited charge carrier then releases the energy to the lattice, generating heat. The eeh and ehh processes are depicted in Figure 3.2 on the left and right, respectively.

Since collision are more likely to occur with a high concentration of free charge carriers, Auger recombination can become the dominant mode of recombination for high injection levels [40]. The most recent parametrization of the rate of Auger recombination R_{aug} is given by [41]

$$R_{aug} = np(1.8 \times 10^{-24} n_0^{0.65} + 6 \times 10^{-25} p_0^{0.65} + 3 \times 10^{-27} \Delta n^{0.8}). \quad (3.8)$$

3. Recombination

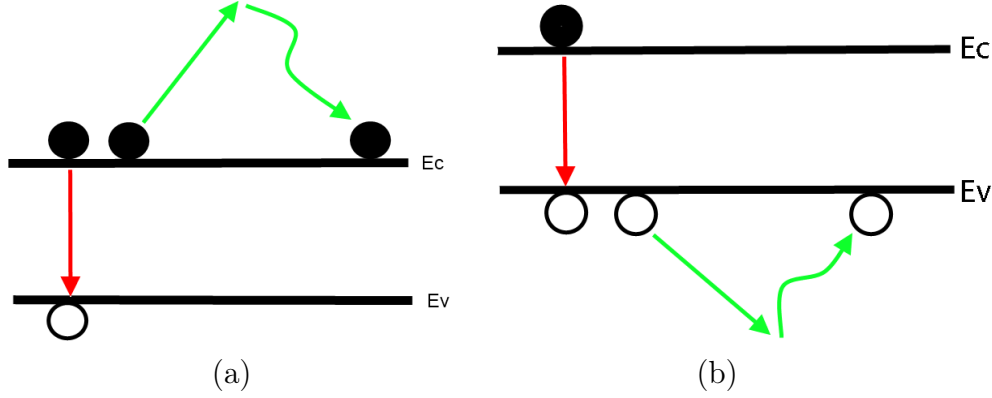


Figure 3.2.: A schematic representation of the Auger recombination process. There are two mechanisms; a collision between two electrons (a) and a collision between two holes (b).

3.2. Recombination through defects

The dynamics of recombination through defects were analyzed simultaneously by Shockley and Read [42] and Hall [43]. It involves the interaction between electrons in the conduction band and holes in the valence band, and a defect with an associated trap energy level E_t . As depicted in Figure 3.3, four transitions are possible:

1. The capture of an electron from the conduction band by the empty trap
2. The emission of a trapped electron to the conduction band from an occupied trap.
3. The capture of a hole from the valence band by an occupied trap
4. The emission of a hole to the valence band from the occupied trap, i.e. the excitation of an electron from the valence band to the trap level

For process (1), the electron capture rate R_{cn} is proportional to the density of electrons in the conduction band and the density of empty trap states:

$$R_{cn} = n \cdot v_{th} \cdot \sigma_n \cdot N_t \cdot (1 - f(E_t)), \quad (3.9)$$

where n is the electron density in the conduction band, v_{th} the thermal velocity, σ_n the electron capture cross-section, N_t the trap density and $f(E_t)$ the Fermi-Dirac distribution function at the trap energy, given by

$$f(E_t) = \frac{1}{1 + \exp(\frac{E_t - E_f}{kT})}, \quad (3.10)$$

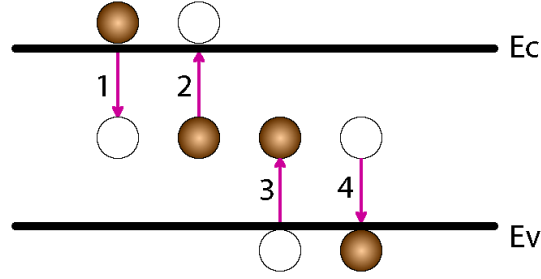


Figure 3.3.: The four basic trapping and emission processes associated to Shockley-Read-Hall recombination statistics.

which denotes the probability that a trap will be occupied by an electron. In this case, $1 - f(E_t)$ denotes the probability that a trap is empty.

For process (2), the electron emission rate R_{en} is proportional to the number of filled traps:

$$R_{en} = e_n \cdot N_t \cdot f(E_t), \quad (3.11)$$

where e_n denotes the emission coefficient for electrons.

Likewise, the hole capture rate of process (3) R_{cp} and emission rate of process (4) R_{ep} be written as

$$R_{cp} = p \cdot v_{th} \cdot \sigma_p \cdot N_t \cdot f(E_t) \quad (3.12)$$

$$R_{ep} = e_p \cdot N_t \cdot (1 - f(E_t)) \quad (3.13)$$

Here σ_p is the capture cross-section for holes and the hole emission coefficient is indicated by e_p .

Under thermal equilibrium, the rate of electron capture from the conduction band must be balanced by the rate of electron emission to the conduction band:

$$R_{cn} = R_{en}, \quad (3.14)$$

from which it follows that

$$n_0 \cdot v_{th} \cdot \sigma_n \cdot N_t \cdot (1 - f(E_t)) = e_n \cdot N_t \cdot f(E_t). \quad (3.15)$$

Combining equation Eq. (3.15) and the Boltzmann approximation of equation Eq. (3.10), the emission coefficient e_n is found as [44]

$$e_n = n \cdot v_{th} \cdot N_c \exp\left(\frac{E_t - E_c}{kT}\right). \quad (3.16)$$

3. Recombination

Similarly, the hole emission coefficient can be derived as

$$e_p = p \cdot v_{th} \cdot N_v \exp\left(\frac{E_v - E_t}{kT}\right). \quad (3.17)$$

In a non-equilibrium steady-state, e.g. under illuminated conditions or when subjected to an external electric field, the net rate at which electrons are captured from the conduction band must be equal to the net rate at which holes are captured from the valence band. It is assumed that the emission coefficients are approximately equal to the values as derived for the thermal equilibrium. The recombination rate R_{srh} is then given by

$$R_{srh} = R_{cn} - R_{en} = R_{cp} - R_{ep}. \quad (3.18)$$

From this the trap occupation $f(E_t)$ can be obtained as

$$f(E_t) = \frac{\sigma_n n + \sigma_p p'}{\sigma_n(n + n') + \sigma_p(p + p')}, \quad (3.19)$$

where

$$n' = N_c \exp\left(\frac{E_t - E_c}{kT}\right), \quad p' = N_v \exp\left(\frac{E_v - E_t}{kT}\right)$$

Substituting equation Eq. (3.19) in equation Eq. (3.18), the Shockley-Read-Hall recombination rate R_{srh} becomes

$$R_{srh} = \frac{\sigma_n \sigma_p N_t (np - n_i^2)}{\sigma_n(n + n') + \sigma_p(p + p')}. \quad (3.20)$$

To simplify this equation, it is useful to examine the case for extrinsic doping and low injection. For an n-type semiconductor under low injection, Eq. (3.20) reduces to

$$R_{srh} = \sigma_p N_t \Delta p. \quad (3.21)$$

Using the definition of the lifetime as given at the start of this chapter, the lifetime for holes in an n-type material due to SRH recombination is

$$\tau_{srh,p} = \frac{\Delta p}{R_{srh}} = \frac{1}{N_t \sigma_p}. \quad (3.22)$$

Similarly, for electrons in a p-type semiconductor, the lifetime can be found as

$$\tau_{srh,n} = \frac{\Delta n}{R_{srh}} = \frac{1}{N_t \sigma_n}. \quad (3.23)$$

3.2. Recombination through defects

Combining Eqs. (3.20)-(3.23), the SRH recombination rate in a p/n junction becomes

$$R_{srh} = \frac{np - n_i^2}{\tau_{srh,p}(n + n') + \tau_{srh,n}(p + p')}. \quad (3.24)$$

4. Current Mechanisms

Depending on the structure of a heterojunction solar cell, applied forward bias and temperature, there are different mechanisms that dominate the observed dark current. Various carrier transport models have been observed by authors of published papers investigating a-Si:H/c-Si heterojunctions. This chapter describes those models and their characteristics to effectively deduce the dominant electronic transport for our HIT cells from the fittings on the dark current measurements as described in Section §6.2.

In this chapter two parts can be distinguished. Sections 4.1-4.3 describe current mechanisms that can dominate the current-voltage curve. Sections 4.4 and 4.5 describe limiting electronic transport, i.e. current mechanisms that suppress the flow of electrons. This distinction is made because while the dominating current mechanisms only have an effect on the dark current and can be superposed on the generated photocurrent, the limiting current mechanisms can inhibit the photocurrent as well. The dominating current mechanisms can be mapped onto the junction rectification model

$$J(V, T) = J_0(T) [\exp(A(T)V) - 1], \quad (4.1)$$

where $A(T)$ is the exponential factor and $J_0(T)$ the saturation current.

In the analysis in Section §8.1, the activation energy of the saturation current is calculated to discern between different current mechanisms. The definition of the activation energy of the saturation current is given by:

$$E_{act} \equiv -\frac{\delta \ln(J_0(T))}{\delta \frac{1}{kT}}. \quad (4.2)$$

Usually, a large part of the activation energy of the saturation current originates from an exponential temperature dependence of the saturation current:

$$J_0(T) = J_{00} \exp\left(-\frac{E_{act, J_0}}{kT}\right), \quad (4.3)$$

where J_{00} is a constant, independent of temperature. Other temperature dependencies can stem from the density of states or the carrier concentration, but are usually negligible compared to the exponential temperature dependence coefficient E_{act, J_0} .

4. Current Mechanisms

4.1. Diffusion

In the case of homojunction p/n solar cells, the dark current is usually governed by charge carrier diffusion in the neutral p-type bulk. Several authors investigating a-Si:H/c-Si heterojunction solar cells have concluded that in their devices, diffusion is also the dominant current mechanisms at operating forward biases [45]. The p/n junction diffusion model was first published by Shockley in 1949 [46]. The derivation starts with the one-dimension ambipolar transport equation, given for an n-type semiconductor as

$$D_p \frac{\delta^2(\Delta p_n)}{\delta x^2} - \mu_p E \frac{\delta(\Delta p_n)}{\delta x} + G - R = \frac{\delta(\Delta p_n)}{\delta t}. \quad (4.4)$$

Where D_p [cm^2s^{-1}] is the diffusion coefficient, Δp_n [cm^{-3}] the excess hole concentration, μ_p [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$] the hole mobility, E [Vcm^{-1}] the electric field, G [$\text{cm}^{-3}\text{s}^{-1}$] the excess carrier generation rate and R [$\text{cm}^{-3}\text{s}^{-1}$] the recombination rate of excess carriers. In the quasi-neutral regions, the electric field $E = 0$ and under dark condition the generation rate of excess charge carriers $G = 0$. The recombination rate R is the sum of all the recombination mechanisms as described in Chapter 3. Assuming steady state conditions so that $\frac{\delta(\Delta p_n)}{\delta t} = 0$, equation Eq. (4.4) reduces to

$$\frac{\delta^2(\Delta p_n)}{\delta x^2} - \frac{\delta \Delta p_n}{L_p} = 0, \quad (4.5)$$

where $L_p^2 = D_p \tau_{p0}$. To solve this equality for $\Delta p_n(x)$, boundary conditions are required. For a pn-junction as shown in Figure 4.1, at the edge of the space-charge region (x_n), the minority carrier concentration p_n is given by [47]

$$p_n(x_n) = p_{n0} \exp\left(\frac{eV_a}{kT}\right). \quad (4.6)$$

Far away from the junction, the minority carrier concentration should be equal to the thermal-equilibrium minority carrier concentration:

$$p_n(+\infty) = p_{n0}. \quad (4.7)$$

Combining Eqs. 4.6 and 4.7 with the definition $\Delta p_n(x) = p_n(x) - p_{n0}$ yields

$$\Delta p_n(x) = p_{n0} \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] \exp\left(\frac{x_n - x}{L_p}\right), \quad x \geq x_n \quad (4.8)$$

The excess minority carrier concentration peaks at the space-region edge and decays exponentially with distance further into the n-type quasi-neutral region due to

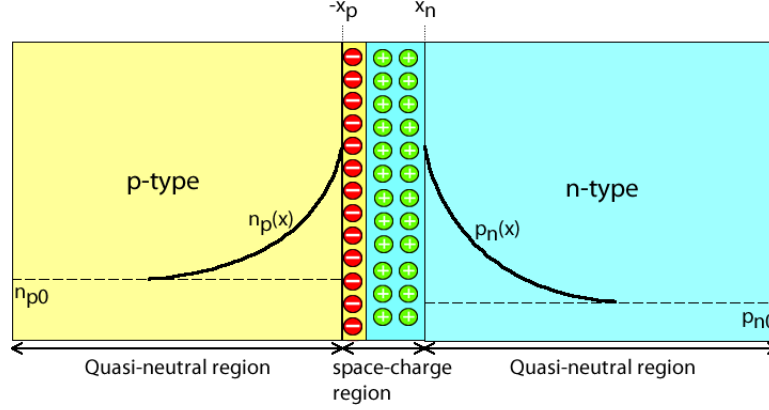


Figure 4.1.: A p/n junction diode. Indicated in the graph is the minority carrier concentration

recombination. The same can be done for the minority carrier concentration in the p-type material:

$$\Delta n_p(x) = n_{p0} \left[\exp\left(\frac{eV_a}{kT}\right) - 1 \right] \exp\left(\frac{x_p + x}{L_p}\right), \quad x \leq -x_p \quad (4.9)$$

Eqs. (4.8) and (4.9) are shown graphically in Figure 4.1.

The concentration gradient that occurs when a voltage is applied, gives rise to diffusion. The total diffusion current is the sum of the hole current at $x = x_n$ and the electron current at $x = -x_p$:

$$J_p(x_n) = -eD_p \frac{p_n(x)}{\delta x} \Big|_{x=x_n} = \frac{eD_p p_{n0}}{L_p} \left[\exp\left(\frac{eV_a}{kT}\right) - 1 \right] \quad (4.10)$$

$$J_n(-x_p) = eD_n \frac{n_p(x)}{\delta x} \Big|_{x=-x_p} = \frac{eD_n n_{p0}}{L_n} \left[\exp\left(\frac{eV_a}{kT}\right) - 1 \right] \quad (4.11)$$

$$J_{dif} = \left[\frac{eD_p p_{n0}}{L_p} + \frac{eD_n n_{p0}}{L_n} \right] \left[\exp\left(\frac{eV_a}{kT}\right) - 1 \right] = J_0 \left[\exp\left(\frac{eV_a}{kT}\right) - 1 \right] \quad (4.12)$$

In a HIT solar cell, the n-type wafer is assumed to be much lower doped than the p-type a-Si:H layer. Hence, $p_{n0} \gg n_{p0}$ and the saturation current J_0 reduces to

$$J_0 = \frac{eD_p p_{n0}}{L_p} = \frac{eD_p n_i^2}{L_p N_d}, \quad (4.13)$$

4. Current Mechanisms

with

$$n_i^2 = N_c N_v \exp\left(-\frac{E_g}{kT}\right). \quad (4.14)$$

From Eqs. 4.12-4.14 it can be concluded that the slope of the logarithmic current-voltage plot $A = \frac{e}{kT}$, implying an ideality factor of 1. Both N_c and N_v have a temperature dependence of $T^{\frac{3}{2}}$. Applying the definition of Eq.(4.2), the activation energy of the saturation current $E_{act} = 3kT + E_g$, where E_g is equal to the bandgap of the wafer (~ 1.12 eV). Note that, for practical temperatures, $E_g \gg 3kT$.

