

École polytechnique de Louvain

Opto-electrical characterization and modelling of defects in thin-film Cu(In,Ga)Se_2 solar cells

**Effect of oxide passivation layers at the front and
window interface**

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Abstract

In this thesis, we model and characterize defects in thin-film $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) solar cells and study the passivation effect of two atomic layer deposited dielectric materials (AlO_x and HfO_x) at the CIGS/CdS (front) and the CdS/TCO (window) interfaces, along with the influence of post-deposition annealing. We use admittance spectroscopy (AS) on simulated and experimental CIGS solar cells to deeply characterize electronic defects in terms of characteristic frequency f_t , activation energy E_A and capture cross section σ . This method is also applied to study other loss mechanisms, such as parasitic resistances and interface barriers. The AS theory is completed with an innovative graphical representation called loss map, enabling to identify the signatures of these loss mechanisms. On top of this, optical experiments are conducted to evaluate relevant CIGS absorbers properties. This large panel of measurements allows to interpret the evolution of solar cells performance. In particular, we show that post-deposition annealing at 150°C has a positive impact on low performance solar cells, leading to a 10% V_{oc} improvement and to an absolute increase of 1.2% efficiency. These cells are further enhanced when a 1nm AlO_x passivation layer is introduced, resulting in a 30% V_{oc} improvement and to an absolute increase of 4% efficiency compared to the reference. Opposite trends are observed for higher performance cells passivated with a 1nm layer of AlO_x or HfO_x . In these structures, we highlight the presence of a N1-type interface defect that is widely observed in the literature, and we extract its characteristic energy $E_A \sim 0.1\text{eV}$ and capture cross section $\sigma \sim 10^{-18}\text{cm}^{-2}$. In the case of front passivation, the N1 defect exhibits a higher response that is probably responsible for the reduced performance and is possibly explained by Fermi level pinning. For window passivation, the N1 defect density is reduced but this positive effect is neutralized by the barrier-induced roll-over that negatively affects the efficiency. Eventually, we also highlight the limitations of these characterization methods and discuss the need for further investigations using more advanced techniques.

List of acronyms

Acronym	Signification
ALD	Atomic layer deposition
AS	Admittance spectroscopy
CdS	Cadmium Sulfide
CIGS	Copper Indium Gallium Diselenide - Cu(In,Ga)Se_2
CV	Capacitance-Voltage
CVf	Capacitance-Voltage-frequency
GhG	Greenhouse gas
ITO	Indium-Tin oxide
IV	Current-Voltage
PL	Photoluminescence
PV	Photovoltaic
SCAPS	Solar cell capacitance simulator
SLG	Soda-Lime glass
SR	Spectral response
SRH	Shockley-Read-Hall
TCO	Transparent conducting oxide
TEMAH	Tetrakis(ethylmethylamino)hafnium (used for ALD of HfO_x)
TMA	Trimethylaluminium (used for ALD of AlO_x)
TRPL	Time-resolved photoluminescence

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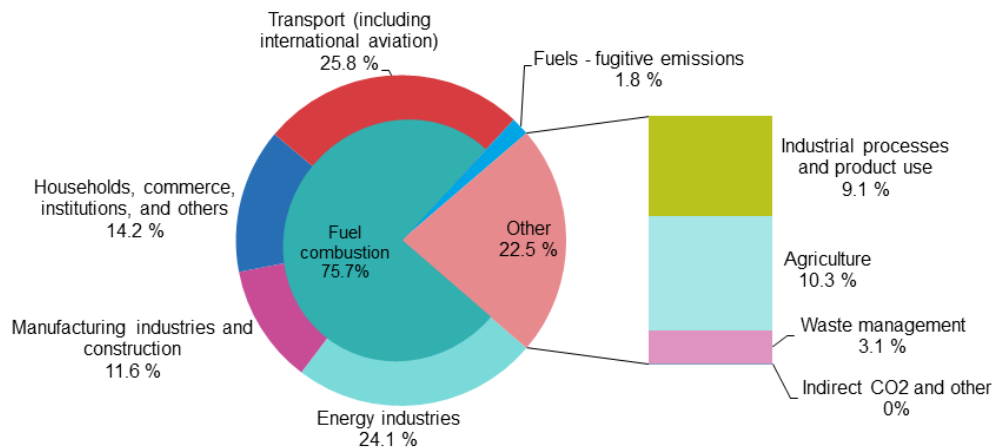
1 Introduction

1.1 Context

On the 4th of April 2022, the IPCC (Intergovernmental Panel on Climate Change) published the final part of its sixth evaluation report [1]. In this report, the most recent and advanced knowledge on climate change is presented. The responsibility of humans activity is extensively discussed and acknowledged. An emphasis is put on the vital necessity to quickly, deeply and durably change our living habits as well as the way our society works. Greenhouse gas (GhG) emissions are found to be largely responsible for the global warming, and therefore need to be strongly reduced in the near following years.

In 2019, the energy industry was responsible for 24.1% of the total GhG emissions in Europe (figure 1.1.1). From this knowledge, and from the data presented in reference [1], it appears that a clean "green" energy and electricity production is key to reducing the global emissions. The availability of green energy could furthermore positively impact other sectors such as transportation and manufacturing industries, which are also largely responsible for the total GhG emissions.

Greenhouse gas emissions by IPCC source sector, EU, 2019



Source: EEA, republished by Eurostat (online data code: env_air_gge)

eurostat 

Figure 1.1.1: Shares of CO₂ emission per activity sector in 2019, from [2]

In the past few years, solar PV technology has shown to be very suitable to achieve clean electricity

production. Photovoltaic panels are cheap, reliable, durable and also easy to integrate at household scale. Despite these advantages, some significant limitations subsist, among which the intermittence of solar production, the ecological footprint of the production process or the efficiency that is not yet high enough to meet the global demand. To tackle these limitations, efficient and sustainable storage solutions are needed, as well as new technological breakthroughs in PV technology.

In this context, thin-film PV has emerged as a promising technology to both enhance the efficiency of solar panels and to reduce their ecological footprint by reducing the quantity of raw material needed [3]. Due to their reduced thickness, these solar cells could also be mounted on flexible substrate to further improve their urban integration. In thin-film PV, there is one particular technology that catches a lot of attention: CIGS solar cells. The name is the one of the absorber material, $\text{Cu}(\text{In,Ga})\text{Se}_2$, that presents very good light absorption characteristics and is thus well suited to the making of solar cells. For this technology to reach its full potential, some challenges still need to be faced, the most complex one being the high quantity of defects that constitutes a major limitation to performance [4].

1.2 Topic overview

Contrarily to Silicon technology that mostly relies on Silicon-based materials, CIGS solar cells are a little more complex. A schematic representation of a CIGS solar cell is represented in figure 1.2.1. On the very bottom, Soda-lime glass (SLG) is used as a mechanical substrate for the solar cell. In some cells, it can also be replaced by steel to make the cell flexible. Directly on top, a Molybdenum (Mo) layer is deposited to act as back electrical contact. On top of the Mo layer, the CIGS/CdS heterojunction is responsible for the absorption of light photons and the generation of the electrical charges. Finally, the window layer and the front electrical contact, generally made of Indium (In) or Silver (Ag), complete the cell structure.

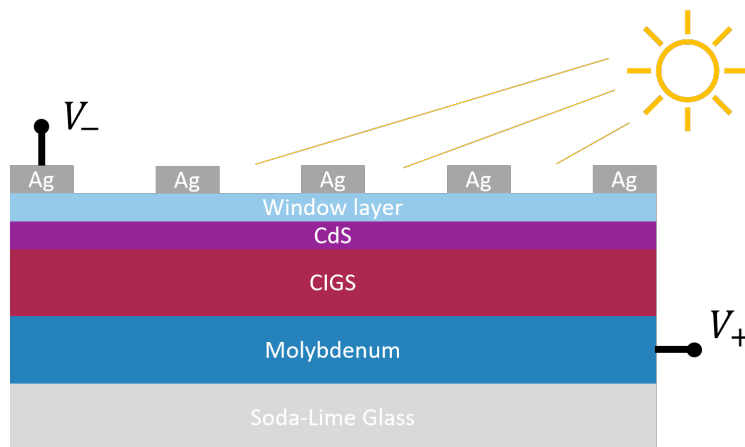


Figure 1.2.1: Schematic representation of a CIGS solar cell (arbitrary scale)

The different interfaces between these materials generally present a significant defect density. More-

over, the polycrystalline nature of CIGS is also responsible for a significant concentration of bulk defects inside the material. These defects are responsible for a consequential reduction of electrical charge generation and thus of overall cell efficiency. Therefore, the study of these defects and their action on the solar cell is key to improving its overall performance.

To mitigate the action of defects at the different interfaces, a technique called interface passivation can be used. In CIGS solar cells, interface passivation is very well documented, especially at the rear interface [5, 6, 7]. Generally, a dielectric layer is inserted between the CIGS and Molybdenum layers. It can either be ultra-thin, about 1nm, or thicker and patterned in order to let the electrical current through. In these references, promising results are shown, with a decreased interface defect density [5], increased current [6] or even increased overall cell efficiency [7]. In this work, the concept of passivation that is already mastered at the back interface is extended to the front interface (CIGS/CdS) and the window interface (CdS/TCO).

1.3 Objectives

This work focuses on the modelling and characterization of defects in CIGS solar cells, as well as on the impact of front and window passivation on these defects and on the cell performance. For this purpose, different leads are investigated.

- Different CIGS absorbers are used, to try to understand how the quality and structure of the absorber influences the performance and the presence of defects. Their influence on the effectiveness of passivation is also studied.
- Passivation is attempted at two interfaces, to see which would help the best with increasing the performance and reducing the influence of defects.
- Two different materials are used for the passivation layer: aluminium oxide (AlO_x) and hafnium oxide (HfO_x). Due to their different bandgap and fixed charge, but also due to their different lattice structure, they should act differently on the solar cell.

For all of these leads, different steps and measurements are undertaken:

- The processing is adapted. This mainly means that the standard processing of a CIGS solar cell is modified to integrate the passivation layers.
- The sample is characterized thoroughly. This means performing numerous measurements such as IV, CV, PL, EQE and others. The aim is to gather various data on the samples and to extract the main figures of merit related to each one of these.
- Using CVf measurements performed on the samples, admittance spectroscopy is used to characterize defects in the structures. This very powerful technique is first developed theoretically in chapter 2 and then put in application in the practical part of this work.

- Simulations are carried out using the SCAPS [8] software and confronted to experimental measurements. The purpose of these simulations is both to predict trends that are then confronted to reality and to help in the interpretation of the experimental observations.

1.4 Structure

The second chapter of this work, after the present introduction, is dedicated to a comprehensive theoretical background on solar cells, the particular case of CIGS and admittance spectroscopy. After that, the methodology of this work is presented, along with the experimental setup and the different techniques that are used. In the fourth chapter, SCAPS simulations are presented for a reference CIGS solar cell. The fifth chapter details the complete characterization process of three experimental CIGS solar cells. There, a performance analysis is first carried out using IV measurements and the defects are then analyzed in more details using admittance spectroscopy. The two following chapters make use of this same characterization process for front and window passivated cells. Finally, the last chapter concludes the discussion and points towards future developments.

2 Theoretical background

This chapter aims at giving a thorough presentation of all the theoretical aspects used in this work, mainly related to solar cells and their characterization. It starts with a general presentation of solar cells, giving a first insight about their operation and faced challenges. After that, the particularities of CIGS solar cells are detailed. The third section is dedicated to a very comprehensive presentation of admittance spectroscopy (AS), a method used for characterizing loss mechanisms in thin-film solar cells. Finally, the last section focuses on ways to mitigate the presented loss mechanisms, and introduces the concept of passivation that is key to this work.

2.1 General theory of solar cells

In this section, a general introduction to solar cells is given. First, the theory behind standard PN junctions is briefly introduced. Then, ideal solar cells are presented, along with their figures of merit. Finally, some details are given about the main loss mechanisms in real solar cells.

2.1.1 PN junctions

The PN junction is one of the most basic and most important building blocks behind modern technology. Its working principle and characteristics are extensively detailed in various reference books, two of which are largely used in this section [9, 10].

A PN junction is built by putting in contact a n-type semiconductor, doped with donor atoms, with a p-type semiconductor, doped with acceptor atoms. This is represented in figure 2.1.1.

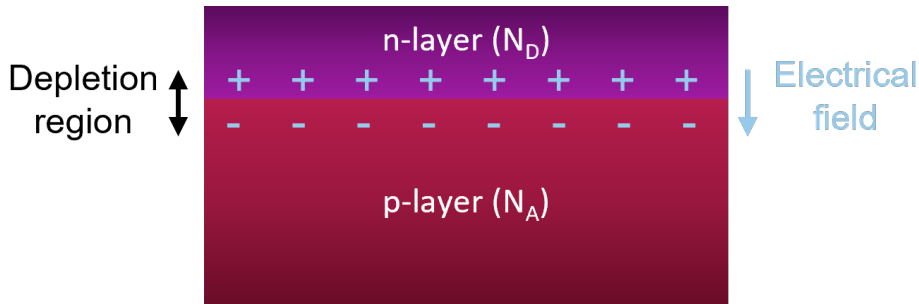


Figure 2.1.1: Schematic representation of a PN junction

The doping of the two semiconductors is N_D [cm^{-3}] and N_A [cm^{-3}] respectively. Because the n-type region is poor in holes but rich in electrons and the p-type region is poor in electrons but rich in holes, a mechanism of diffusion at the junction takes place, leaving only ionized doping atoms in the middle. As a first approximation, it is thus possible to consider that there is an absence of charges in this region. For this reason, it is called the depletion region. The electrical parameters of an ideal abrupt PN junction can be computed for the n- and p-side using the 1D Poisson equation:

$$\frac{d^2\Phi(x)}{dx^2} = -\frac{q}{\varepsilon_s} (p - n + N_D - N_A) \quad (2.1.1)$$

where $\Phi(x)$ is the potential at the junction and p and n are the concentration in holes and electrons derived from the Boltzmann relations. This equation is based on the so-called "depletion approximation" where all doping atoms are ionized in the depletion region [9]. From this equation, the junction potential at equilibrium is computed:

$$\Phi_0 = \frac{kT}{q} \ln \left(\frac{N_A N_D}{n_i^2} \right) \quad (2.1.2)$$

When a bias voltage V_a is applied to the junction, the junction potential (also called internal potential) changes and is simply equal to:

$$\Phi = \Phi_0 - V_a \quad (2.1.3)$$

Positive bias voltage is applied at the p-side of the junction. This equation is based on the assumption that the potential drop across the quasi-neutral regions, that are not in depletion, is negligible. The result of this equation is that the potential barrier at the junction is reduced for positive biases.

After solving the Poisson equation, and by following Gauss' law stating that the electrical field must be continuous at the junction, it is possible to derive the width of the depletion region:

$$w_D = \sqrt{\frac{2\varepsilon_s}{q} \frac{(\Phi_0 - V_a)}{N_A}} \quad (2.1.4)$$

This equation is an approximation accounting for the fact that $N_D \gg N_A$ which is the case in CIGS solar cells. The result of this equation is that the depletion width decreases for a positive bias. Also, the depletion layer capacitance can be derived:

$$C_D = \frac{dQ_D}{dV} = \frac{\varepsilon_s}{w_D} \quad (2.1.5)$$

The analysis of this depletion capacitance is very useful for the characterization of solar cells, as detailed in section 2.3. Finally, by combining the results of the Poisson equation with the charges drift and diffusion equations, it is possible to write the equation for the current density in a PN junction:

$$J = J_s \left(\exp \left(\frac{qV_a}{kT} \right) - 1 \right) \quad (2.1.6)$$

where J_s is the reverse saturation current density.

The current density in an ideal PN junction in function of bias voltage is represented in figure 2.1.2.

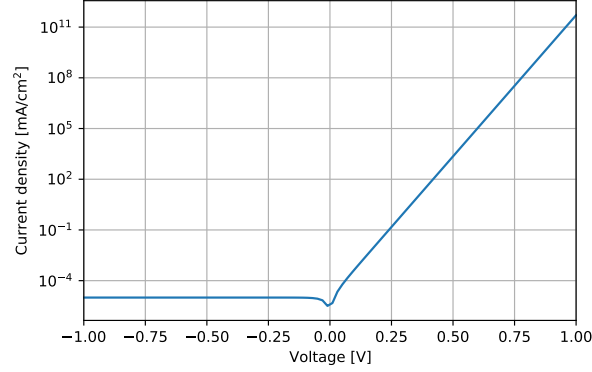


Figure 2.1.2: IV characteristic of a PN junction using equation (2.1.6) and with $J_s = 10^{-5}$ mA/cm².

2.1.2 Ideal solar cells

An ideal solar cell is essentially a PN junction that is illuminated. For understanding its working principle, it is first necessary to present the action of light on semiconductors. This is linked to the charges generation/recombination principle that is presented hereafter.

Charges generation and recombination

In an undoped semiconductor at thermodynamic equilibrium, the valence band is completely populated with electrons, and the conduction band is an empty state. When a sufficient amount of energy is transferred to an electron of the valence band, it can be promoted to the conduction band. In that circumstances, it leaves an unoccupied state which is called a hole. Together they form a so-called electron/hole pair (e^-/h^+). Because the conduction band is originally an empty state, an electron that would be promoted there can move freely. The same is valid for a hole in the valence band. These particles are commonly called "free (charge) carriers" [9]. This situation of a generated e^-/h^+ pair after transfer of energy is represented in figure 2.1.3a.

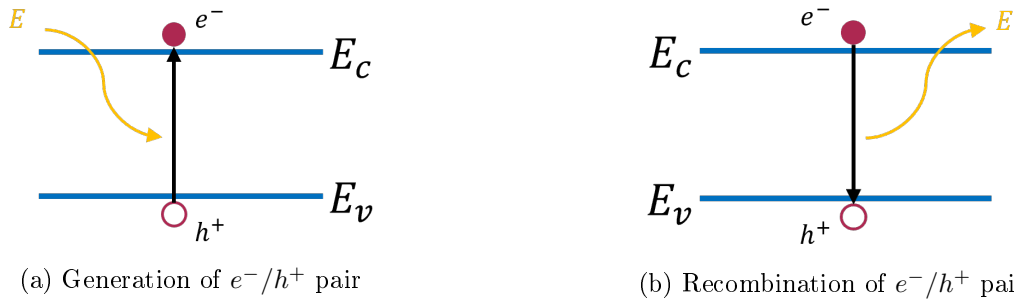


Figure 2.1.3: Schematic representation of the generation/recombination mechanism

After a certain amount of time, if there is no physical mechanism preventing it, the electron returns to its low energy state, releasing that same energy that was absorbed before. This mechanism is called recombination and is depicted in figure 2.1.3b.

Illuminated PN junction: the ideal solar cell

A particular case of generation/recombination applies when a PN junction is illuminated. There, the energy transferred to the e^-/h^+ pair comes from the sun, with value $E = h\nu$. PN junctions present a physical barrier to recombination: the electrical field in the depletion region. It drives the electrons towards the n-type layer and the holes towards the p-type layer, as represented in figure 2.1.4. When they are kept separated, the generated e^- and h^+ contribute to a so-called "photo-generated current".

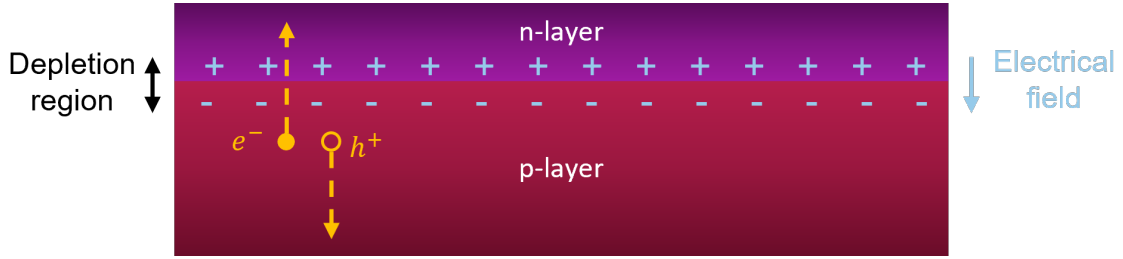


Figure 2.1.4: Schematic representation of an illuminated PN junction, with a generated e^-/h^+ pair pulled away from each other due to the electrical field.

A PN junction under illumination can be represented using the 1-diode model from figure 2.1.5.

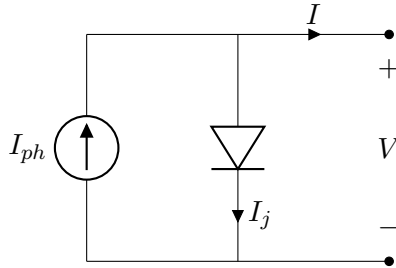


Figure 2.1.5: 1-diode model of solar cell

The photo-generated current I_{ph} depends on the irradiance, the area of the cell and the capability of absorption of the p-type material. It induces an increase in voltage across the PN junction which results in an increased diffusion current I_j . Using the model and equation (2.1.6), the total current in the cell is written as:

$$I = I_{ph} - I_j = I_{ph} - I_s \left(\exp \left(\frac{qV}{kT} \right) - 1 \right) \quad (2.1.7)$$

The current density in an ideal solar cell is represented aside of the current in dark conditions in figure 2.1.6a. It is interesting to note that this representation is not the same as for conventional PN junctions. Here, because the solar cell generates power, the active sign convention is used. It is simply obtained by considering that the $I \cdot V$ product should yield a positive power. This is the case when considering the grey quadrant in the figure, which is also the operation regime of the solar cell. The solar cell under dark condition can also be represented that way, enabling an easier comparison between the two.

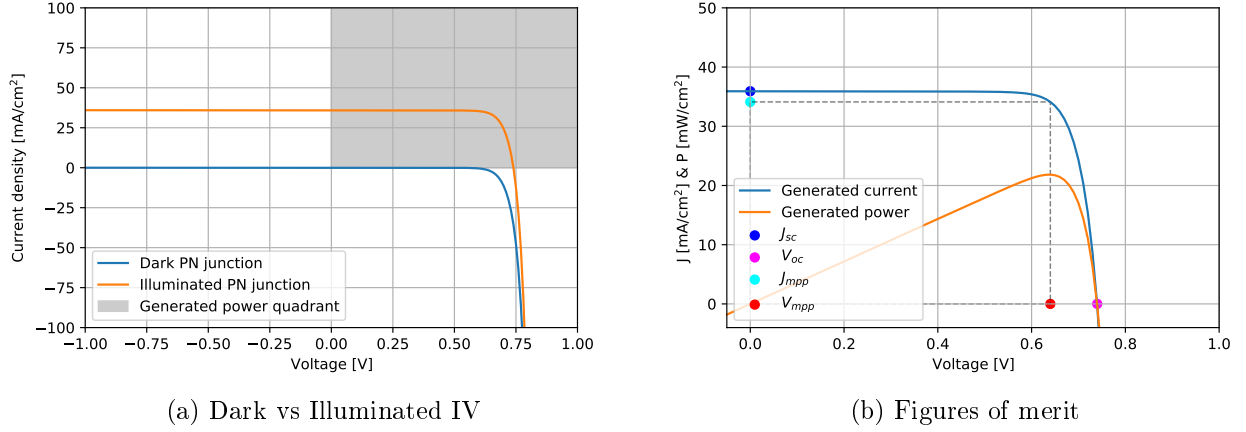


Figure 2.1.6: IV of illuminated ideal solar cell using the SCAPS model from appendix B.1.

Figures of merits of solar cells

Important figures of merit for characterizing the solar cell performance are extracted from the IV curve under light. These are represented in figure 2.1.6b and are the following:

- The open-circuit voltage V_{oc} . This is the voltage at which the current is null.
- The short-circuit current J_{sc} . This is the current at which the voltage is null.
- The maximum power point (V_{mpp} , J_{mpp}) which is the point of highest generated power.
- The fill-factor $FF = \frac{V_{mpp} \cdot J_{mpp}}{V_{oc} \cdot J_{sc}}$. It is a measure of ideality for the solar cell.
- The efficiency of the cell $\eta = \frac{V_{mpp} \cdot J_{mpp}}{G} = FF \cdot \frac{V_{oc} \cdot J_{sc}}{G}$. It depends on the solar irradiance G which is known from the solar cell testing procedure.

This short description of the main figures of merits concludes the presentation of ideal solar cells. The next section steps away of the ideal case, by introducing the main loss mechanisms existing in real solar cells.

2.1.3 Loss mechanisms in solar cells

First, the 1-diode model of solar cells is adapted, allowing to present the action of external losses. Secondly, SRH recombination and defects are introduced, along with their impact on charges recombination.

An important mention is that this work focuses on the electrical characterization of solar cells. For this reason, optical considerations are mostly not taken into account. Optical losses, even though they are not detailed here, are also a big part of solar cells losses. In this section and the rest of this work, all references to losses only consider their electrical part.

External losses

The 1-diode model is very commonly used for modelling of solar cells [11]. It gives an easy representation of the currents and voltages inside it, decoupled from the external electrical losses. The adapted 1-diode model, taking these losses into account, is represented in figure 2.1.7.

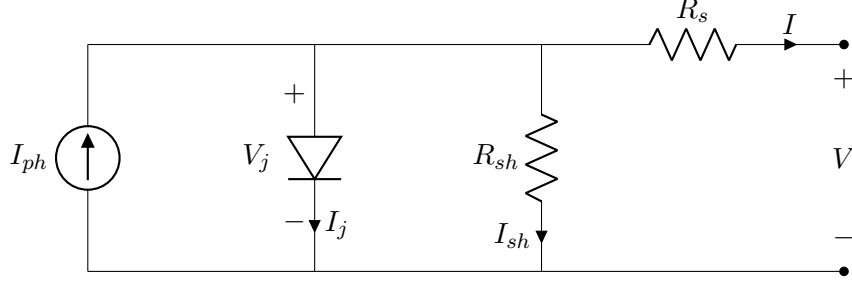


Figure 2.1.7: Adapted 1-diode model for solar cells, taking into account the effect of series resistance and shunt resistance. R_s is the series resistance, R_{sh} is the shunt resistance and V_j and I_j are the junction voltage and current.

Using this model, the external measured current can be separated into its different parts using the following equations:

$$\begin{cases} I = I_{ph} - I_j - I_{sh} \\ V = V_j - R_s \cdot I \\ I_j = I_s \cdot \left(\exp\left(\frac{qV_j}{kT}\right) - 1 \right) \end{cases} \quad (2.1.8)$$

Putting it all together, this leads to:

$$I = I_{ph} - I_s \cdot \left(\exp\left(\frac{q(V + IR_s)}{kT}\right) - 1 \right) - \frac{V + IR_s}{R_{sh}} \quad (2.1.9)$$

This 1-diode model puts into light the two main sources of external electrical losses: series resistance and shunt resistance. Series resistance, as for many electronic devices, mainly comes from the electrical contacts at the front and rear side of the device. Shunt resistance, on the contrary, has a very different origin depending on the technology of solar cell that is used. Their origin is developed in more details further, in the context of CIGS solar cells.

SRH recombination and defects

In section 2.1.2, the principle of recombination is introduced. It is mentioned that recombination is the action of an electron returning from the conduction band to the valence band, emitting a previously absorbed photon in the process. Because recombination reduces the amount of carriers contributing to the photo-generated current, its action is critical for cell performance. In that section, band-to-band recombination is presented, but this mechanism can be facilitated in a process that is called Shockley-Read-Hall (SRH) recombination [9].

Instead of having an electron directly go from the conduction band to the valence band, it passes by an intermediate energy state (a so-called "trap") located somewhere in the bandgap. This situation is represented along with the band-to-band recombination mechanism in figure 2.1.8.

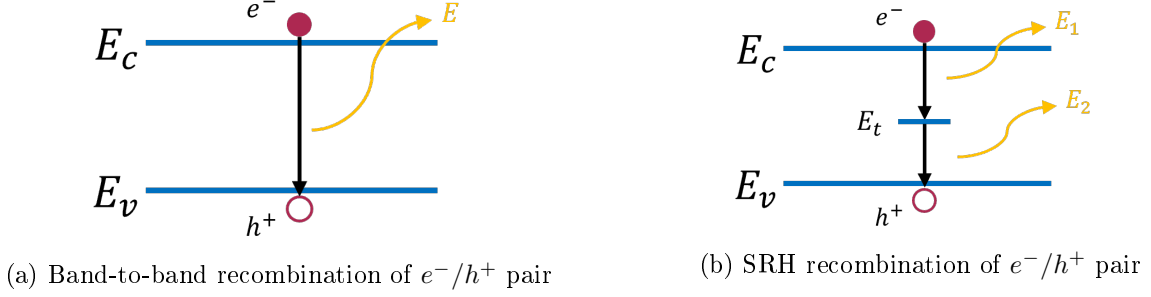


Figure 2.1.8: Schematic representation of the band-to-band and SRH recombination mechanism

The electron is first captured by the trap, going from the conduction band to an intermediate energy state E_t . It is then reemitted from that state into the valence band where it recombines with a hole. This process is the predominant recombination process in solar cells.

For SRH recombination to take place, the trap state needs to be able to capture and emit charges, interacting with both the conduction and valence band. This is the case of defects which have their energy level inside the bandgap. They can capture and emit charges, therefore acting as intermediate states for recombination. This mechanism is described in section 2.3.1.

Two different types of defects exist: bulk defects and interface defects. Bulk defects are present inside a material, depending on the quality and the nature of the material. Interface defects are present between different layers, originating from the fabrication process and the potential lattice incompatibility between the different layers. Lattice incompatibilities can result in vacancies or dangling bonds that act as recombination centers. In CIGS solar cells, defects have a particularly great impact on performance. This is introduced in the next section, and extensively discussed in this work.

Mathematically, the SRH recombination rate is expressed as [9]:

$$U = \frac{pn - n_i^2}{\tau_0 \left(p + n + 2n_i \cdot \cosh \left(\frac{E_t - E_i}{kT} \right) \right)} \quad (2.1.10)$$

where τ_0 is the minority carrier lifetime given by:

$$\tau_0 = \frac{1}{\sigma_0 \cdot v_T \cdot N} \quad (2.1.11)$$

with σ_0 [cm^2] the capture cross section, which is in this case assumed to be the same for electrons and holes, v_T [cm/s] the thermal velocity and N [cm^{-3}] the total density of states available, among which the ones of the defects. Qualitatively, it makes sense that the lifetime of the carrier depends

on these parameters. The lifetime of a carrier would be high if

- (a) σ_0 , a measure of how close a carrier must be to the trap for being captured, is small.
- (b) v_T , the speed of the charge in the lattice, is small.
- (c) N , the number of available states for the charge to occupy, is small.

In equation (2.1.10), the recombination rate is lower for a higher carrier lifetime. Moreover, the recombination rate also depends on the position of the trap state in the bandgap, and more precisely on the difference $(E_t - E_i)$. The closer the trap is to the centre of the bandgap, the higher the recombination rate is. Physically, this can be explained knowing that SRH recombination is a two-step process: first a charge must be captured from one band and then it needs to be re-emitted to the other. For both steps to be the most likely and the fastest, the intermediate state must be close to each of the two bands it is exchanging charges with, hence be close to the centre of the bandgap.

Defects and non-radiative recombination in general also have an impact on the IV characteristic of the solar cell. The introduction of SRH recombination leads to a modified current in the solar cell. Also from [9], the junction current of the solar cell becomes:

$$I_s \cdot \left(\exp \left(\frac{q(V)}{m k T} \right) - 1 \right) \quad (2.1.12)$$

with m the junction ideality factor. When no SRH recombination is considered, $m = 1$. When recombination currents are introduced, $m = 2$.

In this section, a general theory of solar cells was presented. Because the focus of this work is the study of CIGS solar cells, the next section presents their main characteristics, and the necessary adaptation to the general theory.

2.2 CIGS solar cells

The structure of CIGS solar cells was introduced before in section 1.2. They fundamentally work in the same way as basic solar cells. In a first section, the main particularities of CIGS solar cells are described. In a second section, loss mechanisms are adapted to the CIGS case.

2.2.1 CIGS/CdS heterojunction

The main difference between CIGS solar cells and the more traditional cells is that the PN junction is not a homojunction. These are composed of two layers of the same material, that are doped with different impurities to constitute a p- and n-type layer. In an heterojunction, such as the CIGS/CdS junction, two different materials are used.

The CIGS layer is a p-type semiconductor and is called the absorber, because it is the layer where the charge carriers are generated. The CdS layer is a n-type semiconductor and is called the buffer layer. Together, these two layers create a depletion region at their interface, and thus also an electrical field that is responsible for charge separation. As mentioned in section 2.1.1, the doping of the n-type layer N_D is much greater than the doping of the p-type layer N_A . For this reason, equations (2.1.4) and (2.1.5) are also valid for CIGS solar cells.

As presented in [9], the main particularity of an heterojunction compared to a standard PN homojunction is the difference of bandgap between the two materials. The bandstructure of the junction is different, with a barrier present at the interface between the two layers. The complete bandstructure of a CIGS solar cell is represented in figure 2.2.1.

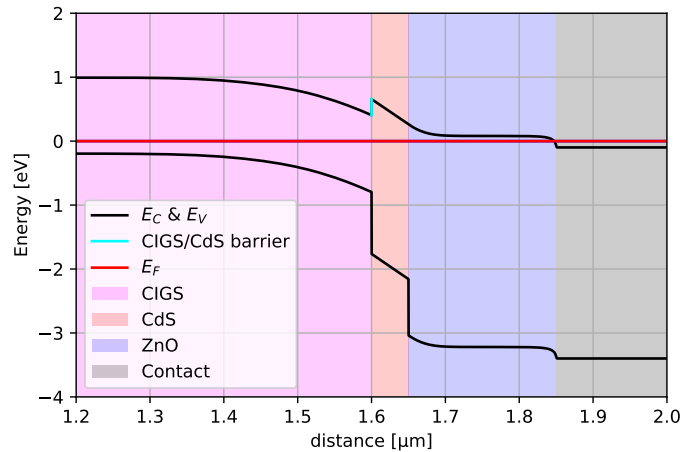


Figure 2.2.1: Simulated bandstructure of a CIGS reference solar cell using the SCAPS model from appendix B.2.

The CIGS/CdS barrier alters the behaviour of charges at the interface between the two materials,

compared to an homojunction where there is no discontinuity in the bands. The barrier and its impact on the solar cell is developed in section 2.3.8 and 2.4.3.

2.2.2 Bandgap grading

Another very particular aspect of the CIGS layer is that its bandgap is not uniform over the entire thickness, as explained in [12]. This is called bandgap grading, and it is realized by changing the Ga/(In+Ga) ratio over the thickness of the CIGS layer. Different possibilities of grading exist, such as normal grading with the bandgap increased at the back or double grading with a minimum bandgap at a certain place in the layer and higher bandgap at the edges.

The light spectrum being constituted of higher and lower energy light, depending on its frequency, it is important that the bandgap of CIGS is not too high. Indeed, increasing the bandgap increases the energy necessary to promote electrons to the conduction band, reducing the range of photons that can be absorbed. On the flip side, a great benefit from a higher bandgap at the back is the improvement of charges separation, thanks to the additional generated electrical field. Moreover, the bandgap close to the edges also has a big influence on the interface structure, with the CdS at the front and the Molybdenum at the back, which can also help with increasing the efficiency of the cell. Bandgap grading is an important feature of CIGS solar cells and must therefore be carefully designed and executed. The action of bandgap grading on cell performance is discussed in section 2.4.2.

2.2.3 Electrical losses

External losses

Series and shunt resistances are also present in CIGS solar cells, and their presence can also significantly impact the performance. They are briefly introduced here and discussed in more details further in this work.

Series resistance is mostly related to the front and rear contacts, as in other PV technologies. At the front, the Schottky contact that is formed at the interface between the metallic grid and the ZnO layer is associated with a certain non-negligible resistance [9]. A metal that has a work function adapted to the ZnO layer is thus essential to lower this resistance. At the rear side, the CIGS and Molybdenum layer form together another Schottky contact that must be correctly engineered. On top of this, oxidation of the grid also plays a role and can increase the series resistance contribution with time.

Shunt resistance is related to the inherent roughness of CIGS absorbers [13]. Because they do not have a flat surface, the coverage of the absorber when depositing the thin CdS and ZnO layers on top is generally not uniform. When depositing the front electrical contacts afterwards, there can be places where a direct connection between the front contact and the CIGS exists. This results in current leakages.

Bulk and interface defects

The main challenge and limiting factor in terms of performance for modern thin-film, and more specifically, CIGS solar cells is the high quantity of defects in the device [3, 4]. In particular, the high number of defect states at the different interfaces as well as a high bulk defects concentration in the absorber layer lead to an increased recombination rate and reduction of cell performance. Two different types of defects can be present: bulk and interface defects.

Bulk defects inside the CIGS layer can cause very significant performance loss, because charges are capable of recombining directly where they are generated. The presence of these defects is partly linked to the polycrystalline nature of CIGS. It is constituted of grains of various shapes, sizes and crystallographic arrangements. In function of the growth process and conditions that are used, the overall structure can vary greatly, leading to a very different concentration in bulk defects [4].

The most significant recombination losses in high efficiency CIGS cells happens at the different interfaces [3]. At the front interface (CIGS/CdS), the different lattice constants of the materials as well as the fabrication process are mostly responsible for increased defect density [14]. At the rear interface (Mo/CIGS), the bandgap grading in CIGS induces strain in the lattice leading to point defects, dislocations and lower absorber quality overall that enhances recombination [4].

Overall, the mitigation of these defects in CIGS is a very important research aspect in this field. Different ways of reducing the action of these defects are presented in section 2.4. In order to identify them, a characterization methodology is needed. The technique used in this work, admittance spectroscopy, is presented in details in the next section.

2.3 Admittance spectroscopy for defects characterization

It is underlined in the previous section that defects play an predominant role in the reduction of performance in thin-film PV cells. This is why a method for characterizing these defects is necessary. More precisely, it would be of interest to know the nature of the defect (bulk, interface), its activation energy E_A and capture cross-section σ as well as other parameters that are presented further.

One particularly powerful method that can be used for this characterization is the analysis of admittance measurements. Because defects capture and release electrons, their charge state vary. This has a direct influence on the total admittance of the device and more particularly on its capacitive part. By measuring the device under different voltage biases, at different frequencies and at different temperatures, the parameters of interest can be extracted. The development of this method is greatly inspired by [15, 16] and is completed by [17].

For the presentation and the illustration of this method, a SCAPS [8] solar cell model is used. Its characteristics are detailed in appendix B.2 and it is simply described throughout this entire section as the "reference CIGS model".

2.3.1 Charge state of defects

There are two types of defects, donors and acceptors. Each of these can be either ionized, i.e. carrying a positive or negative charge, or neutral. For an acceptor defect (A), the ionization equation is:



Where A^0 is the neutral acceptor atom and A^- is the negatively charged acceptor ion. The acceptor defects considered in this work are typically exchanging holes with the valence band. The charge state of the impurities is deduced from the probability of occupancy of the acceptor level, which follows the Fermi-Dirac distribution as explained in [9]. The statistics is adapted by using the acceptor energy level E_a and using a degeneration factor of 1/2. This accounts for the fact that the acceptor energy level can only host one electron and not two as stated by the Pauli exclusion principle, leading to the following Fermi-Dirac distribution:

$$f(E_a) = \frac{1}{1 + \frac{1}{2} \exp[(E_F - E_a)/kT]} \quad (2.3.2)$$

where E_F is the energy of the Fermi level. Since this distribution gives the probability for the defect state to be occupied, it also is the complementary of the probability for the defect to be ionized. The direct consequence of (2.3.2) is that for a certain value of E_a , the probability of ionization is either very close to 0 (for $E_a > E_F$) or very close to 1 (for $E_a < E_F$). This is also visible in figure 2.3.1a.

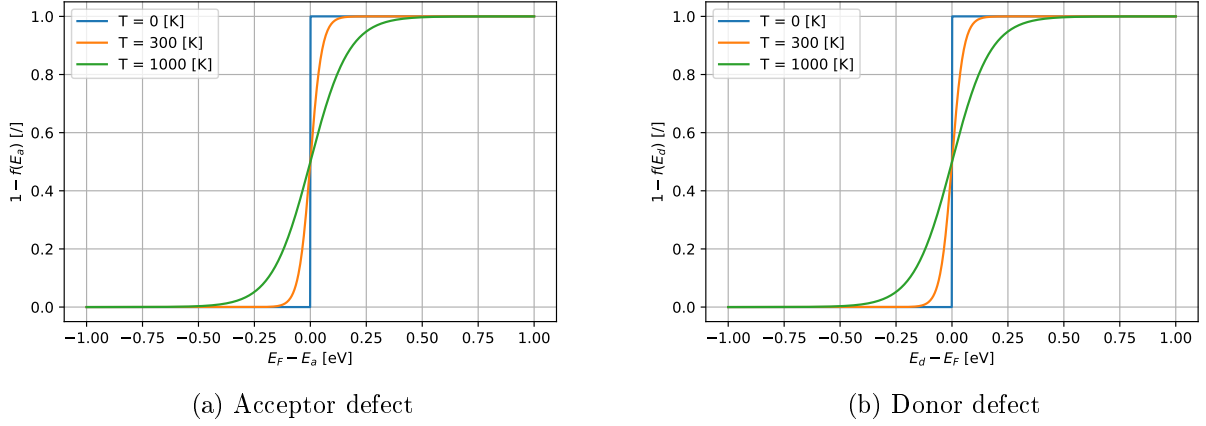


Figure 2.3.1: Probability of ionization of a defect (complementary of Fermi-Dirac distribution)

The same reasoning applies to a donor defect (D) for which the ionization equation is:



Where D^0 is the neutral donor atom and D^+ is the positively charged donor ion. The donor defects considered in this work are typically exchanging electrons with the conduction band. Following the same reasoning as hereabove and with an energy level E_d , its probability of occupancy is:

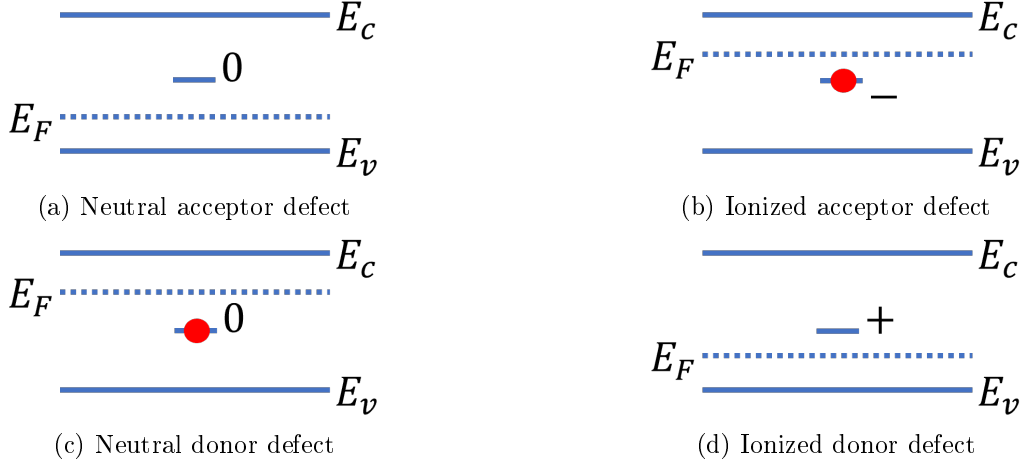
$$f(E_d) = \frac{1}{1 + \frac{1}{2} \exp[(E_d - E_F)/kT]} \quad (2.3.4)$$

Again, the probability for the defect to be ionized is the complementary of the probability of occupation of the state. It is either very close to 0 (for $E_d < E_F$) or very close to 1 (for $E_d > E_F$). This is also visible in figure 2.3.1b.

At this point, the impact of temperature on the probability of ionization of the defect must be shortly discussed. Its impact is clearly visible in figure 2.3.1. It is negligible when the Fermi level is far from the energy state of the level, but more important when the Fermi level is closer. For the sake of simplicity, the rest of this section considers defects to be either ionized or not, disregarding the probability function, even though this is not exactly correct and impacts the actual defects response.

A summary of the different possible charge states of the defects, depending on the position of the Fermi level, is presented in figure 2.3.2. Acceptor defects are ionized when the Fermi level is above them ($E_F - E_a > 0$) and donor defects are ionized when the Fermi level is below them ($E_d - E_F > 0$).

The concept of charge state of the defects is really fundamental to understand the concept of AS. Indeed, because defects only contribute to the total capacitance when they are ionized, a change of fixed charge is observed when the Fermi level moves across the defect state. The next section focuses on defects time constant, a metric of the kinetics of charge capture and release.


 Figure 2.3.2: Possible charge states of defects depending on E_F

2.3.2 Time constant of defects

Defect change their charge state through two different processes: capture and emission. Charge capture happens when an ionized defect attracts a charge. Charge emission happens when a neutral defect gives away its charge. The type of carrier involved depends on the type of defect: a hole for an acceptor defect and an electron for a donor defect. Each of these two phenomena are linked to a different time constant, as developed further.

Charge capture is a relatively straightforward process as the carrier goes from a high energy level state to a lower energy level state, with the release of a photon in the process. For this reason, the associated time constant τ_c , as explained in [9], is simply the carrier lifetime τ_0 from equation (2.1.11):

$$\tau_c = \frac{1}{2\pi f_c} = \tau_0 \quad (2.3.5)$$

In CIGS, τ_0 is generally in the order of 1-100ns. Typical values $\sigma_0 = 10^{-15} \text{ cm}^2$; $v_T = 10^{-7} \text{ cm/s}$; $N_c = 10^{-18} \text{ cm}^{-3}$ give $\tau_0 = 10 \text{ ns}$. Admittance measurements on solar cells are generally done in the 1 kHz - 1 MHz range, for reasons that are detailed in section 2.3.6. This implies that the charge capture mechanism, that has a response frequency in the order of GHz, is too fast to be observed.

Charge emission on the other hand, is a slower process because it requires energy absorption from the lattice. The time constant τ_e has an added term corresponding to the thermal activation of the process. It leads to:

$$\tau_e = \frac{1}{2\pi f_e} = \tau_0 \cdot \exp\left(\frac{E_A}{kT}\right) \quad (2.3.6)$$

with E_A the activation energy of the defect. It is defined as the difference between the defect's energy state, previously called E_a for an acceptor and E_d for a donor, and the band it is exchanging charges with, E_V or E_C . The exponential term in equation (2.3.6) is always greater than one because E_A is always taken positive. This implies that $\tau_e > \tau_c$.

Following this development, it appears that the emission process mostly determines the defect time response τ_t , and thus its characteristic frequency f_t . This leads to the following equation:

$$f_t = \frac{1}{2\pi\tau_t} = \sigma \cdot v_T \cdot N \cdot \exp\left(\frac{-E_A}{kT}\right) \quad (2.3.7)$$

It depends on two parameters that vary from one defect to the other: E_A and σ , as well as on one external parameter: the temperature. E_A and σ are unknown and can hopefully be extracted from admittance measurements. The temperature can be used as a variable of adjustment on the measurement (section 2.3.7).

With the value $\tau_0 = 10\text{ns}$ taken at room temperature, it is possible to make a plot of the response frequency versus the activation energy E_A for defects in CIGS, as shown in figure 2.3.3. There, it appears that some defects have indeed a response frequency in the range of the admittance measurement. This further motivates the use of this technique.

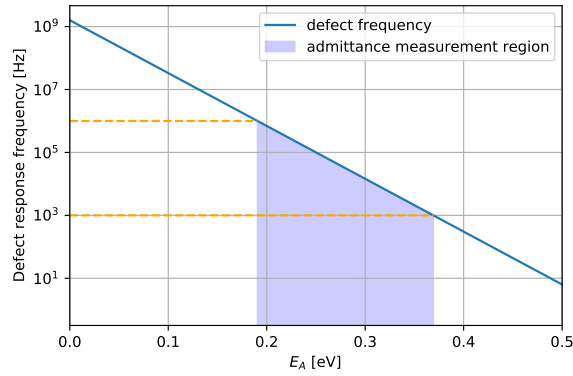


Figure 2.3.3: Response frequency of defects with usual values for CIGS, inspired from [16]

2.3.3 Shallow and deep defects

Before developing the AS method, the notion of defects depth in the bandgap must be introduced. In the previous section, the importance of E_A , which is linked to the defect position in the bandgap, is underlined. This enables another classification for defects: shallow defects that are close to the bandgap edges, and deep defects that are closer to the middle of the bandgap. Shallow defects have a small E_A and thus respond to higher frequency excitations. Deep defects have a great E_A and thus respond to lower frequency excitations.

Quantitatively, the limit between shallow and deep defects is set at $E_A = 40\text{ meV}$. Because $kT \approx 26\text{ meV}$ at room temperature, the position of the quasi-Fermi level for these defects is such as they are permanently ionized. Therefore, these shallow defects are often considered to act as doping elements. Their contribution to the total charge is constant and thus not relevant to AS measurements. On the contrary, deep defects are ionized at room temperature only if the position of the quasi-Fermi level is modified, for example when applying a bias. Because of this, they sometimes cause a change

of fixed charge in the device, which is detected with AS. The region for shallow and deep defects is represented in figure 2.3.4.

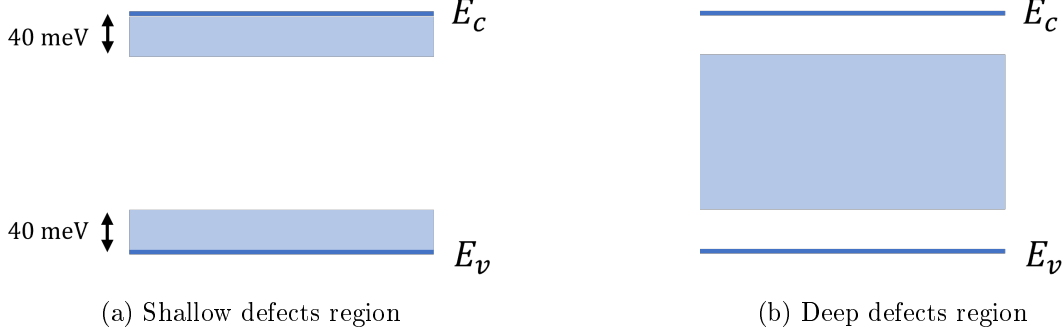


Figure 2.3.4: Type of defect vs their position in the bandgap, inspired from [16] (not to scale)

2.3.4 Admittance measurement

Admittance measurements are used in numerous applications and fields of research. This section aims at presenting its use in the context of solar cells characterization and more precisely to justify how it helps detecting defects and other loss mechanisms.

An admittance $Y(\omega)$ is an electrical quantity representing the parallel connection of a capacitance and a conductance, that both depend on the measurement frequency [17]. It is expressed as:

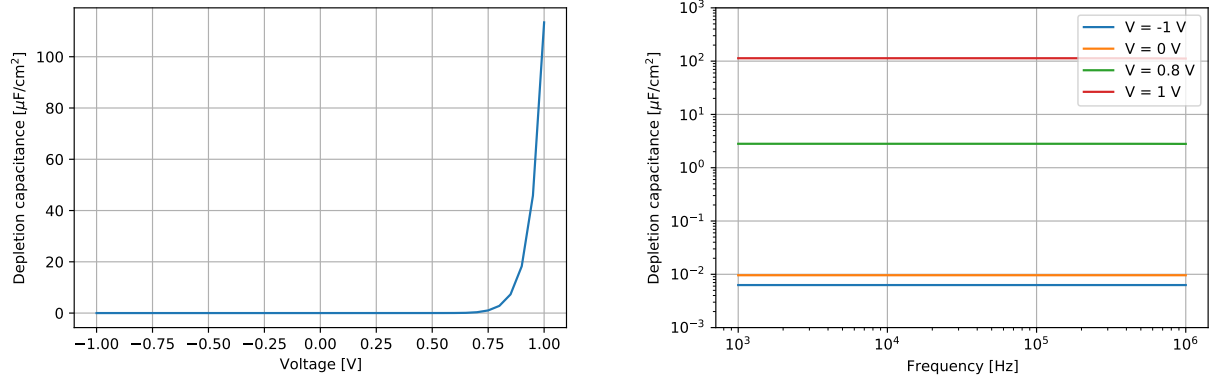
$$Y(\omega) = G(\omega) + j\omega C(\omega) \quad (2.3.8)$$

The two parts of this admittance, the conductance $G(\omega)$ and the capacitance $C(\omega)$, are linked to each other through the Kramers-Kronig relations. These prove mathematically that the analysis of the two quantities is equivalent [18]. In this work and in the literature [15, 17, 19], the focus is typically put on capacitance measurements because they are less affected by parasitic conductive elements.

Intuitively, the capacitance of an ideal solar cell is linked with the charge separation in the depletion region of the PN junction. For an ideal PN junction, the depletion capacitance, that is derived in section 2.1.1 is the following:

$$C_d = \frac{\varepsilon_s}{w_d} = \sqrt{2q\varepsilon_s \cdot \frac{N_A}{(\Phi_0 - V_a)}} \quad (2.3.9)$$

An example of the evolution of C_d in function of the voltage is represented in figure 2.3.5a. When the voltage is increased in forward bias, the depletion width decreases, resulting in an increased capacitance. Moreover, the value of capacitance at a certain bias point does not vary with frequency, as shown in figure 2.3.5b. This is normal since the depletion length is independent from frequency.

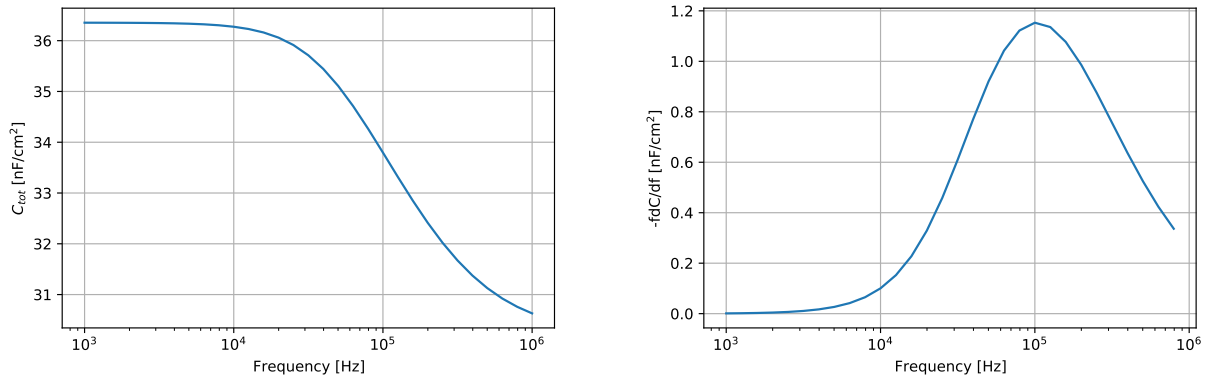


(a) Depletion capacitance in function of applied voltage (b) Depletion capacitance in function of frequency

Figure 2.3.5: Behaviour of the depletion capacitance for a reference PN junction (SCAPS)

In real solar cells, because of the presence of multiple other contributors to the total capacitance such as defects, the total capacitance becomes frequency dependent. These contributions all have a characteristic frequency beyond which they do not contribute to the capacitance anymore.

Suppose a defect in a solar cell, the energy state of which would be the same as the Fermi level. If an AC voltage is applied, the defect state successively charges and discharges as the Fermi level is moving across it. A condition for this to happen is that the carriers are fast enough to follow the AC signal. It is possible to establish that there is a certain frequency, the response frequency of the defect, above which it does not contribute to the capacitance anymore. Indeed, at high frequencies, the emission process is not fast enough for the carriers to follow the AC signal anymore. This is represented in figure 2.3.6a, where a bulk defect is responsible for an increased capacitance at low frequency and stops contributing at higher frequency.



(a) Total capacitance in function of frequency

 (b) $-dC/df$ in function of frequency

Figure 2.3.6: Total capacitance and its derivative, at 0V bias and for a reference CIGS model where an acceptor bulk defect has been added (SCAPS)

The response frequency of the acceptor defect f_t is computed using the parameters of the defect from

appendix B.2 and equation (2.3.6):

$$\begin{aligned} f_t &= \frac{1}{2\pi} \cdot \sigma_0 \cdot v_T \cdot N_v \cdot \exp\left(\frac{-E_A}{kT}\right) \\ &= \frac{1}{2\pi} \cdot 10^{-15} \cdot 10^7 \cdot 1.8 \cdot 10^{19} \cdot \exp\left(\frac{-0.326}{0.35}\right) \approx 100 \text{ kHz} \end{aligned} \quad (2.3.10)$$

This is the frequency at which the step occurs in figure 2.3.6a. Another way of representing the defect response is to take the opposite of the capacitance derivative with respect to frequency, multiplied by the frequency ($-f dC/df$). This is done in figure 2.3.6b and results in a peak at the frequency response of the defect. This representation isolates the change in capacitance, allowing an easy extraction of the response frequency of the defect.

In this development, it is shown that capacitance measurements can yield interesting information about defects frequency response and contribution to the device total charge. In the presented example, only one single bulk defect is added to the structure. In a real solar cell, the total capacitance is the sum of the different contributions (defects, series resistance, barriers at interfaces, ...), which results in a frequency response that generally is much harder to interpret. This is discussed further in section 4.2.

2.3.5 Voltage dependency

In the previous section, only the frequency dependence of defects is taken into account. A 0V bias voltage is considered and the added defect has an energy level that is crossed by the Fermi level at that bias point. This section introduces another dimension in the measurement, with the variation in bias voltage.

From the PN junction theory, it is known that the quasi-Fermi level for holes and electrons can be moved by changing the bias voltage [9, 10]. The effect of different voltages on the bandstructure is represented in figure 2.3.7.

At zero bias voltage (figure 2.3.7b), the Fermi level crosses the energy state of the defect which then becomes ionized and contributes to the total charge. This situation is the same as in figure 2.3.6. When changing the bias voltage, the Fermi level splits into two quasi-Fermi levels, for holes and electrons. Here, because the defect is an acceptor, its behaviour is determined by F_p , the quasi-Fermi level for holes. When it is above the defect level, the defect is ionized and contributes to the total capacitance (figure 2.3.7a & 2.3.7b). On the contrary, when it is below the defect level, the defect stays neutral and does not contribute to the total capacitance (figure 2.3.7c & 2.3.7d).

2.3. ADMITTANCE SPECTROSCOPY FOR DEFECTS CHARACTERIZATION

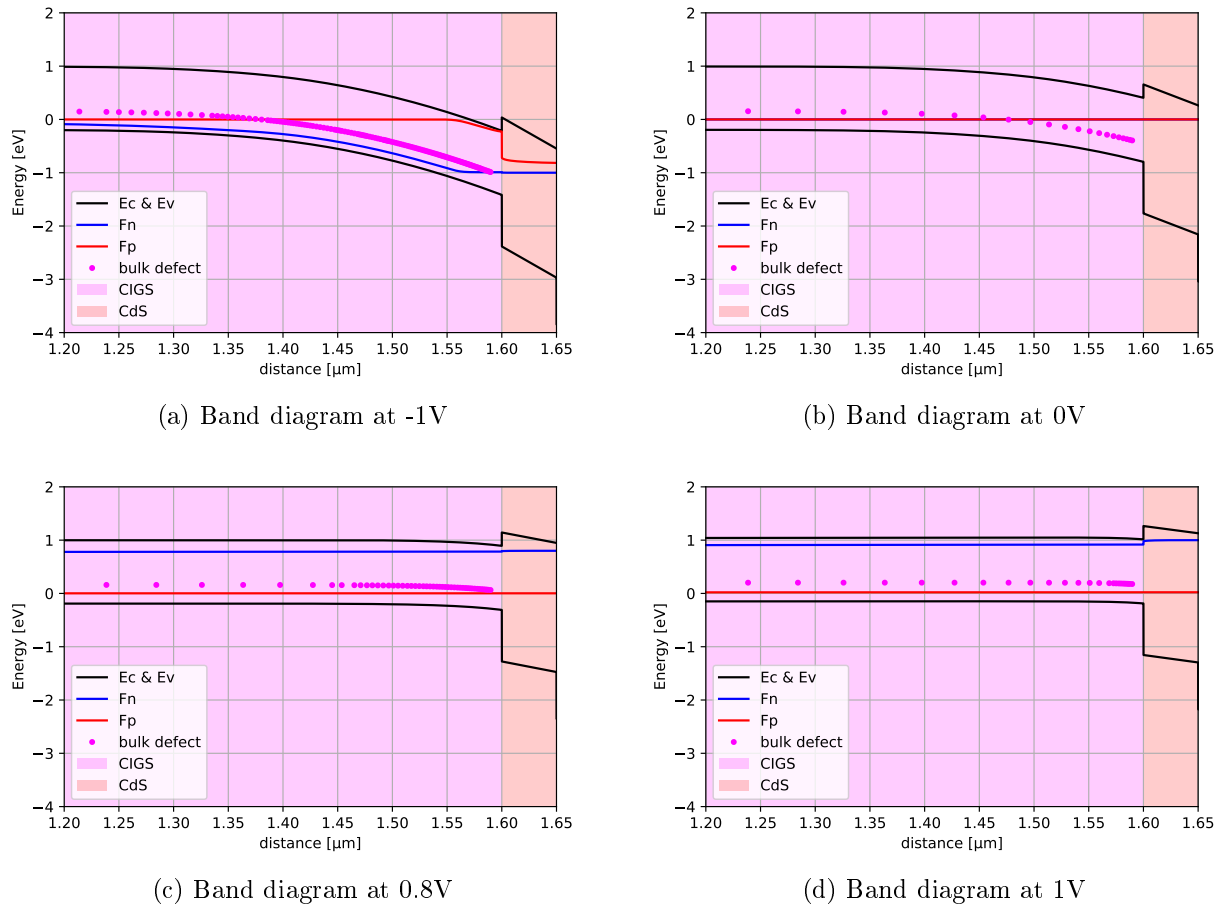


Figure 2.3.7: Band diagram for a reference CIGS model with the same acceptor bulk defect as in previous section, at different voltage biases (SCAPS).