4.2. Generation-Recombination

Whereas diffusion is determined by the recombination in the bulk, a generation-recombination current is caused by generation and recombination in the space charge region. It is assumed that in the space-charge region the defect density is relatively high, especially for a-Si/c-Si heterojunctions, so the recombination is dominated by Shockley-Read-Hall recombination as derived in Section §3.2 [47]:

$$R_{srh} = \frac{np - n_i^2}{\tau_{srh,p}(n + n') + \tau_{srh,n}(p + p')}. \quad (4.15)$$

Reverse-bias generation current Under reverse bias, it can be assumed that there are no charge carriers in the space charge region, i.e. $p \approx n \approx 0$, so the SRH recombination equation Eq. (4.15) reduces to:

$$R_{srh} = \frac{-n_i^2}{\tau_{srh,p}n' + \tau_{srh,n}p'}. \quad (4.16)$$

The minus sign in Eq. (4.16) indicates a negative recombination rate. That implies that the junction actually thermally generates charge carriers at a rate of $G = -R_{srh}$. The electrons and holes are subject to the electric field in the space charge region and are immediately separated, generating a current; the reverse-bias generation current. If it is assumed that the energy level of the trap is located near the middle of the bandgap, i.e. $E_t \approx E_{Fi}$, it follows that $n' \approx p' \approx n_i$. This is not necessarily true, but it gives sufficient insight to be useful for the analysis later on. The current generated in the space-charge region with width W may be determined from

$$J_{gen} = \int_0^W eGdx. \quad (4.17)$$

Defining an effective lifetime $\tau_{eff} = \frac{\tau_{srh,p} + \tau_{srh,n}}{2}$ and assuming the generation is

constant throughout the space charge region, Eq. (4.17) can be written as:

$$J_{gen} = \frac{e \cdot n_i \cdot W}{2\tau_{eff}},$$

The depletion region width W is proportional to the square root of the applied reverse bias $V_{a,rev}$ so that $J_{gen} \propto \sqrt{(V_{bi} + V_{a,rev})}$. However, it has been frequently reported that the reverse bias generation current has more of a $J_{gen} \propto KV_{a,rev}^m$ behaviour, where $0.5 < m < 0.8$ [48, 49]. The activation energy of the current is mainly determined by the temperature dependence of the intrinsic carrier concentration:

$$n_i = \sqrt{N_c N_v} \exp\left(-\frac{E_g}{2kT}\right). \quad (4.18)$$

In this case, the activation energy for a reverse-bias generation current $E_{act,gen} = 1.5kT + \frac{1}{2}E_g$, where for HIT solar cells E_g is approximately the bandgap of the crystalline silicon, since the depletion region mainly extends in the crystalline wafer.

Forward-bias recombination current Under forward-bias, electrons and holes are injected in the space-charge region and recombination can occur. If injected holes and electrons are lost because of recombination, additional charge carriers are injected in from the p- and n-type regions, respectively, to maintain equilibrium. This current is called a recombination current and was first described by Sah et al. in 1957 [50]. In this case the Shockley-Read-Hall rate of recombination of Eq. (3.24) remains the same:

$$R_{srh} = \frac{np - n_i^2}{\tau_{srh,p}(n + n') + \tau_{srh,n}(p + p')}. \quad (4.19)$$

The electron and hole concentrations are given as

$$n = n_i \exp\left[\frac{E_{Fn} - E_{Fi}}{kT}\right] \quad p = n_i \exp\left[\frac{E_{Fi} - E_{Fp}}{kT}\right], \quad (4.20)$$

with E_{Fn} and E_{Fp} being the quasi-Fermi energy levels of the electrons and holes, respectively. Here, too, it is assumed that the trap energy level is located near the middle of the band gap, implying $n' \approx p' \approx n_i$ and that the electron and hole lifetimes are equal; $\tau_{srh,n} = \tau_{srh,p} = \tau_{srh}$. Eq.(4.19) then becomes:

$$R_{srh} = \frac{n_i}{\tau_{srh}} \frac{\left[\exp\left(\frac{E_{Fn} - E_{Fp}}{kT}\right) - 1\right]}{\exp\left(\frac{E_{Fn} - E_{Fi}}{kT}\right) + \exp\left(\frac{E_{Fi} - E_{Fp}}{kT}\right) + 2} \quad (4.21)$$

It may be noted that the difference between the quasi-Fermi levels is equal to the applied forward bias; $E_{Fn} - E_{Fp} = V_a$. The recombination rate is maximum when the

4. Current Mechanisms

denominator of Eq.(4.21) is lowest. This occurs when $E_{Fn} = E_{Fp} = E_{Fi}$, which is at the metallurgical junction. At the metallurgical junction $E_{Fn} - E_{Fi} = E_{Fi} - E_{Fp} = \frac{eV_a}{2}$. The maximum recombination rate for $V_a \gg \frac{kT}{e}$ can then be written as

$$R_{srh,max} = \frac{n_i}{2\tau_{srh}} \exp\left(\frac{eV_a}{2kT}\right) \quad (4.22)$$

The generation-recombination current density J_{rec} is the integral of the recombination in the space-charge region over the width of the space-charge region:

$$J_{rec} = \int_0^W (eR)\delta x.$$

Since the recombination is not constant throughout the space-charge region, this is a difficult integration. However, by using the maximum recombination rate from Eq.(4.22) and approximating the width for which this is valid $x' < W$, the generation-recombination current density becomes

$$J_{rec} = ex' \frac{n_i}{2\tau_{srh}} \exp\left(\frac{eV_a}{2kT}\right). \quad (4.23)$$

The effective depletion region width x' has the same square root voltage dependence. This was relevant for the derivation of the reverse-bias generation current, but in this case it is negligible compared to the exponential factor in Eq.(4.23). Therefore, the ideality factor for a recombination current is found to be 2. In practice, the observed ideality factor is usually lower. This is because the trap energy levels are actually a range of values instead of being close to the intrinsic Fermi level, as assumed for the derivation of Eq.(4.23). The activation energy is again mostly determined by the temperature dependence of the intrinsic carrier concentration. With again

$$n_i = \sqrt{N_c N_v} \exp\left(-\frac{E_g}{2kT}\right), \quad (4.24)$$

the expected activation energy of the saturation current $E_{act,rec} = 1.5kT + \frac{1}{2}E_g$. Similar to the reverse-bias generation current, the value for the bandgap is mostly determined by the bandgap of the wafer for HIT solar cells.

4.3. Multitunneling capture and emission

Several tunneling mechanisms have been described and suggested for heterojunctions. Riben et al. in 1966 believed that tunneling through the spikes in the conduction band was the dominating mechanism in their Ge-GaAs heterojunction diode

[51]. This is shown schematically as mechanism (A) for an inversely doped heterojunction, where the valence band spikes, in Figure 4.2. Another tunneling mechanism is multistep tunneling, which has originally been presented for excess currents in tunnel diodes [52]. This model assumes tunneling through defects to the other in the interface between the two semiconductors and is shown as mechanism (B) in Figure 4.2. In 1984, Matsuura et al. investigated a-Si/c-Si heterojunctions and found that no tunneling mechanism could satisfactorily model the observed temperature dependence. They proposed a new tunneling model, multitunneling capture and emission (MTCE), where carriers tunnel through defects until they are emitted to the conduction band or recombine with a hole from the valence band, shown as mechanisms (C.1) and (C.2) in Figure 4.2, respectively [53]. Various authors investigating a-Si/c-Si heterojunctions have reported MTCE as the dominating current at low forward biases [48, 54, 55, 56].

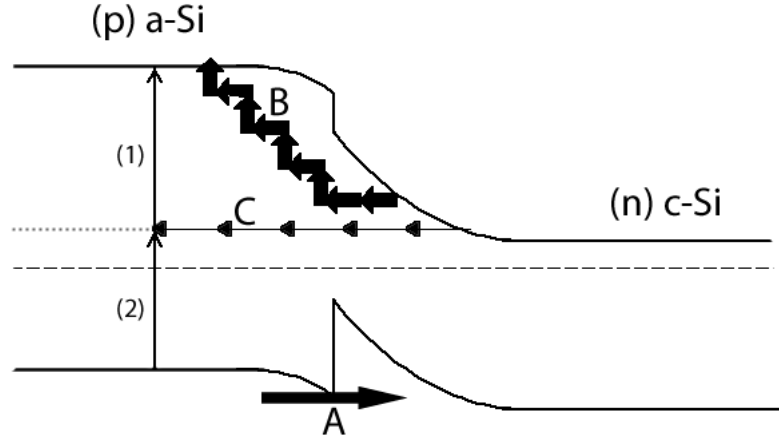


Figure 4.2.: Three tunneling mechanisms are depicted; tunneling through the band spikes (A), multistep tunneling (B) and multitunneling capture and emission (C).

A tunneling current can be described by

$$J_{mtce} = J_0 [\exp(AV_a) - 1], \quad (4.25)$$

where A is temperature independent and generally much lower than for diffusion and recombination. This also implies that a calculated ideality factor $n > 2$. The saturation current is given by:

$$J_0 = B[\sigma_n v_{th} N_c \exp(-\frac{E_c - E_t}{kT}) + \sigma_p v_{th} N_v \exp(-\frac{E_f - E_v}{kT})], \quad (4.26)$$

where B is a constant independent of applied voltage and temperature, $\sigma_{n,p}$ the

4. Current Mechanisms

capture cross-section for electrons and holes, v_{th} the thermal velocity and $N_{c,v}$ the effective density of states at the conduction and valence band. The activation energy of the saturation current depends on whichever of the exponential arguments is smaller, $E_c - E_t$ or $E_f - E_v$.

4.4. Space-charge limited

Space-charge limited currents (SCLCs) have been investigated from as early as 1940 by Mott and Gurney and their theoretical framework was extended mostly by Rose and Lampert [57, 58, 59]. SCLC has been observed to occur in amorphous/crystalline silicon heterojunction diodes [49, 60, 54] and solar cells [48].

Up to this point, it was assumed that the semiconductors were in low injection, i.e. $\Delta n_n \ll n_{n0}$ in the n-type and $\Delta p_p \ll p_p$ in the p-type material. However, it is possible, at sufficient applied bias and a thin enough layer, that the entire region is swamped with excess carriers and the entire semiconductor is in high injection. In this case, the electric field is not zero in the quasi-neutral region and the drift current becomes much larger than the diffusion current so that the total current can be approximated by the drift current alone [61]:

$$J_{scl} = e\mu_n n(x) \frac{\delta E(x)}{\delta x}, \quad (4.27)$$

where $E(x)$ is the electric field in the material. From this the standard space-charge-limited current equation can be derived:

$$J_{scl} = \varepsilon_s \frac{\mu_n V_a^2}{2L^3}, \quad (4.28)$$

with ε_s as the dielectric constant of silicon, μ_n the electron mobility and L the length of the space-charge region. Eq. (4.28) is derived for a situation without traps, which is not very realistic. In general, a space-charge limited current can be described by the generic equation

$$J_{scl} = K \cdot V^m, \quad (4.29)$$

where $m > 2$ [49].

4.5. Resistances

Parallel resistance The effect of a parallel resistance under illuminated conditions has already been considered in Section §1.5. However, the parallel resistance has to

be very low for the current through it to be noticeable compared to the photogenerated current; in the order of $100\ \Omega$, as explained in Section §1.5.

Usually, this only occurs in case of an error in the fabrication of the cell. Such severe shunts can be induced by the production process, such as edge shunts and cracks, holes or scratches in the wafer, so most can be avoided [62]. Therefore, state-of-the-art HIT solar cells typically exhibit a parallel resistance is in the order of several $M\Omega$ and consequently, the shunt current is generally much lower than the other current paths.

Series resistance Unlike a parallel resistance, series resistance can not be ignored. At low forward bias, the current through the device is very small and the voltage drop across the series resistance is negligible. Due to the exponential current-voltage relation of the aforementioned dominating current mechanisms, however, the voltage drop can become quite pronounced. This imposes an upper limit on the exponential current behaviour, after which a linear, ohmic behaviour can be observed in the dark current-voltage curve.

Basically, the voltage drop across the series resistance is the part of the applied bias that is not across the pn-junction, i.e. across the conductive oxide, metal contacts and the bulk. Since the conductive oxide and the metal are both much thinner and more conductive than the bulk, the majority of the series resistance is due to bulk resistivity. As the silicon bulk is a semiconductor, the resistivity decreases exponentially with temperature, as will be explained in Section §6.1. This gives rise to a temperature dependence in the current-voltage curve which is similar, but not necessarily the same, as that of the current mechanisms that can be described by the junction rectification model.

Part II.

Experimental

5. Deposition methods

The deposition methods that have been employed in fabricating a HIT solar cell can be classified in two groups: chemical vapour deposition (CVD) and physical vapour deposition (PVD). In a chemical vapour deposition, a chemical reaction such as the dissociation of a molecule occurs in the reaction chamber [63]. Frequently used CVD methods are low pressure CVD (LPCVD), atmospheric pressure CVD, also known as epitaxy, and plasma-enhanced CVD (PECVD). This last method is the process that is employed for depositing the amorphous layers in a HIT solar cell as is therefore described in Section §5.1.

In case of a physical vapour deposition the material that is deposited is not chemically altered for deposition. Often, the material is present in the deposition chamber in the form of a target. Here also different implementations exist. The two employed methods in the fabrication of HIT solar cells are sputtering and electron-beam evaporation, described in Secs. 5.2 and 5.3.

5.1. Radio-Frequency Plasma-Enhanced Chemical Vapour Deposition

A RF PECVD deposition has several significant useful properties for deposition of amorphous silicon. Due to the fact that the deposition can be done at relatively low temperatures (100-400°C), the material quality is excellent and the choice of substrates is substantial, including glass, steel, aluminium foil and plastics. The low deposition temperature is also important for a HIT solar cell, it doesn't cause wafer bowing that might introduce stress between the layers in case of an asymmetric device. For the industry additional advantages of PECVD are the low cost, the possibility to deposit large areas and the prospect of mass-producibility. PECVD is already a widely employed deposition technique in the thin film silicon solar cell industry.

The PECVD deposition of amorphous silicon makes use of a silane gas (SiH_4) as the source of silicon, which is decomposed by an RF (13.56 MHz) plasma. From the plasma, electrons emerge which are accelerated by an electric field. These electrons collide with the silane, forming radicals that attach to the surface of the growing film. Doping is accomplished by mixing the silane with diborane (B_2H_6) for p-type

5. Deposition methods

or phosphane (PH_3) for n-type layers. Sometimes the energy that is transferred from the accelerated electrons to the silane is radiated as visible light, which is why PECVD is also known as the glow discharge method.

An illustration of a PECVD deposition system is shown in Figure 5.1. The substrate is placed in the reaction chamber, where the deposition takes place. The reaction chamber is pumped vacuum to reduce the number of unwanted contaminants. The heater then increases the substrate temperature to typically $200\text{--}250^\circ\text{C}$ and an RF signal is capacitively coupled to the electrodes by an RF power source, generating an alternating electric field in the chamber. Finally, a gas system regulates the flow of the deposition gases which is necessary to control the deposition rate and dopant levels.

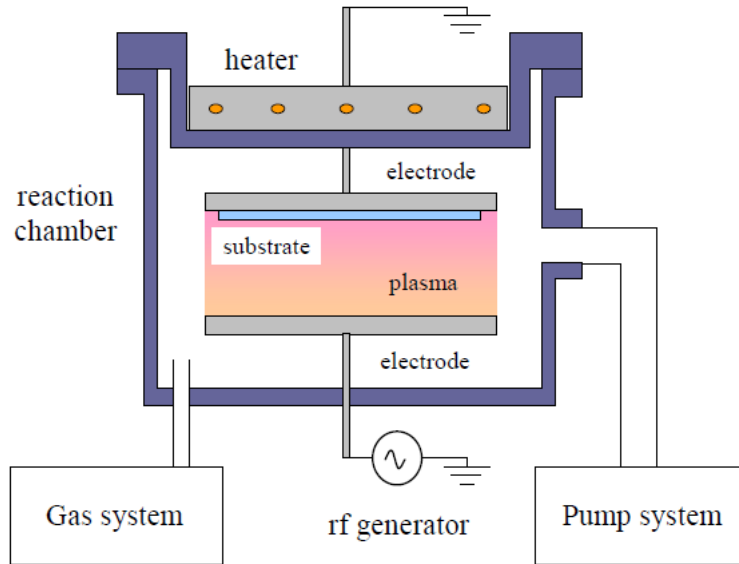


Figure 5.1.: An illustration of a plasma-enhance chemical vapour deposition system. Image taken from ref [1].

5.2. Radio-Frequency Sputtering

The transparent conductive oxide (TCO) is deposited using an RF sputtering method. Sputtering is a physical vapour deposition method, so a target with the TCO, in this case Indium Tin Oxide ($\text{In}_2\text{O}_3\text{: Sn}$, or ITO), is present in the deposition chamber. The substrate is positioned in the chamber facing the target and a gas, usually argon (Ar) is injected in the chamber. The sputtering process starts by applying

5.3. Thermal and electron-beam Evaporation

a negative bias to the target, which causes a plasma to ignite. Positively charged argon ions, generated in the plasma region, are accelerated to the negatively biased target. The resultant collision created a momentum transfer which propels atomic size particles from the target to the substrate, forming a layer of the material [64]. An illustration of a sputtering system is shown in Figure 5.2.

There are two operating modes for sputtering. A DC sputtering is done as described above and will only work for a conductive target. In case of a non-conductive target, because the positive charge from the bombardment ions will cause a charge buildup and stop the sputtering process. During an RF sputtering an RF oscillating signal is applied on the electrodes. Instead of direct bombardment of the gas plasma atoms, the energy is used to remove electrons from the outer shell of the gas atoms, which then collide with the target. An advantage of this system is that the pressure that is maintained in the chamber can be much lower than for a DC sputtering system and that there is no charge buildup on the target.

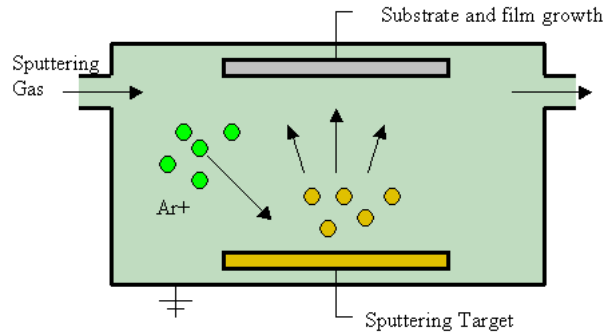


Figure 5.2.: An illustration of a sputtering system.

5.3. Thermal and electron-beam Evaporation

For evaporation the target is heated up, causing it to melt and evaporate onto the substrate. With thermal evaporation the target is settled in a boat, which is heated up by conducting a current through it. In case of electron-beam evaporation, the target is bombarded by electrons. The transferred energy causes the atoms at the surface of the target heat up and evaporate. The evaporated particles deposit on any solid surface, amongst which the substrate. The electrons are generated by an electron gun, which generally consists of a charged tungsten filament.

6. Characterization Methods

6.1. Layer characterization

Solar cell performance is determined by the quality of the layers it is made up of. Therefore, these layers are examined individually to outline where the most progress can be made. Similarly, to investigate and optimize a certain deposition parameter efficiently, the deposited layer has to be analyzed to determine which property is affected in which way. This is both beneficial to streamlining the optimization process and yields an advance in scientific insight.

Determining the layer properties is also crucial for effective modeling of a solar cell. Semiconductor simulators such as ASA[65] and AFORS-HET [66, 67], developed by Delft University of Technology and Helmholtz-Zentrum Berlin, respectively, have as input the structure of the device, which is a list of the layers and their properties and use that to simulate the behavior of the complete device. When the layer properties are well-known and the solar cell behavior can be predicted correctly, film optimizations can be done using software, which can significantly speed up the development as it is no longer necessary to manufacture complete solar cells.

6.1.1. Activation energy

During the deposition of the p-type amorphous layer, diborane is inserted as the dopant gas. Since the doping of amorphous silicon is not as effective as that of crystalline silicon, there is no linear relation between the dopant gas flow and the concentration of active impurity atoms. To calibrate the p-layer deposition, the doping level needs to be measured. Also, due to drift in the deposition facilities, it is necessary to re-evaluate the doping efficiency at a regular interval. This can be done with an activation energy measurement, where the conductivity of a deposited layer is measured at different temperatures.

The conductivity of a semiconductor is given as

$$\sigma(T) = q(\mu_p p(T) + \mu_n n(T)). \quad (6.1)$$

The temperature dependencies of the carrier mobilities are assumed to be negligible. In a doped semiconductor, the concentration of one of the charge carriers is much larger than the other. For instance in a p-doped layer, $p \gg n$, so Eq.(6.1) reduces

6. Characterization Methods

to

$$\sigma(T) = q\mu_p p(T). \quad (6.2)$$

Under low-level injection and sufficient doping level, the hole concentration can be assumed to be always at the thermal equilibrium level. The hole concentration at thermal equilibrium is a function of the difference between the Fermi energy level and the valence band edge:

$$p_0 = N_v \exp\left[\frac{-(E_f - E_v)}{kT}\right] \quad (6.3)$$

The activation energy of a doped p-layer is usually defined as:

$$E_{act} = E_f - E_v. \quad (6.4)$$

Therefore, the temperature dependence of the conductivity is directly related to difference between the Fermi energy level and the valence band. Since the Fermi energy is a function of the dopant concentration, this measurement yields doping efficiency of the deposited layer.

For an activation energy measurement, a layer of doped material is deposited on an insulator, typically glass. Two contacts, strips of metal with fixed dimensions and distance, are then evaporated on top of the deposited layer. Then the electrical conductance of the layer is measured by applying a voltage on the contact strips and measuring the resultant steady-state current. This is done for several, well-controlled temperatures. The activation energy of the layer can then be extracted by taking a linear fit in the $\ln[\sigma(T)]$ vs. $\frac{1}{kT}$ plot, also known as an Arrhenius plot, as shown in Figure 6.1.

6.1.2. Minority charge carrier lifetime

As discussed in Chapter 3, an important characteristic for a solar cell is the effective minority charge carrier lifetime. This measurement is usually performed on the a-Si/c-Si stack directly after the deposition of the amorphous layer and is a indication of the passivation of the interface by the a-Si. An incorrectly passivated interface contains a high concentration of defects. As defects act as efficient recombination centers, this has a significant negative impact on the open circuit voltage V_{oc} .

The techniques that are used to measure the minority carrier lifetime are usually based on either quasi-steady state (QSS) or quasi-transient (QT) conductance, depending on the expected lifetime [68]. Both of them take advantage of the change in conductivity of semiconductor material under illumination due to an increase in excess charge carriers. The ambipolar transport equation for excess charge carriers

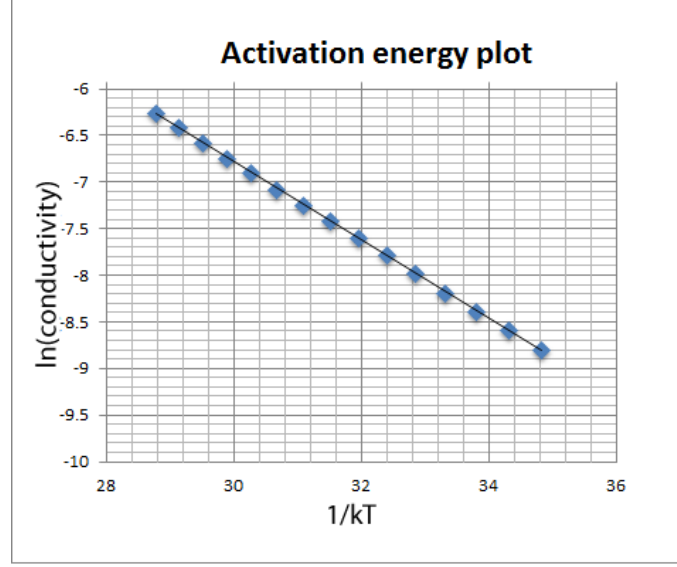


Figure 6.1.: An Arrhenius plot showing the $\ln[\sigma(T)]$ vs. $\frac{1}{kT}$. The activation energy is the slope of the linear fit through the data points.

is

$$\frac{\delta \Delta n}{\delta t} = G - R + \frac{\nabla J}{q}, \quad (6.5)$$

where Δn is the excess carrier concentration, G the photogeneration rate of charge carriers, R the recombination of charge carriers and J the electron current density. Assuming spatially uniform photogeneration and no electric field, the last term on the right-hand side of equation Eq. (6.5) vanishes. The relation between recombination rate R and lifetime τ_{eff} is classically given by [47]:

$$R \equiv \frac{\Delta n}{\tau_{eff}} \quad (6.6)$$

Combining Eq.(6.5) and Eq.(6.6) and rearranging terms yields [69]

$$\tau_{eff}(\Delta n) = \frac{\Delta n(t)}{G(t) - \frac{\delta \Delta n(t)}{\delta t}}. \quad (6.7)$$

During the measurement the sample is illuminated using a flash lamp. Depending on the expected minority carrier lifetime, one of two operating modes of the light source can be chosen. A QSS measurement is effective for measuring short lifetimes, while a QT measurement is most suitable for measuring long lifetimes. The difference between these two modes of measurement is the duration of the illumination,

6. Characterization Methods

indicated by the decay time constant of the flash lamp τ_{flash} . For QSS measurements, a 'long' decay constant, i.e. $\tau_{flash} \gg \tau_{eff}$, is selected. In this case the excess carrier concentration is in steady-state, i.e. $\frac{\delta \Delta n}{\delta t} \approx 0$. so equation Eq. (6.7) reduces to

$$\tau_{eff}(\Delta n) = \frac{\Delta n}{G}. \quad (6.8)$$

A calibrated reference diode measures the flash lamp intensity. With that data, the photogeneration rate G can be easily estimated using computer programs or look-up tables, so measuring the excess carrier concentration directly yields the effective minority carrier lifetime. This method can be used to measure lifetimes between $10ns$ to $60\mu s$ [70].

For quasi-transient measurements, a 'short' time decay constant of the flash lamp, i.e. $\tau_{flash} \ll \tau_{eff}$, is selected. In this case equation Eq. (6.7) reduces to

$$\tau_{eff.trans}(\Delta n) = -\frac{\Delta n(t)}{\frac{\delta \Delta n(t)}{\delta t}}. \quad (6.9)$$

In this case the flash lamp photo-generates an initial excess carrier concentration which then start to recombine. The decay constant of the $\Delta n(t)$ curve, as shown in Figure 6.2, yields the lifetime.

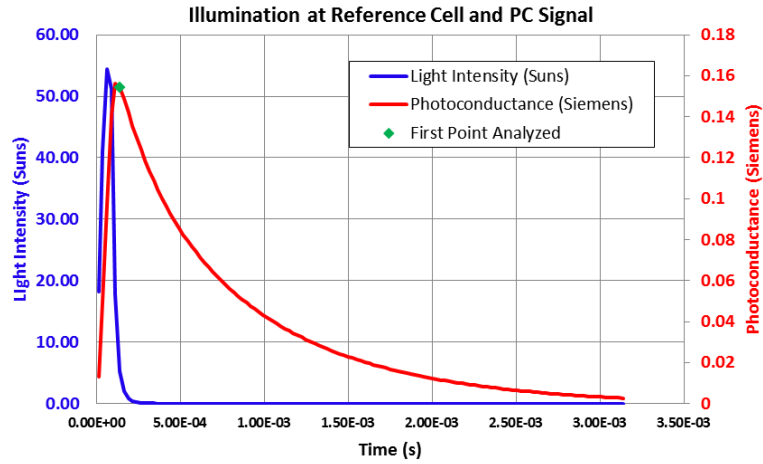


Figure 6.2.: The result of a quasi-transient lifetime measurement of sample A6114. The excess carrier concentration can be directly deduced from the photoconductance.

For both the transient and the quasi-steady state measurements the minority charge carrier concentration has to be determined. This can be done by capacitively or inductively coupling the conductivity of the sample to a bridge circuit. The excess conductivity is a function of the excess carrier concentration as

$$\sigma_L = q(\Delta n_{av}\mu_n + \Delta p_{av}\mu_p), \quad (6.10)$$

Since the excess electrons and holes are generated in pairs by the light, equation Eq. (6.10) can be simplified to

$$\sigma_L = q\Delta n_{av}(\mu_n + \mu_p). \quad (6.11)$$

Here, too, the electron and hole mobilities for silicon and their dependencies on doping and injection level and are well-known and can be found in literature [68].

6.2. Device characterization

The purpose of device characterization is to determine the performance of a finished device. Most interesting for practical applications are the solar parameters under standard illumination conditions; the open circuit voltage V_{oc} , the short circuit current J_{sc} and the fill factor FF . However, to establish a theoretical framework for these devices, other parameters, such as dominant current mechanisms and defect distributions, are also required [71, 72]. An advance in the understanding of the device mechanics is necessary to satisfactorily simulate this type of solar cell. There is an abundance of possible device measurements, so this section is limited to the measurements performed that are of importance for this research.

6.2.1. Illuminated current-voltage relation

The standard measurement for determining the solar parameters is a current-voltage (JV) measurement while the solar cell is illuminated by a lamp. This light source has a spectral distribution and intensity is similar to the operating conditions to give an impression of real-world performance. Therefore all illuminated JV measurements are done with a light source that emits the AM1.5 standard. The AM number of light refers to the number of times the light has passed through the earth's atmosphere. The AM1.5 spectrum is chosen because it reflects the spectrum of sunlight that reaches the earth in the temperate latitudes, where the majority of the world's population is settled.

The equivalent circuit for a solar cell under illumination from Section §1.5 is repeated in Figure 6.3. An external voltage source is connected to the contacts. The applied voltage is varied typically from $-0.1 < V < 0.9$ and at every setting the current is measured.

An example of an illuminated IV-curve measurement is shown in Figure 6.4. The short-circuit current density is the maximum current density that the solar cell can provide, which occurs at zero bias. The maximum voltage of the solar cell is

6. Characterization Methods

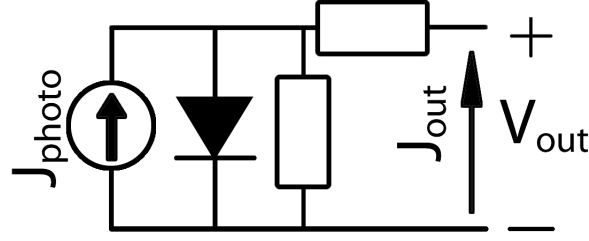


Figure 6.3.: The equivalent circuit of an illuminated solar cell.

the open-circuit voltage, when no current flows through the contacts. At a certain voltage the $V \times J$ -product peaks, which is the optimal operating voltage. This is known as the maximum power point and is indicated in Figure 6.4 as V_{mpp} , with a corresponding current J_{mpp} . The fill factor is defined as $FF = \frac{V_{mpp}J_{mpp}}{V_{oc}J_{sc}}$. The conversion efficiency can then be calculated as

$$\eta = V_{oc}J_{sc}FF \times 100\%, \quad (6.12)$$

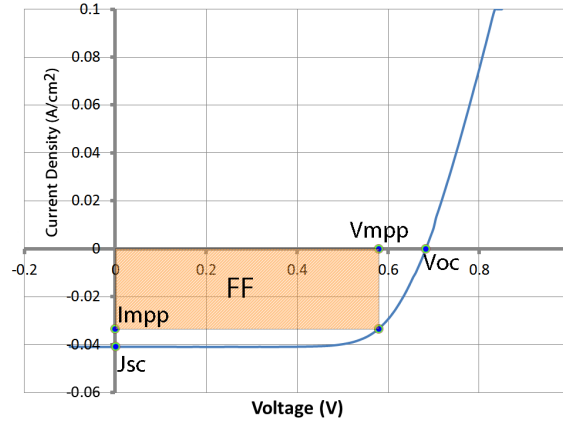


Figure 6.4.: A typical IV-curve under illuminated conditions. Indicated in the graph are the solar parameters.