This contribution to the total capacitance is visible when looking at the C_f characteristic at different voltage biases, in figure 2.3.8a. For the sake of clarity, the normalized capacitance curves are shown.

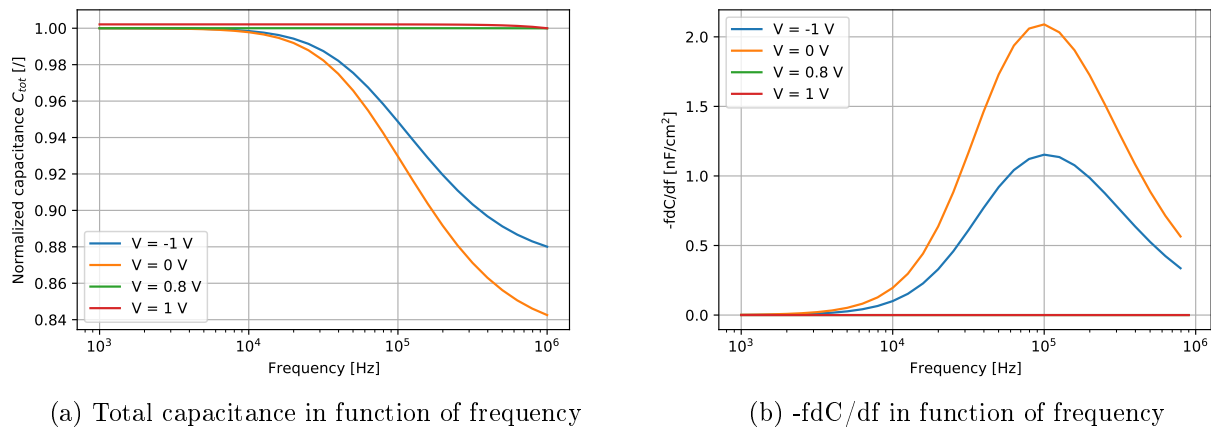


Figure 2.3.8: Total capacitance in function of frequency, at different biases and for a reference CIGS model where a bulk acceptor defect has been added (SCAPS).

For $V = -1V$ & $V = 0V$, there is a step in capacitance due to the action of the ionized defect that contributes only at low frequencies. On the contrary, for $V = 0.8V$ & $V = 1V$, the capacitance is constant which suggest an inactive (neutral) defect. The response of the defect is also visible when considering the $-f dC/df$ characteristic such as in figure 2.3.8b. A peak in capacitance indicates an active defect. On the contrary, an inactive defect results in a constant capacitance with frequency, and thus a derivative equal to zero.

In this section, the impact of voltage bias on the defects and the way they contribute to the total capacitance is shown. Two different parameters, the frequency and the voltage, can be changed to try characterize the defect. Next section goes one step further, by proposing a visual representation that helps with defects characterization.

2.3.6 CVf loss maps

It is now established that the derivative of capacitance with respect to frequency ($-f dC/df$) is an efficient way of representing the response of defects. This is also suggested in [15]. Using this metric, is also possible to represent an entire voltage sweep from $-1V$ to $1V$, such as in figure 2.3.9a.

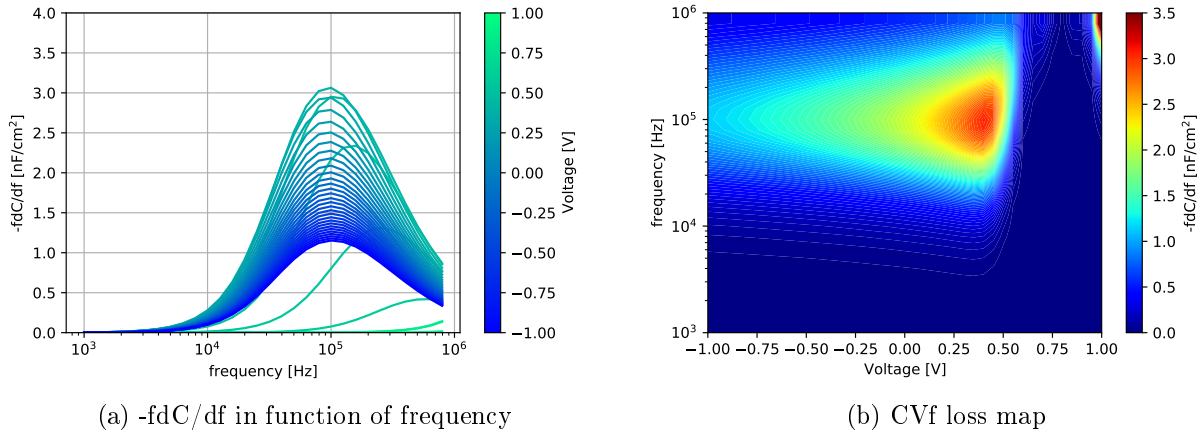


Figure 2.3.9: $-f dC/df$ in function of V & f for a reference CIGS model where a bulk acceptor defect has been added (SCAPS).

By looking closely, it is possible to see that the contribution in capacitance increases from $-1V$ to reach a maximum around $0.5V$ and then decreases to finally have no contribution anymore at $1V$. Also, the defect response is localized at higher frequencies. Even though the defect's peak is clearly visible, this representation is not yet the most easy to read and to interpret. The same information can be represented differently on a so-called "loss map" [15], such as in figure 2.3.9b, where the response of the defect appears in a more visual way. The name of this representation comes from the fact that every signature corresponds to a charge loss event. The present defect has a large signature in voltage bias, coming from the fact that the Fermi level is crossing the defect state at many different biases. In the frequency range, it is mostly concentrated around the 100kHz response frequency that characterizes the defect.

An important limitation to the interpretation of these loss maps is the conductive behaviour of solar cells in forward bias [17]. Because a solar cell is a PN junction, there are high current that flow through the device beyond the threshold voltage. Capacitance is typically measured with a LCR meter (see section 3.3.2), whose accuracy is only preserved when the amplitudes of the capacitive and conductive parts of admittance have similar orders of magnitude. This can be monitored through the dissipation factor D defined as [20]:

$$D = \frac{G_m}{2\pi f C_m} \quad (2.3.11)$$

where G_m and C_m are the measured values of conductance and capacitance, and f is the measurement frequency. This factor must typically be lower than 10 in order for the measurement to be accurate [21]. In figure 2.3.10, the dissipation factor from an experimental measurement is represented.

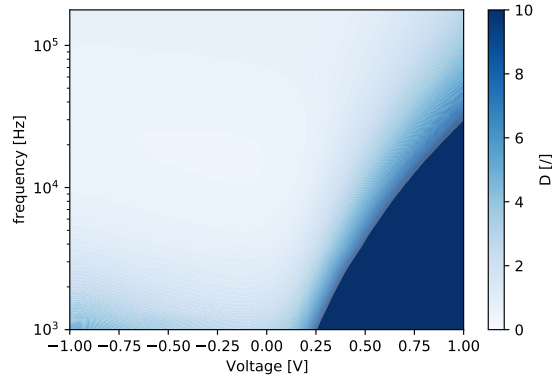


Figure 2.3.10: Dissipation factor in function of V & f for a CIGS cell (experimental data).

In forward bias, the dissipation factor is large due to the high DC current. The measurement accuracy is poor in that region. For negative bias and low frequencies, the dissipation factor also increases due to reverse leakage current. The best measurement, over an entire range of frequencies, occurs around 0V when there is no current. This dissipation factor is commonly used to determine the regions of the loss map where the capacitance data are reliable and accurate [15].

Another restriction in the AS method is the usable frequency range for the measurement. This range is mostly determined by the accuracy of the measurement that is done on the capacitance. For high frequencies, the measurement is limited due to the action of the series resistance that plays an important role in the total measured capacitance [22]. This is detailed in section 2.3.8. For this reason, admittance measurements are generally not performed above 1MHz. At low frequencies, there is no real physical limitation preventing the measurement, but the capacitance extraction can become more difficult due to the tool sensitivity to noise that is more important [21]. For this reason, admittance measurements are generally not performed below 100Hz, or 1kHz in the case of this work.

Even though they offer a very visual representation, loss maps are not so easy to interpret. Very different contributions could have a similar effect on the capacitance and result in a very similar

signature. In order to facilitate the interpretation of these measurements, SCAPS simulations are often used as a sensitivity analysis tool to understand the impact of the different contributions to the capacitance on the loss map. This is done in section 4.2.

2.3.7 Temperature dependency

In a previous section, it was pointed out that the frequency response of defects depends on two parameters: the capture cross-section σ and the activation energy E_A . Unfortunately, using room temperature measurements, it is impossible to extract these two parameters independently from each other. For this reason, a new dimension is introduced: the variation of the measurement temperature.

The kinetics of a thermally activated process is commonly described by the Arrhenius equation [23]:

$$k = k_0 \cdot \exp\left(\frac{-E_A}{RT}\right) \quad (2.3.12)$$

where k is the kinetic reaction rate, k_0 is the pre-exponential factor, E_A is the activation energy, R is a thermodynamic constant and T is the absolute temperature. In the case of the charge emission rate e_t from a certain energy level, here the defect level, the equation is rewritten as [24]:

$$e_t = 2\pi f_t = \xi_0 T^2 \cdot \exp\left(\frac{-E_A}{kT}\right) \quad (2.3.13)$$

with f_t the trap characteristic frequency as defined before, and $\xi_0 T^2$ the pre-exponential factor. This can directly be related to equation (2.3.7) deriving the expression of f_t . By association:

$$\xi_0 T^2 = \sigma \cdot N_0 \cdot v_{T,0} \quad (2.3.14)$$

The T^2 contribution here comes from the temperature dependency of both the thermal velocity ($v_T = T^{1/2} \cdot v_{T,0}$) and the density of states ($N = T^{3/2} \cdot N_0$). Finally, the Arrhenius equation is derived in the two following ways:

$$\frac{\omega_t}{T^2} = \sigma \cdot v_{T,0} \cdot N_0 \cdot \exp\left(\frac{-E_A}{kT}\right) \quad (2.3.15)$$

$$\log\left(\frac{\omega_t}{T^2}\right) = \log(\sigma \cdot v_{T,0} \cdot N_0) - \frac{E_A}{1000k} \cdot \frac{1000}{T} \quad (2.3.16)$$

Equation 2.3.16 is usually preferred because it puts in evidence the two parameters used for graphical representation, in [blue](#). By using admittance measurements versus bias and frequency, different characteristic frequencies can be extracted for each measurement temperature. These points are then plotted on the so-called Arrhenius plot, such as in figure 2.3.11.

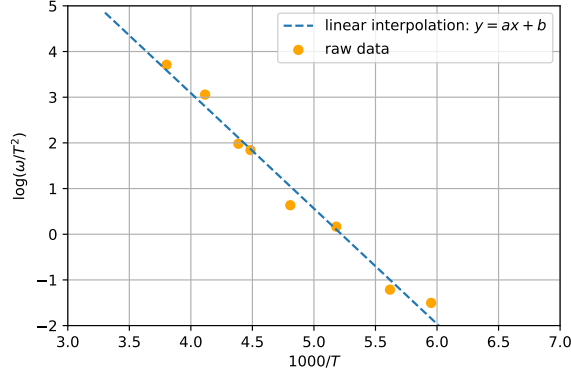


Figure 2.3.11: Arrhenius plot made from low temperature experimental data.

The raw data is then fitted to a linear model that allows the extraction of σ and E_A as follows:

$$\begin{cases} \sigma = \frac{e^b}{v_{T,0} \cdot N_0} \\ E_A = -a \cdot 1000k \end{cases} \quad (2.3.17)$$

This methodology enables an almost full characterization of the defect. The last defect's parameter, the defect density, could also be extracted but this requires a more complex and thorough analysis that is beyond the scope of this work.

The complete characterization of defects using AS was presented. The two next sections focus on additional considerations: the extension of this method to other loss mechanisms and the use of admittance measurement to compute the apparent doping of the CIGS layer.

2.3.8 Other loss mechanisms

Besides defects, other loss mechanisms contribute to the total measured capacitance. Two mechanisms that are well documented for solar cells are the effect of series resistance R_s at high frequencies, and the presence of a barrier at the interface between two layers. These two mechanisms and their impact on room temperature admittance measurements are presented in this section.

Series resistance

It is well known, also from the MOS theory, that series resistance plays a big role in devices frequency response. Solar cells are no exception and the impact of R_s is very often visible in admittance measurements. A simple electrical model for the solar cell that takes the series resistance into account was presented in [22] and is represented in figure 2.3.12. This model considers that the cell is placed in depletion regime and that there is a single capacitance, the depletion capacitance.

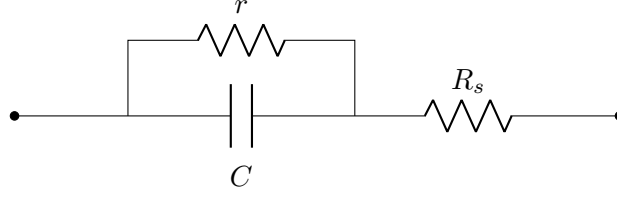


Figure 2.3.12: Model for the solar cell, taking into account the effect of series resistance. R_s is the series resistance, C is the depletion capacitance, and $r = 1/G$ is the inverse of the conductance.

From the previous model, the complex admittance is derived as:

$$Y(j\omega) = Z^{-1}(j\omega) = \left(R_s + \frac{r \cdot (j\omega C)^{-1}}{r + (j\omega C)^{-1}} \right)^{-1} \quad (2.3.18)$$

The measured capacitance C_m and conductance G_m of the device are isolated by separating equation (2.3.18) into its real and imaginary part. Here, only the capacitance is considered:

$$C_m(j\omega) = \Im \{Y(j\omega)\} = C \cdot \frac{1}{(1 + \lambda)^2 + (\omega R_s C)^2}, \text{ with } \lambda = \frac{R_s}{r} \quad (2.3.19)$$

The ratio of resistances λ is supposed to be $\ll 1$, which is a reasonable assumption since the series resistance is small (about $1\Omega \cdot \text{cm}^2$) and the conductance even smaller (about $1\text{mS} \cdot \text{cm}^2$ so $r = 1\text{k}\Omega \cdot \text{cm}^2$). In that case, it is possible to write:

$$C_m(j\omega) = C \cdot \begin{cases} 1, & \text{if } \omega \text{ is small} \\ 1/(\omega R_s C)^2, & \text{if } \omega \text{ is large} \end{cases} \quad (2.3.20)$$

This implies that for large measurement frequencies, the series resistance acts together with the depletion capacitance as a low-pass filter. On the other hand, for small measurement frequencies, the measured capacitance is simply equal to the depletion capacitance, with no effect of R_s .

It is important to note that this model stays valid when other loss mechanism of the solar cell add up to the capacitance, if the assumption is made that these contributions are purely capacitive. In that case, C that was used in previous equations is a combination of these contributions. Typically, this is the case when combining a series resistance with defects. Additional loss mechanisms that are not only purely capacitive necessitate a more complex model that depends on the type of contribution, but this is beyond the scope of this analysis.

Barrier at the CIGS/CdS interface

Another mechanism that contributes to losses in CIGS solar cells is the presence of a barrier at the CIGS/CdS interface. The parameter that has an influence on the barrier height is mainly the magnitude of the conduction band offset [25]. It changes when the electron affinity of the two materials are altered, which is itself impacted by the processing and the stoichiometry of the materials.

The barrier height has an impact on the charge flow at the interface. It is interesting to note that this phenomenon can be detrimental, such as presented in this section, or beneficial when the barrier modification is done to promote separation of charges and carrier lifetime in the solar cell. This beneficial aspect is discussed in section 2.4.3 dedicated to mitigation of loss mechanisms.

A closer view of the CIGS/CdS interface is presented in figure 2.3.13a. In this figure, a barrier limiting the electron flow from the CIGS to the CdS is visible. The barrier height can be increased by changing the electron affinity of the CdS and the ZnO such as in figure 2.3.13b. The electron affinity increased from 0.3 eV and as a consequence, the barrier increases from 0.3 eV. Charges accumulate behind the barrier which constitutes a contribution in capacitance, but also in conductance since it becomes more complicated for the charges to flow through the barrier [17].

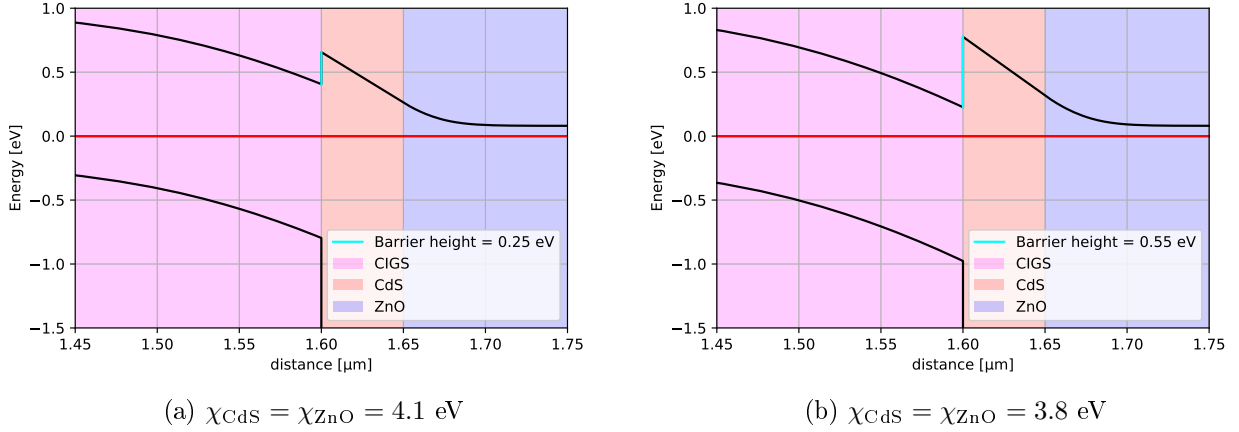


Figure 2.3.13: Bandstructure of the CIGS/CdS interface at 0V, for two different electron affinities of CdS, simulated with the reference CIGS model (SCAPS).

2.3.9 Apparent doping

The AS method already makes extensive use of the CVf measurements to characterize loss mechanisms in the solar cell. Still, other information can be extracted from such data, one of which is the analysis of the apparent doping profile described in this section.

The doping of a semiconductor layer can be deduced from CV measurements using a standard technique called "capacitance-voltage profiling" [26]. For an ideal solar cell, when considering that the device is in depletion regime, the charge density at the edge of the depletion region is written as:

$$N_A(w) = \frac{2}{q \cdot \epsilon_s \epsilon_0 \cdot A^2} \cdot \left(\frac{d(1/C^2)}{dV} \right)^{-1} \quad (2.3.21)$$

where w is the width of the depletion region and A is the area of the junction capacitance. This

doping profile is usually plotted against w which is itself derived from the measured capacitance as:

$$w(V) = \frac{\varepsilon_s \varepsilon_0 A}{C(V)} \quad (2.3.22)$$

In the case of real solar cells, the same technique and equations can be used, but the doping profile that is extracted has additional contributions [27]. These contributions come from the impact of defects and other loss mechanisms on the total capacitance. Therefore, the extracted doping profile constitutes an upper bound of the real doping and is then called "apparent doping profile".

In figure 2.3.14, the doping profile of the reference CIGS model was presented, along with the doping profile when a bulk defect is added.

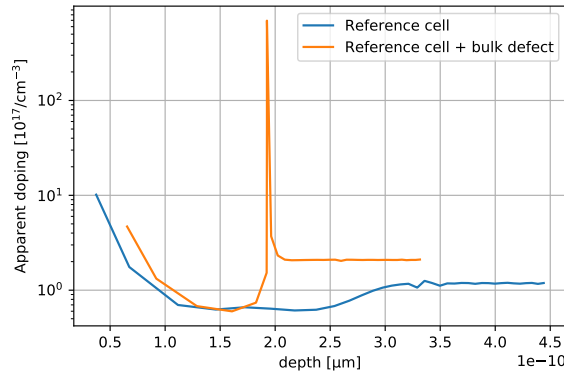


Figure 2.3.14: Doping profile extracted from CV data at $f = 10\text{kHz}$ for the reference CIGS model with and without bulk defect added (SCAPS).

As anticipated, the overall doping profile when a bulk defect is present in the structure is higher than when there is no defect. This confirms the idea that the doping profile extracted from CV measurements is a higher bound of the actual doping of the CIGS layer.

If the actual doping of the CIGS layer needs to be extracted, another technique called DLCP should be used. Measurements extracted from this technique are independent from the defects action. Moreover, the comparison between DLCP result and apparent doping profile can yield some interesting information about defects [27]. This is not developed further, as this is not the focus of this work.

This part concludes the use of admittance spectroscopy, and more generally CVf measurements, as a technique to characterize loss mechanisms in CIGS solar cells. The next section presents different mitigation mechanisms that can be used to improve solar cells efficiency.

2.4 Strategies for recombination mitigation

In section 2.2.3, the different loss mechanisms in CIGS solar cells are presented. As underlined, most of these losses have as a main effect to increase recombination at the cell interfaces and in the absorber, which itself results in reduced performance. Acting against recombination is thus essential in many ways, and this is the focus of this section.

Four general ways of reducing recombination are presented. For the first three, annealing, bandgap grading and modification of the interface barrier, the structure of the solar cell remains unchanged and care is taken about the engineering of the different layers. For the last one, interface passivation, additional layers are introduced in the device for improving interface recombination in particular.

2.4.1 Post-deposition annealing

As presented before, CIGS is a polycrystalline material that is constituted of grains of various sizes, shapes and crystallographic orientations. It is known from theory that grain boundaries are the predominant place where defects appear [14]. There is thus a direct correlation between the proportion of grain boundaries and the bulk defect density. Moreover, the bigger the grains in the CIGS, the less boundaries there are overall in the layer. In order to have a high quality absorber with low defect density, the focus must thus be put on increasing the grain size in the CIGS.

The impact of grain size on cell performance is also mathematically established, by considering the diffusion length of minority carriers in CIGS. The relation between the diffusion length for polycrystalline and monocrystalline material is given by [28]:

$$\frac{1}{(L_D^{poly})^2} = \frac{1}{(L_D^{mono})^2} + \frac{2S_g}{D_n g} \quad (2.4.1)$$

where $(L_D^{poly})^2$ and $(L_D^{mono})^2$ are the minority carriers diffusion length of the polycrystalline and monocrystalline materials respectively, D_n is the diffusion constant of electrons and S_g is the recombination velocity at the boundaries of grains with size g . This equation shows that for lower grain size, the diffusion length is also lower. The diffusion length is itself directly related to the minority carriers lifetime, through [10]:

$$L_D = \sqrt{D_n \tau_0} \quad (2.4.2)$$

A decreased diffusion length thus induces a reduced minority carrier lifetime and according to section 2.1.3 thus reduces solar cell performance.

Absorber annealing was introduced in early stages of CIGS solar cells development [3]. In [29], the impact of annealing temperature is investigated. It appears that grain growth is improved when annealing is performed, and when the temperature is increased. The impact of annealing is also validated by the experimental work of this thesis. To underline this, scanning electron microscope (SEM) pictures of a bare CIGS absorber are taken before and after annealing. This is depicted in figure 2.4.1.

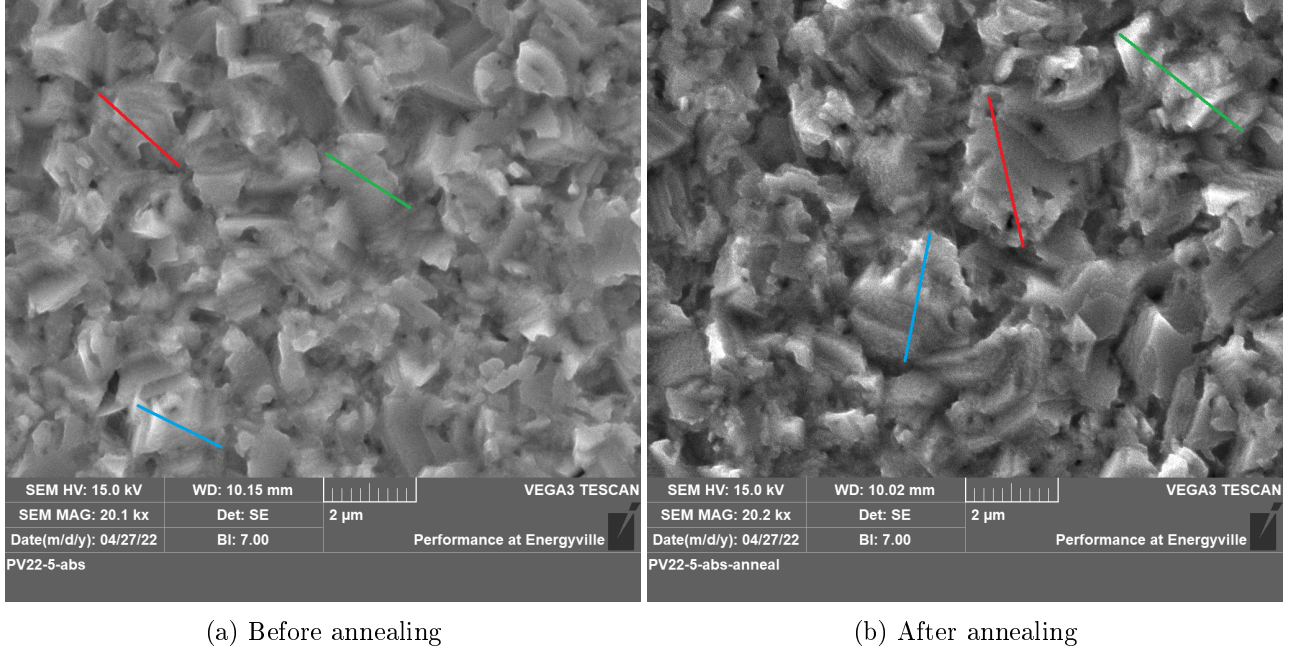


Figure 2.4.1: SEM pictures of a bare CIGS absorber, before and after annealing (150°C during 15 minutes). The bigger grains are underlined for each picture.

It appears from this picture that annealing does indeed have a positive impact on grain size. Moreover, in the present case, the annealing temperature is not very high compared to temperatures presented in [29]. It is possible that the grain size would increase even more with further annealing of the absorber. The impact of annealing on performance is presented further in this work, in chapter 5.

Even though annealing has a positive impact on performance, by increasing grain size, the temperature cannot be increased indefinitely. Indeed, when the temperature is too high, selenium vacancies appear in the CIGS which increases the recombination rate of free carriers [29]. Particular care must thus be taken for choosing the most appropriate annealing temperature, duration and environment.

2.4.2 Bandgap grading

Bandgap grading was already mentioned in section 2.2, as a tool for reducing recombination at the front and the back interfaces of the CIGS layer. The bandgap in the CIGS layer is altered by changing the Ga/(In+Ga) ratio during fabrication. One main effect results from this bandgap grading [12].

In the region where the bandgap is increased, an additional electrical field ξ_A is created [30]:

$$\xi_A = \frac{d\Delta E_g}{dx} \quad (2.4.3)$$

where ΔE_g is the bandgap variation over the distance x due to the bandgap grading. Usually, this is done at the rear interface of CIGS. Physically, the explanation is quite straightforward. When

increasing the bandgap at the rear, the conduction band is bent. This situation is represented in figure 2.4.2.

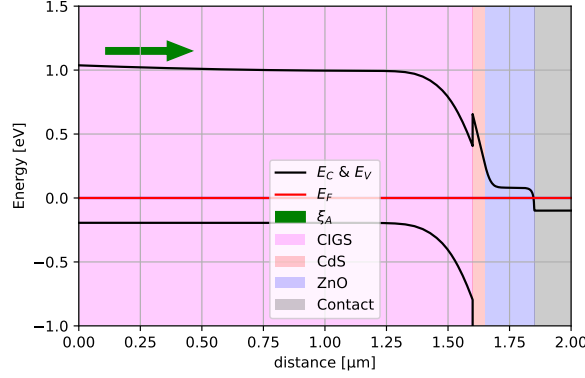


Figure 2.4.2: Bandstructure of the CIGS reference model at 0V (SCAPS). The conduction band bending at the rear contact ($x=0$) and the direction of the additional electrical field ξ_A are shown.

As a result of the band-bending, the photo-generated electrons are pushed away from the high energy zone towards the lower energy zone (green arrow) where they should be collected. Moreover, holes must be extracted at the rear side of the device which is easier in the absence of electrons with whom they would recombine. This is shown in equation (2.1.10) where U decreases when n is reduced compared to p .

Bandgap grading can also be used at the front interface, between CIGS and CdS. This is usually done through double grading, in order to preserve the beneficial characteristics from the back grading. This grading impacts the barrier at the CIGS/CdS interface which is detailed just below.

2.4.3 Interface barrier modification

As presented before, one particularity of CIGS solar cells is that there is a barrier present in the conduction band at the CIGS/CdS interface. This barrier limits the electron flow from the CIGS to the CdS, which limits the photo-generated current and results in an accumulation of charges at this interface. The effect of this barrier can be altered in different ways.

First, the height of the barrier can be altered such as in section 2.3.8 by changing the electron affinity of the CIGS or the CdS. An increased barrier height leads to a lower electron flow and a higher accumulation of charges at the interface, thus reduced performance.

Secondly, bandgap grading can be used, as mentioned hereabove. It consists in increasing the CIGS bandgap close to the interface. The grading then acts in the same way as at the back interface, by bending the conduction band upwards. This decreases the barrier height at the interface, which helps with the extraction of electrons and reduces recombination with holes.

Another possibility is to change the doping in either the CIGS or the CdS layer. This modifies the

Fermi level position, such as represented in figure 2.4.3.