6.2.2. External quantum efficiency

Not all incident photons have a contribution to the photogenerated current. Photons with insufficient energy, i.e. an energy lower than the band gap of the absorber layer, and reflected photons do not generate electron-hole pairs. Generated charge-carriers are subject to recombination before reaching the contacts. These losses are reflected

in the external quantum efficiency (EQE), which is defined as the number of charge carriers collected per incident photon at each wavelength λ [1].

The result of a typical quantum efficiency measurement on a HIT cell is shown in figure Figure 6.5.

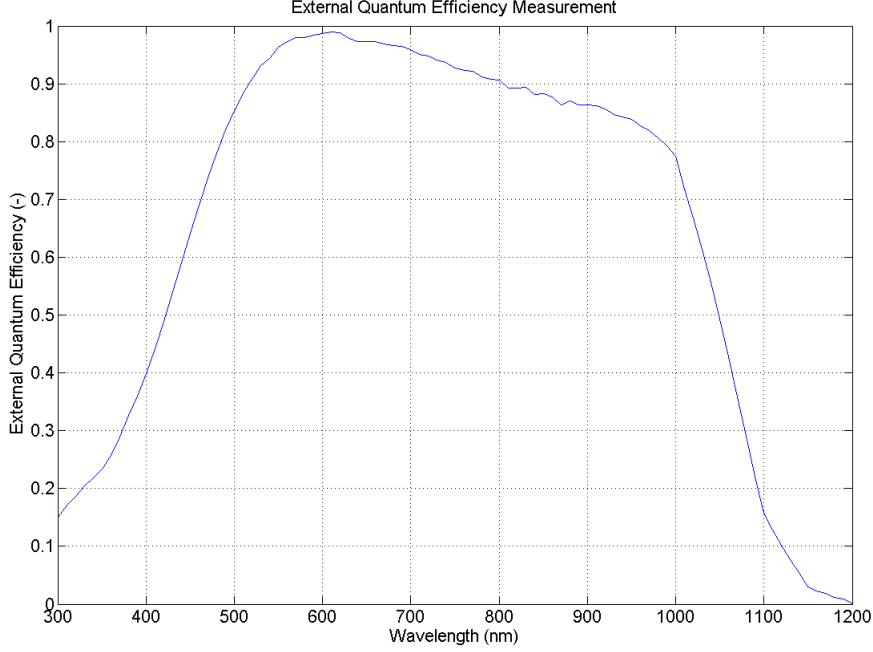


Figure 6.5.: The result of a typical external quantum efficiency measurement on a HIT cell

A quantum efficiency measurement has two purposes. For device characterization it is interesting because it shows where many of the losses occur. For instance, a low response in the short wavelength region indicates photon absorption in the TCO or the emitter layer, where generated electron-hole pairs are restricted in contributing to the current. The quantum efficiency for longer wavelengths is usually limited by reflection. Therefore, changes in the thickness of a layer or in material properties such as the band gap are directly reflected in the external quantum efficiency. This makes it an ideal tool for optimizing the optical properties of the layers to maximize the current of the solar cell.

Another function of a quantum efficiency measurement is to calibrate the short-circuit current. Even though the lamp that is used for the illuminated IV measurement has a spectrum as close as possible to the AM1.5 standard, slight deviations are inevitable. Since the J_{sc} has a linear dependence on the light intensity, this deviation significantly reduces the reliability of this parameter. The V_{oc} has a logarithmic

6. Characterization Methods

dependence on the light intensity, so it is not affected significantly.

A more reliable J_{sc} can be obtained from the external quantum efficiency by multiplying it with the AM1.5 spectrum and integrating over the wavelength:

$$J_{sc} = \int [EQE(\lambda) \times \Phi(\lambda)] \delta\lambda, \quad (6.13)$$

where $\Phi(\lambda)$ is the light spectrum as defined by the AM1.5 standard.

The measurement is performed by illuminating the solar cell with light of a certain wavelength. A particular wavelength is selected from a normal light source by a monochromator. The intensity of the light at every wavelength has been measured using a reference diode. The resultant current in the short-circuited solar cell is measured using a setup that generally includes a lock-in amplifier to improve the signal-to-noise ratio. Combining the current and the number of incoming photons, which is known from the reference diode, yields the external quantum efficiency.

$$EQE(\lambda) = \frac{J_{measured}(\lambda)}{J_{refdiode}(\lambda) \cdot \frac{1}{H(\lambda)}}, \quad (6.14)$$

where $H(\lambda)$ is the known response of the reference diode so that $J_{refdiode}(\lambda) \cdot \frac{1}{H(\lambda)}$ yields the measured incoming photons per second per wavelength.

6.2.3. Dark current-voltage relation and fitting procedure

The method to measure the dark current-voltage relation (JV) is very similar to that of an illuminated JV measurement, except under circumstances dark enough so that the photogenerated current is nihil compared to any other current that might exist in the material. During an illuminated IV measurement the photocurrent can be several orders of magnitude larger than the dark current, especially in the low forward bias region (LFB). For instance, as mentioned in Section §4.3, a tunneling current can dominate the dark current at low forward biases, but is generally very small and is negligible in comparison to a photocurrent. Even though small dark currents will not have an effect on the solar cell output, information about the device can be extracted from it.

An example of a DIV measurement at a single temperature is shown in Figure 6.6(a). To clearly discern the small values for the reverse and low forward bias, the current is plotted on a logarithmic scale. On a logarithmic scale, a straight line indicates an exponential voltage dependence, which is true for several current mechanisms, as explained in Chapter 4. The voltage is swept from -1.2 to 0.9V. From direct inspection of the curve, several current regions can be distinguished, indicated 1-4. In every region, a different current mechanism dominates. These regions are

recognized by various authors having done similar measurements or predicted by theoretical evaluation [73, 74]. An overview of the reported dominating currents is given in Table 6.1:

Region	Current mechanism
1	Reverse-bias Generation, Parallel resistance
2	MTCE, Generation-Recombination, Parallel resistance
3	Generation-Recombination, Diffusion
4	Space-charge limited, Series resistance

Table 6.1.: A listing of the reported current mechanisms for each of the regions of Figure 6.6(a).

As introduced in Chapter 4, current mechanisms can be distinguished by their temperature behaviour. The temperature dependences of the logarithmic slope A and saturation current J_0 are important parameters in determining the type of current. Therefore, the dark current-voltage measurements are carried out in an environment where the temperature is actively controlled. To acquire these parameters the temperature is varied with a certain step size and a measurement is performed at every single temperature. The result of a temperature-varied dark JV measurement is shown in Figure 6.6(b).

The next step is to extract the important parameters; the ideality factor or slope of the curve and the activation energy of the saturation current, from the measurement. In certain cases it is possible to derive these parameters directly from the graph, for instance with the thermal ideality factor method described first by Pieters for μc -Si:H p-i-n solar cells and recently adopted by Kind et al for a-Si:H p-i-n solar cells [75, 76]. The reason that this can not be done for the samples discussed in this thesis can be found in Figure 6.6(b). There it can be observed that the boundaries between regions, with the exception of the boundary between regions 1-2, shift to lower voltages as temperature is increased. The consequence of this shift is that for a certain voltage setting, not all the measurements are in the same region or are so close to a neighbouring region that the effect of the other current mechanism cannot be neglected. This has a pronounced effect on determining the activation energy directly. The graph with the directly derived activation energy as shown in Figure 6.7(a) has been calculated by:

$$E_{act}(V, T_n) = \frac{\ln[J(V, T_n)] - \ln[J(V, T_{n-1})]}{\frac{1}{kT_n} - \frac{1}{kT_{n-1}}} + \frac{\ln[J(V, T_{n+1})] - \ln[J(V, T_n)]}{\frac{1}{kT_{n+1}} - \frac{1}{kT_n}} \quad (6.15)$$

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Eq. (6.15) is a discrete approximation of the general activation energy derivation equation for a current:

$$E_{act}(V) = \frac{\delta \ln[J(V, T)]}{\delta \frac{1}{kT}}, \quad (6.16)$$

If at a certain voltage range the same current dominates at every temperature, the curves in Figure 6.7 should overlap. Obviously that is not the case and therefore, the thermal ideality factor method can not be used here.

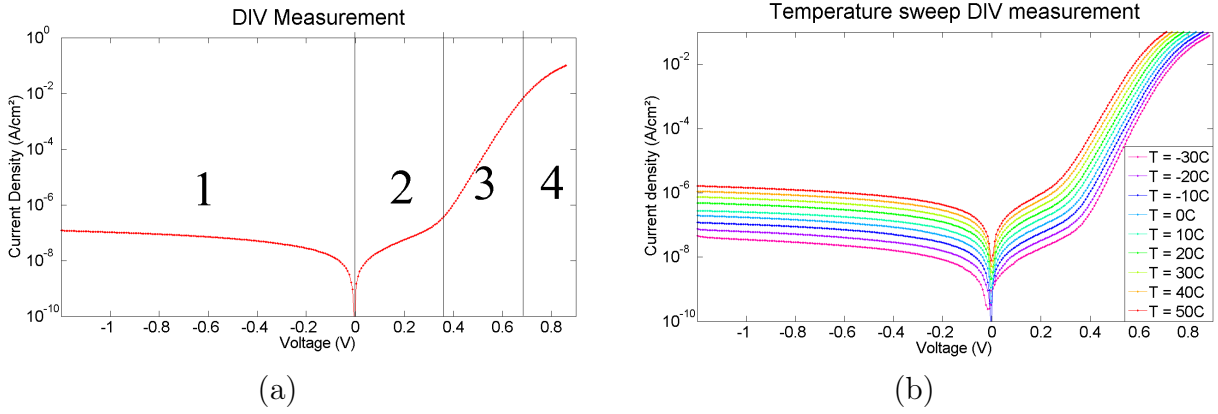


Figure 6.6.: The current-voltage relation under dark conditions. Indicated in (a) are regions with a different dominating current mechanism. A full temperature-varied measurement is shown in (b).

Even though the activation energy cannot be deduced from the curves directly, it is possible to find the voltage dependences of the exponential regions 2 and 3 by calculating the slope when the curve is straight in the logarithmic plot. Extrapolating the slope can yield the saturation currents from which the activation energy can be calculated. However, another consequence of the shifting region boundaries is the decreased width of the exponential regions, causing the voltage range where the curve is straight, i.e. completely dominated by one current mechanism, to decrease for high temperatures. Especially for region 2 the uncertainty of the acquired values is quite high. Published studies that employ this method do indeed indicate this [77].

An alternative to direct observation is to fit the measurement. The goal of a fitting is to map a certain fitting function onto the measurement, with minimal difference. A fitting function has a set of variables that are free to be optimized to accomplish this. If the chosen function is suitable for the measurement, the resultant set of optimal variables of the fitting contains a lot of information.

The standard procedure for determining the goodness of a fitting is the sum of

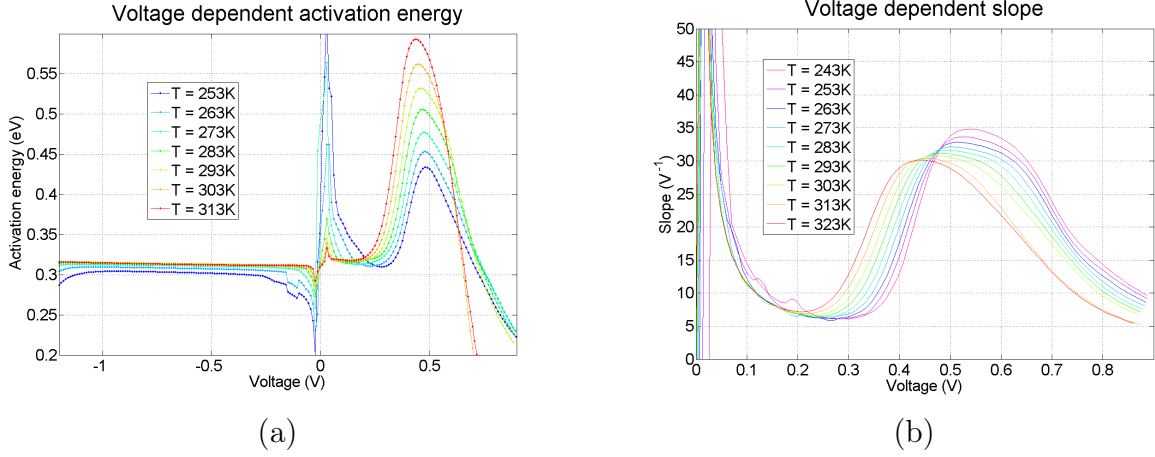


Figure 6.7.: The (a) voltage dependent activation energy as calculated by Eq. 6.15 and the (b) voltage dependent slope of the logarithmic plot

squared errors:

$$f_{cost} = \sum_{V=a}^b [J_{meas}(V) - J_{fit}(V)]^2 \quad (6.17)$$

in the voltage range $a < V < b$ that is being fitted. Ideally, by using Eq.(6.17) as the cost function that is minimized by the fitting optimization, the fitted curve should be a narrow fit. However, this particular cost function is not suitable for fitting the DIV measurement of Figure 6.6(b). The measurement shows a large range of values; the difference between low and high forward bias being seven orders of magnitude. A relatively small error in the high current region is therefore a more significant contribution to the cost function than a comparable relative error in the low current region. Consequently, this optimization algorithm will fit the high current region more accurately than the low current region, while actually both are equally as important for the analysis. To overcome this, Eq. (6.17) is adapted to be the sum of squared relative errors:

$$f_{cost} = \sum_{V=a}^b \left[\frac{J_{meas}(V) - J_{fit}(V)}{J_{meas}(V)} \right]^2 \quad (6.18)$$

As mentioned before, the choice of the fitting function is important for the validity of the fitting. Any function with sufficient free variables can be fit onto any measurement, without yielding any information. Therefore, the current mechanisms in Table 6.1 will be leading. Since the theory of every listed current mechanism is known and described in Chapter 4, the fitting functions can be derived from there.

Since the slope of the reverse bias current, region 1, is not horizontal, as predicted

6. Characterization Methods

by the diode model, either a generation current or a current through a parallel ohmic path is present. Both current mechanisms have a $J \propto KV^m$ behaviour, where $m = 1$ in case of a parallel resistive path and an exponent $m = 0.5 - 0.8$ for a generation current, as claimed by previous studies. The fitting of the forward bias has to be done in two steps. The first is to fit the two exponential regions 2 and 3 simultaneously with a double diode equation with an added parallel ohmic path:

$$J_{fit} = J_{0,1}[\exp(A_1 V_a) - 1] + J_{0,2}[\exp(A_2 V_a) - 1] + \frac{V_a}{R_p} \quad (6.19)$$

The next step is the addition of the series resistance to fit region 4. This brings about some difficulties, as the fitting equation becomes implicit and can no longer be calculated directly:

$$J_{fit} = J_{0,2}[\exp(A_2(V_a - R_s J_{fit})) - 1]$$

The parallel resistance is assumed to be sufficiently large and the current through the first diode negligible compared to the second diode in the region where the series resistance needs to be considered. An implicit equation can still be calculated, but it is considerable slower than a direct calculation, which increases the fitting time considerably. It is even more difficult to include a space-charge limited current, because the effect cannot be calculated as easily as the voltage drop across a series resistance. Therefore, only a series resistance is fitted. If the fitting cannot satisfactorily approximate the measurement, it is assumed that the current in region 4 is space-charge limited.

7. Experimental Details

The HIT solar cells that were fabricated for this study all have the structure of our currently standard cell as shown in Figure 7.1. However, for both optimization and modeling purposes, the thickness and activation energy of the (p)a-Si:H emitter layer was varied. For optimization the goal is to achieve the best solar device, while for modeling it is necessary to know the influence of the p-layer parameters on the device characteristics. Since the activation energy of the p-layer can not be measured accurately in the device, instead the flow of the dopant gas, diborane (B_2H_6), is used as a parameter. Activation energy measurements on a p-layer deposited on glass show that the activation energy decreases with increased diborane flow. The different p-layer thicknesses are 5, 9, 13 and 17 nm. Every thickness was deposited using 1, 2, 3 and 4 sccm dopant gas flow, so in total solar cells with sixteen combinations of deposition parameters have been made.

This chapter reports the details of the experimental techniques that have been employed for this study. Section §7.1 lists the steps of fabrication of the devices and Section §7.2 details the methods of characterization.

7.1. Deposition

In this section the fabrication steps for a standard HIT cell as shown in Figure 7.1 are presented. A high quality floating zone (FZ) wafer is used. The resistivity of the 300 μm thick n-type wafer is 2-5 Ωcm . To remove any contaminants, the wafer is cleaned chemically, after which dipping in an HF solution removes the native oxide and passivates the surface with hydrogen.

The prepared wafer is then transferred to a PECVD multi-chamber deposition system to deposit the amorphous layers. The substrate is preheated to 180°C for about 50 minutes after which the 5 nm thick intrinsic, 9 nm thick p-type and 9 nm thick n-type layers are deposited in separate chambers by RF-PECVD deposition. As described in Section §5.1, the process gases used are SiH_4 for the intrinsic layer, mixed with either B_2H_6 or PH_3 for the doped layers. The dopant level of the doped layers can be adjusted by changing the flow of the dopant gas. The doping efficiency is occasionally calibrated by an activation energy measurement employing a Temptronic heating stage and a Simac high-temperature hot-chuck. To verify that the intrinsic amorphous layer has passivated the interface sufficiently, a lifetime

7. Experimental Details

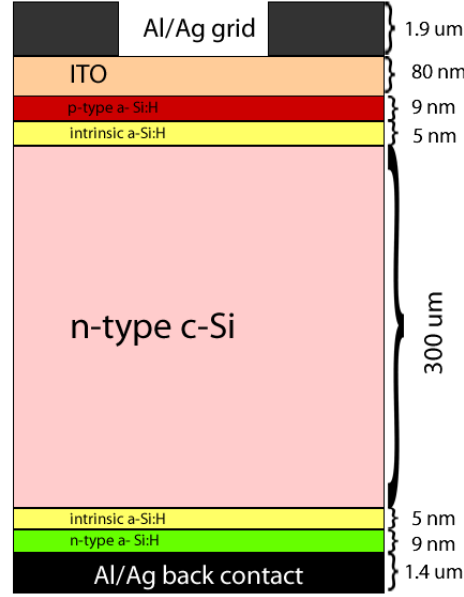


Figure 7.1.: A schematic of a HIT solar cell

measurement is done using a Sinton WCT-120 photoconductance lifetime tester.

Subsequently, an 80nm-thick layer of ITO is sputtered on the front side of the cell, which acts as a current collector and antireflective coating. During the ITO deposition, the substrate is masked to create $1 \times 1 \text{ cm}^2$ and $0.4 \times 0.4 \text{ cm}^2$ areas. These solar cell dots are separated such that they are not influenced by each other during measurement. This allows individual testing on several places of the wafer. Using thermal e-beam evaporation in a Provac PRO500S PVD facility the front and back are covered with silver, chromium and aluminium, which has been found to make the best contact. The grid on the front of the device is obtained by masking the sample during aluminium deposition. The finished device is then annealed at 170°C for one hour to improve the passivation and reduce the contact resistance.

7.2. Characterization

The solar cell performance is measured in the illuminated IV setup, which consists of an Oriel AM1.5 illumination lamp and an HP4145B semiconductor parameter analyzer. To avoid current generation by other dots, the wafer is masked to only illuminate the dot under inspection. To avoid heating of the sample due to the

lamp, the sample is only subjected to the light during the actual measuring.

For certain small $0.4 \times 0.4 \text{ cm}^2$ dots the aluminium is deposited around the sample, so that it does not interfere with the dot of monochromatic light of the quantum efficiency setup. The light is generated using an Oriel Apex monochromator illuminator and an Oriel 1/8m cornerstone monochromator. The EQE is then measured using a EG&G 7260 DSP lock-in amplifier and a chopper which operates at 123 Hz.

The dark IV measurements are always performed on $1 \times 1 \text{ cm}^2$ dots on the same location on the wafer to eliminate the offset of layer parameters due to spacial variation of the deposition. The measurement chamber is a Cascade Microchamber enclosure, where the temperature is controlled by a Temptronic TPO3200 thermochuck push-pull system. The temperature is varied from -30 to 50°C . Ideally, the inside of the measurement chamber is completely dark, but for consistency the entire system is covered completely with a black canvas. The measurement is performed with a three-point probe method, which involves a grounded chuck and two measurement probes. The first probe applies a voltage on the device, while other probe senses the actual applied voltage on the solar cell to account for the potential drop across contact resistance between the first probe and the aluminium of the sample. The current was measured as the current through the chuck. The probes are connected to an Agilent 4156C precision semiconductor parameter analyzer with an HP41501B SMU & pulse generator expander. Finally the measured curves were fitted using MATLAB with a fitting function that is applicable to the current region, as explained in the next chapter.

Part III.

Results and Discussion

8. Experimental Results

In this chapter the experimental results are analyzed. In Section §8.1, the dominant electronic transport mechanisms in the HIT solar cells for each current region are derived from the dark current-voltage measurements. Section §8.2 explores how the process parameters influence the device characteristics.

8.1. Electronic Transport

As can be observed in Figure 6.6(a), most dark-current voltage measurements have four distinct regions, from here on called the reverse bias (RB) region, low forward bias (LFB) region, high forward bias (HFB) region and the current limited (CL) region. In this section, for every region of the fitting results are examined to determine the dominating current and give, if possible, a physical interpretation. An example of a fitted full-temperature (-30 to 50°C) variation measurement is shown in Figure 8.1.

To put the results in the correct context, occasional references to articles and publications of authors that have done research on HIT solar cells with a similar approach are used to interpret the results. Especially Schulze has published an extensive study on fittings of dark current-voltage measurements on HIT solar cells that are very similar to ours in which several interesting analyses have been employed [78].

8.1.1. Low forward bias region

There is some disagreement amongst previous studies concerning the dominant current mechanism in the LFB region. The greater part of the studies that have investigated heterojunction structures with thin amorphous layers, including the most recent report on dark current-voltage measurements on state-of-the art HIT solar cells from Sanyo, claim tunneling to be dominant [48, 54, 56, 60, 77, 78], as reflected in a gradual, temperature-independent slope and a relatively low activation energy (~ 0.4 eV). However, some studies report a recombination current with an ideality factor of 2 and an activation energy of half the band gap of either the crystalline absorber layer $\frac{1}{2}E_{g,c-Si}$ (~ 0.56 eV) [55] or the amorphous layer $\frac{1}{2}E_{g,a-Si}$ (~ 0.88 eV) [49, 79].

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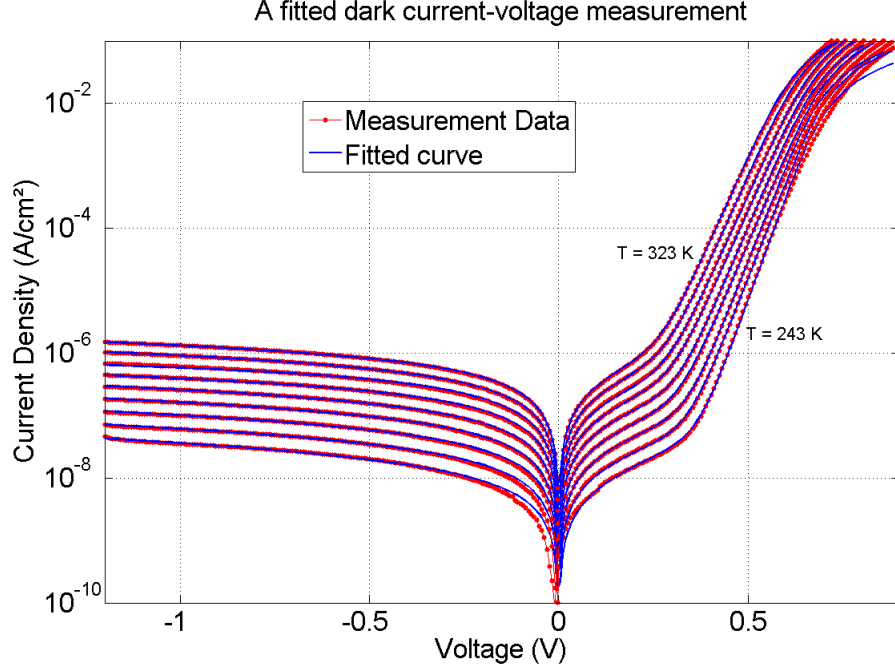


Figure 8.1.: An example of a fitted full-temperature variation measurement

As mentioned in Section §6.2, for our sample the LFB region is fitted simultaneously with the HFB region with the double diode equation with an additional ohmic path:

$$J_{fit} = J_{0,1}[\exp(A_1 V_a) - 1] + J_{0,2}[\exp(A_2 V_a) - 1] + \frac{V_a}{R_p}. \quad (8.1)$$

The current through the parallel path is very small compared to that of the LFB diode, which lead to a poor fitting of the resistance. As a consequence, a large inaccuracy is present in the obtained values and therefore the parallel path will be omitted in the LFB behaviour analysis. So this fitting results in a low forward bias slope A_1 and saturation current $J_{0,1}$ for every temperature. From this, first the activation energy of the saturation current is determined for every sample. Recalling that the temperature dependence of a saturation current is given by

$$J_0(T) = J_{00} \exp\left(-\frac{E_{act}}{kT}\right), \quad (8.2)$$

the activation energy can be found as the slope of the graph $\ln([J(T)])$ vs $\frac{1}{kT}$, which is similar to the procedure of determining the activation energy of a layer as described in Section §6.1. Figure 8.2(a) shows an example of such a graph. The slope is found with the least mean square (LMS) approximation.

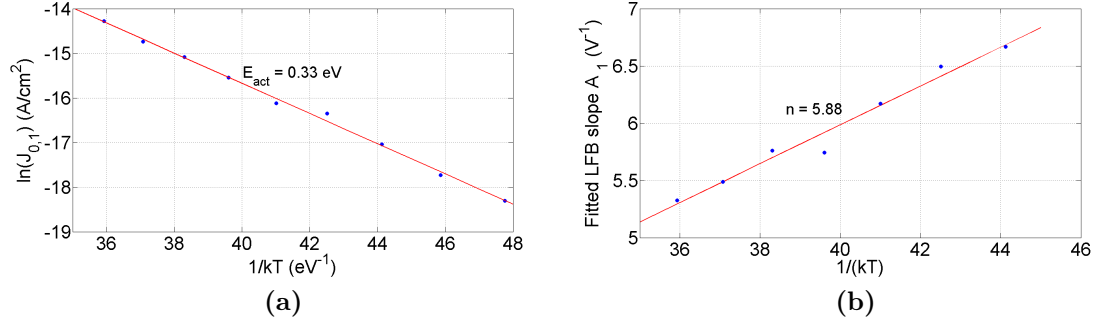


Figure 8.2.: An example of the temperature dependence of the LFB saturation current (a) and slope (b)

The ideality factor can be obtained from the temperature dependence of the LFB slope A_1 from the relation

$$A_1(T) = \frac{1}{n} \cdot \frac{1}{kT}. \quad (8.3)$$

For a tunneling current the slope is ideally temperature-independent, which translates to a high, temperature-dependent ideality factor ($n > 2$). For a recombination current the ideality factor is expected to be around 2. Figure 8.2(b) shows a graph an example of the LFB slope A_1 vs. $\frac{1}{kT}$. According to Eq.(8.3), the slope of this curve yields the ideality factor.

The procedure of extracting the LFB activation energy $E_{\text{act,LFB}}$ and ideality factor n_{LFB} from the fitted parameters has been performed for every sample. An overview of all the results for the low forward bias is shown in Figure 8.3. Indicated in the graph are the areas where the ideality factor $n < 2$ and where $n > 2$. From the graph it is clear that most samples exhibit a very small slope of A_1 vs. the inverse temperature (i.e. a very high ideality factor) and an activation energy of $0.30 - 0.45 \text{ eV}$. The high ideality factor in combination with the extracted values for the activation energy are consistent with the multi-tunneling capture-emission process as described in Section §4.3.

However, the MTCE theory for a tunneling current predicts a slope of zero. Also, there is an apparent correlation between the slope and the activation energy. There are several explanations for these observations. The simplest is that they are fitting artifacts and not real. The LFB region can be very small, especially for high temperatures. This makes the discrimination of the contributions of the fitting parameters $J_{0,1}$ and A_1 the less pronounced, which leads to a higher interchangeability. As Schulze explains in the aforementioned paper, this interchangeability can lead to an apparent correlation of the fitting parameters.

A different explanation is the existence of two current regimes in the low forward

8. Experimental Results

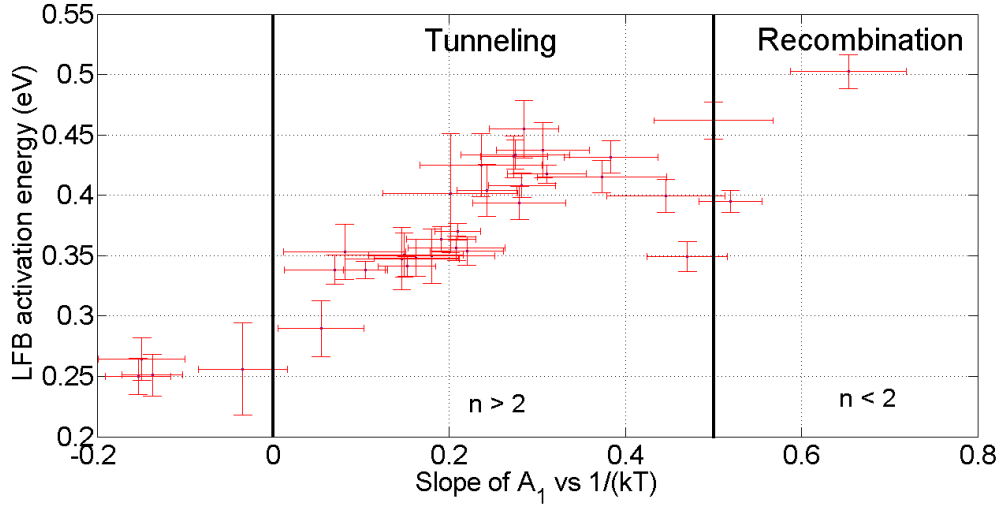


Figure 8.3.: An overview of the LFB fitting results

bias. It is conceivable that a tunneling current with $E_{act} = 0.3$ eV and a slope of zero coexists with a recombination current with $E_{act} = 0.55$ eV and a slope of 0.5 (ideality factor $n = 2$). The ratio of the magnitudes of the current mechanisms would then determine the value of the activation energy and ideality factor. If this model is correct, it can be concluded from the graph that the magnitude of the tunneling current is much higher than the recombination current and thus that the LFB region is dominated by an MTCE mechanism.