With a higher CIGS doping than in the base case (figure 2.4.3a), the Fermi level crosses the interface at a very low position in the bandgap. This enables the charge and discharge of deep defects that heavily contribute to the SRH recombination [17]. With a higher CdS doping than in the base case (figure 2.4.3b), the Fermi level is pulled in a very high position at the interface. This has a positive impact since the Fermi level ability to move across deeper defects is limited and their impact is then also reduced.

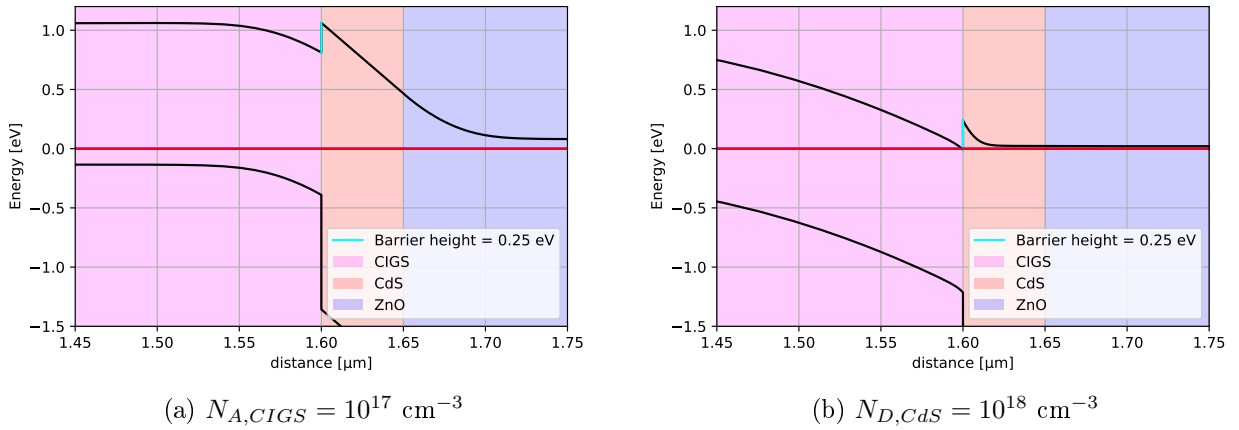


Figure 2.4.3: Bandstructure of the CIGS/CdS interface at 0V, when changing the CIGS & CdS doping, simulated with the SCAPS standard CIGS model.

The CIGS/CdS interface is very critical in terms of performance. As explained, its barrier has a direct impact on charge transport, but also on defects inside the bandgap. For optimized performance, changing only the internal parameters of the CIGS solar cell might not be enough. It might be necessary to introduce other layers whose purpose are to optimize the interfaces: a passivation layer. This is detailed in the next section.

2.4.4 Interface passivation

Interface passivation in solar cells is a concept that is nor new nor limited to CIGS applications, as it is already quite extensively used in crystalline silicon technology [31, 32]. The goal of solar cell passivation is to reduce the SRH recombination at the interfaces of the solar cell. This can be done in two ways:

1. **Field-effect passivation.** For reducing SRH recombination in solar cells, it is sufficient to strongly reduce the surface concentration of either e^- or h^+ . By imposing an electrical field directly at the interface, it is possible to repel one of the two types of carriers and therefore reduce the recombination. This electrical field is generally built using an added fixed charge of value Q_f .
2. **Chemical passivation.** For SRH recombination to take place, the density of defects must

be sufficiently large. If the density of traps D_{it} at the interface is reduced, then the SRH recombination is also reduced.

It is possible to pursue these two goals at the same time, and this is generally done using an additional thin dielectric layer at the interface that needs to be passivated. This dielectric layer has:

1. A fixed charge of density Q_f . The material can have a positive or negative charge and is chosen depending on the type of carrier that must be repelled from the interface.
2. An adequate D_{it} , that makes it compatible with both materials of the interface and makes it suitable for reducing the density of defects.

The choice of material for the passivation layer is very crucial [33]. AlO_x and HfO_x are very popular materials, because they allow to reach a very low D_{it} . SiO_x is also interesting because it can have either a positive or negative Q_f , depending on x . This means it can be used either for hole or electron passivation. Generally, a metal-insulator-semiconductor (MIS) structure is used for choosing the right passivation material. This structure enables the same growth of dielectric layer as for solar cells, but in a much simpler structure [34]. From CV measurements, it is then possible to extract Q_f and D_{it} to estimate if the layer would be a good candidate for passivation of the solar cell, such as shown in [35].

In this work, passivation of CIGS solar cells is investigated. Because passivation at the rear interface (CIGS/Mo) is already extensively discussed in the literature, passivation is tried at the front interface (CIGS/CdS) and at the interface with the window layer (CdS/TCO). Two materials are investigated: AlO_x and HfO_x . These materials both present a very low D_{it} [34]. Unfortunately, it is likely that their fixed charge is not adapted for front interface passivation. Indeed, at the front of the solar cells e^- must be extracted, which would be increased with a positive fixed charge at the interface. AlO_x and HfO_x both have a negative fixed charge [34] which makes them less suitable on that standpoint. Still, they could act as chemical passivation layers. This is investigated further in the experimental part of this work.

3 Methodology

A great methodology is important when performing experimental work. It enables an efficient coordination of the different experimentation aspects, which is essential to produce meaningful conclusions in the end. The methodology used in this work is presented in figure 3.0.1.

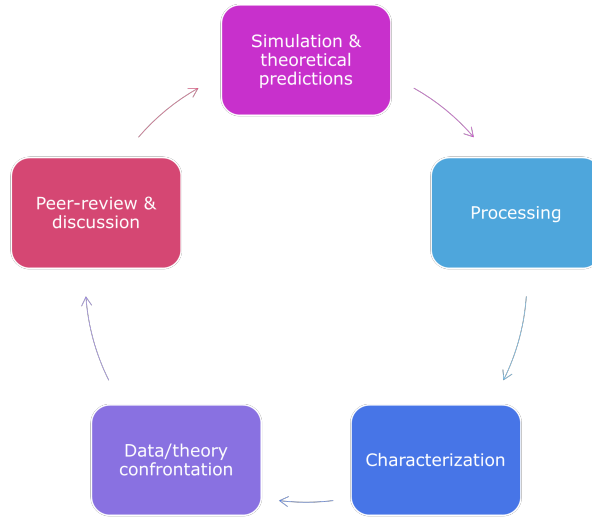


Figure 3.0.1: Work methodology

Simulation & theoretical predictions are the starting point in this work. Mainly, SCAPS simulations are undergone in order to predict the behaviour of the cells. After that, the **processing** of the cells is performed. The purpose of the actual solar cells is to validate the theoretical predictions using real-life data. Multiple **characterization** tools are used on the processed cells, to try to obtain as much data as possible, and extract the important figures of merit. By **comparing the experimental data with the data from SCAPS**, it is then possible to make educated guesses about the mechanisms at play inside the cells. Particular care must be taken when making the comparison, because these simulations are often not entirely trustworthy. Finally the conclusions drawn from the previous steps are submitted to **discussion**, in order to receive feedback and input on the quality of the analysis. From this feedback and the previous conclusions, the workflow is restarted from the beginning with a new set of experiments.

In this chapter, the different parts of the methodology and the setup used at each step is detailed.

3.1 SCAPS simulations

In this section, the SCAPS [8] software is introduced as a simulation setup for the modelization of solar cells. First, SCAPS is presented along with its main characteristics. Secondly, the motivations behind the use of this software in this work are detailed. The CIGS solar cell model is also explained. Finally, the limitations of SCAPS are discussed.

3.1.1 Presentation

SCAPS is a 1D solar cell simulator, that is developed at the Department of Electronics and Information Systems (ELIS) of the University of Gent, Belgium [8]. It enables the electrical simulation of solar cells, among which CIGS solar cells. Several types of simulations can be performed, such as bandstructure analysis, IV, CV and Cf. Furthermore, it integrates several non-idealities such as bulk and interface defects as well as series and shunt resistances, accounting for non ideal solar cells.

A solar cell model in SCAPS is built layer by layer. The different layers composing the cell are added, along with their specific characteristics: electrical properties, thickness, possible bulk defects, recombination model. The different interfaces between the layers can be customized, and interface defects in particular can be added. Finally, the work functions of the electrical contact can be adjusted.

For the electrical simulation part, numerous parameters are available. A static working point in temperature, voltage and frequency is first set. Series and shunt resistances are then added to the model. After that, the choice is made between the simulation of the solar cell in dark or illuminated conditions, with broad customization of the light spectrum. Finally, the measurement type is adjusted, with its various parameters: voltage bias range, frequency bias range and number of points. The next section focuses on the use that is made of SCAPS in this work.

3.1.2 Sensitivity analysis

The structure used in the SCAPS model is represented in figure 3.1.1. This base model of a CIGS cell is first composed of a CIGS absorber layer, with integrated bandgap grading. On top of it, a CdS buffer layer and a ZnO window layer are added. Finally, the front contact is simulated. The positive back contact represented at the bottom has its metal work function aligned with the adjacent CIGS. This is done for convergence reasons, as explained further. All the parameters used for the different materials are detailed in appendix B.2.



Figure 3.1.1: SCAPS model of the reference CIGS cell.

Because of the great customizability of the SCAPS model, it is a perfectly suited tool for sensitivity analysis. The different parameters are changed one by one, in order to identify their impact on the solar cell behaviour. Two main objectives are pursued with this sensitivity analysis:

- *Predicting experimental trends.* This includes the effect of the doping, bandgap, presence of defects and many others. It is simulated through IV and CVf measurements, but also through analysis of the bandstructure.
- *Interpreting experimental observations.* This is more specific to admittance measurements for which it is sometimes tricky to interpret the obtained signature. The purpose of SCAPS simulations here is to try to understand which loss mechanisms could correspond to a certain experimental observation.

For this second objective, defects that are not present in the ideal CIGS cell are introduced. It can be a bulk defect in the CIGS layer, or a defect present at one of the different interfaces, generally between CIGS & CdS. The AS method can also be used in SCAPS, as presented before in section 2.3.

SCAPS is thus mainly used as a way of validating the analysis of experimental data, and gather some intuition about the physical phenomena at play. Naturally, because it is a 1D simulation of a very complex device, there are some important limitations that are detailed in the next section.

3.1.3 Limitations

The first main limitation is linked to the intrinsic nature of SCAPS, as a simulation software. All the parameters that need to be introduced in the model are often based on educated guesses because of the empirical methods used to obtain them. Typical examples are the bandgap and the doping. Because the bandgap is graded, the general profile should be extracted, which is not straightforward. Generally, only a single value close to the CdS interface can be extracted [36]. In similar fashion, the doping of the CIGS layer can be deduced from CV measurements (section 2.3.9), but the value is

impacted by the presence of defects. This emphasises the fact that theoretical or simulation models are not always a perfect representation of reality, which justifies why they should not be used as absolute references to compare with experimental data.

Another big limitation of SCAPS is the mathematical convergence of the model. It impacts the ability to modify some parameters and to simulate some specific aspects of solar cells such as dielectric layers. Two main phenomena can cause convergence failures:

- The Fermi level moving outside of the bandgap. This is typically observed when the metal work function of a contact is too different from the one of the adjacent layer. It is the reason why a real work function is not used for the back contact. Problems with the position of the Fermi level also occur when too high values of doping are used in one of the layers.
- The absence of non-negligible currents in one of the layers. This is a major limitation for the simulation of dielectric layers in SCAPS, because they only let low currents through them. One way to fix this issue is to increase the defect density in the layer, inducing more recombination current.

To act against convergence issues under specific circumstances, workarounds are generally used in the simulation of the cell. This has the obvious disadvantage of going even further away from the experimental cell, sometimes making the interpretation of simulations even more complicated. Some of these workarounds were used in this work, and are detailed further.

Finally, a last limitation of SCAPS is the interpretation of some parameters inside the model itself. Their effect on the model is not always easy to understand and to interpret physically, and it would need further investigation for them to be used for sensitivity analysis.

From this introduction, it appears that even though SCAPS is not perfect in terms of simulation of solar cells, its great customizability and functionalities makes it very suitable to be used in this work. If a more precise and accurate model of the solar cell is needed, it would be interesting to use a more sophisticated software. SCAPS probably offers a good compromise between accuracy of the model and simplicity of use.

3.2 Samples processing and overview

In this section, the processing of a reference CIGS solar cell is first presented. Secondly, modifications to the processing for including the passivation layers is detailed. Finally, the different samples used in this work are presented.

3.2.1 Processing of reference samples

Standard CIGS solar cells are made of several stacked layers, detailed from top to bottom in table 3.2.1.

Layer	Material	thickness	Deposition technique
Front contact	NiAgNi	200 nm	Sputtering
Window (TCO)	IZnO & ITO	200 nm	Sputtering
Buffer	CdS	50 nm	CBD
Absorber	CIGS	1.6 μm	Sputtering/Co-evaporation
Back contact	Mo	300 nm	Sputtering
Substrate	SLG	2-3 mm	/

Table 3.2.1: Composition of the reference (baseline) solar cell from EnergyVille

Absorber The first step in the processing of a CIGS cell, after deposition of the back-contact, is the making of the absorber. Two different techniques can be used, either co-evaporation or sputtering. In co-evaporation, the different elements (Cu, In, Ga, Se) are placed in separate effusion cells. Each cell is heated at a certain temperature for precise control of the evaporation rate. Typically, this process is made of 2 or 3 stages during which different elements are evaporated concurrently on the sample. In sputtering, 3 different targets are used for making the absorber: CuIn, CuGa and Se. The targets are first hit by an ion beam that ejects particles onto the sample. After that, selenization and sulfurization is performed to complete the absorber. In both cases, as mentioned before, the ratio of Ga/(In+Ga) is adjusted during the process for realizing the bandgap grading.

Cleaning of the absorber Before depositing the CdS layer, the substrate is cleaned using a $(\text{NH}_4)_2\text{S}$ solution. This allows the removal of the Cu_xSe_2 secondary phase that forms at the surface of the absorber after the deposition process [37]. It must be removed because it negatively impacts performance.

CdS deposition The CdS deposition is performed using CDB. The samples are dipped in a heated solution. The deposition time depends on the thickness, in this case about 50nm. At the end of the process, the sample is rinsed in a de-ionized water bath and dried using a nitrogen gun.

Sputtering of window and grids The window layer and the grids are deposited one after the other by sputtering. In the standard process, a stack made of i-ZnO and ITO is used for the window

3.2. SAMPLES PROCESSING AND OVERVIEW

layer and a combination of Ni and Ag is used for the contacts. The use of Ni in this case is important for limiting the oxidation of the contacts with time.

Scribing and back-contact The last step in the processing is the scribing and making of the back contact. At the end of processing, the different cells are not separated. This is why the scribing is performed, to isolate the 0.5cm^2 cells from each other. Because this is done by hand, the real area of the cell generally varies a little bit, which can have consequences on the extracted value of J_{sc} , as explained further. After scribing, the back-contact is made by removing part of the stack to reach the Mo layer. A metal, generally Ag or In, is then deposited on top of this Mo to prevent oxidation while ensuring a good electrical contact.

Final cell The structure and a picture of the final solar cell are presented in figure 3.2.1.

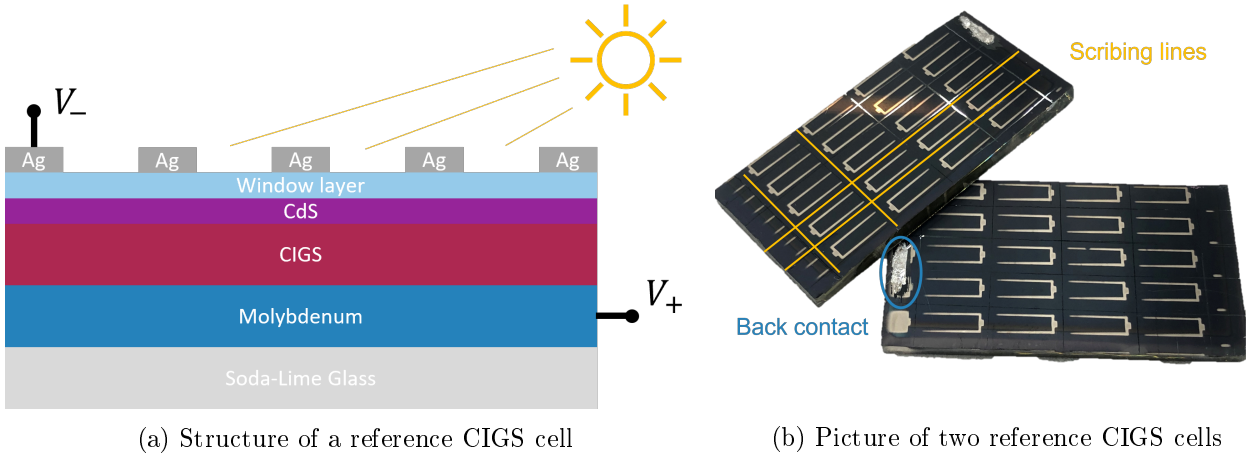


Figure 3.2.1: Structure and picture of a reference CIGS cell

3.2.2 Processing of passivated samples

In this work, passivation of CIGS solar cells is investigated. It requires to add additional layers to the reference cell design. In practice, this means that the standard processing steps are interrupted before addition of the layer, and finished after that. This is described hereafter.

Front passivation Here, the passivation layer is introduced between the CIGS and the CdS layer. The process is interrupted after the substrate cleaning, then the passivation layer is deposited and finally the rest of the process is performed, starting with the CdS deposition.

Window passivation Here, the passivation layer is introduced between the CdS and the TCO layer. The process is interrupted after the CdS deposition, then the passivation layer is deposited and finally the rest of the process is performed, starting with the TCO deposition.

Passivation layer deposition Two different dielectric materials are used as passivation layers: AlO_x and HfO_x . They both are 1nm thick, to allow current to flow via electrical tunnelling, and

3.2. SAMPLES PROCESSING AND OVERVIEW

deposited using ALD. This step is performed in the imec cleanrooms in Leuven. ALD is a processing technique that enables the deposition of very thin oxide layers. It is a sequential technique in which atomic layers are deposited one by one. Two chemicals (precursors) are used in the process: water and TMA or TEMAH, for AlO_x and HfO_x respectively. The sample is placed in a vacuum pumped chamber, which is then heated to stimulate the reaction. After that, the two precursors are sequentially pulsed into the chamber, and chemically react one after the other with the atoms present at the surface of the wafer. At this stage, a unique layer of atoms is present on the surface. The process is then repeated until a 1nm layer is grown.

Structure of passivated samples The structure of the front and window passivated samples is represented in figure 3.2.2.

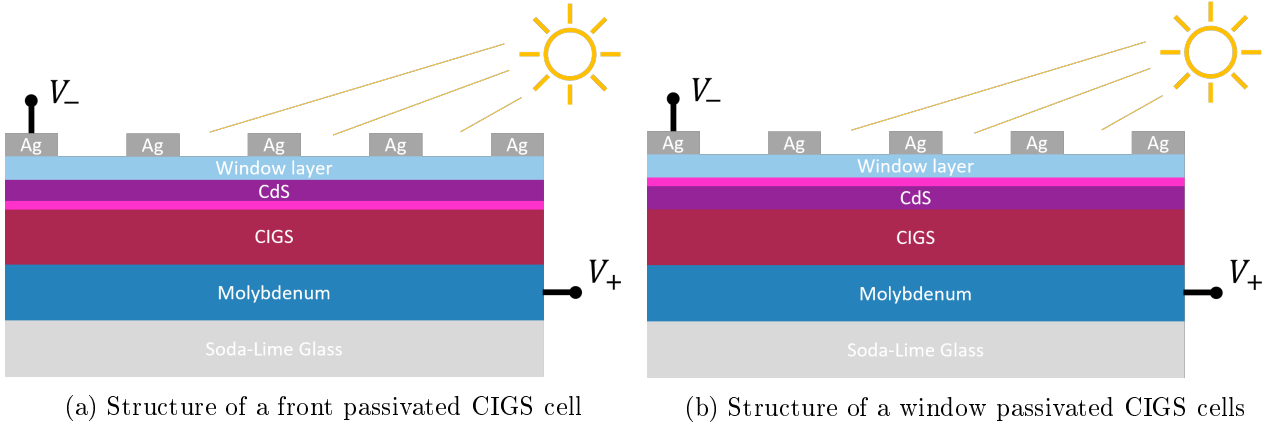


Figure 3.2.2: Structure of passivated CIGS cells. The passivation layers are represented in pink, and can either be AlO_x or HfO_x 1nm layers.

3.2.3 Overview of the samples

For the reader to have a global view of the samples used in this work, this section makes a comprehensive list of the different processed samples that are then used in the experimental characterization part.

The samples are classified by the type of absorber. In total, 3 different absorbers are used:

- Absorber 1: Research-level CIGS, made by sputtering
- Absorber 2: Commercially available high quality CIGS made by co-evaporation
- Absorber 3: Commercially available high quality CIGS made by chalcogenization of metal precursor layers.

Three different structures are investigated: Reference (figure 3.2.1a), front passivation (figure 3.2.2a) and window passivation (figure 3.2.2b). On top of these 3 structures, 2 different passivation materials are used: AlO_x and HfO_x . All the different samples are presented in table 3.2.2.

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Absorber	Sample name	Type of cell	Annealing [°C]	Passivation layer
1	Reference 1	Reference	/	/
1	Reference 1A	Annealed reference	150	/
1	FP1	Front passivation	150	AlO _x
1	WP1	Window passivation	150	AlO _x
2	Reference 2	Reference	/	/
2	Reference 2A	Annealed reference	150	/
2	FP2-AlO _x	Front passivation	150	AlO _x
2	WP2-AlO _x	Window passivation	150	AlO _x
2	FP2-HfO _x	Front passivation	300	HfO _x
2	WP2-HfO _x	Window passivation	300	HfO _x
3	Reference 3	Reference	/	/
3	Reference 3A	Annealed reference	150	/
3	FP3-AlO _x	Front passivation	150	AlO _x
3	WP3-AlO _x	Window passivation	150	AlO _x
3	FP3-HfO _x	Front passivation	300	HfO _x
3	WP3-HfO _x	Window passivation	300	HfO _x

Table 3.2.2: Processed samples, with type of cell, annealing temperature (taking into account the annealing during ALD processing) and passivation layer

The presentation of these samples concludes the section about cells processing and overview. This large set of samples then allows to study the impact of passivation layers as compared to unpassivated references, while including the effect of absorber processing and quality. The next section focuses on solar cells characterization.

3.3 Experimental characterization

In this section, the experimental characterization techniques used in this work are presented. Three aspects are covered for each technique:

- Description of the experimental setup and limitations
- Description of the experiments performed on the setup
- Analysis of the data from the experimentation

Four different techniques are detailed: IV, CV, PL and EQE.

3.3.1 IV

IV measurement is generally the first characterization step that is performed after processing of the samples. The goal is to have an overview of each sample performance. Two different types of measurements are performed: IV in the dark and under light conditions.

Experimental setup

For measuring the sample, a *Keithley 2401 sourceMeter*[®] is used, along with the *Rera Solutions Tracer software* for data acquisition. In order to avoid parasitic series resistance from the setup, four point probes are used. The two high potential probes are placed on the Mo back-contact, and the two low potential probes are placed on the NiAgNi front-contact.

For measurements in the dark, a black cloth is placed on top of the sample, ensuring as little light reaching the sample as possible. The data acquisition software is placed in "dark measurement" mode, which is important for data processing and analysis afterwards.

For measurements under light, an *Oriel solar simulator* is used. It simulates the action of sun illumination, following the AM 1.5G spectrum. This is considered in most research fields to be the standard for solar irradiation [38]. The tool is calibrated using a calibrated reference cell for an irradiance $G = 100\text{mW/cm}^2$. The data acquisition software is placed in "light measurement" mode, which is again important for data processing and analysis afterwards.

The main limitation does not come from the experimental setup, but rather from the use of IV as a performance analysis tool. As mentioned before, variations due to the scribing step can affect the current that is read and thus affect the extracted J_{sc} . This also impacts the efficiency of the cell that is based on the assumption that every cell has an area of 0.5cm^2 . Correction to these values must be made, and this is discussed in more details further in section 3.3.4.

Description of experiments

For each sample, three different cells are measured, and for each cell three measurements are done both in the dark and under light. This methodology allows to have a real understanding of the performance of the cell, as well as put process variations in evidence.

First, the measurement in the dark is performed. The contacts is done between the cell and the probes, and the black cloth is put on top. The measurement is performed in the range $[-1V, 1V]$ and the IV curve is plotted directly in the software, in log-scale. From this measurement in the dark, the curve should look like the one of a PN junction. Typical parameters that are extracted are R_s and R_{sh} , using the dJ/dV vs V characteristic [39]. This is usually not done in light condition, because the derivative is in that case much noisier, making the extraction more complicated. From measurement in the dark, it is also theoretically possible to extract J_0 and m . In CIGS, it is generally complicated and not very reliable due to the high recombination currents coming from the defects [40].

In a second moment, measurements under light are performed. The black cloth is removed and the solar simulator is activated. The measurement is also done in the range $[-1V, 1V]$ and the IV curve is plotted directly in the software using the active sign convention. From this measurement, the other parameters of performance are extracted: J_{sc} , V_{oc} , FF and η . This enables to have a first insight about the performance of the cell, directly after measurement. Bad cells can be put in evidence and then discarded from the analysis.

Data analysis

Data from the measurement is extracted in a single file, compiling experiments in the dark and under light. They are flagged differently, which is understood by the routine used for analysing the data and extracting the parameters. Different plots are made from the extracted data:

- IV curves of the dark and light measurements.
- Corrected IV curves, removing the effect of R_s and R_{sh} extracted from the measurement in the dark. This is done using the 1-diode model presented in section 2.1.3.
- Boxplots for each of the important figures of merit. This highlights the cell-to-cell variation in one sample, which is very important to control the quality of the process and the accuracy of the measurement procedure.

Overall, the IV data is mainly used for evaluation of the solar cell performance. If more detail is needed about the mechanisms happening inside the cell, IV curves are not sufficient. For this, CV and PL measurements are mainly used, as described further.

3.3.2 CV

The purpose of CV measurements is to try to understand the loss mechanisms at play inside the solar cell. CV measurements can be performed both at room temperature and low temperature.

Experimental setup

For measuring the sample, a *Agilent E4980A* LCR meter is used. It is controlled using a *Labview*® routine, in which the parameters of voltage bias, frequency and AC amplitude are set. The widest frequency measurement range is [20Hz, 2MHz]. Since the 4 point probes do not work with this setup, a simpler 2 probes configuration is used.

Low temperature measurements are performed using liquid nitrogen and a temperature controller, linked to a thermocouple and a resistive heater. The sample is placed on a thermally conductive stand, in a box filled with liquid nitrogen. The temperature is read by the controller using the thermocouple, and the heater is used for adapting it in function of the requested setpoint. The measurement can be performed down to 133K. The data acquisition is carried out by the same setup as before.

This setup has two main limitations. First, the fact that a 2 probes setup must be used induces a parasitic series resistance. An additional $R_s = 1\Omega$ is added to the measurement. This particularly impacts the CV measurement at high frequencies, as detailed in section 2.3.8. Secondly, low temperature measurements are performed in open air. The very low temperature of the sample and its surroundings leads to the formation of ice on the probes and on the sample. The measurement procedure can become more complex, and the sample can be degraded when the ice melts. For this reason, low temperature CV measurements are generally performed at the very end of the characterization process, to not impact other measurements.

Description of experiments

For each sample, two informations are concurrently measured: the parallel capacitance C_p and the parallel conductance G_p . As previously mentioned, mainly C_p is used in the analysis. For each sample, only one cell is measured, as it takes time to do a sweep over different voltage and frequency biases. The cell is chosen using the IV measurement, as the one that has median performance.

For room temperature measurements, the sample is placed on a stand and contact is made between the probes and the cell. In the same way as for IV measurements, the high potential probe is placed on the back-contact and the low potential probe is placed on the front-contact. The measurement is generally done in the [-1V, 1V] voltage range with 41 measurement points, and in the [1kHz, 1MHz] frequency range with 31 measurements points. A 50mV AC voltage is applied during the entire measurement. To obtain these 41x31 measurement points, the tool measures from the lowest frequency to the highest, doing an entire voltage sweep at each frequency. There is a 2 seconds delay between each measurement point, to enable the cell to return to equilibrium when switching from one voltage bias to the other. The data is plotted on 4 graphs, CV, Cf, GV and Gf which allows to control if the measurement is successful or not. From there, it is possible to export the data in a text file for further analysis.

For low temperature measurements, the same procedure described just before is applied, with the exception that no waiting time is used between each measurement point. Before going to low temper-

ature, a first room temperature measurement is done to ensure the setup is performing properly and also to have a comparison with low temperature data. After that, the setup is brought at the lowest temperature, 133K, and a first measurement is made. After each measurement, the data is saved and the temperature is risen by 20K. The last one is made just below 273K, temperature after which the ice formed on the sample melts, rendering any further measurement impossible.

Data analysis

One file is created for each measurement. A Python routine is used for analysis of the data, and in particular the following plots are made:

- CV, Cf, GV and Gf for a first general analysis of the cell behaviour.
- $-fdC/df$ vs frequency and voltage, in the form of a loss map for understanding the effect of the different loss mechanisms.
- Apparent doping vs w , to visualize in another way the action of defects.
- Arrhenius plots from low temperature measurements, to extract the activation energy and capture cross section of the defects.

3.3.3 PL and TRPL

PL and TRPL measurements are purely optical measurements, in which the sample is illuminated with very fast laser pulses. In the first one, the steady-state behaviour of the sample is analyzed. In the second one, the transient response of the sample is studied.

Experimental setup

The setup used for PL and TRPL is a *Picoquant Fluotime 300*, described as a "high performance fluorescence lifetime and steady state spectrometer". It is essentially composed of two parts: an emitter and a receiver. The emitter is composed of a laser source of wavelength $\lambda = 532\text{nm}$, a lens decomposing the light source into different wavelength and an adjustable monochromator that can let only one selected wavelength through. This light is then emitted on the sample, and reflected back into the system where it is captured by the receiver. The laser light is pulsed at 3MHz, and the purpose of the detector is to count the number of times the light is reemitted per second.

The main limitation of PL and TRPL is linked to their nature of optical measurements. When going through and reflecting on the sample, the light follows a very complex path. The light signal is altered by interferences and contributions from the different layers. For this reason, PL data can be very tricky to interpret, as a lot of very different informations are hidden inside it. Moreover, the PL signal is very much subject to layers deterioration and ageing, as these directly impacts the way light is transmitted and reflected. Finally, due to the impact of the very high energy laser light, the sample degrades over time, which leads to two successive runs possibly yielding a different result.