8.1.2. High forward bias region

Similar to the situation for the low forward bias region, there is no consensus regarding the dominating current in the high forward bias region in previous studies. Both diffusion and recombination currents are reported to dominate. Interestingly, there appears to be a correlation between the dominant current in the HFB region and the solar cell parameters, in particular the open circuit voltage V_{oc} . Samples for which the HFB current is dominated by a diffusion current [56, 78, 80, 81] exhibit in general higher values for the V_{oc} than samples where a recombination current dominates [77, 82]. This is probably related to an increased interface passivation, which reduces the recombination current and increases the V_{oc} .

The results for the HFB region for our cells are derived from the same double diode equation fitting employed for the LFB region. The advantage of this equation as opposed to fitting the HFB region only is that the region where the transition from LFB to HFB occurs is also included. Thus, more information is extracted

from the measurement, which has a positive effect on the quality and accuracy of the analysis.

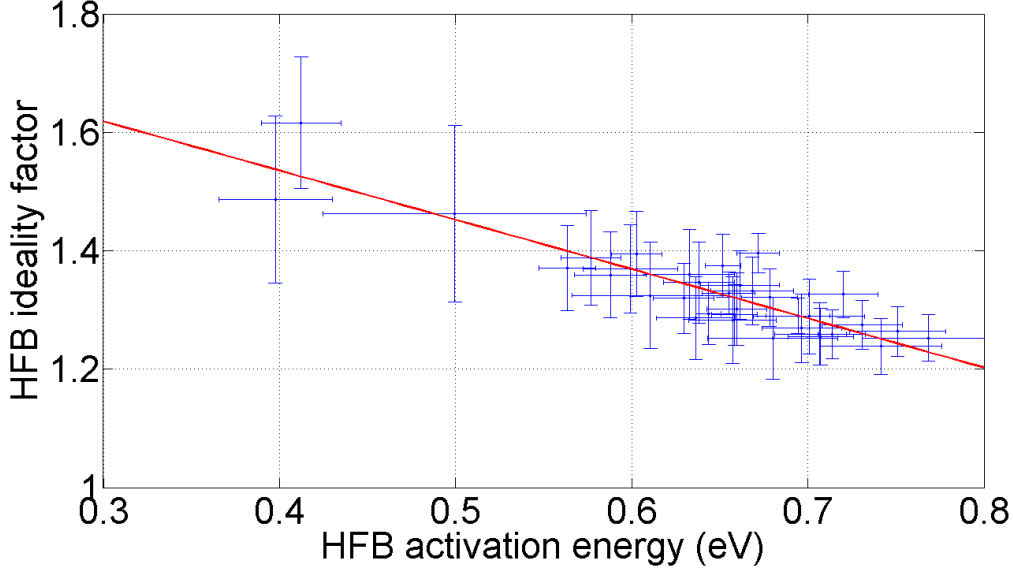


Figure 8.4.: An overview of the HFB fitting results. The red line shows the apparent correlation between the HFB ideality factor and activation energy.

Figure 8.4 shows an overview of the values for the HFB activation energy $E_{act,HFB}$ and ideality factor n_{HFB} . The activation energy has been calculated from the fitted HFB saturation current density $J_{0,2}(T)$ by a linear fit through the $\ln(J_{0,2})$ vs. $\frac{1}{kT}$ plot, as shown as the blue line in Figure 8.5. The HFB ideality factor n_{HFB} is the average of $n(T)$, which is calculated from $A_2(T)$ as

$$n(T) = \frac{1}{A_2(T) \cdot kT}. \quad (8.4)$$

Theoretically, $n(T)$ is independent of temperature. However, as shown in Figure 8.7(a), this is not entirely true. The implications of this deviation will be elucidated upon later in this section. For now, the derived values are sufficient for a proper analysis.

Several interesting observations can be made in Figure 8.4. The majority of the samples appears to be grouped with an HFB ideality factor $n_{HFB} = 1.25 - 1.4$ and activation energy $E_{act,HFB} = 0.55 - 0.75$ eV. As explained in Chapter 4, an ideality factor in this range corresponds to a diffusion current, however, the activation energy agrees with a recombination current mechanism. This is an odd combination and it not predicted by any theory, but it has been observed before by other authors

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[55, 77], who argue that the current is a recombination current. The explanation is that the ideality factor deviates from the classical value of $n_{HFB} = 2$, because the standard Shockley-Read-Hole theory does not take into account the continuous distribution of trap states in the amorphous silicon and the nonidentical electron and hole capture cross-sections. This is indeed observed in amorphous p-i-n structures, but there the ideality factor never decreases below $n_{HFB} = 1.45$ [75, 83, 84], while our cells are consistently below $n_{HFB} = 1.4$, so the explanation does not seem likely.

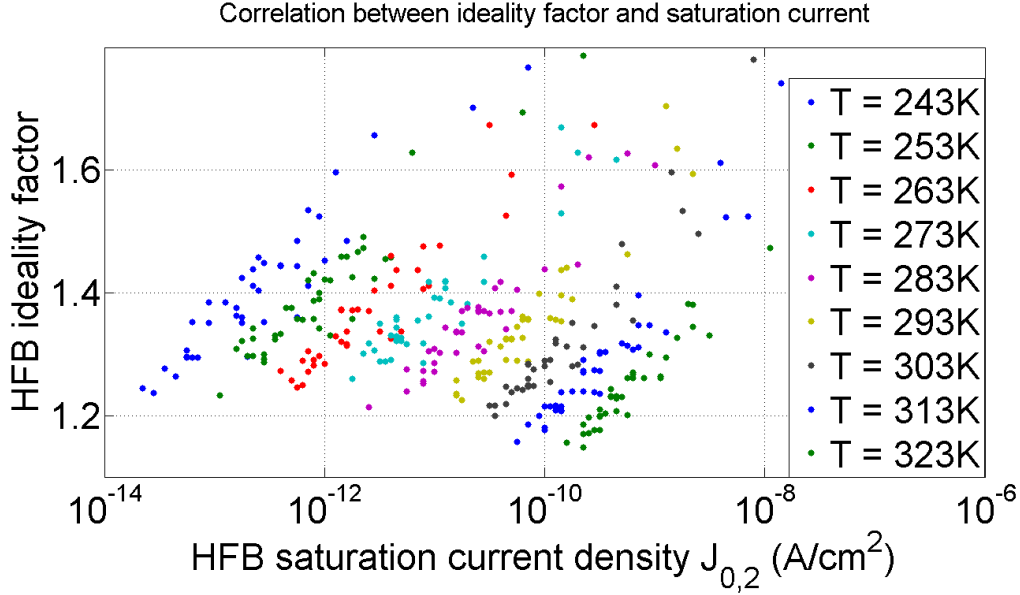


Figure 8.5.: Illustration of the correlation between the fitted ideality factor and the saturation current at every temperature.

Another characteristic of the graph in Figure 8.4 is the apparent correlation between the HFB ideality factor and activation energy. It is even more obvious when the ideality factor n_{HFB} is plotted against the fitted saturation current $J_{0,2}$ for every temperature, as shown in Figure 8.5. Such a correlation between fitting parameters was also observed in the low forward bias region and attributed to a fitting artifact or the coexistence of two current mechanisms. For the HFB region, however, there is evidence that there is no coexistence of two current mechanisms. To have any effect, the diffusion and recombination currents should be in the same order of magnitude. Theoretically, the coexistence of two currents similar in magnitude but with a different ideality factor and activation energy would cause two details that are not observed. The first is a slight curve in the exponential region from where one current overtakes the other in magnitude, which is can not be seen in Figure 8.1 or in any of the other measurements. The other unobserved consequence of the two-current model is a temperature dependence of the activation energy, which would

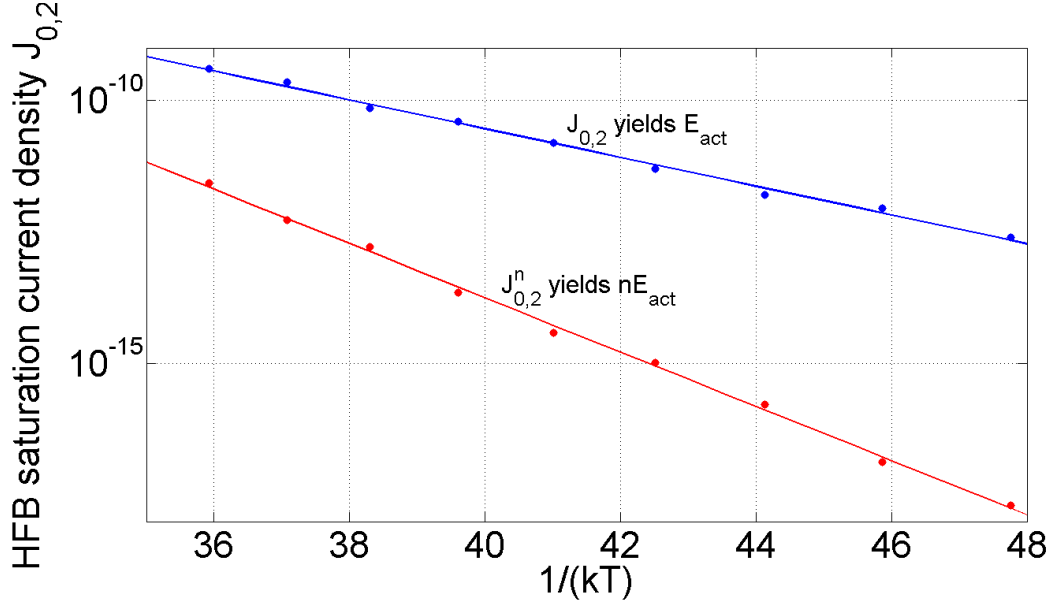


Figure 8.6.: Two methods of finding the HFB activation energy

be reflected in the $\ln(J_{0,2})$ vs. $\frac{1}{kT}$ plot as a slight curve. As shown in Figure 8.5, the line is very straight.

Therefore, it is in this case worthwhile to perform a transformation on the data as devised by Schulze, who observed a similar correlation between the HFB ideality factor and activation energy. Instead of examining the $\ln(J_{0,2}(T))$ vs. $\frac{1}{kT}$ plot to find the activation energy $E_{act,HFB}$ and the $A_2(T)$ vs. $\frac{1}{kT}$ plot to find the ideality factor n_{HFB} , it takes the $\ln(J_{0,2}^{n(T)}(T))$ vs. $\frac{1}{kT}$ plot as shown in Figure 8.5, where $n(T)$ is calculated with Eq.(8.4), which yields $(nE_{act})_{HFB}$. As explained by Schulze, this transformation attempts to reduce the effect of the interchangeability of the fitting parameters $J_{0,2}$ and A_2 on the analysis.

It turns out that this transformation indeed has a beneficial effect on the accuracy of the extracted parameters. The average relative standard deviation drops from 3.62% for $E_{act,HFB}$ and 4.78% for n_{HFB} to 2.39% for $(nE_{act})_{HFB}$, which is an indication that it is a useful way to decrease the inaccuracy due to the interchangeability of the fitting parameters. Also other interesting conclusions can be based on the value of $(nE_{act})_{HFB}$. However, it is first necessary to address the validity of the transformation. Schulze writes:

"[...] by exponentiating j_0 with n_1 we can reduce the scatter in the fit parameter j_0 stemming from the uncertainty in n_1 , [...] while the activation energy derived from $j_0(T)$ is then multiplied with an 'average' ideality factor."

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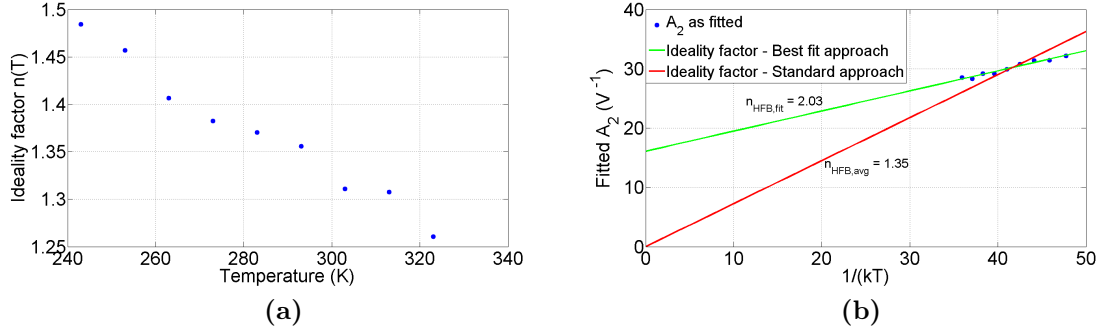


Figure 8.7.: Figure (a) shows temperature dependence of the ideality factor of $n(T)$ as calculated with Eq.(8.4). Figure (b) shows the alternative method of calculating the ideality factor.

The phrase 'average ideality factor' is not entirely accurate. To understand this, Figure 8.7(a) shows an example of $n(T)$ as calculated with Eq.(8.4) for one sample. Even though $n(T)$ is expected to be temperature-independent, there is a clear downward trend. To investigate why this occurs, Figure 8.7(b) shows the plot of A_2 vs. $\frac{1}{kT}$. If the standard model that produces Eq.(8.4) is correct, a linear fit through the data points should yield a line through the origin and with a slope of the inverse ideality factor $\frac{1}{n_{HFB}}$. The red line in Figure 8.7(b) shows the best fit through the origin. The ideality factor derived from this fit is the same as the average of the values of the ideality factor in Figure 8.7(a). It is quite obvious that this line does not fit the data points correctly. A best fit that follows the data points more accurately is shown in green. This fit corresponds to the equation

$$A_2(T) = \frac{1}{n_{HFB}kT} + C. \quad (8.5)$$

It is clear the constant C in Eq.(8.5) allows a much more accurate modeling than Eq.(8.4). The problem is that the origin of the constant can not be found in any existing theory. Attempts to correlate the constant to an other parameter have also not resulted in any more information regarding its origin.

This is relevant for the derivation of $(nE_{act})_{HFB}$ because the 'average ideality factor' mentioned by Schulze is actually the fitted ideality factor from Eq.(8.5). This is illustrated in Figure 8.8, where the correlation between $(nE_{act})_{HFB}$ and $n_{HFB,fit} \cdot E_{act}$ is much more pronounced than between $(nE_{act})_{HFB}$ and $n_{HFB,avg} \cdot E_{act}$. This implies that the validity of the transformation that calculates $(nE_{act})_{HFB}$ relies on the validity of Eq.(8.5). It should be noted that if it is valid, $(nE_{act})_{HFB}$ is more accurate than the product of $n_{HFB,fit}$ and $E_{act,HFB}$ because the first one reduces the error introduced by fitting parameter interchangeability, while the latter increases

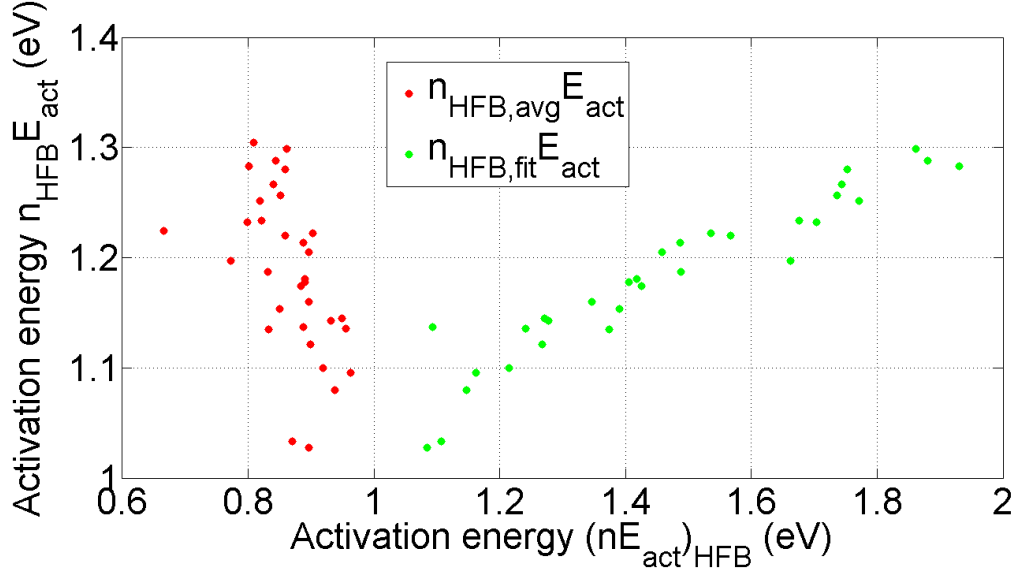


Figure 8.8.: Illustration of the correlation between $(nE_{act})_{HFB}$ and the fitted, $n_{HFB,fit}$, and averaged ideality factor, $n_{HFB,avg}$.

it.

The validity of Eq.(8.5) depends on whether the constant C can be explained as being another fitting artifact or if a physical interpretation can be found. At this moment an acceptable explanation is lacking and further research is required. However, it is possible to make certain careful observations.

For instance, the new ideality factor $n_{HFB,fit}$ has an average of 1.8, which would indicate that the current is a recombination current. An other observation is the apparent correlation between $(nE_{act})_{HFB}$ and the open circuit voltage V_{oc} , as show in Figure 8.9. Regardless of the current mechanism, for a homojunction solar cell the product of the ideality factor and the activation energy should yield the bandgap of the crystalline wafer, i.e. $n \cdot E_{act} = E_{g,c-Si} = 1.12$ eV. The deviation from this value for our samples can indicate that the passivation of the a-Si:H/c-Si interface has been improved to the point where the heterostructure, i.e. the band offsets, becomes more important and the value increases away from the ideal homojunction value. This is also supported by simulation [45].

8.1.3. Current-limited region

Literature suggests that the current in the very high forward bias, or current-limited, region is limited by either a series resistance or space-charge limited (SCL) current. There appears to be a historic separation between the two. State-of-the-art solar cells from Sanyo and Schulze show a series resistance to be the dominant limiting

8. Experimental Results

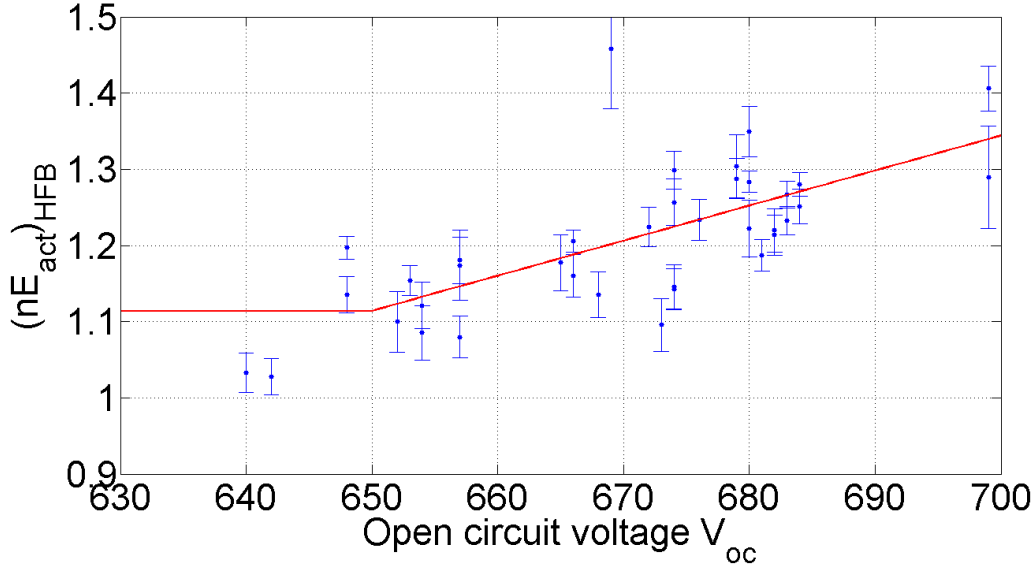


Figure 8.9.: The correlation between $(nE_{act})_{HFB}$ and V_{oc} . The correlation is attributed to an increase interface passivation and a more important heterostructure aspect.

factor, while older HIT cells exhibit a space-charge limited current.

Predicting how the SCL current limits the dominating current of the HFB region is difficult, but the effect of a series resistance is well-known. Therefore, as explained in Section §6.2, only a fitting that incorporates series resistance is performed:

$$J_{fit} = J_{0,2}[\exp(A_2(V - JR_s)) - 1]. \quad (8.6)$$

The initial values for HFB saturation current $J_{0,2}$ and slope A_2 are taken from the HFB fitting, but they are free fitting parameters for increased current-limited region fitting accuracy. Eq.(8.6) is an implicit equation, which makes direct calculation impossible and reduces speed of the fitting optimization considerably. Therefore, the resolution of the fitting parameters is not as fine as for the other current regions. However, in this case it does not degrade the quality of the analysis, as will be explained later in this section.

The inability of fitting a SCL current means that the analysis of the CL region is different from the other regions. For high currents, the curve approximates $J = KV^m$. For the series resistance $K = \frac{1}{R_s}$ and $m = 1$, while for a SCL current $m > 2$, as explained in Section §4.4. The curvature of the line in the logarithmic plot is set by the exponent m . A high value for m leads to a gradual curve and thus a steep slope. This is important because even though the value for the series resistance in

Eq.(8.6) can change the magnitude of the current, the curvature is fixed. This can be used to analyze the fit qualitatively. For every sample Eq.(8.6) is used to fit the CL region. The result is then visually inspected to determine the goodness of the fit. If the current is indeed limited by a series resistance, Eq.(8.6) will result in a good fit. If the current is limited by SCL, Eq.(8.6) does not describe the correct model and the fitting will fail. So even though a quantitative analysis is not possible due to the lack of a SCL fitting procedure, the current can be correctly classified by checking for a series resistance.

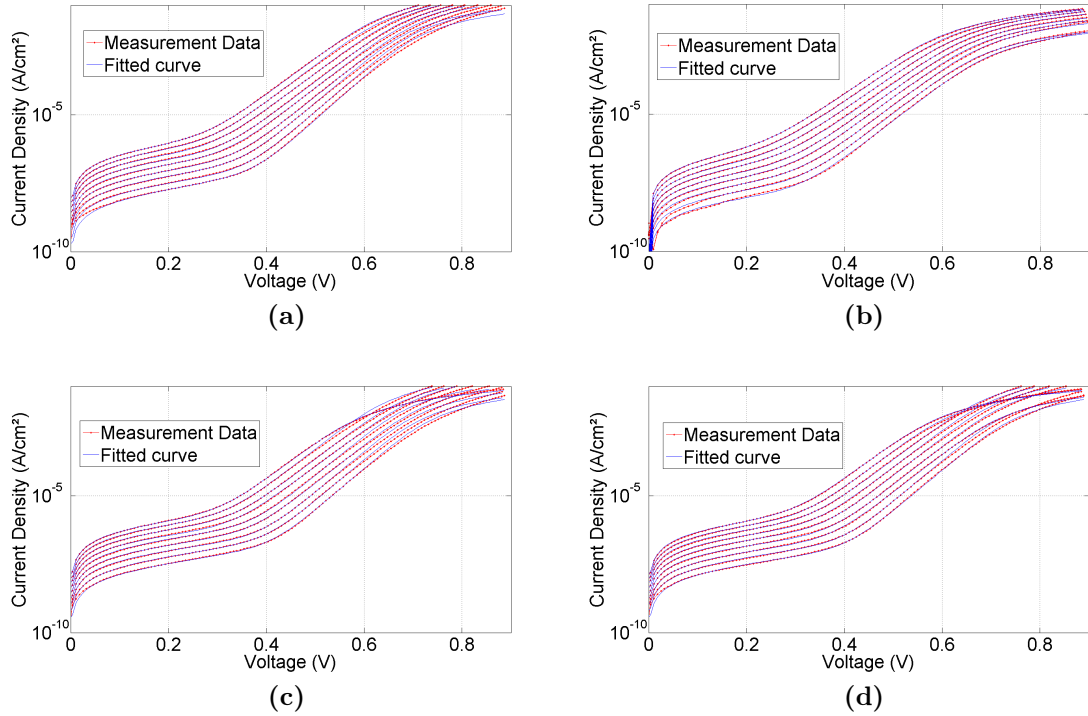


Figure 8.10.: The fitting results of the CL region. The measurement shown in (b) is not possible to fit with Equation Eq. (8.6), so it can be stated that the current is limited by an SCL current. An example of the current-limited by a series resistance is shown in (a). Presented in (c) and (d) are examples of samples of which the measurement at a certain temperature(s) is limited by a series resistance while the other temperatures show a SCL behaviour. This is attributed to a failure of the voltage sensing probe.

Four examples of the result of the aforementioned procedure are shown in Figure 8.10(a - d). An example of a sample of which the CL region is limited by SCL is shown Figure 8.10(a). It is very clear that the blue fitting line displays a stronger curvature than the measurement data points. Visual inspection of all the results in-

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indicate that this is the case for most samples. In fact, the only sample that exhibits a series resistance limited behaviour is shown in Figure 8.10(b).

Occasionally, a measurement shows that at certain temperatures the current is limited by a series resistance, while measurements performed at an other temperature reveal a SCL current. It is believed that this is a measurement artifact, where the third, voltage sensing probe fails and somehow senses a series resistance. The anomalous measurements are confirmed to be limited by series resistances, because unlike the measurements at other temperatures, they can be fitted by (8.6). It can go unnoticed during the measurement and only come to light when the measurements at all temperatures are plotted in the same graph.

The conclusion of the CL region analysis is that practically all the samples are limited by a space-charge limited current. So the question is, why do the Sanyo state-of-the-art HIT solar cells show a series resistance limitation? A possible explanation is that the measurements were performed without a third probe to sense the voltage. Sanyo does not explicitly report the setup for the dark current-voltage measurements. As reflected in the anomalous curves in Figure 8.10(c) and (d), without this probe the contact resistance between the probe that applies the voltage and the aluminium contact pad of the solar cell is not eliminated. However, Sanyo reports a dependence of the series resistance on the intrinsic a-Si:H layer and temperature, neither of which can be justified by the exclusion of the third probe.

A better explanation relies on the fact that the cells of which Sanyo has measured the dark current-voltage are much larger than ours; $10 \times 10 \text{ cm}^2$. A large area corresponds to a large current, which increases the voltage drop across the contacts. Beside this, they also noticed a temperature dependent part of the series resistance, caused by a relatively thick intrinsic amorphous layer [56]. The samples with thin intrinsic layers did not show this temperature dependence and the series resistance was dominated by the resistance of the contacts and TCO. Concluding, it is safe to assume that our cells did not show a series resistance in the current limited region because of the small area of the samples and that the intrinsic layers are thin enough to avoid a significant contribution to the series resistance.

8.1.4. Reverse bias region

Regarding the reverse bias region, several studies have found that this region can be accurately modeled by $J = KV^m$. A recurring value for the exponential factor m is between 0.6-0.8 and the activation energy E_{act} is reported to be between 0.3-0.45 eV. Even though these values differ from the theoretical values of $m = 0.5$ and $E_{act} = \frac{1}{2}E_{g,c-Si} = 0.56 \text{ eV}$, most studies agree that the reverse bias is dominated by a reverse bias generation current.

In our case, as a first approach the previous studies were followed, with a fitting function of

$$J_{fit,1} = KV_a^m, \quad (8.7)$$

where K and m as free fitting variables. The result of a single fitting with Eq.(8.7) and the extracted parameters m and $E_{act,RB}$ from the entire measurement set are shown in Figure 8.11.

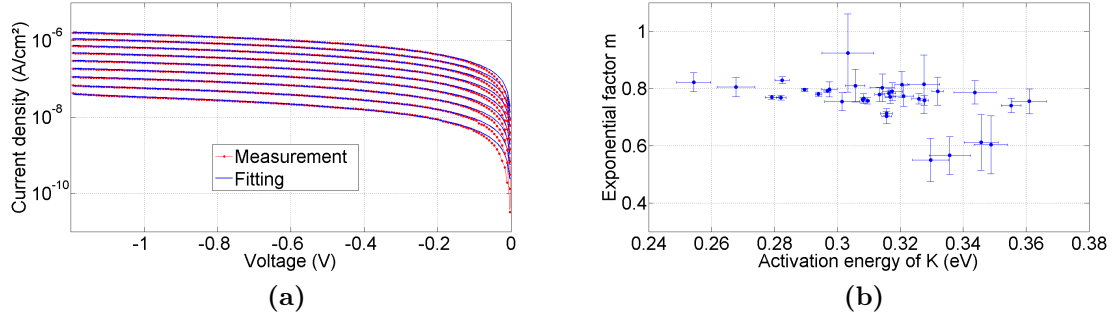


Figure 8.11.: The result of a fitting of the reverse bias region with Eq.(8.7)

Similar to the previous studies, the average exponential factor $m = 0.65 - 0.85$ and the activation energy $E_{act,RB} = 0.28 - 0.33$ eV. Even though these values have been reported before and attributed to a generation current, the large deviation from the theoretical values can not be ignored. Some ascribe the difference to the heterostructure, but this does not seem plausible because the space-charge region, the origin of the generation current, extends mostly in the crystalline silicon wafer.

Other peculiarities have been reported by Schulze. In his article he notes that for the samples of which the fitting does not yield the theoretical generation current values, the exponent m has a temperature dependence. For high temperatures the exponent saturates toward a value of 0.5. This is also observed in our sample, as illustrated in Figure 8.12.

Another observation by Schulze is that only the samples that exhibit a tunneling behaviour in the LFB region can not be described adequately by a generation current and that for these samples there is a correlation between the activation energies of the LFB and the RB region. He proposes that an 'inverse MTCE' mechanism is at work.

However, we think that the apparent correlation between the reverse bias and the low forward bias regions is much simpler; the reverse bias current is caused by the same mechanisms responsible for the low forward bias current. This would imply that the diode equation derived for MTCE in Section §4.3 also holds for a reverse applied bias. To check this, the measurement in Figure 8.11(a) is fitted again with the same fitting function as for the LFB, except that the second diode is excluded, because the reverse bias current through it would be much lower than the first diode.