Description of experiments

For PL steady-state measurements, the sample is first placed under the light source. Before starting the measurement, the focal point must be adapted. An arbitrary wavelength, estimated to be close to the one yielding a maximal response, is chosen and the sample response over time is shown. The height of the sample with respect to the light source is then changed, until a maximum in response is reached which means that the correct focal point is set. After that, the steady-state measurement can be performed. The wavelength is swept in the range [950nm, 1350nm]. This measurement should result in a peak around the maximum absorption wavelength of the sample.

For the TRPL measurements, the sample is maintained in the same conditions as previously. The wavelength is fixed to be the one that shows the highest response in the steady-state measurement. The very fast laser pulse is exploited to measure the decay of the light re-emission with time, which is then recorded by the software.

Data analysis

Data from PL and TRPL measurements is captured by the software of the manufacturer. It can then be extracted in the form of a text file, and further analyzed. Two important informations are deduced from PL measurements. The optical bandgap can be extracted from the steady-state measurement, and the lifetime of the carriers can be extracted from the time-resolved measurement.

From the charges generation/recombination theory detailed in section 2.1.2, it is known that the energy emitted by an electron going from the conduction band to the valence band is equal to E_g . In the case of a solar cell, this energy is emitted under the form of light, whose wavelength is then related to E_g through $E_g = hc/\lambda$. Following this reasoning, a peak in PL intensity should lead to the value of the bandgap. Indeed, the peak indicates the wavelength for which the light absorption and re-emission is maximal, and thus for which the charge generation/recombination is maximal. This is the case when the energy of the light is the same as the energy of the bandgap. It is important to mention that this bandgap is not the actual bandgap of the device, which is why it is called "optical bandgap". Considering that there is a bandgap grading in the absorber, the extracted bandgap is usually a lower bound of the real bandgap [36]. Furthermore, it integrates the phenomenon of optical interference, whose impact is usually complex to evaluate.

In TRPL measurements, the light re-emission with time is measured. This should directly be linked to carrier lifetime, since re-emission of the light happens during the recombination process. In an ideal case, the PL decay is exponential with time [41]. In reality, because the recombination is mostly non-radiative due to the action of defects, the decay has a double exponential shape [42]. The intensity of the PL response with time can be modelled as:

$$I_{\text{PL}}(t) = C_1 e^{-t/\tau_1} + C_2 e^{-t/\tau_2} \quad (3.3.1)$$

where τ_1 and τ_2 are the decay times corresponding to the two parts of the PL response. In an ideal case, where there is only radiative recombination happening, $\tau_1 = \tau_0$ and $\tau_2 = 0$ [43]. This is also valid when there is low defect density. For high defect density, the correlation between τ_1, τ_2 and τ_0 can no longer be easily established. There is an impact of the type of defect, its distribution, the intensity of the laser pulse, the mobility of the carriers and others. Some models like the one presented in [44] try to predict the value of τ_0 from TRPL measurements, but this is beyond the scope of this work. Instead, τ_1 and τ_2 are used here as effective lifetime of carriers. They overall give information about an apparent recombination rate. A high PL lifetime is the sign of good performance, because it indicates a low recombination rate and thus a low density of defects.

3.3.4 EQE

The last characterization tool that is used for the sample analysis is the EQE (external quantum efficiency) tool. EQE is used to quantify the absorption of light and carrier extraction over a range of wavelength. In this measurement, a light source with varying λ is used and the generated current is monitored. This does not directly yield the EQE of the cell, but rather the spectral response (SR) from which it can be computed, as explained further.

Experimental setup

The tool used for EQE measurements is the *Bentham PV300* spectral response tool. It can be used in two configurations: for reflection/transmission measurements (not used in this work) and for EQE measurements. It has a xenon-quartz tungsten halogen dual light source that allows to sweep λ in the [300nm, 2500nm] range. This light passes through a monochromator that let a specific wavelength through and then is redirected onto the sample using lenses and mirrors. The sample is placed in a black-box, to ensure no other light reaching the sample. The photo-current is measured using two-point probes and is recorded through the software.

The main limitation of this setup is that it has to be recalibrated each time it is used, and that a 30 minutes heating process is needed each time. Moreover, the ageing lamp that was present at the time of measurement sometimes resulted in a drift of data accuracy with time, meaning that a second calibration was needed after a few measurements.

Description of experiments

For each sample, different cells are measured. These cells are selected on basis of the IV curves, typically when an unexpected value of J_{sc} is obtained, requiring further analysis.

Before starting the cell measurement, the setup is calibrated using two reference cells. A Si reference cell is measured over the [300nm, 1100nm] wavelength range, and a Ge reference cell is measured over the [800nm, 1200nm] range. These two are then combined and the data is passed to the software, to be used as calibration for correcting the experimental data. After that, the cell is placed into the black box and under the light source. Contact is made with the probes. The cell SR is then measured

in the range [300nm, 1200nm] which is the typical absorption range of CIGS solar cells. SR data is recorded into the software and converted into EQE data which is then extracted for further analysis.

Data analysis

As explained previously, the photo-generated current is recorded with respect to the wavelength of the light. Several steps are needed in order to obtain the EQE information, as detailed in [45]. First, SR [A/W] is obtained as the ratio between the generated current and the power of the incident light. From this, the external quantum efficiency is computed using the relation:

$$\text{EQE}(\lambda) = \frac{hc}{q\lambda} \cdot \text{SR}(\lambda) \quad (3.3.2)$$

An interesting point, also highlighted in [45], is that the SR and EQE value are directly related to J_{sc} by the following relation:

$$J_{sc} = \int_{\lambda_{min}}^{\lambda_{max}} \text{SR}(\lambda) \cdot h(\lambda) \, d\lambda \quad (3.3.3)$$

$$= \int_{\lambda_{min}}^{\lambda_{max}} \text{EQE}(\lambda) \cdot h(\lambda) \cdot \frac{q\lambda}{hc} \, d\lambda \quad (3.3.4)$$

where $h(\lambda)$ is the spectral irradiance of AM 1.5G spectrum. This relation is very useful, because it enables the validation of J_{sc} using data that is independent of the cell area and thus of scribing process variation.

This concludes the chapter about the work methodology. In the next chapters, it is put into application, starting with the SCAPS simulations, and continuing with the analysis of the experimental data for the reference and passivated cells.

4 SCAPS sensitivity analysis

In this chapter, SCAPS is used as a sensitivity analysis tool for evaluating the effect of the different loss mechanisms on the solar cell parameters. As a reminder from the previous chapter, the role of these simulations is twofold:

1. Predict experimental trends.
2. Interpret experimental observations.

The SCAPS solar cell model that is used is the same that is presented in section 3.1.2. Its characteristics are detailed in appendix B.2.

In the first section, IV curves are used to understand the impact of losses on both performance and the main figures of merits of the solar cell. In the second section, the impact of these same losses is investigated on CVf loss maps to try to understand their signature and be able to identify them further in the experimental work.

4.1 Performance evaluation

4.1.1 External losses

In this first section, the impact of R_s and R_{sh} is studied. In SCAPS, external losses are modelled using the 1-diode model from section 2.1.3. As a reminder, the equation for the current in this model is given by:

$$J = J_{ph} - J_s \cdot \left(\exp \left(\frac{q(V + JR_s)}{mkT} \right) - 1 \right) - \frac{V + JR_s}{R_{sh}} \quad (4.1.1)$$

The particular consequence of this model is that the effect of the resistances is completely decoupled from the simulation of the solar cell internal structure. In practice, this is not the case since part of the action of R_s and R_{sh} is intrinsic to the solar cell. Results must thus be taken with care, as for all simulation predictions.

Series resistance R_s

The contribution of R_s for a dark and illuminated solar cell is represented in figure 4.1.1.

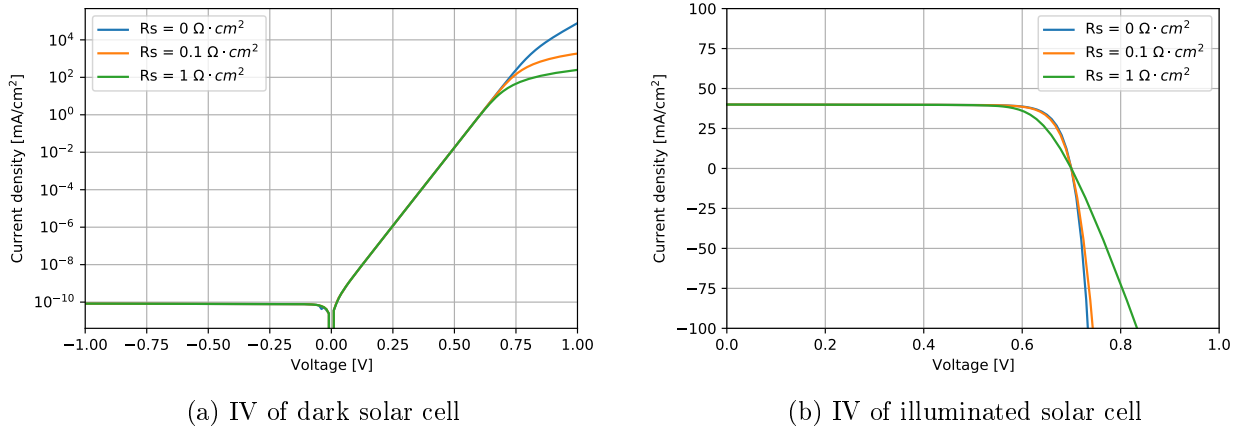


Figure 4.1.1: Effect of R_s on a solar cell IV curve (SCAPS)

It appears that the main contribution of the series resistance happens at high voltage biases. This is quite straightforward from equation (4.1.1), in which the action of R_s is coupled to the total current. At low voltage bias, the current is low and the impact of the resistance is thus limited. On the contrary, at high voltage bias, the current increases exponentially, which increases the impact of R_s and finally leads to a saturation of the current. This is also known from the general theory of diodes.

By looking at the IV curve under light, it is possible to deduce the effect of R_s on the different figures of merit of the solar cell. It appears that J_{sc} and V_{oc} are not affected by R_s . For J_{sc} , it is explained with the reasoning hereabove, since it is computed at 0V and the effect of the resistance only affects higher biases. Concerning V_{oc} , since it is computed when no current is passing through the cell, there cannot be any impact of R_s because every $J \cdot R_s$ term in the equation is null.

On the contrary, FF and thus also η are negatively affected by an increased R_s . This comes from the change in the exponential slope at high voltages induced by R_s , leading to a reduction of both V_{mpp} and I_{mpp} . Qualitatively, it makes sense that the efficiency would be reduced, because more energy is dissipated through R_s while the energy supplied to the solar cell is still identical.

Shunt resistance R_{sh}

The contributions of R_{sh} for a dark and illuminated solar cells are represented in figure 4.1.2.

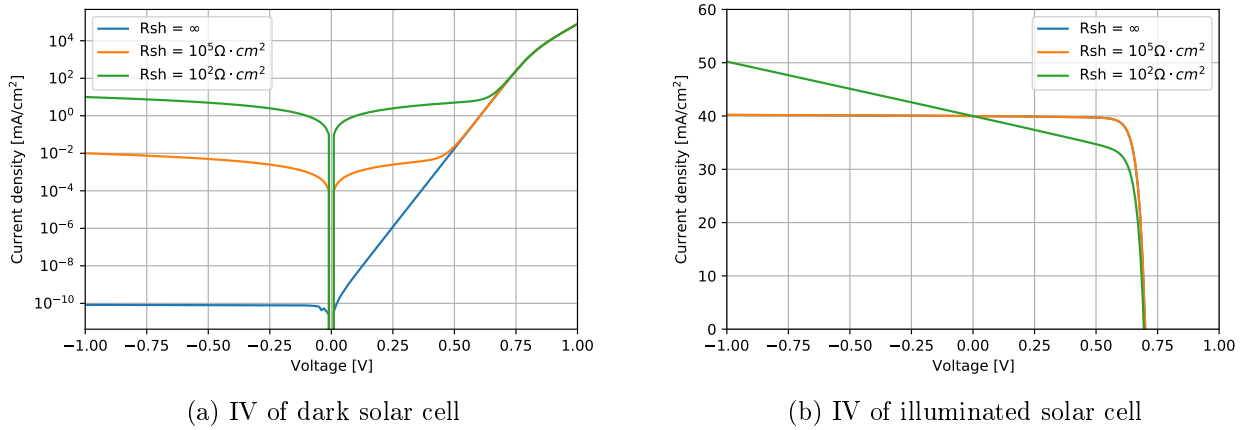


Figure 4.1.2: Effect of R_{sh} on the solar cell IV curve (SCAPS)

Contrarily to series resistance, it appears that the contribution of the shunt resistance happens at low and reverse voltage bias, when the current is low. Looking again at equation (4.1.1), this is justified by the fact that R_{sh} only influences the linear term. The total current is dominated by the linear term at lower biases, hence increasing the effect of R_{sh} .

Similarly to R_s , R_{sh} does not impact J_{sc} and V_{oc} . For the latter, this comes from the fact that R_{sh} has no impact at higher voltage bias, and thus V_{oc} that is very close to this regime remains unchanged. Concerning J_{sc} , the external voltage is null, meaning that in absence of R_s , the voltage across R_{sh} is also null and there is no contribution of this resistance.

The reduction of R_{sh} has a negative impact on FF and η . This comes from the impact of R_{sh} on the sub-threshold slope of the IV curve. A steeper slope reduces the maximal power point and thus also FF and η . Again, it qualitatively makes sense that a reduced R_{sh} impacts negatively the performance because more power is dissipated through it.

4.1.2 Contribution of defects

In this section, two different defects are added to the reference structure, and their impact on the solar cell performance is studied. First, a bulk defect in the CIGS layer is added. Then, it is replaced by an interface defect between the CIGS and the CdS layer.

Bulk defect in CIGS

The contribution of a bulk defect for a dark and illuminated solar cell is represented in figure 4.1.3.

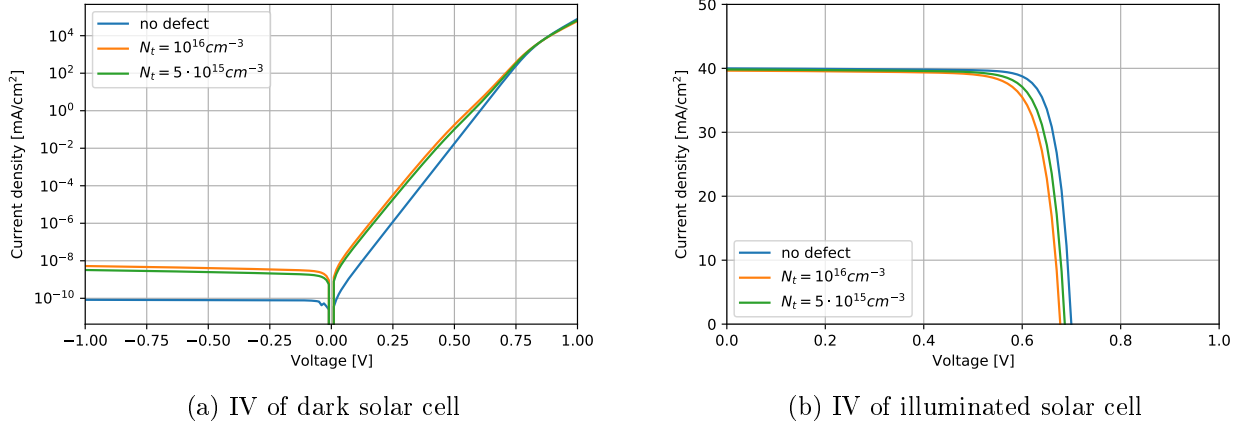


Figure 4.1.3: Effect of a bulk defect in CIGS on the solar cell IV curve using SCAPS. The bulk defect parameters are: $E_A = 0.35\text{eV}$, $\sigma = 10^{-15}\text{cm}^2$, $N_A = 10^{16}\text{cm}^{-3}$ and N_t is varied.

As explained in section 2.1.3, defects have a negative impact on recombination in the device. Increasing the density of defects increases the SRH recombination rate and thus also the recombination current. This has a impact on both V_{oc} and J_{sc} , as explained hereafter.

From the 1-diode equation (4.1.1) and by removing external losses, V_{oc} is expressed as:

$$V_{oc} = \frac{kT}{q} \cdot \ln \left(\frac{J_{ph}}{J_s} \right) \quad (4.1.2)$$

In this equation, V_{oc} is impacted by two parameters of the solar cell: J_s the reverse saturation current and J_{ph} the photo-generated current. When J_s increases, such as in figure 4.1.3a, V_{oc} decreases, such as in figure 4.1.3b. This current has two main contribution: one that is related to diffusion of minority carriers and one that is related to the recombination current. When the last one increases due to the action of the bulk defect, it leads to a higher J_s and a lower V_{oc} . The recombination rate does not affect much J_{ph} . Indeed, the value of J_{ph} is mostly determined by the illumination and as first approximation it is considered to be constant at constant irradiation. A higher J_s is thus mostly responsible for the V_{oc} lowering.

From equation (4.1.1) and by removing external losses, J_{sc} is simply expressed as:

$$J_{sc} = J_{ph} - J_s \quad (4.1.3)$$

Where J_{sc} reduces when J_s increases, as explained just before. Due to the reduction in V_{oc} and J_{sc} , the maximum power point is negatively affected and η is also reduced. On the contrary, FF seems to not be much impacted by the presence of defects as shown in figure 4.1.3b.

Interface defect

The contribution of an interface defect for a dark and illuminated solar cell is represented in figure 4.1.4.

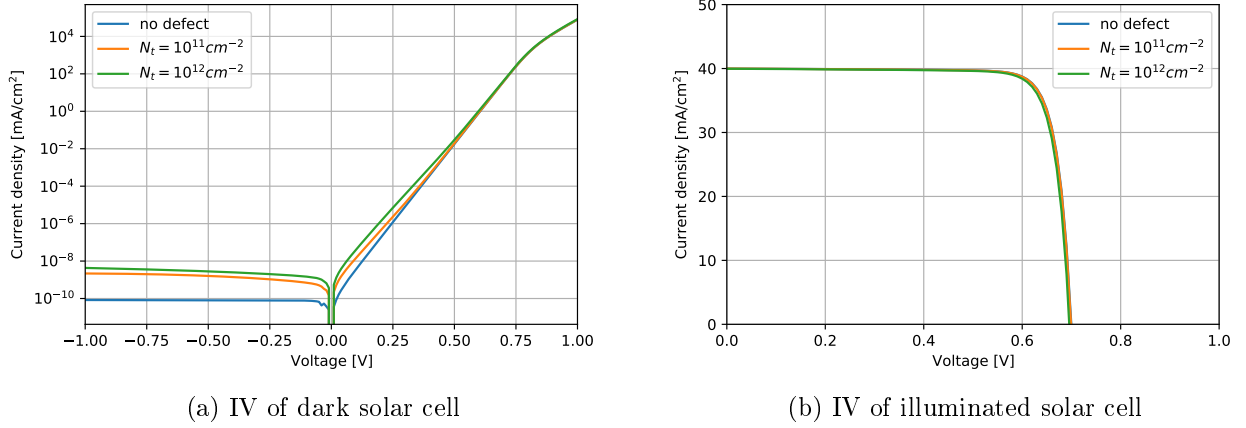


Figure 4.1.4: Effect of an interface defect on the solar cell IV curve using SCAPS. The interface defect parameters are: $E_A = 0.35\text{eV}$, $\sigma = 10^{-15}\text{cm}^2$, $N_A = 10^{16}\text{cm}^{-3}$ and N_t is varied.

From this figure, the impact of interface defects seems to be similar to the impact of bulk defects, even though the changes are very small. Interface defects also mainly affect recombination in the device. V_{oc} , J_{sc} and η are reduced, while FF remains the same. The smaller parameter change than for bulk defects is probably coming from the simulation in SCAPS, since it is clear from literature that interface defects can have a very significant impact on performance [3, 4]. It is possible that the parameters chosen for this interface defect are not optimal for seeing real changes in the figures of merit. Other parameters were tried, but did not lead to conclusive results either.

4.1.3 Other contributions

In section 2.2.1 about the peculiarities of CIGS solar cells, it is underlined that the presence of a barrier at the CIGS/CdS interface can greatly influence the performance of the solar cell. In spite of that, the simulation of the solar cell IV curve on SCAPS with different barrier heights does not give meaningful results. This shows one of the limitations of SCAPS. Nevertheless, from the theory, it is expected that this barrier should impact the current flow as well as increase recombination by blocking the electron flow towards the CdS layer. This would result in a decreased J_{sc} , V_{oc} and η .

4.2 Admittance spectroscopy

In this section, simulations of admittance measurements are used to understand the effect of the different loss mechanisms on CVf loss maps. This should yield some insight on how to interpret these maps when they are used with experimental data in the next chapters.

As already mentioned before (section 2.3.6), high dissipation factors in the positive bias range make the interpretation of loss maps above 0.5V and at high frequencies difficult. This is generally not an issue in SCAPS. Nevertheless, in this high forward bias region, the total capacitance is not only composed of the depletion contribution anymore. Indeed, the junction capacitance becomes also significant above 0.5V, making the physical analysis much more complex [15]. For this reason, the SCAPS measurements are only analyzed for the the bias range [-1V, 0.5V].

4.2.1 External losses

Two external losses are presented in section 4.1, R_s and R_{sh} . As underlined in [15], the shunt resistance has no influence on the loss map, because its action is not frequency dependent. Its only contribution on the device admittance is to increase the dissipation factor, which makes the measurement less accurate. This stresses the importance of monitoring the dissipation factor when performing CVf measurements, in order to validate the measurement reliability.

The series resistance, on the contrary, does have an impact on the CVf map, as presented in section 2.3.8. It is possible to simulate it on the loss map using SCAPS, such as in figure 4.2.1.

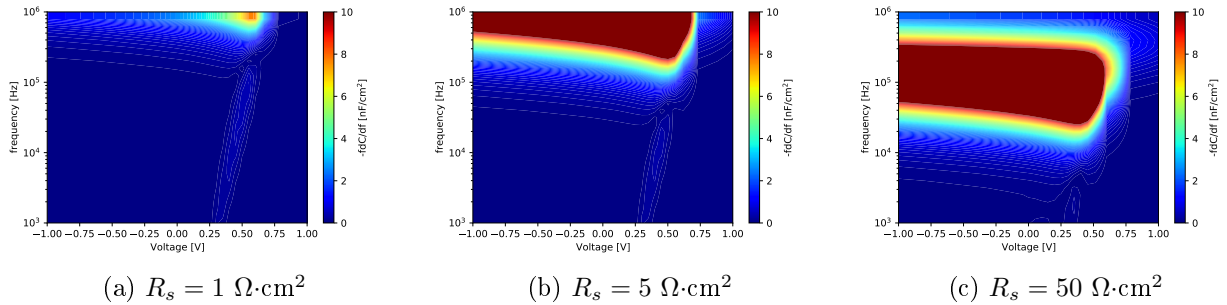


Figure 4.2.1: reference CIGS model with added series resistance (SCAPS).

The change in capacitance happens at high frequencies and is constant with respect to voltage bias. This is normal since there is no direct relation between the bias voltage and R_s other than through the capacitance itself (equation (2.3.20)). Moreover, when R_s is increased, the signature is lowered in frequency. This also makes sense since R_s and C act together as a low-pass filter in which an increased resistance results in a reduced cut-off frequency.

4.2.2 Contribution of defects

At first, a bulk defect is introduced and its different parameters are varied. In a second time, it is replaced by an interface defect placed at the CIGS/CdS interface, and its parameters are also varied. These defects are the same as in section 4.1.

Acceptor bulk defect

The different parameters of interest in the case of a bulk defect in SCAPS are:

- The defect type: acceptor or donor. In this case, a single acceptor defect is considered.
- The defect capture cross section σ [cm^2]. It may differ for holes and electrons but is kept equal for both in this model.
- The defect activation energy E_A [eV]. It is taken as the difference between the energy level of the defect and the valence band; $E_A = E_t - E_v$.
- The defect density N_t [cm^{-3}].
- The doping of the CIGS N_A [cm^{-3}].

The other SCAPS parameters have a lower influence on the response of bulk defects and are thus not studied here. It is also worth mentioning that because convergence in SCAPS can sometimes be an issue, it is a limiting factor in the choice of the studied range of values for each parameter.

First, the activation energy of the defect is varied. This is represented in figure 4.2.2. When E_A changes, the response moves in frequency. This makes sense since E_A is directly linked to the frequency response of the defect. When E_A is higher, the defect is deeper in the bandgap, and its characteristic frequency is lower. This moves down the signature of the defect.

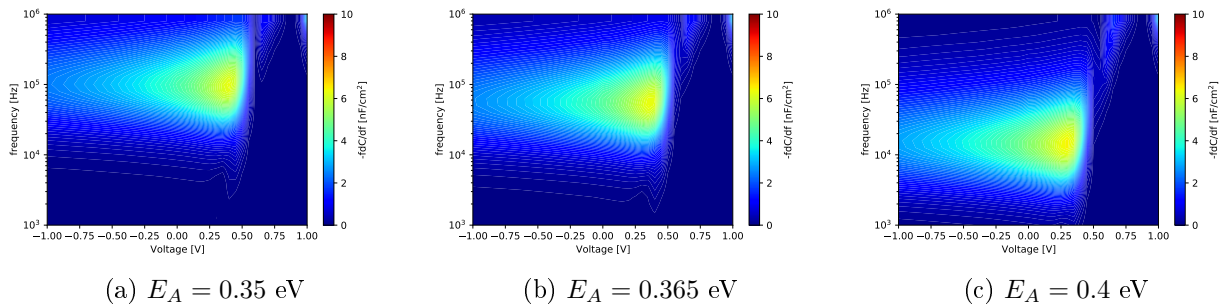


Figure 4.2.2: Bulk defect with E_A changed. The other parameters that are kept constant are: $\sigma = 10^{-15} \text{cm}^2$, $N_t = 10^{16} \text{cm}^{-3}$, $N_A = 10^{16} \text{cm}^{-3}$ (SCAPS).

Secondly, the capture cross section of the defect is varied. This is represented in figure 4.2.3.

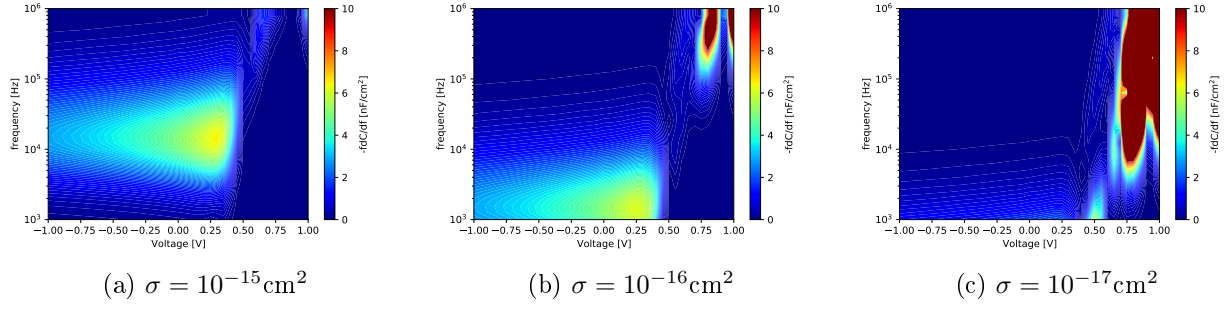


Figure 4.2.3: Bulk defect with σ changed. The other parameters that are kept constant are:
 $E_A = 0.4 \text{ eV}$, $N_t = 10^{16} \text{cm}^{-3}$, $N_A = 10^{16} \text{cm}^{-3}$ (SCAPS).

When σ changes, the response also moves in frequency. Again, σ is directly linked to the characteristic frequency of the defect. When σ decreases, the probability for electrons to be trapped also decreases and the characteristic frequency decreases. On figure 4.2.3c, the response is almost not visible anymore, because it has moved to very low frequencies. The signature visible at higher biases, as previously mentioned, is probably linked to the junction capacitance and is more difficult to interpret.

Thirdly, the defect density is varied. This is represented in figure 4.2.4.

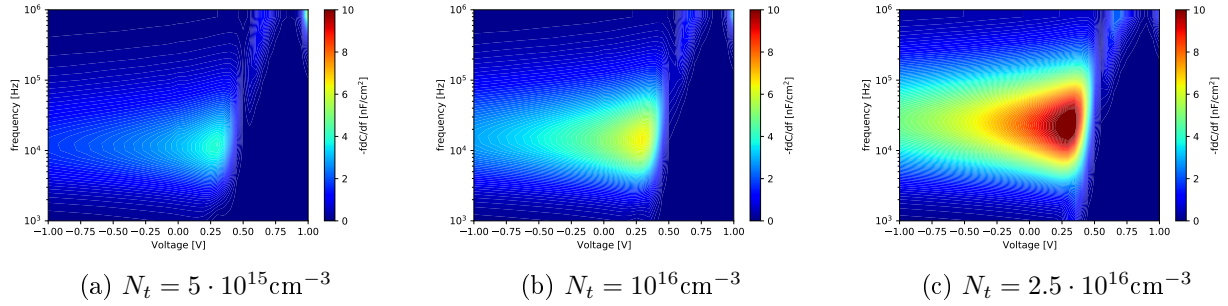


Figure 4.2.4: Bulk defect with N_t changed. The other parameters that are kept constant are:
 $E_A = 0.4 \text{ eV}$, $\sigma = 10^{-15} \text{cm}^2$, $N_A = 10^{16} \text{cm}^{-3}$ (SCAPS).

Changing N_t mainly affects the amplitude of the defect response. For a higher defect density, more charges enter the capture/release process and the contribution to the capacitance is increased. The same applies to the capacitance variation on the loss map, leading to a larger peak height. Another consequence of increasing N_t is the defect response slightly moving up in frequency. This can be explained by the carriers having more energy states where they can be trapped, and the defect time constant therefore being reduced.

Finally, the doping of the CIGS layer is varied. This is represented in figure 4.2.5.

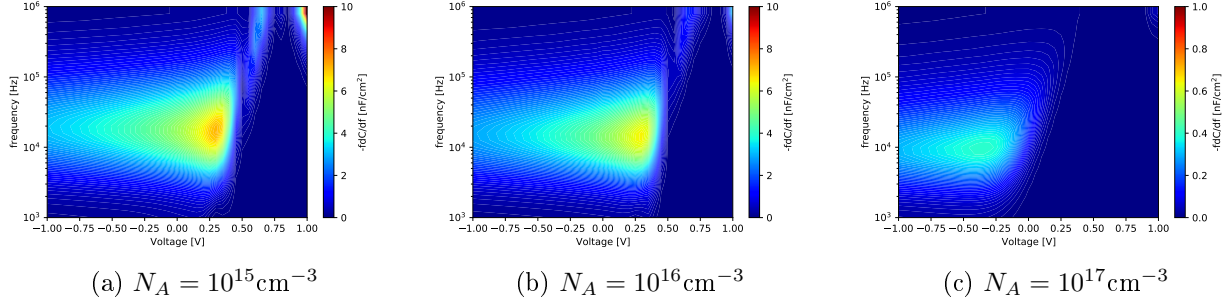


Figure 4.2.5: Bulk defect with N_A changed. The other parameters that are kept constant are:
 $E_A = 0.4 \text{ eV}$, $\sigma = 10^{-15} \text{cm}^2$, $N_t = 10^{16} \text{cm}^{-3}$ (SCAPS.)

The first impact of a variation of N_A is the change in the response amplitude (the scale of figure 4.2.5c had to be reduced or the signature would not have been visible). It appears that when the doping density becomes higher than the defect density (figure 4.2.5c), the defect response is much lower in amplitude. Indeed, for $N_A > N_t$, the total capacitance is dominated by the frequency-independent fixed charge of doping atoms, rather than by ionized defect states. Thus, the capacitance derivative is mostly equal to zero, except for the smaller bulk defect response. The second impact of a variation of N_A is the little shift of the response in voltage. Looking at equation (2.1.4), it appears that increasing the doping reduces the depletion width. This results in a different band bending and in the Fermi level crossing the defect state at different voltage biases.

As a conclusion, bulk defects have a generally broad signature on the loss map. In the voltage range, it comes from the defect energy level following the band alignment, as seen previously in figure 2.3.7, therefore leading to the Fermi level crossing it at various biases. In the frequency range, the position of the response is governed by the characteristic frequency of the defect.

Donor defect at CIGS/CdS interface

The different parameters of interest for interface defects in SCAPS are :

- The defect type: acceptor or donor. In this case, a donor defect is considered.
- The defect capture cross section $\sigma \text{ [cm}^2\text{]}$. It is equal for holes and electrons.
- The defect activation energy $E_A \text{ [eV]}$. It is taken as the difference between the conduction band and the energy level of the defect; $E_A = E_c - E_t$.
- The defect density $N_t \text{ [cm}^{-2}\text{]}$. Here, as an interface defect is considered, it makes sense to use the sheet density rather than the volume density.

In this study, the doping of the CIGS and the CdS are not altered, because the focus is on the response of the interface defect itself. The change of these parameters has also an impact on the response that is investigated more in detail in section 2.3.8. It is worth mentioning that a trace coming from another interface defect than the one considered is also visible on the map. It is vertical and with a small

4.2. ADMITTANCE SPECTROSCOPY

signature around the 0.5V bias range. The presence of this defect was necessary for the convergence of the SCAPS model. More precisely, it is an acceptor defect with $E_A = 0.2$ eV, $\sigma = 10^{-15}\text{cm}^{-2}$ and $N_t = 10^{10}\text{cm}^{-2}$. Due to its low density, it is very likely that its impact on performance is limited.

First, the activation energy of the donor defect is varied. This is represented in figure 4.2.6.

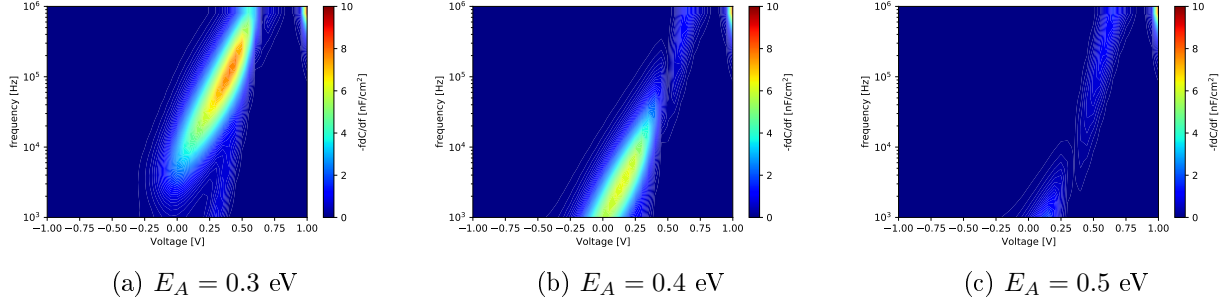


Figure 4.2.6: Interface donor defect with E_A changed. The other parameters that are kept constant are: $\sigma = 10^{-15}\text{cm}^2$, $N_t = 10^{11}\text{cm}^{-2}$ (SCAPS).

Changing the activation energy of an interface defect has the same effect as for a bulk defect. The characteristic frequency decreases when the activation energy increases, which is directly derived from equation (2.3.7). From these figures, it is also possible to deduce that the response of an interface defect is typically very narrow in voltage and broad in frequency. This broadness in frequency is generally less pronounced in the experimental work.

Secondly, the capture cross section of the defect is varied. This is represented in figure 4.2.7. Changing the capture cross section for an interface defect yields the same frequency dependency as for bulk defects. Indeed, when σ is higher, there is an increased probability for electrons to be captured and the defect has thus a higher frequency response. For interface defects, the frequency response is broader when σ is large. The explanation of this phenomenon is less straightforward, especially that the very broad frequency dependence for high σ does not seem to be supported by experimental work. A hypothesis is that a higher σ allows the capture of charge carriers with various lifetimes which increases the frequency response.

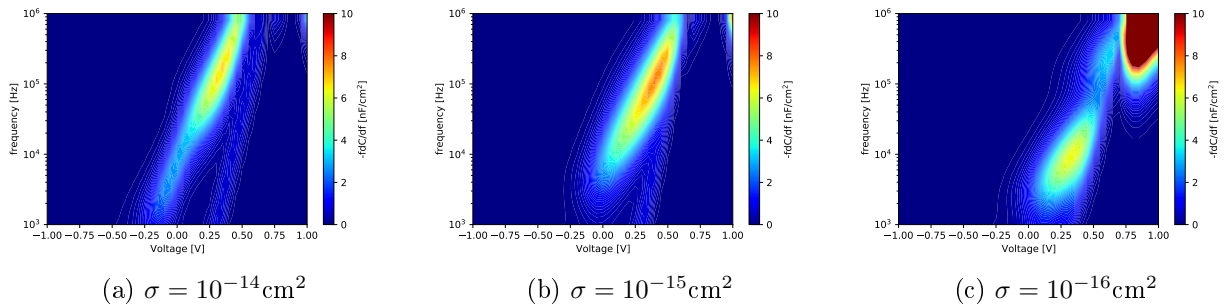


Figure 4.2.7: Interface defect with σ changed. The other parameters that are kept constant are: $E_A = 0.3$ eV, $N_t = 10^{11}\text{cm}^{-2}$ (SCAPS).

Finally, the defect density is varied. This is represented in figure 4.2.8.

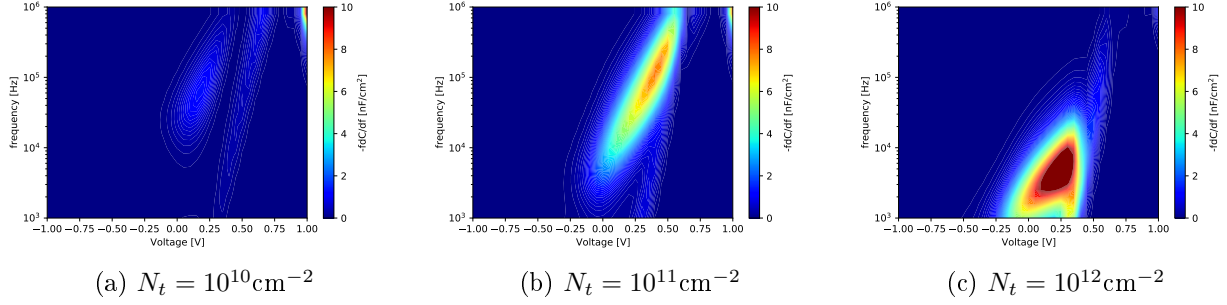


Figure 4.2.8: Interface defect with N_t changed. The other parameters that are kept constant are: $E_A = 0.3$ eV, $\sigma = 10^{-15}\text{cm}^2$ (SCAPS).

The action of the defect density change is a little more complex than for bulk defects. Below a certain density, generally between $10^{11} - 10^{12}\text{cm}^{-2}$, the behaviour is similar to bulk defects in the sense that an increased density corresponds to a greater signature on the map (figure 4.2.8a & 4.2.8b). This is because more charges enter the capture/release process of the defect. The response in voltage stays in that case very localized, due to the the Fermi level crossing that takes place at a very particular voltage bias point.

For higher trap densities, there is another phenomenon that enters into play. In that case, the response in voltage that is normally very localized becomes broader (figure 4.2.8c). The exact physics behind this is not entirely certain, but a good hypothesis is that it is linked to Fermi level pinning [15]. This hypothesis states that when the defect density is very high, the Fermi level gets stuck when crossing the interface defect level, which is why the response also extends at different biases.

In conclusion, contrarily to bulk defects, interface defects have a very localized response in voltage bias. They may also present a broader response in frequency, as well as an ability to extend their response in voltage bias when they have a very high density.

4.2.3 Other contributions

Interface barrier

Another contribution to CVf measurements that is presented in section 2.3.8 is the action of the barrier at the CIGS/CdS interface. The main parameter influencing the signature in that case is the height of the barrier. This can also be modelled on SCAPS, such as in figure 4.2.9.

Since the flow of charges through a barrier is a thermally activated process, it makes sense that the signature on the map is frequency dependent. When the barrier is higher, in the same way as when a defect is deeper in the bandgap, more energy is needed for the charges to move across the barrier and thus the characteristic frequency of the response is lower.

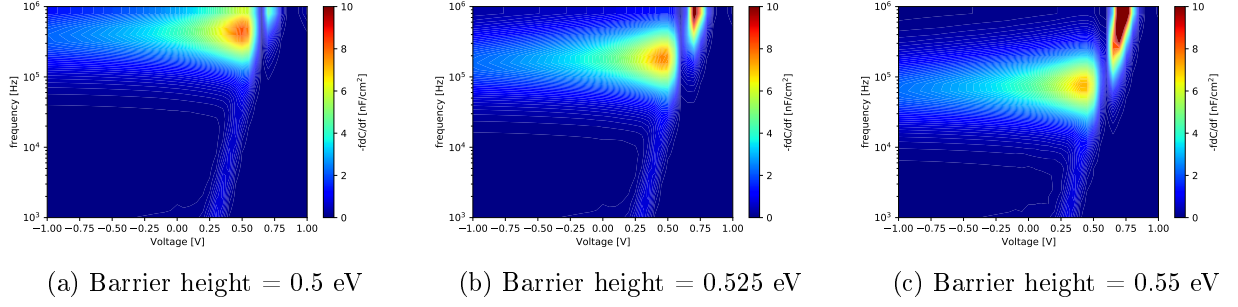


Figure 4.2.9: reference CIGS model with an added barrier at CIGS/CdS interface (SCAPS).

Simultaneous contribution of multiple losses

As a conclusion to this section about simulation of admittance measurements on SCAPS, it is of particular interest to consider the effect of multiple losses on one map. This is typically what happens in real solar cells, where a series resistance can, by example, be coupled with a bulk or an interface defect. This was done in figure 4.2.10. It appears that the different loss mechanisms have their signature that is simply added on top one of another, which is confirmed in the literature [15, 17, 46]. In function of the loss mechanisms the map can quickly become more complex, which is a well known limitation of loss maps.

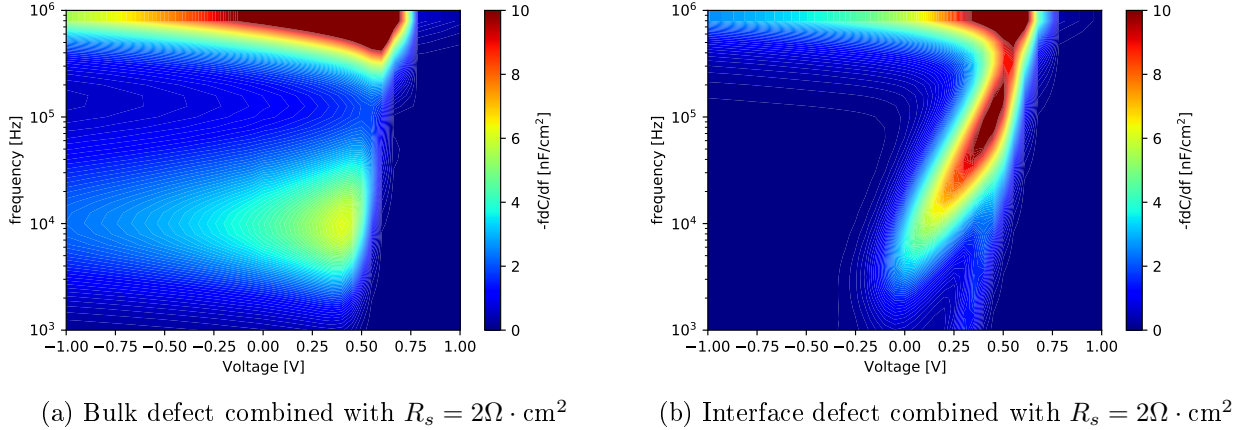


Figure 4.2.10: Multiple contributions to the capacitance. The bulk defect is the same as in figure 4.2.2c with σ changed to 10^{-16}cm^2 . The interface defect is the same as in figure 4.2.7b (SCAPS).

4.3 Conclusion

In this chapter, SCAPS simulations are performed in order to try to understand the impact of several loss mechanisms on the solar cell characteristics.

In a first section, the impact of losses on the solar cell performance and figures of merit is studied. There, it appears that external losses mainly influence FF and η , while other figures of merits remain unchanged. This must be interpreted with care, as SCAPS makes use of the 1-diode model for modelling the external losses, which is not completely in line with the reality. As expected, an increased R_s and a decreased R_{sh} are both detrimental to the performance. The impact of internal losses is also studied, by adding both a bulk and an interface defect in the device. These two have a negative impact on V_{oc} and on J_{sc} . This comes from the increased recombination induced by the defects, that influences J_s and J_{ph} . Because of the reduced V_{oc} and J_{sc} , η is also reduced. Contrarily to external losses, it appears that FF remains mostly unaffected by the presence of defects. This is probably only true for the defects simulated in this work and not general to all types of defects [17].

In a second section, the impact of these different losses on the CVf loss maps is investigated. The goal is to identify their signature to be able to recognize them in real measurements in the next chapters. Only one of the two external losses has an impact on the loss map: R_s . As already explained in the theory, it acts together with the depletion capacitance as a low-pass filter and presents a clear trace at high frequencies, which is not bias dependant. Bulk defects have a very broad response in voltage bias. Their frequency response changes with E_A and σ while the intensity of the response changes with N_t . Interface defects have a very narrow response in voltage bias, that comes from the Fermi level crossing the state of the defect at a very particular point. Their frequency response also changes with E_A and σ . When their concentration N_t increases, the response amplitude on the map also increases. For very high N_t , the signature on the map is broader in the voltage bias range, which could indicate Fermi level pinning. Finally, it is shown that when combining several loss mechanisms in one structure, their signature simply add up on the map.

5 Base case study: Reference CIGS cell

This chapter and the following aim at making a thorough analysis of the real CIGS solar cells presented before. In this first experimental chapter, the characterization methodology is used for the first time with reference solar cells. It is then repeated in the next two chapters, with front and window passivated solar cells respectively.

Six different samples are analyzed in this chapter (table 5.0.1). They all have the structure of a standard CIGS solar cell shown in figure 5.0.1. Three different absorbers are used, and for each one a reference and an annealed version is made. In a first section, the comparison is made on a performance standpoint, with analysis of the IV curves and EQE measurements. After that, the cells are analyzed in detail, using the AS method and PL measurements.

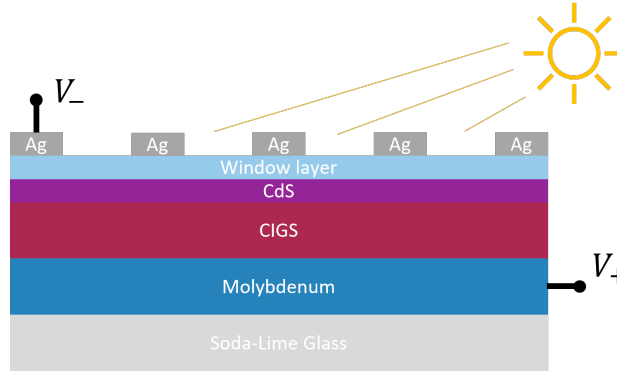


Figure 5.0.1: Schematic representation of the reference CIGS cell.

Absorber	Sample name	Type of cell	Annealing temperature [°C]	Passivation layer
1	Reference 1	Reference	/	/
1	Reference 1A	Annealed reference	150	/
2	Reference 2	Reference	/	/
2	Reference 2A	Annealed reference	150	/
3	Reference 3	Reference	/	/
3	Reference 3A	Annealed reference	150	/

Table 5.0.1: Samples used in this chapter

5.1 Performance evaluation

In this section, performance of the reference samples are first presented and analyzed. The impact of external losses on performance is then discussed. After that, the limitations of performance characterization in real solar cells are detailed. EQE measurements are then presented as a way to counteract part of these limitations. Finally, the effect of annealing on performance is discussed.

5.1.1 Samples performance

The IV curve in the dark and under light for the champion cell¹ of each reference sample are represented in figure 5.1.1.

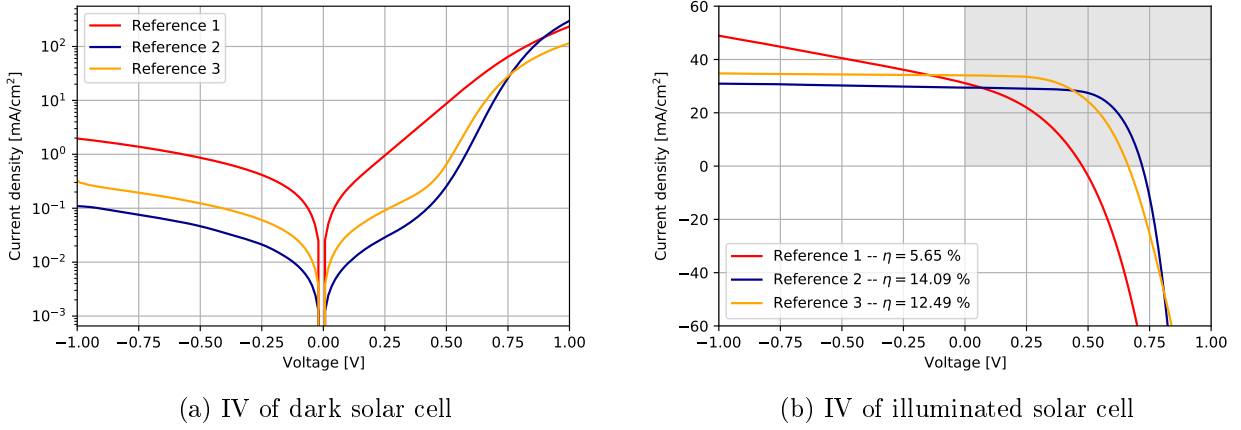


Figure 5.1.1: IV curve of the three different references

At first glance, it is directly noticeable that the same cell structure with different absorbers can yield very different results in terms of performance. In figure 5.1.1b, reference 2 & 3 have a high efficiency while reference 1 has a much lower efficiency.

The main figures of merit of each sample are directly extracted from figure 5.1.1b.

- J_{sc} is extracted by looking at the value of the current at zero voltage bias.
- V_{oc} is extracted by looking at the value of the voltage at zero current.
- η is computed by taking the maximal power divided by the irradiance, which is 100mW/cm².
- FF is computed by taking the ratio between the maximal power and the product $J_{sc} \cdot V_{oc}$.

These extracted figures of merit are presented in table 5.1.1.

¹The champion cell in a sample is the cell that provides the best performance, after removal of the outliers. More detail about this is given in section 5.1.3

Parameter	Reference 1	Reference 2	Reference 3
J_{sc} [mA/cm ²]	31.28	29.24	34.1
V_{oc} [mV]	476.8	719.9	663.3
η [%]	5.65	14.09	12.49
FF [%]	37.9	66.5	55.2

Table 5.1.1: Figures of merit for the three different samples

The best cell in this case is reference 2. Despite having a lower J_{sc} than the two others, it has better efficiency both thanks to its high V_{oc} and FF. Reference 1, the worst performing cell, has these two parameters much lower than reference 2 & 3, which explains why it is performing poorly. It is known from the theory and also from SCAPS simulations that these parameters vary due to the presence of losses inside the solar cell, both extrinsic and intrinsic. The first step in the loss analysis, using the IV measurement, is to extract the external losses R_s and R_{sh} .

5.1.2 External losses

From the SCAPS simulations in section 4.1.1, it is known that R_s and R_{sh} negatively affect the efficiency of the cell through a reduction of FF. It is often interesting to be able to understand the impact of these external losses but also to decorrelate them from the internal losses, as presented in [39]. For this purpose, the values of R_s and R_{sh} are extracted from the IV measurements, and a corrected version of the curve is then made using the 1-diode model.

Extraction of R_{sh} In order to extract the shunt resistance, a plot of dV/dJ vs V is made [39]. For this purpose, the data in dark conditions is used in order to avoid parasitic effects of I_{ph} on the extracted value. In the case of an ideal solar cell with shunt resistance, this representation should yield a constant line in the negative voltage bias range, whose value is the one of R_{sh} . In reverse bias, there are three main current contributions in the solar cell: the shunt current, the diffusion current of the minority carriers and the SRH recombination current originating from the action of defects. When the defect density is low, the reverse bias current flowing through the shunt resistance should normally be dominant over the other two.

The dV/dJ vs V characteristic is represented for the reference cells in figure 5.1.2a. In this figure, the behaviour in reverse bias is not exactly constant as expected, but the general trend is still linear in average. Typically, noise induced by the measurement makes derivatives like the dV/dJ presented here a little noisy. For reference 1, this is less the case than for the two others. This comes from the lower shunt resistance, and thus from the higher reverse current flowing through the device that is easier to measure accurately. The value of R_{sh} is extracted from figure 5.1.2a by taking an average value over a small range of voltages, generally around 0V. These extracted values of R_{sh} are presented further in the completed table of performance (table 5.1.2).

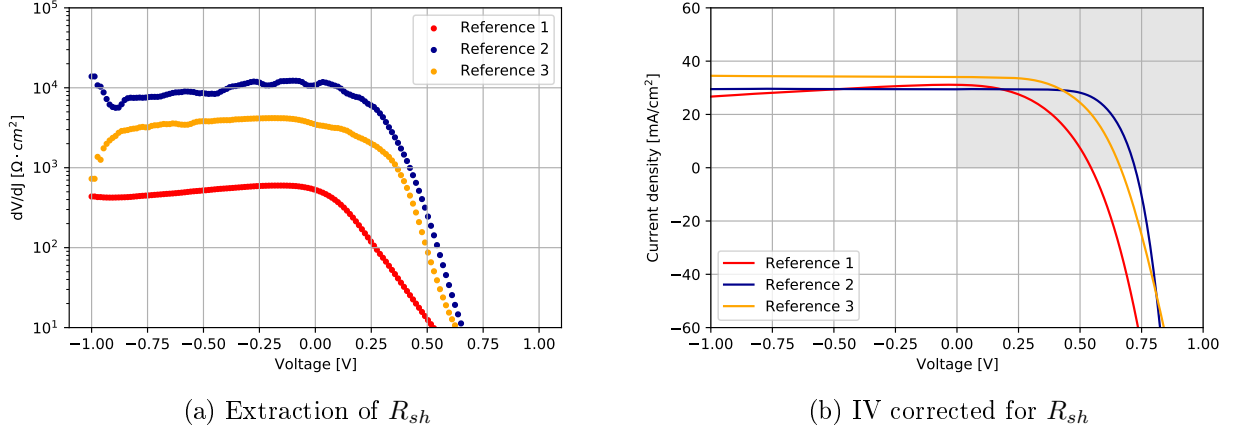


Figure 5.1.2: Extraction of shunt resistance and correction of the IV curve

After extraction of R_{sh} , the IV curve is corrected using the 1-diode model equations, leading to figure 5.1.2b. There, it is possible to see that the impact of R_{sh} has completely disappeared for reference 2 & 3, leading to a completely flat curve in reverse bias. For reference 1, the extraction of R_{sh} is not properly done, which leads to a wrong correction and a negative slope in the reverse bias range. This highlights the complexity of extracting R_{sh} . In the case of reference 1, the value of R_{sh} changes quite a lot between dark and light condition, leading to this overestimation of R_{sh} .

Extraction of R_s For the extraction of the series resistance, the data corrected for the shunt resistance is used as starting point [39]. The derivative dV/dJ is plotted as a function of $(J + J_{sc})^{-1}$. This is chosen from equation 4.1.1, and by considering $J_{ph} = J_{sc}$, leading to:

$$R_s(J) = \frac{dV}{dJ} = R_s + \frac{q}{mkT}(J + J_{sc})^{-1} \quad (5.1.1)$$

Plotting dV/dJ as a function of $(J + J_{sc})^{-1}$ should thus ideally yield a straight line intercepting the y-axis at the value of R_s . Due to the photo-generated current not being constant with voltage, from the action of defects and other intrinsic losses, this is not the case in practice. Therefore, a linear fit to the data at low $(J + J_{sc})^{-1}$ is performed, and the intercept of this fit with the y-axis gives the value of R_s .

The dV/dJ vs $(J + J_{sc})^{-1}$ characteristic is represented for the reference cells in figure 5.1.3a. As expected, the derivative is not directly a straight line and the linear fit is therefore used for extracting R_s at the intersection with the y-axis. These extracted values of R_s are also presented further in the completed table of performance (table 5.1.2). Here, Reference 1 & 2 both present a rather low R_s while it is higher for reference 3.

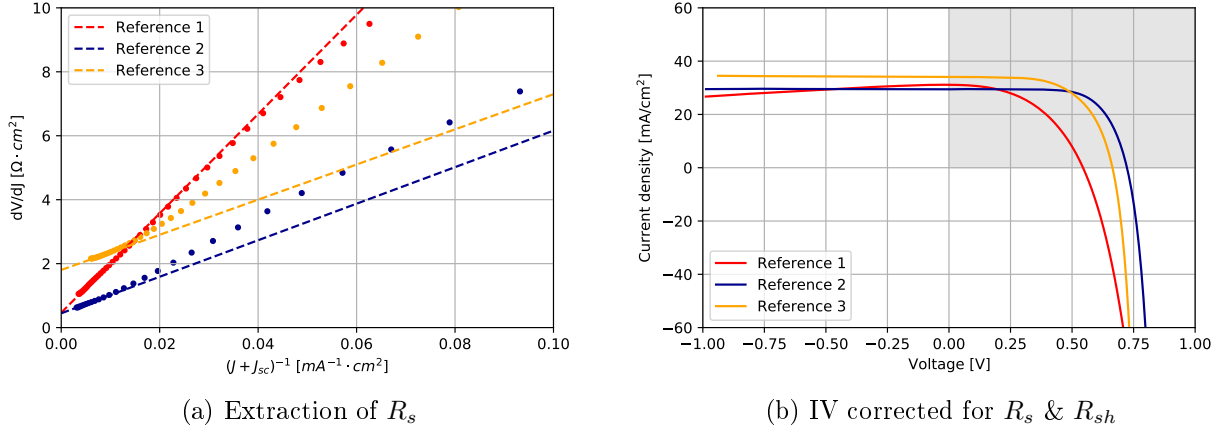


Figure 5.1.3: Extraction of series resistance and correction of the IV curve. The linear fits are represented in dashed lines.

Using the 1-diode model equation, it is also possible to correct the IV curve to remove the action of R_s . This is done in figure 5.1.3b. The correction is not as good as for the shunt resistance, and this is a well know problem of IV measurements on solar cells: the extraction of the series resistance is quite difficult. This is due to the extraction process being affected by the intrinsic losses of the solar cell [39]. Nevertheless, the correction does work to a certain extend, certainly for reference 2 & 3.

Corrected values of FF and η Using the IV curve corrected for R_s & R_{sh} , new values of FF and η can be computed. These are supposedly independent from the external losses. In figure 5.1.4, the corrected vs non-corrected IV curve is represented for reference 1. There, it clearly appears that the external losses are responsible for a big reduction in FF of about 10%. Their removal constitutes a big improvement in terms of performance. The values of corrected FF_c & η_c for the three references are presented in the completed table of performance (table 5.1.2).

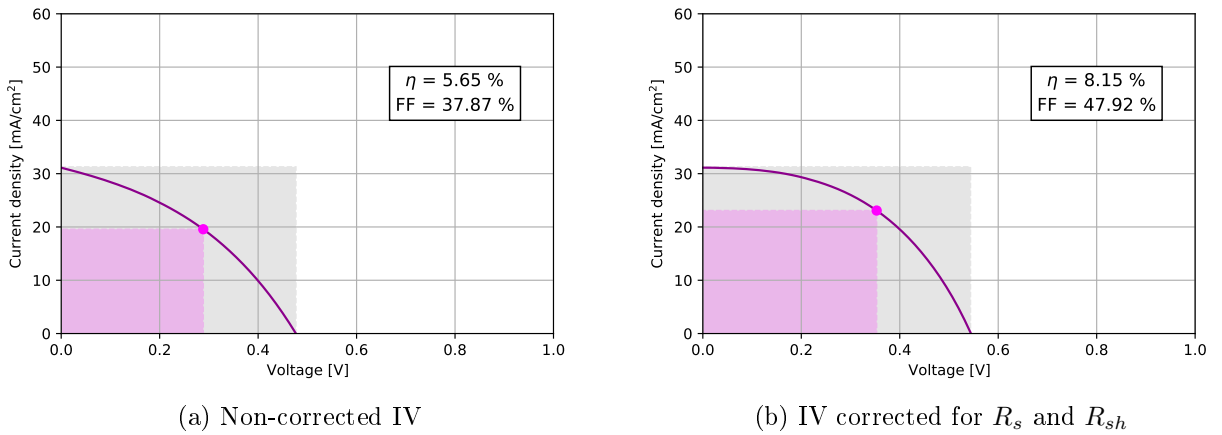


Figure 5.1.4: Correction of the IV curve for extraction of intrinsic FF_c and η_c (Reference 1)

Completed table of performance The complete summary of performance for the three reference cells is presented in table 5.1.2. The important figures of merit are presented, as well as the external losses R_s and R_{sh} .