8. Experimental Results

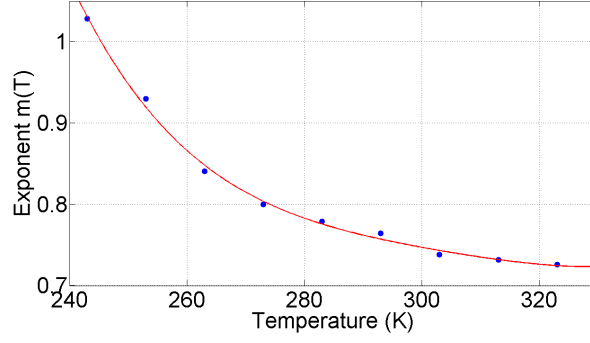


Figure 8.12.: The temperature dependence of $m(T)$. The red line is drawn to guide the eye.

$$J_{fit,2} = J_{0,1}[\exp(A_1 V) - 1] + \frac{V_a}{R_p}. \quad (8.8)$$

The initial values of the saturation current $J_{0,1}$, slope A_1 and parallel resistance R_p are taken from the LFB fitting, but employed as free fitting variables. The result of a single fitting of the RB region Eq.(8.8) is shown in Figure 8.13. It is clear that the quality of the fit is also very good. The extracted parameters $E_{act,LFB}$ and A_1 are the same as that of the LFB. More intriguingly, the activation energy $E_{act,Rp}$, as calculated from the temperature dependence R_p is very close to the activation energy of the crystalline wafer. This gives rise to the speculation that the origin of R_p can be a small area, direct path from the contacts to the crystalline silicon wafer.

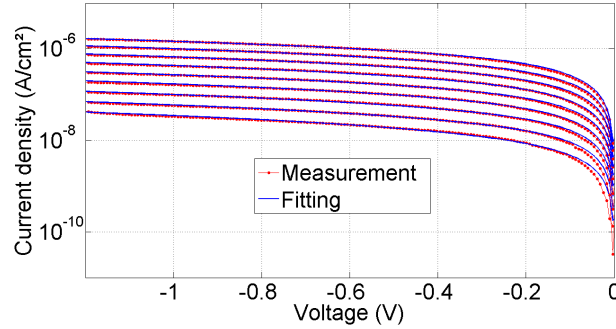


Figure 8.13.: A single fitting of the RB region with Eq.(8.8).

To investigate whether the current is indeed modeled correctly by Eq.(8.8), some

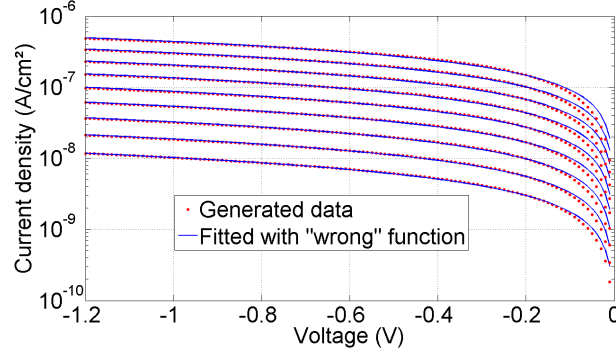


Figure 8.14.: Data generated with Eq.(8.8) fitted with Eq.(8.7)

artificial data has been generated with Eq.(8.8):

$$J_{fit}(V_a, T) = J_0(T)[\exp(AV_a) - 1] + \frac{V_a}{R_p(T)}, \quad A = 4$$

$$J_0(T) = J_{00} \exp\left(-\frac{E_{act,j0}}{kT}\right), \quad J_{00} = 5 \cdot 10^{-2}, \quad E_{act,j0} = 0.35$$

$$R_p(T) = R_{p,0} \exp\left(\frac{E_{act,Rp}}{kT}\right), \quad R_{p,0} = 80, \quad E_{act,Rp} = 0.3$$

The temperature was varied the same as for the measurements, i.e. from -30 to 50°C in steps of 10°C. The resultant data were subsequently fitted with Eq.(8.7) and (8.8) as a control. As expected, the generated data could be fitted perfectly with Eq.(8.8) and would yield the exact activation energies and slopes with which it has been generated. However, Eq.(8.7) was also able to fit the data perfectly, as illustrated in Figure 8.14.

Interesting is the behaviour of the extracted values for the activation energy $E_{act,RB}$ of K and the exponent m , shown in Figure 8.15. $E_{act,RB}$ had a value between the activation energies of the generated saturation current $E_{act,j0}$ and parallel resistance $E_{act,Rp}$. Another interesting result is that the exponent m shows a decrease with increased temperature, with an average of $m = 0.72$, just as observed by Schulze and in our own samples when fitted with Eq.(8.7),

The conclusion that can be drawn from this section is that the reverse bias region is probably not dominated by a generation current, as opposed to what many other authors believe, but actually the reverse bias characteristics of the dominant LFB current mechanism. The reverse bias region also allows for a much more accurate derivation of the parallel resistance. Based on the activation energy that has been extracted from the fitting with Eq.(8.8), it can be concluded that the most likely origin is a direct path from the contacts to the crystalline wafer.

8. Experimental Results

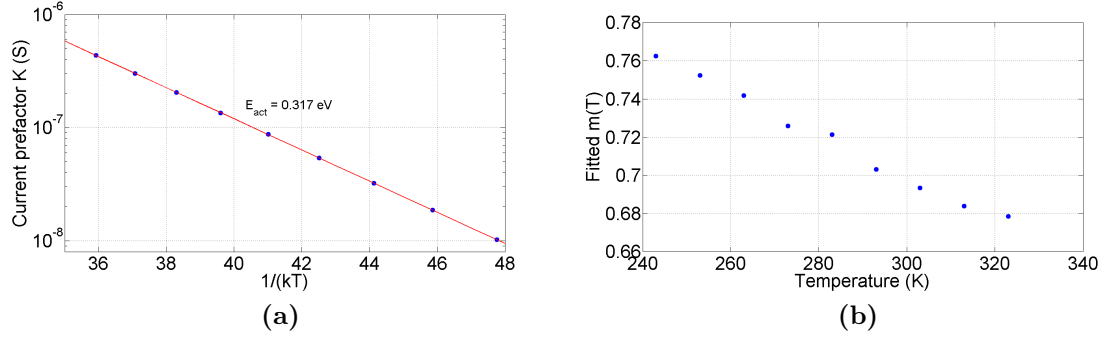


Figure 8.15.: The parameter extractions from fitting the generated data with Eq.(8.7).

8.2. Influence of deposition parameters

Besides investigating the dominant current mechanisms in our HIT solar cells, this study is intended to derive a model that can be used to simulate the solar cells accurately. To adequately model a semiconductor device, it is necessary to understand how certain changes in the layers that make up the solar cell influence the device characteristics. To this end, as explained in Chapter 7, a set of samples was prepared with a variation in the thickness of the amorphous p-layer and in the diborane flow during deposition the amorphous p-layer to change the activation energy. In this section any observed trends of the device parameters with respect to these variations will be shown and interpreted.

8.2.1. Diborane flow

An increase doping level of the p-type amorphous layer, as regulated by the diborane flow, can have a positive and a negative effect on the open circuit voltage V_{oc} . The positive effect is that a decrease of the activation energy causes a higher built-in voltage V_{bi} . In general a higher V_{bi} implies a higher V_{oc} . The negative effect is due to the nature of doping of amorphous silicon. As explained in Section §2.3, substitutional doping of amorphous silicon creates additional defects, dangling bonds, in the material. A larger number of defects in the p-layer can affect the passivative qualities of the i-layer by H_2 effusion under certain elevated temperatures, such as during the ITO sputtering. This increases the interface recombination, which leads to a lower V_{oc} . One of the goals of the HIT solar cell research in our group is to find the diborane flow that balances the two effects to yield the highest V_{oc} . Figure 8.16(a) shows the effect of B_2H_6 flow on the V_{oc} . Apparently the effect of the decrease of defect density is stronger than the decrease of the built-in voltage. This is also reflected in Figure 8.16(b). Combined with the correlation between $(nE_{act})_{HFB}$

and V_{oc} as observed in Figure 8.9 in Section §8.1.2, this makes the speculation from Schulze that $(nE_{act})_{HFB}$ is a measure for passivation more plausible. A logical consequence of this would also be that the tunneling through defects is affected. Such a correlation was not observed, however.

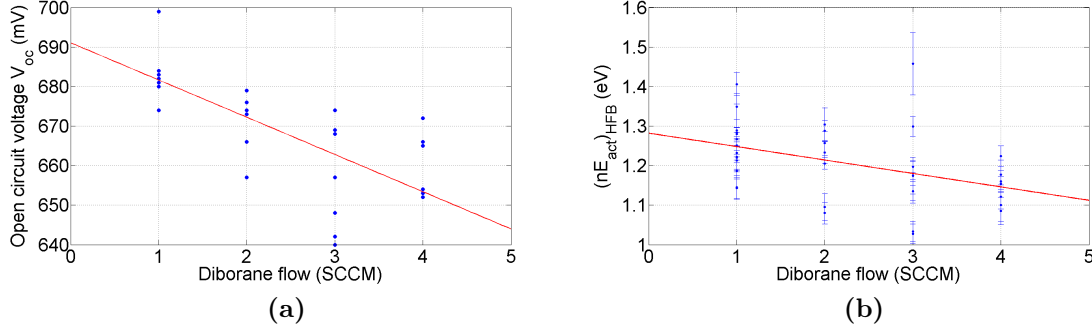


Figure 8.16.: The effect of the diborane B_2H_6 flow on the open circuit voltage V_{oc} (a) and $(nE_{act})_{HFB}$ (b).

8.2.2. Layer thickness

Theoretically, the p-layer thickness does not influence the dark current significantly, unless the layer becomes so thin that it is depleted. This does not seem likely, because due to the high doping level of the emitter the junction can be regarded as being one-sided; the depletion region barely extends into the p-layer. The p-layer thickness does have an effect on the short circuit current; a thicker layer absorbs more photons that do not contribute to the current, but that effect is not evaluated in this study.

Interestingly, whereas the diborane flow did not influence the low forward bias region, a change of layer thickness does appear to have an effect, as shown in Figure 8.17. According to the MTCE theory, the activation energy is either $E_c - E_t$ or $E_f - E_v$, whichever is smaller. It is unclear how the thickness of the p-layer can influence this. One attempt at an explanation is that the doping is not entirely homogeneous. This could be due to a 'ramp-up' at the start of the deposition, where the growth and doping of the amorphous layer is not yet stable. This would affect only extremely thin layers and the influence would decrease with increasing thickness, which could explain the correlation as observed in Figure 8.17. This could perhaps be measured by in-situ spectral ellipsometry, but such an equipment was not available for this study.

8. Experimental Results

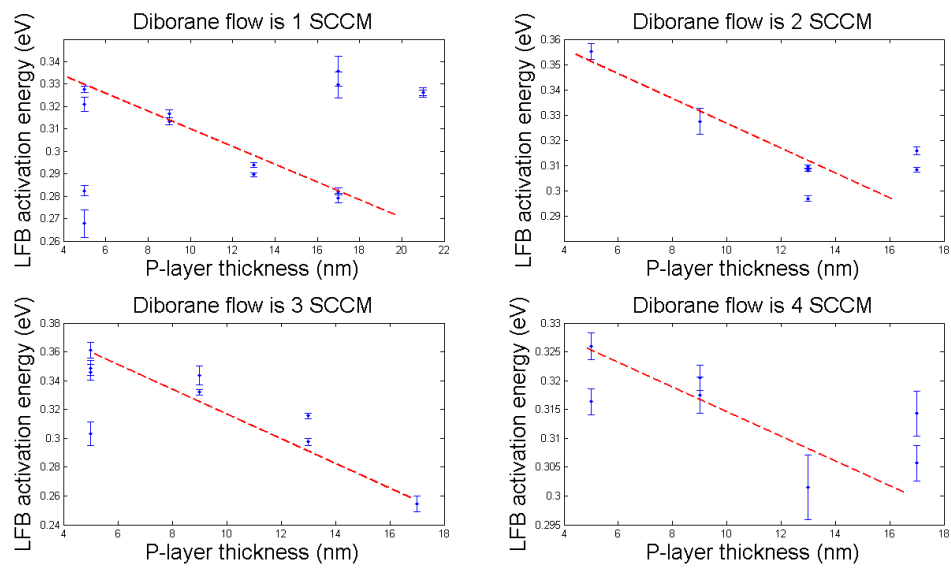


Figure 8.17.: P-layer thickness dependence of the LFB activation energy. The red line is only intended to guide the eye.

9. Discussion and Conclusion

9.1. Dominant current mechanism determination

The dominant current mechanism in the low forward bias region is determined to be consistent with multitunneling capture-emission model, with an activation energy $E_{act,LFB} = 0.3 - 0.45$ eV and a slope $A_{LFB} = 3.5 - 6.5$ V⁻¹. The apparent correlation between the activation energy and the slope of A_1 vs. $\frac{1}{kT}$ can be attributed to a fitting artifact or the existence of a second, smaller current with a higher activation energy and ideality factor, such as a recombination current.

The determination of the dominant current mechanism in the high forward bias needs further research. The observed activation energy $E_{act,HFB} = 0.55 - 0.75$ eV in combination with the ideality factor $n_{HFB} = 1.25 - 1.4$ does not correspond to any theory as discussed in Chapter 4. However, another method calculates the average ideality factor to be $\sim 1.8 - 1.9$, which would lead to the conclusion that the current is dominated by a recombination current. The issue is that the validity of this alternative method is questionable and should be examined in more detail. However, if further research shows that it is acceptable, it also validates the calculation of $(nE_{act})_{HFB}$, which has shown to be a measure of the defect density and passivation of the interface and therefore to be related to the open circuit voltage V_{oc} .

The current limited region of the curve is for almost all samples space-charge limited. The current record holder of the highest efficiency HIT solar cells, Sanyo, reports that their devices are limited by a series resistance. The reason for that is not clear, though bad contacts or an inaccurate measurement setup have been identified as unlikely. A more plausible cause should probably be found in the characteristics of the amorphous layers or the choice of wafer type, but this requires further research and is outside the scope of this study.

The reverse bias region is probably not dominated by a generation current, even though the fitted parameters agree with previous studies that have classified it as such. It has been shown that the reverse bias current is most likely caused by the combination of the low forward bias diode that models the tunneling and an ohmic path through the crystalline wafer. This probably also applies to the other studies, so perhaps the conclusions there need to be revisited.

9.2. Influence of deposition parameters

Unfortunately, the important section of this study to derive a model of the HIT solar cell did not bring forth many results. The only correlations that were found were between the flow of the dopant gas for the p-layer, diborane (B_2H_6), and $(nE_{act})_{HFB}$, which appears to confirm the relation between $(nE_{act})_{HFB}$ and the defect density, and between the p-layer thickness and the low forward bias activation energy $E_{act,LFB}$.

This low yield can be caused by several things. The first is the stability of the deposition setup. Any variation in the deposition over time can seriously degrade the reproducibility and disguise any correlations that may have been present. To minimize this, all the depositions were done between two cleanings of the chamber, but that might not have been sufficient. Another problem is that sporadic thickness measurements with spectral ellipsometry have shown that the thickness of the amorphous layers can differ from what was intended. The deposition rate is calibrated using relatively thick layers, masking any irregularities at the start of the deposition.

Both of these issues could be solved by instead of relying on calibrated doping levels and layer thicknesses, to measure the properties of the layers in the device. This is already possible for the thickness, to a certain extent. Using ellipsometry it is possible to measure the thickness of an amorphous layer grown on top of a crystalline layer. It is, however, impossible to distinguish between the doped emitter and the intrinsic passivation layer, but this could be worked around with enough depositions.

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