Parameter	Reference 1	Reference 2	Reference 3
J_{sc} [mA/cm ²]	31.28	29.24	34.1
V_{oc} [mV]	476.8	719.9	663.3
η [%]	5.65	14.09	12.49
FF [%]	37.9	66.5	55.2
R_{sh} [$\Omega \cdot \text{cm}^2$]	558.49	10865.3	3717.7
R_s [$\Omega \cdot \text{cm}^2$]	0.42	0.42	2.06
η_c [%]	8.15	14.83	13.99
FF _c [%]	47.92	70.07	62.49

Table 5.1.2: Updated table of performance, after extraction of the external losses and correction of the IV curve.

From this table, the impact of external losses is deduced. It appears to be very small for reference 2. It has a very low series resistance as well as a very high shunt resistance. Also, there is little difference between the real values of FF & η and the corrected values of FF & η for reference 2. This is the sign that R_s and R_{sh} do not have much impact on the efficiency, only about 0.74%.

The impact of external losses is the greatest for reference 1. There, the low R_{sh} is responsible for a big efficiency drop of about 2.5%. The lower quality of absorber is probably at the origin of these shunt losses. When looking at absorber 1 under a SEM microscope, it presents a rougher surface than absorber 2 and 3. This greater roughness might be responsible for the shunt losses, as explained previously in section 2.2.3. An increased roughness leads to a worse coverage and homogeneity when depositing the CdS and ZnO layers, which leads to direct paths for the current between the front contact and the absorber and might explain this lower shunt resistance. In this case, removing the external losses significantly improves FF & η , a sign that they are indeed significant.

For reference 3, the higher series resistance is in that case responsible for the reduced performance. The impact on performance is not as important as for reference 1, but there is still 1.5% efficiency drop due to non-ideal R_s and R_{sh} .

IV measurements are quite useful to easily quantify the impact of external losses. Nevertheless, as mentioned hereabove, the extraction techniques are not perfect and the results must thus be taken with care as well as completed with other types of measurements for validation. This is especially true when considering cells that are measured at different times and ageing stage. The next section goes into more details about the limitations of performance evaluation in real solar cells.

5.1.3 Limitations to sample performance evaluation

An easy extraction of the most important figures of merit makes IV measurements very suitable for performance analysis. Nevertheless, there are a few points that need to be taken into account in order to correctly interpret the results. The three important limitations that are presented here are J_{sc} variation, varying R_s due to contacts and performance homogeneity over the whole sample.

J_{sc} variation This first limitation is inherent to the use of IV as performance evaluation tool, and also specific to the setup used in this work. As a reminder, an *Oriel solar simulator* is used to simulate the action of the sun illumination, following the AM 1.5G spectrum at $G = 100\text{mW}/\text{cm}^2$. In order for this value to be correct, the tool must be calibrated. The irradiance directly influences the photo-generated current and thus also J_{sc} . Hence, if the tool is not calibrated properly, the extracted value of J_{sc} is incorrect. In the context of this work, the tool is not calibrated every time an IV measurement is done. This means that the value of J_{sc} for some of the cells may vary with respect to the actual value. For this reason, EQE measurements are performed in order to validate the value of J_{sc} . This is developed in the next section.

On top of calibration, another parameter has an impact on the extracted value of J_{sc} : the solar cells area. For computing the current density J , the current through the device is measured and is then divided by the area of the cell: $A = 0.5\text{cm}^2$. In the computation of J , it is assumed that this value of A is the same for every cell. This is in practice not correct, due to the scribing process that is done by hand (section 3.2.1). It is thus possible that the value of J_{sc} varies virtually quite a lot on one sample, only because the actual value of A is different from the one that is used for computing J . This is illustrated in figure 5.1.5a.

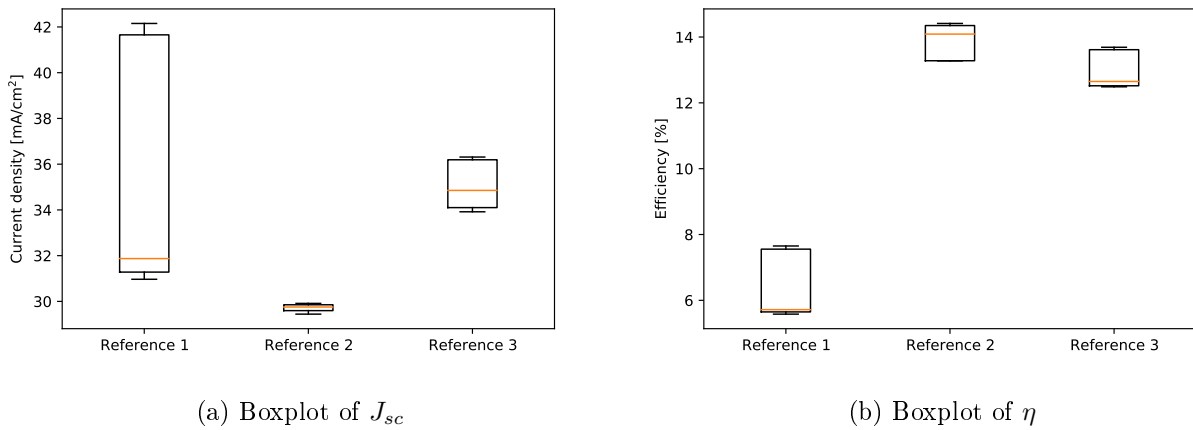


Figure 5.1.5: Boxplot of J_{sc} & η measured for different cells of each of the three reference samples

In this figure, an important increase of J_{sc} is visible for some cells of reference 1. Because the highest value, above 40 mA/cm^2 , is much higher than the median value, around 32 mA/cm^2 , and also higher than the best performing cells on the market, it is very unlikely. Here, this high value of J_{sc} is probably coming from a scribing error, which is confirmed when performing a visual check on the sample.

This very high value of J_{sc} has also an impact on η , as illustrated in figure 5.1.5b. For reference 1, it is very probable that the high value of η for some of the samples comes from the virtually high current density. For this reason, the outlier value of J_{sc} must be discarded, and another cell should be considered as champion cell for this sample.

In opposition, the values of reference 2 are very much concentrated around 30 mA/cm^2 . This indicates that the scribing process yielded cells of even area, but does not yet confirm the median value of J_{sc} . Indeed, as all the data is coming from one measurement batch, it is still possible that the tool was not calibrated properly at the time of measurement. The value should thus be confirmed using EQE measurements. It must be noted, when looking at figure 5.1.5b, that for reference 2 the variation in efficiency between the different samples does not come from a variation in current. It must thus be further interpreted by looking at other figures of merit.

Variation of R_s due to contacts As explained in section 3.2.1, at the end of processing, part of the cell is removed for exposing the Mo back contact. At this moment, a metal is deposited on top of the Mo for preventing its oxidation with time. In the scope of this work, In is always used, except for reference 3 where Ag and In are both tried. The series resistance for reference 3 with In and Ag contacts is represented in figure 5.1.6a.

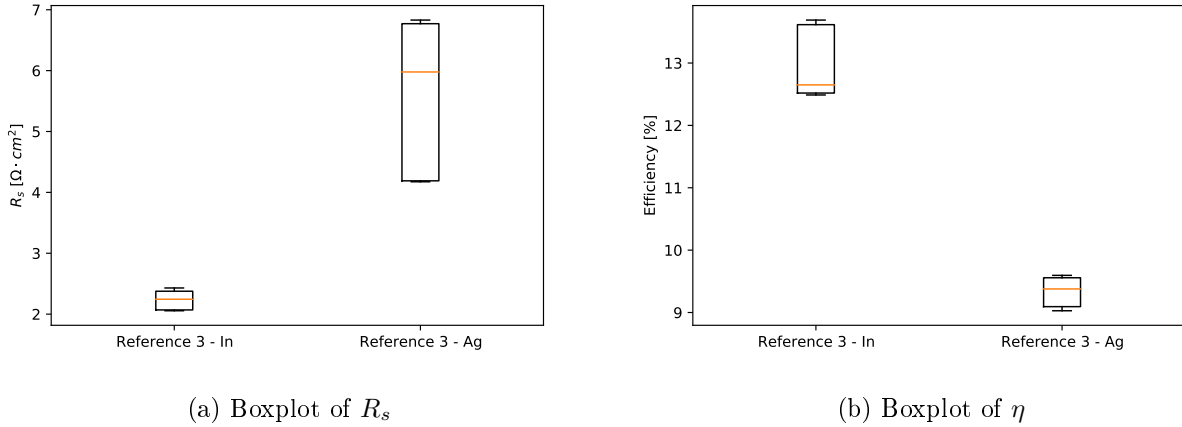


Figure 5.1.6: Boxplot of R_s & η measured for different cells of reference 3

The impact of the contact material on the series resistance is visible. When using the Ag contact, the series resistance is much higher and there is also more variation for the different cells of the sample. This directly results, in figure 5.1.6b, in a reduction of the efficiency of the cell. The reason why Ag contacts are performing poorly is probably due to the fact that a conductive paint containing Ag is used, which is less reliable in terms of homogeneity and performance than pure metal such as In. This result also illustrates the importance of a good contact on the value of R_s , and more generally on the solar cell performance. If the contact is not chosen properly or if it oxidizes with time, the reduction in efficiency can be dramatic.

Performance homogeneity on the sample In addition to J_{sc} and R_s , the other figures of merit can vary in different cells of one sample. Their variation is more difficult to precisely interpret, but it overall leads to the conclusion that performance are not homogeneous over the entire sample. This is due to the processing and the deposition techniques. This variation is illustrated for the main figures of merit in figure 5.1.7.

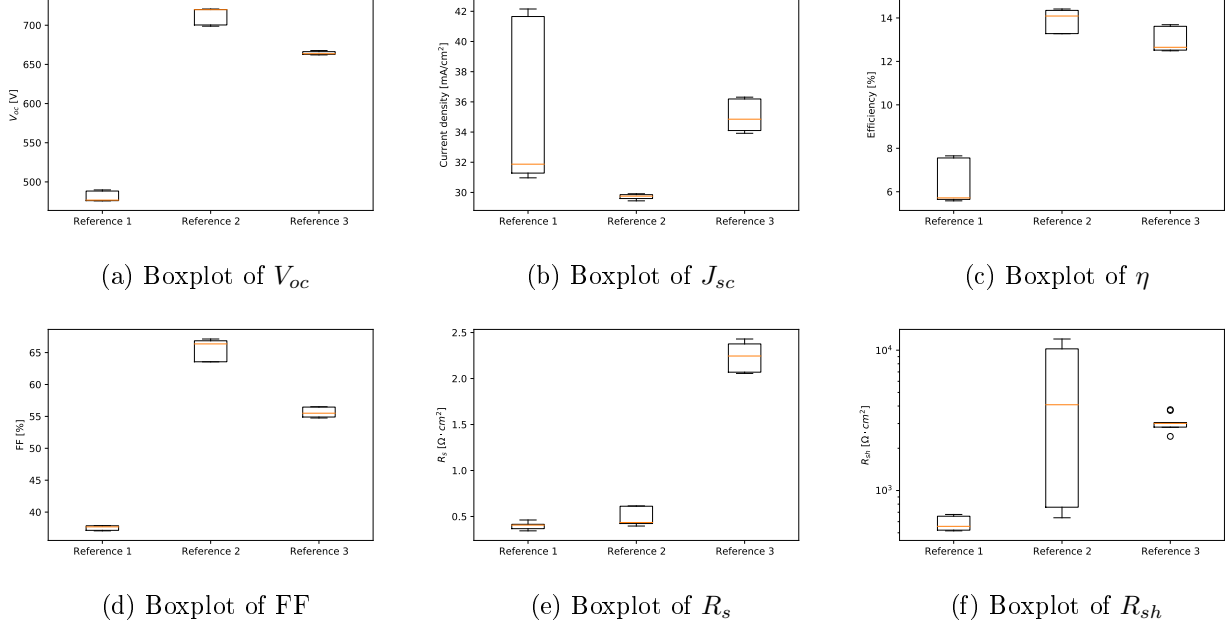


Figure 5.1.7: Boxplot of the figures of merit measured for different cells of each of the three reference samples

Even though the exact phenomenon behind each of the variations in these boxplots is not always clear, it generally can provide some insight about the quality of the processing. For example, in figure 5.1.7f, reference 2 presents a great variation in R_{sh} . Because it is linked to the coverage of the absorber with the CdS layer, it is likely in this case that the coverage is not optimal over the entire sample. Some cells present a very high R_{sh} , sign of a good cell stack, while some other cells have a much lower R_{sh} . This leads to the hypothesis that maybe the CdS and ZnO/ITO deposition is not optimal over the whole sample. In this precise case, the impact on the performance is not dramatic, as it can be deduced from figure 5.1.7c.

Selection of the champion cell As a conclusion on the sample performance evaluation, it appears that having an overview of not only the performance of one cell but also multiple cells on one sample is important. While the selection of one champion cell is useful for comparing the cells between them, it is also important to look at the variations to be able to fully characterize the sample performance and to obtain a potentially reproducible or even up-scalable process. In the rest of this work, champion cells are mostly used for the sample to sample comparison, but they are always chosen comparatively to the other cells. The outliers are discarded and all the figures of merit are taken into account so that the selected cell is representative of the overall sample performance.

5.1.4 EQE measurements for J_{sc} evaluation

On top of providing information about the absorption of light and extraction of carriers in function of the light wavelength, EQE measurements can also be used to estimate the value of J_{sc} . This can be done using equation (3.3.4) from section 3.3.4:

$$J_{sc} = \int_{\lambda_{min}}^{\lambda_{max}} \text{EQE}(\lambda) \cdot h(\lambda) \cdot \frac{q\lambda}{hc} d\lambda \quad (5.1.2)$$

where $h(\lambda)$ is the spectral irradiance of AM 1.5G spectrum. This integral is numerically computed for reference 2 & 3, with the curves of EQE and $h(\lambda)$ shown in figure 5.1.8. The comparison between the obtained J_{sc} using IV and EQE measurement is given in table 5.1.3.

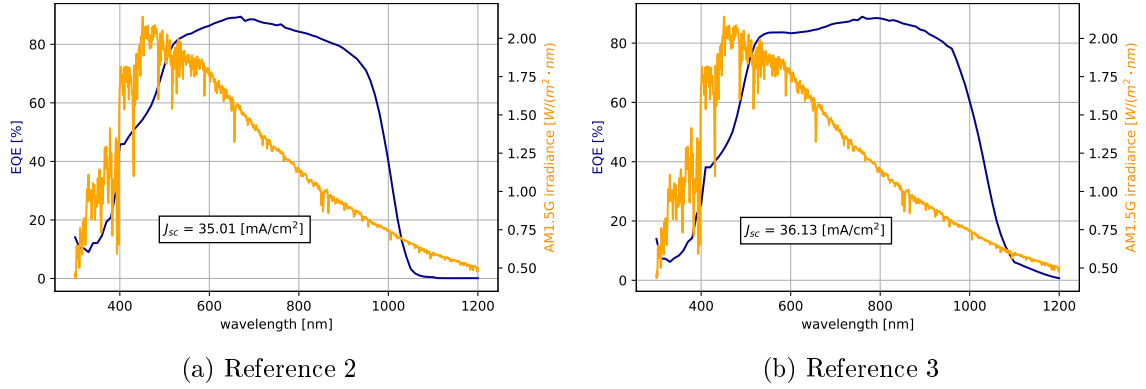


Figure 5.1.8: EQE and AM1.5G spectrum for one cell of reference 2 & 3

Sample	EQE measurement	IV champion cell	IV median value
Reference 2	35.01	29.24	29.5
Reference 3	36.13	34.1	34.45

Table 5.1.3: J_{sc} value in $[\text{mA}/\text{cm}^2]$ for EQE and IV measurements

For reference 3, the values obtained using the two methods are quite close to each other. Normally, the value obtained using the EQE measurement should be more accurate than the one from IV measurements because it is not subject to cell area variation and lamp calibration. Because the results are quite close, no real further action is needed and the IV curves are kept as such.

For reference 2, the results are a little further from the IV experimental results. One possible explanation would be that the solar simulator used for IV was at the time of measurement slightly under its nominal operation. It is also possible that other factor have influenced this difference, but it would need further investigation of the EQE technique which is beyond the scope of this work.

5.1.5 Effect of annealing on the solar cell performance

In the previous sections, the entire process of performance evaluation is developed for the three reference cells. In this section, the impact of annealing on these cells performance is discussed, using the condensed form of this methodology.

The IV curves of the three references, before and after annealing, are represented in figure 5.1.9.

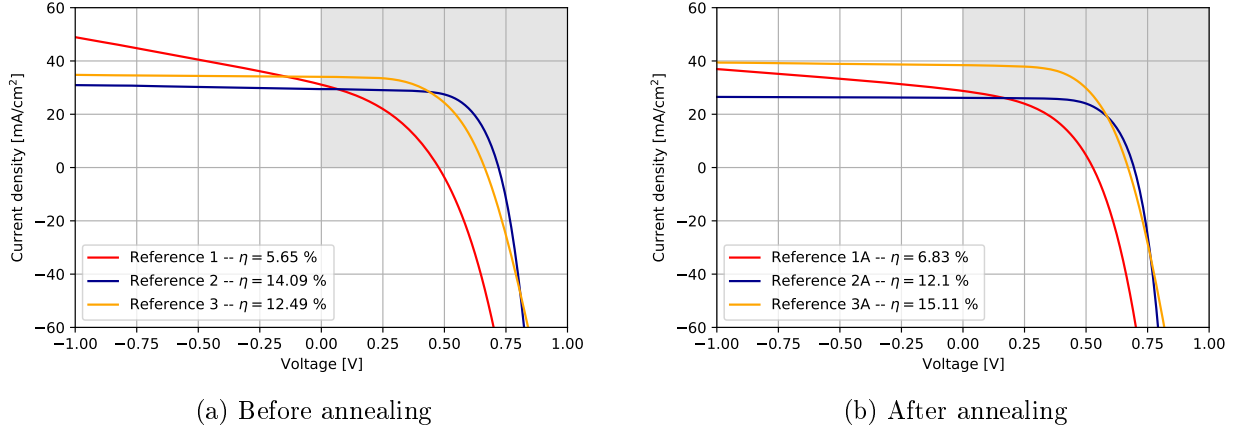


Figure 5.1.9: IV curve under light of the three different references, before and after annealing

It appears that annealing has a positive impact on the efficiency of reference 1 & 3 and a negative impact on the efficiency of reference 2. Before even looking at the extracted figures of merit, intuition on the graphs shape already provide insight about the reason of these performance change. For reference 1, the reduced slope in reverse bias indicates an increased R_{sh} which is probably at the origin of the increased performance. For reference 2, J_{sc} is reduced after annealing which is the main reason of reduced performance. For reference 3, the improved efficiency certainly comes from the increased J_{sc} . In order to go one step further, all the figures of merit related to these three IV curves are presented in table 5.1.4.

Parameter	Reference 1	Reference 1A	Reference 2	Reference 2A	Reference 3	Reference 3A
J_{sc} [mA/cm ²]	31.28	28.84	29.24	26.19	34.1	38.45
V_{oc} [mV]	476.8	527.5	719.9	694.4	663.3	670.4
η [%]	5.65	6.83	14.09	12.1	12.49	15.11
FF [%]	37.9	44.9	66.5	66.5	55.2	58.6
R_{sh} [$\Omega \cdot \text{cm}^2$]	558.49	256.54	10865.3	19321.5	3717.7	2127.3
R_s [$\Omega \cdot \text{cm}^2$]	0.42	0.34	0.42	0.43	2.06	1.93
η_c [%]	8.15	8.37	14.83	12.17	13.99	16.78
FF _c [%]	47.92	52.12	70.07	67.19	62.49	65.33

Table 5.1.4: Table of performance with comparison between the reference cells (Reference x) and the annealed reference cells (Reference xA).

Annealing of Reference 1 For reference 1, the annealing impacts most of the figures of merit. Overall, even though J_{sc} is a little bit reduced, the efficiency is improved. This is mainly due to a much better FF and a little bit to an increased V_{oc} . Following what is predicted by the SCAPS simulations, the external losses may be responsible of this FF increase if R_s is reduced or R_{sh} is increased. In this case, R_s is indeed decreased, but this is not the most significant contributor to the improved FF.

Even though in the table it seems like R_{sh} has decreased, it is necessary to remember that this value is extracted from dark measurements. Due to the action of the photo-generated current, the extracted value of R_{sh} always varies between dark and light measurements. This is illustrated in figure 5.1.10. There, it is visible that even though R_{sh} is lower after annealing in the dark, the value under light is higher after annealing. This also corresponds to what is deduced from figure 5.1.9 where the slope of reference 1 in reverse bias is indeed higher before annealing. A possible interpretation of different R_{sh} in the dark and under light is that the mechanisms in the structure that lead to shunt losses are activated in light conditions, and are thus current dependent. After annealing, it appears that this difference between the two R_{sh} is smaller. The conclusion is thus that even though the extracted value in the dark is worse after annealing, the value that matters for performance, R_{sh} under light, is better after annealing. This contributes significantly to the improvement of FF.

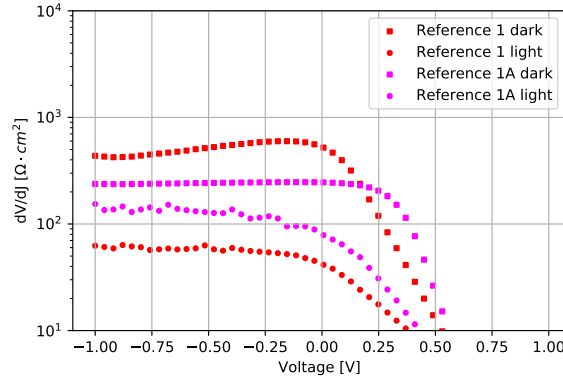


Figure 5.1.10: Extraction of R_{sh} from dark and light IV measurements, for reference 1 before and after annealing

Annealing of Reference 2 For reference 2, the annealing has mostly an impact on J_{sc} , V_{oc} and R_{sh} . The two first parameters become worse after annealing and the last parameter becomes better, but not sufficiently to increase the efficiency. An important question to ask is whether there is indeed a sensible reduction in J_{sc} , which appears to be mostly responsible for the drop in performance, or if it is an artefact of the measurement. For this purpose, an EQE measurement is used. The comparison between the two EQE spectra is given in figure 5.1.11. In that case, it appears that the value of J_{sc} is not lower but actually higher for the annealed sample. This wrong value of J_{sc} is possibly coming from a wrong scribing process, but this is not the best hypothesis in this case as the selected cell is already the champion cell and thus the one presenting the best characteristics. It is also not probable that this comes from tool calibration as the samples are measured one after the other and the settings

of the solar simulator are not changed in between. It is thus complicated to conclude on the reason of this wrong J_{sc} extraction. The direct consequence of J_{sc} not being reduced and even being increased is that the efficiency of reference 2 after annealing is not reduced as presented in table 5.1.4.

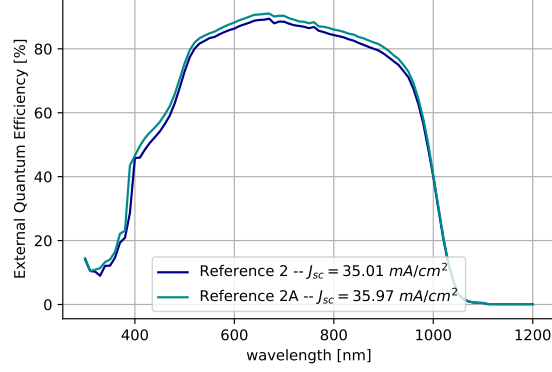


Figure 5.1.11: Comparison of EQE for reference 2 before and after annealing

Annealing of Reference 3 For reference 3, the annealing mostly affects J_{sc} and FF. Because R_s & R_{sh} are not affected, it is probable that the increase in FF is coming from improvements that are intrinsic to the solar cell, by example defects action that is reduced. This needs to be further investigated using other characterization techniques. In the same way as for reference 2, it is possible to confirm using EQE measurements that J_{sc} is actually improved after annealing. This is represented in figure 5.1.12. In this case, the EQE measurements confirm an increase in J_{sc} , even though it is not as high as the one predicted in the IV measurements. This means that the efficiency gain is lower than predicted. A possible explanation would be a wrong scribing process that increases artificially the value of J_{sc} .

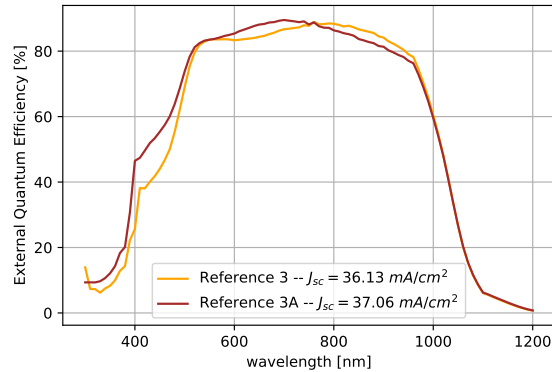


Figure 5.1.12: Comparison of EQE for reference 3 before and after annealing

This concludes this first section about performance of the reference CIGS cells. A lot of information is already extracted from these measurements, but in order to study the impact of defects on performance, it is necessary to go one step further and to look at CV and PL measurements.

5.2 CV measurements

In this section, the three reference cells are analyzed using CVf measurements and the AS method. This, combined with the simulation results from SCAPS presented in section 4.2, should provide useful information about defects mechanisms in these structures. First, room temperature measurements are considered. After that, a comment is made on correction of R_s for CVf loss maps. Then, low temperature measurements are performed to extract the defects parameters. Finally, a comparison is made between the reference cells and the annealed reference cells.

5.2.1 Room temperature measurements

Before introducing the results of the AS characterization, it is interesting to look at the CV and Cf curves separately and compare them for the different references. Even though they do not enable the defects full characterization, they provide some interesting information about the general capacitive behaviour of the solar cells.

CV characteristics The CV characteristics for the three reference cells are shown in figure 5.2.1.

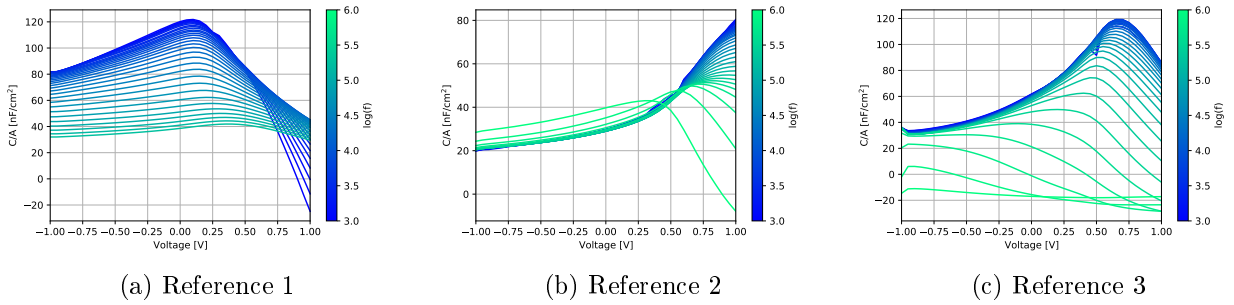


Figure 5.2.1: CV characteristics of the three reference cells

At first glance, it is already clear that these solar cells behave very differently on a capacitance perspective. These differences can be studied using the theory developed in section 2.3. Solar cells are working in depletion regime. This means that the capacitance should normally look like the one in figure 5.2.1b where the capacitance increases with bias voltage. The presence of a peak in capacitance such as in figure 5.2.1a and 5.2.1c is typical of the presence of intrinsic losses in the structure. There, the total capacitance is not only constituted of the depletion capacitance, but also of additional capacitances related to the presence of charge traps. This tends to indicate that reference 2 would have less intrinsic losses acting on the capacitance than the two other references.

These cells also differ when looking at the frequency behaviour. Reference 1 & 3 present a high dispersion in frequency, contrarily to reference 2 that only presents frequency dispersion at high voltage bias. This is also a sign of the presence of intrinsic losses, or for higher frequencies the sign of a higher series resistance. Normally, when the total capacitance is only constituted of the depletion capacitance, it should be frequency independent. This is mostly the case of reference 2. When there are

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other contributors such as defects, the capacitance tends to decrease with the frequency increasing. This is quite straightforward: when the frequency increases, the AC excitation that is responsible for the defects charge and discharge is faster and the amount of carriers that are able to follow this excitation reduces. This is observed for reference 1 & 3. This reducing capacitance with respect to frequency is also visible in the case of reference 2, but only at high voltage bias. There is probably also a loss mechanism acting in that region.

As these are experimental measurements, some comments must be made about the accuracy of the setup and the measurement. Two main problems can be identified from figure 5.2.1. First, a slight measurement error from the tool is observed at 0.5V for low values of frequency. This error is present in all the CV measurements, and always at the same voltage and frequency biases. It does not impact the interpretation of the measurement, but it is interesting to note that it is present and specific to the setup that is used. The second problem is the negative value of capacitance recorded for some voltage and frequency biases. This is not specific to the setup, but is typically caused by the presence of a frequency dependent R_s combined to a high DC current at high voltage biases [47]. As the AS method makes use of the $-fdC/df$ derivative, this negative value of capacitance should normally not impact the interpretation of the results. Also, the high dispersion factor at high DC current generally implies that this range where the negative values appear is discarded from the analysis.

Cf characteristic The same information can also be represented in a Cf characteristic, and this is done for the three reference cells in figure 5.2.2.

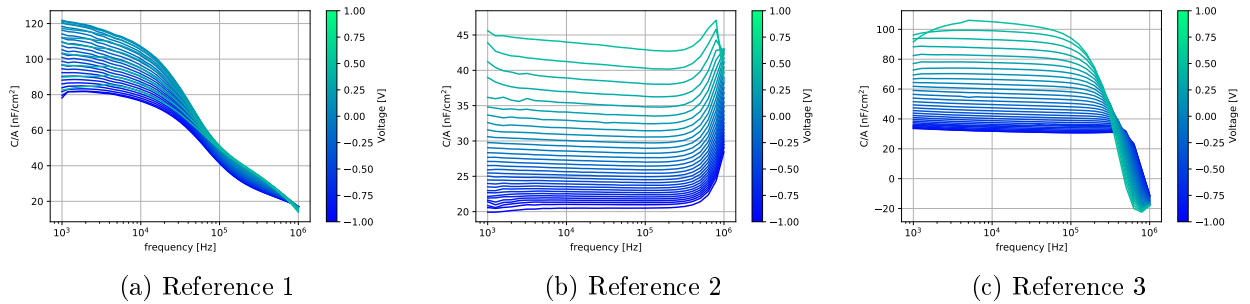


Figure 5.2.2: Cf characteristics of the three reference cells

These curves confirm what is already deduced hereabove from the CV characteristics. As anticipated, reference 2 (figure 5.2.2b) is the closest to an ideal solar cell, composed of a depletion capacitance only. The curves at each voltage bias are almost constant, except at very high frequency. Reference 1 (figure 5.2.2a) clearly presents a certain cut-off frequency at which the capacitance drops. This is a clear sign of the presence of a charge trap in the device, as already presented in section 2.3.4. Reference 3 (figure 5.2.2c) also has a certain cut-off frequency, which is higher than for reference 1. Such a high frequency response is probably coming from the effect of a series resistance which acts together with the depletion capacitance as a low-pass filter. This is suggested by the high frequency at which the drop in capacitance happens, and the sharp decline. Moreover, it is further motivated by the capacitance dropping in the negative values which is also the sign of a significant series resistance.

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CVf loss maps Even though CV and Cf characteristics provide some useful information on the cells, it is often tricky to extract all the information needed from them. Loss maps are thus used and are represented for the three reference cells in figure 5.2.3. The three signatures are detailed hereafter.

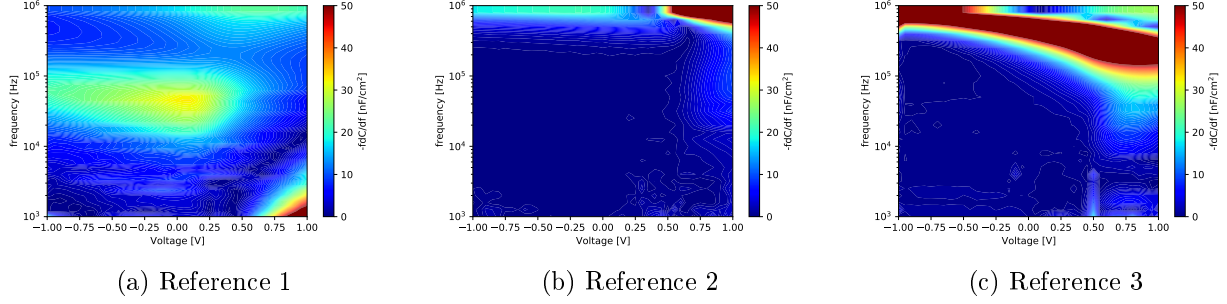


Figure 5.2.3: Loss maps of the three reference cells

Reference 1 Figure 5.2.3a presents a very broad signature in the center of the device. For interpreting this signature, the theory and the SCAPS simulations must be used. From simulation results in section 4.2.2 and 4.2.3, it is very probable that this signature is either a bulk defect or a barrier at the CIGS/CdS interface. These two are represented aside of reference 1 in figure 5.2.4.

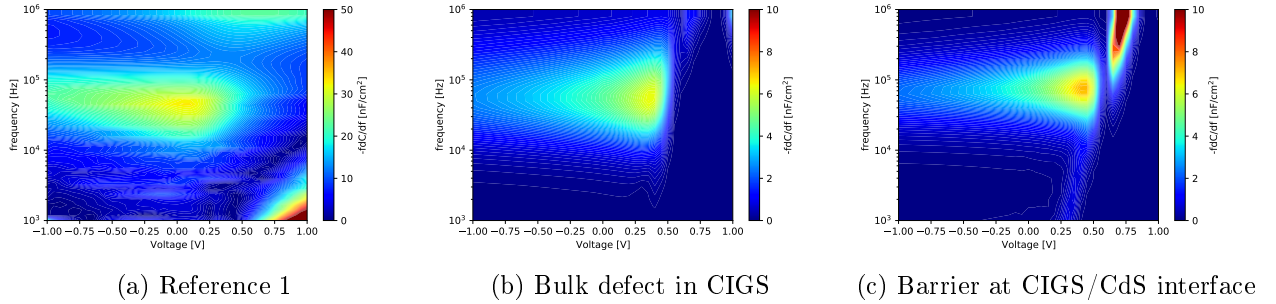


Figure 5.2.4: Comparison between the loss map of reference 1 and SCAPS simulations

It is quite complicated to determine at this stage which of the two types of losses is present in reference 1. From what is known of the absorber, it is not of the best quality, and it is possible that its concentration in bulk defect is sufficiently high to be responsible for the signature on the map. It is also possible that, due to the mismatch between the CIGS and the CdS, the barrier at the interface is very high and in that case the second option is also possible. To be able to conclude about reference 1, it is necessary to go one step further with the analysis of other structures having the same absorber.

Even though the exact loss mechanism is not yet known, the map confirms that charge trapping is responsible for part of the lower performance of reference 1 compared to the other two. The typical working region of the solar cell, between 0V and 0.7V, is a region where the trap is active. This means that a lot of carriers are trapped in this region which then impacts the efficiency. Indeed, when carriers get trapped and cannot get extracted properly, the photo-generated current is lower which highly impacts V_{oc} . This is the reason why $V_{oc,1}$ is much lower compared to $V_{oc,2}$ & $V_{oc,3}$.

Reference 2 There is not much information in the loss map of figure 5.2.3b. There is a little signature present at higher frequencies, which is probably the effect of the small series resistance extracted in the performance analysis. In the active region of the solar cell, there is almost no signature, meaning that there is almost no charge trapping. This sustains the high value of V_{oc} & η obtained for this sample. Because of this already quite ideal capacitive behaviour, it is probable that using passivated structures for improving performance is not critical in this case.

Reference 3 The loss map of figure 5.2.3c presents a broad signature at high frequency bias. Based on the SCAPS simulations from section 4.2.1, it is very probable that this signature is mainly caused by a high series resistance. This is confirmed by the Cf measurements presented hereabove, as well as by the performance analysis where the extracted R_s is much higher than for the other two references. Overall, similarly to reference 2, the signature on the map is not that much present in the active area of the solar cell. This justifies the high V_{oc} & η , but also that reference 3 has a slightly lower performance than reference 2.

On the right of the map, the signature becomes broader and lower in frequency. It is not typical of the action of series resistance and it may thus come from the action of another loss mechanism. Using this figure only, it is difficult to confirm this with certainty, which is why it needs to be further investigated. This is done in a next section presenting low temperature measurements.

5.2.2 Correction of R_s

When performing CVf measurements on MOS or MIS structures, it is very common to correct these measurements to remove the effect of the series resistance [48]. It can affect the measured value of capacitance, such as presented in section 2.3.8, by acting together with C_{ox} as a low-pass filter. This is particularly true when performing measurements at high frequency. By using an equivalent model that takes this series resistance into account, it is possible to derive the equations for the corrected values of capacitance C_c and conductance G_c as [48]:

$$C_c = \frac{(G_m^2 + \omega^2 C_m^2) \cdot C_m}{a^2 + \omega^2 C_m^2} \quad (5.2.1)$$

$$G_c = \frac{(G_m^2 + \omega^2 C_m^2) \cdot a}{a^2 + \omega^2 C_m^2} \quad (5.2.2)$$

where $a = G_m - (G_m^2 + \omega^2 C_m^2) \cdot R_s$ and C_m and G_m are the measured values of capacitance and equivalent parallel conductance as already defined before.

It is also possible to perform this correction in the case of solar cells, but some very important limitations can occur. The most important one is that the conductance is much higher in the case of a solar cell, which leads to more uncertainty on the measured capacitance. This can easily result in a wrong computation of C_c . Furthermore, the extraction technique of R_s used here is based on IV measurements and is also not perfect, potentially leading to a wrong evaluation of R_s .

The loss maps corrected for series resistance are represented for the three references in figure 5.2.5.

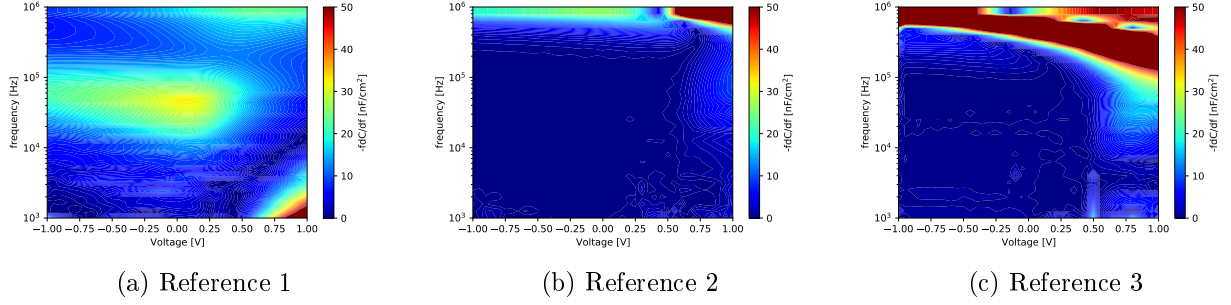


Figure 5.2.5: Loss maps of the three reference cells corrected for series resistance

This figure presents very few difference with figure 5.2.3 where the uncorrected maps are represented. It illustrates the fact that correcting R_s in the case of solar cells is a complex matter and that it is not particularly suitable to the CVf maps application. This is not really an issue. Indeed, the absolute value of capacitance is not relevant for loss maps, and the trace of R_s on the map is quite straightforward to identify. This makes the correction for R_s less critical in the scope of this work. For this reason, it is not investigated further in the following chapters.

5.2.3 Low temperature measurements

As detailed in section 2.3.7, low temperature measurements can be used to extract the defects activation energy E_A and capture cross-section σ . They can also be used to spot shallower defects, whose response is not directly visible on room temperature measurements. In the scope of this work, room temperature measurements are performed on the samples made with absorber 3. The measurements done on reference 3 are presented in figure 5.2.6.

These measurements confirm what is sensed already in figure 5.2.3c: the contribution to the CVf map for reference 3 does not only come from R_s but also from another type of loss. The contribution of R_s is visible at each temperature bias, on the very top of the map. With the temperature increasing, it merges with the other signature coming from the bottom. This last signature is the one of a defect, probably of an interface defect. Indeed, it seems to be concentrated around a certain value of voltage which is the one at which the Fermi level would cross the interface state of the defect. In the case of a bulk defect, the response would necessarily be much broader in the voltage bias range. This is confirmed by the fact that the quality of absorber 3 is very high and it is thus very unlikely that there is a sufficient concentration of bulk defects inside it to give such a response on the map.

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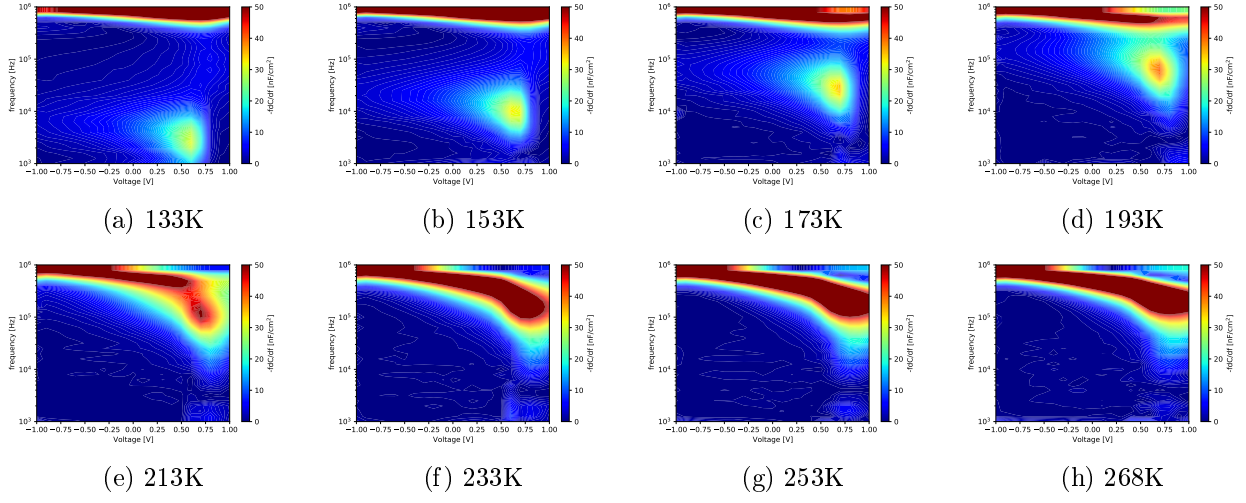


Figure 5.2.6: Loss maps of reference 3 at different temperatures

Because the signature is the one of a defect, it is interesting to try to extract E_A & σ . In order to do that, the characteristic frequency of the defect must first be extracted at each temperature bias. For this purpose, the $-f dC/df$ plots of figure 5.2.7 are used.

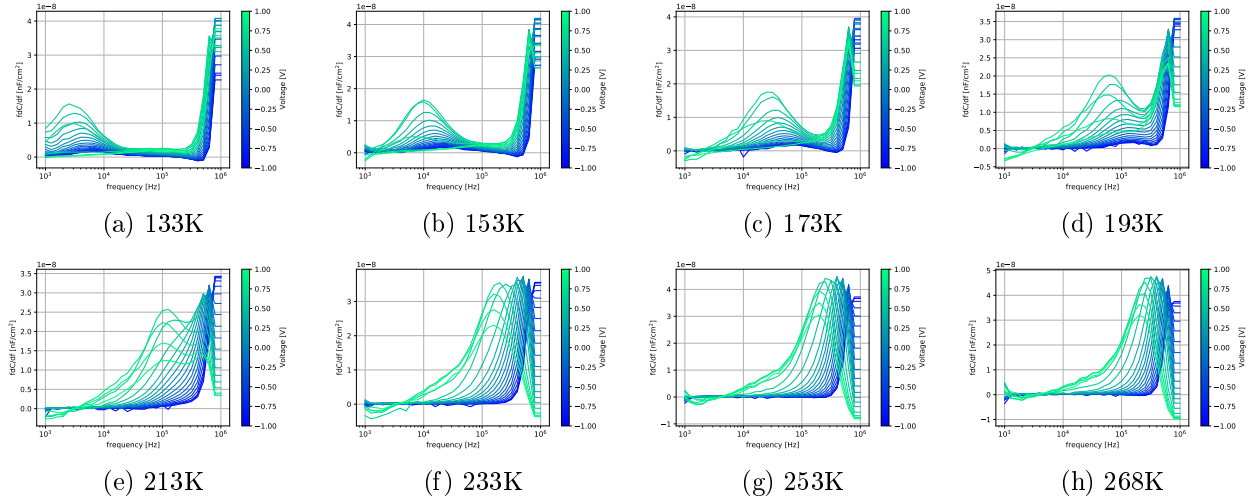


Figure 5.2.7: $-f dC/df$ curves of reference 3 at different temperatures

At each temperature bias, the characteristic frequency is the one at which the highest peak is present. The extracted characteristic frequency in function of the temperature is shown in table 5.2.1. Some values, at higher temperatures, cannot be extracted because it is almost impossible to dissociate the action of the defect from the one of R_s . Nevertheless, the five values extracted here should be sufficient to characterize the defect.

Temperature [K]	133	153	173	193	213	233	253	268
Characteristic frequency [kHz]	2.5	10	25	60	150	/	/	/

Table 5.2.1: Extracted values of characteristic frequency vs temperature

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These values are used to make an Arrhenius plot that is shown in figure 5.2.8. In this plot, a linear fit is made and E_A & σ are extracted using the equations from section 2.3.7.

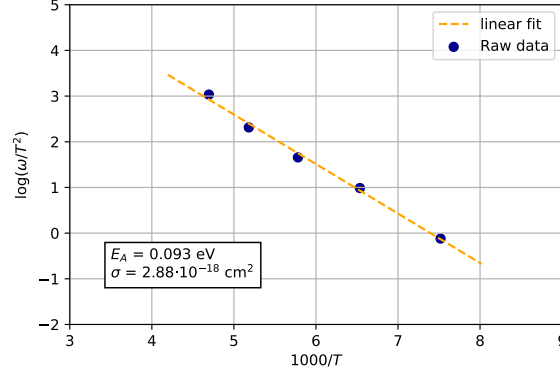


Figure 5.2.8: Arrhenius plot made from the low temperature CV data of reference 3

From this representation, it is possible to conclude about the interface defect of reference 3. It is a quite shallow defect ($E_A = 0.093 \text{ eV}$) which does not have a very high σ . Therefore, it should not impact the performance of the device in a critical way. This is confirmed by the rather high value of V_{oc} and η . It is interesting to analyze how this defect evolves when the structure is changed, i.e. when annealing is performed or when a passivation layer is introduced. Annealing is studied in the next section, and passivation is studied in the next two chapters.

5.2.4 Effect of annealing on the internal losses

The effect of annealing on each reference can be studied using loss maps. The loss maps for the three reference cells after annealing are represented in figure 5.2.9. They must be compared to figure 5.2.3 showing the same structures before annealing.

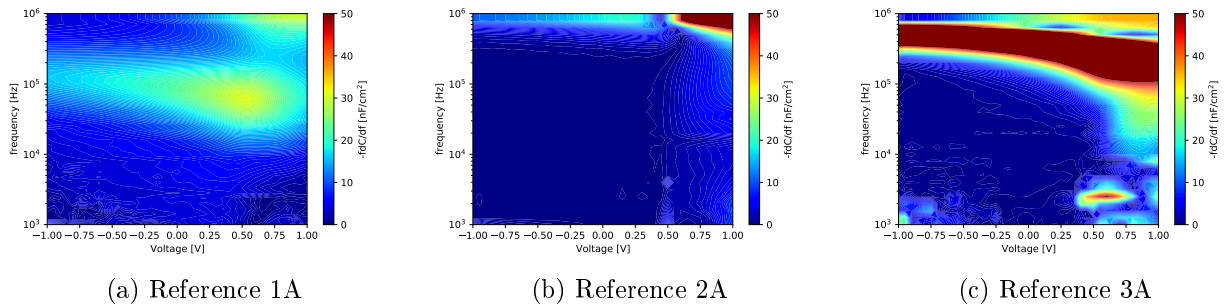


Figure 5.2.9: Loss maps of the three reference cells after annealing

The observed trend is quite similar than for the performance analysis. The annealing has a significant impact on reference 1, whilst it does not impact much reference 2 & 3.

For reference 1, the signature in the middle of the map moves to the left, displacing the active area of the defect a little outside of the active area of the solar cell. This is probably at the origin

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of the little V_{oc} increase observed in section 5.1.5. It is still not really possible to conclude about the nature of this signature. On one side, it is known that annealing impacts the absorber and thus it is possible that it reduces the defect density. On the other side, the signature intensity on the map does not change, only the voltage bias at which the signature responds changes. It is also possible that the annealing affects the barrier at the interface, but the SCAPS simulations suggest that it would change the signature in frequency bias, not in voltage bias. Further investigation is thus again needed, which is not done in this work.

For reference 2 & 3, the signature does not change much. This is also in the continuity of the performance analysis, since V_{oc} for these two cells does not change significantly with annealing. For reference 3, it is possible to look at the low temperature measurements, to see if the interface defect response is modified with annealing. The Arrhenius plot of reference 3 before and after annealing is represented in figure 5.2.10.

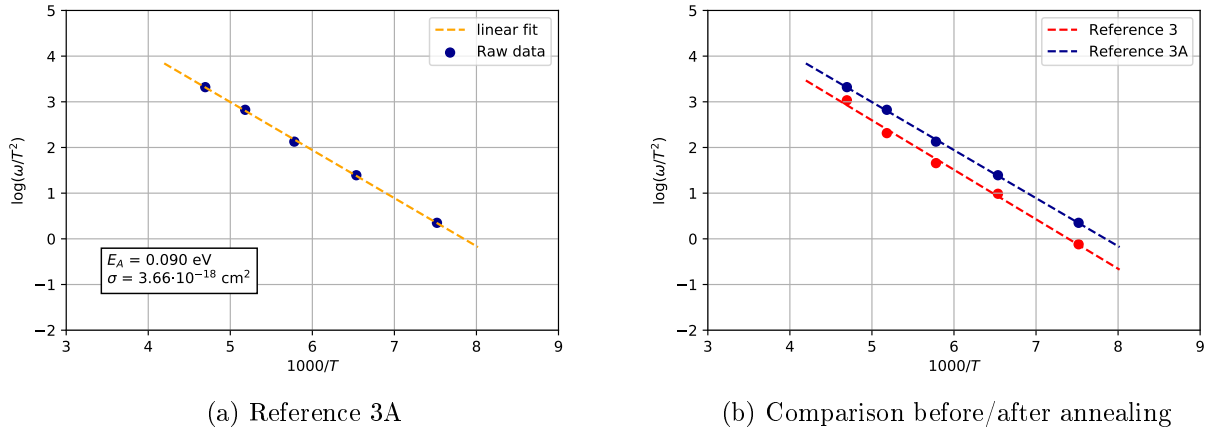


Figure 5.2.10: Arrhenius plot of reference 3A and comparison before/after annealing

The conclusion of this figure is that there is not much impact of annealing on the response of the defect. It is very probable that the differences in E_A & σ are coming from the measurement and its quantitative analysis rather than from the annealing itself. This confirms that the annealing of reference 3 does not have much impact on the intrinsic losses in the sample, as suggested before.

This concludes the section about analysis of the internal losses of the three references using the AS method. The next section provides another way of analyzing the solar cells, in a purely optical way, with the PL and TRPL measurements.

5.3 PL & TRPL measurements

In this section, PL and TRPL measurements are used to characterize the three reference cells. As mentioned in section 3.3.3, these measurements inherently contain a lot of information about very different mechanisms in the solar cell, both electrical and optical. This makes them suited for the analysis of intrinsic phenomena to the solar cell, but also renders the interpretation sometimes difficult. In this section, the validation of the absorber quality on basis of PL steady-state measurements is first briefly discussed. Secondly, TRPL measurements are performed on the three references. Finally, the impact of annealing is presented.

5.3.1 PL steady-state measurements

In this first section, the different references are compared on the basis of their PL steady-state response. This is represented in figure 5.3.1.

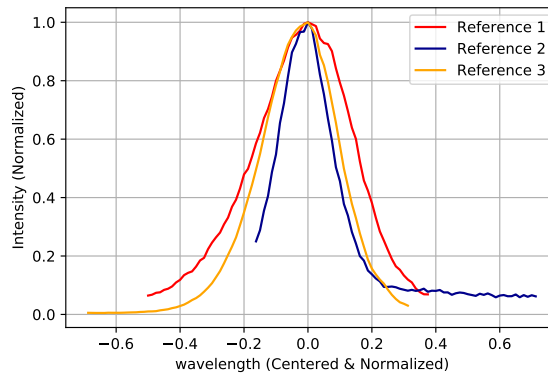


Figure 5.3.1: Normalized PL steady-state response of the three references

The main information that can be extracted from PL measurements with this figure is the so-called "Normalized width at half maximum" (NWHM). It is computed by taking the width of the normalized curve at 0.5 intensity. It is the lowest for reference 2, and the highest for reference 1. In reference [36], it is mentioned that a broader PL peak is a sign of higher bandgap fluctuation in the device. Bandgap fluctuation is an unwanted effect in CIGS solar cells. It can cause light interference in the device, therefore reducing light absorption. Also, for high fluctuation, E_g may, in certain places, become too high for the light to create e^-/h^+ pairs. NWHM is thus another way of validating the quality of a solar cell and of its absorber.

In terms of performance for the three reference cells, it makes sense that reference 2 presents the lowest fluctuation and reference 1 the highest. Indeed, the best performance are obtained for reference 2 and the lowest performance for reference 1. Unfortunately, there is not much more information that can be extracted from these measurements. In the following section and in the following chapters, the focus is put on TRPL measurements, as they provide more information on the samples, and more precisely on the carriers lifetime.

5.3.2 TRPL measurements

The TRPL measurements of the three reference cells are shown in figure 5.3.2.

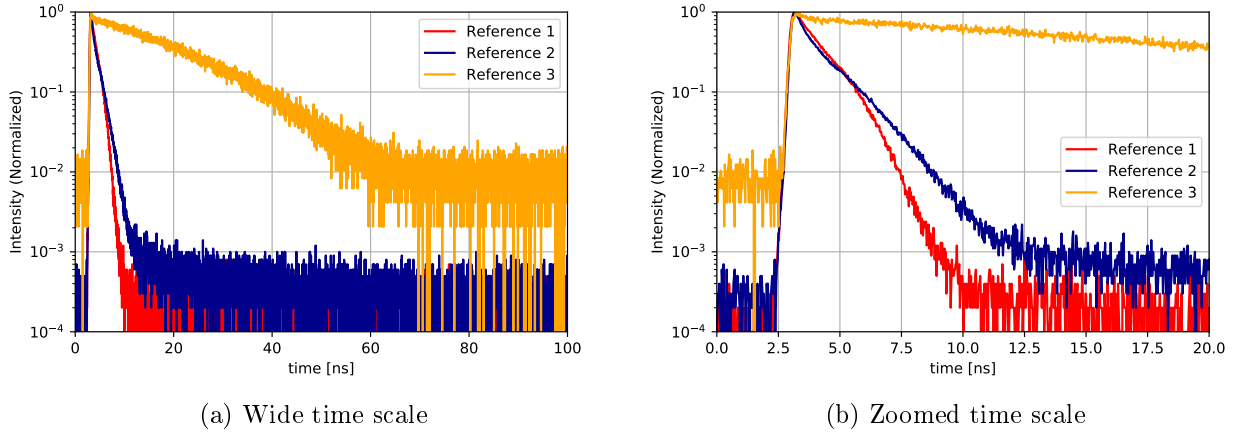


Figure 5.3.2: TRPL measurements of the three reference cells

TRPL decay In section 3.3.3, the theory of TRPL is developed and the focus is put on the double exponential decay of TRPL characterized by the two time constants τ_1 & τ_2 . This double exponential behaviour is visible for reference 1 & 2 in figure 5.3.2b, where the slope of the TRPL decay changes for the two samples around 5ns. Each of the τ_i is actually related to a different lifetime in the device [41]. First, shortly after the laser pulse ends, the electrical charges are separated from each other due to the action of the electrical field at the junction. At that time, there is a high density of electrons and holes, resulting in a high np product. The time constant τ_1 is thus mainly controlled by the radiative part of recombination, which is proportional to np , and is close to the intrinsic time constant of the carriers. In a second time, later after the laser pulse ends, the concentration of electrons and holes has decreased and the radiative recombination is not dominant anymore. The time constant τ_2 that is associated to this part of the curve is thus mainly controlled by the action of non-radiative (SRH) recombination that is influenced by defects and other losses. The most important figure of merit in this case is thus τ_2 . A high τ_2 is beneficial because it is related to a lower SRH recombination rate. As said previously, other phenomena than generation/recombination influence the time constants, which are important to keep in mind when performing the analysis.

Extraction of τ_1 & τ_2 for reference 1 & 2 To extract the time constants of the TRPL decay, two exponentials are fitted to the curve. In advanced TRPL analysis, mathematical models are used to try to link these time constants to intrinsic carrier time, defects time constants and others. In the scope of this work, the values of τ_1 and τ_2 are mainly used as such to compare the cells between themselves. The fitting of TRPL data with exponentials is shown in figure 5.3.3. In the figure, the time constants are given and it appears that τ_2 is greater for reference 2 than for reference 1. This makes sense since reference 2 is performing better. For reference 1, $\tau_1 > \tau_2$. This kind of behaviour is

observed, as explained in [43], when there is a very high defect density in the device. This is sustained in this case by the CVf loss map presented in the previous section. The fit with the exponentials is not perfect for reference 2. Therefore, it is possible that another type of decay is present on top of the double exponential. This is even more pronounced in the case of reference 3 and is developed hereafter.

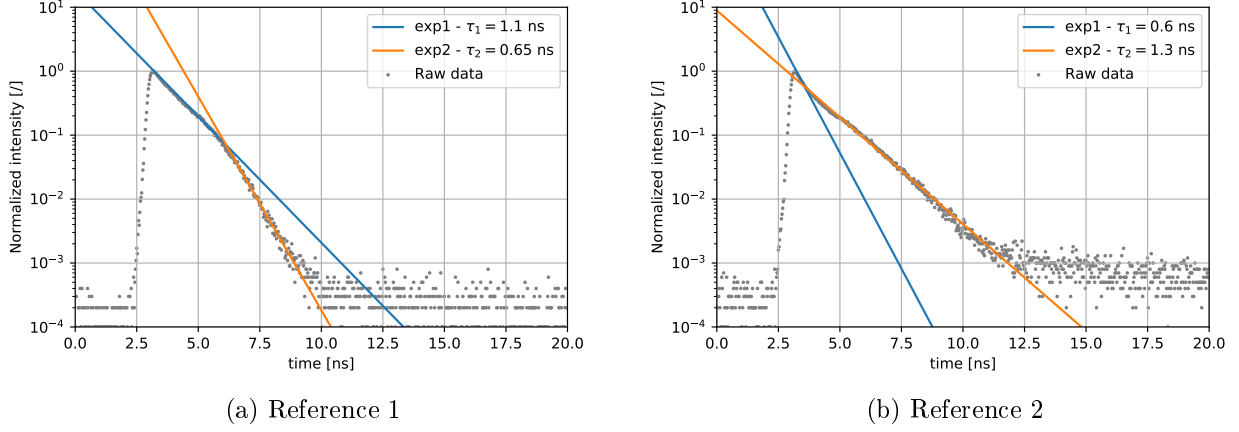


Figure 5.3.3: Fitting of the TRPL measurement with double exponential model

Analysis of reference 3 In the case of reference 3, the curve does not look like it is only a sum of two exponentials such as for reference 1 & 2, but it looks like there is a Gaussian component added to it. By fitting this curve with 2 exponentials and a Gaussian, figure 5.3.4 is obtained.

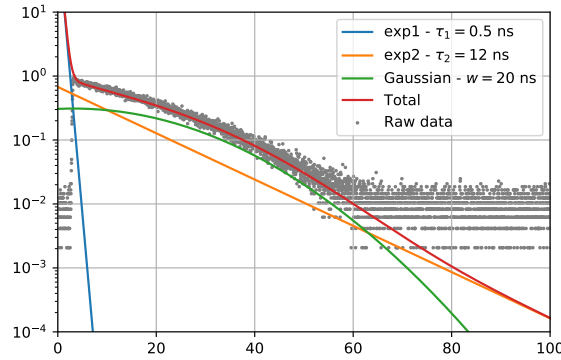


Figure 5.3.4: Fitting of the TRPL measurement of reference 3 with a double exponential and a gaussian

In terms of lifetime, it appears that the obtained τ_2 is much higher than for the two other references. This is the sign of a very low recombination rate in the absorber. The Gaussian shape visible in this case is something that is not common in TRPL measurements and not very well documented in references. For this reason, it is complicated to give exact information on its origin. An hypothesis that can be formulated is that this shape is linked to the presence of defects inside the structure. To try to confirm this, TRPL at different injection regimes is used.

Injection regimes of TRPL In TRPL, the sample is excited with very fast laser pulses. One parameter that can be tuned is the amount of light that is emitted onto the sample in one pulse, measured via the photon surface density D_{ph} [cm^{-2}]. The higher D_{ph} , the more e^-/h^+ pairs are generated. In function of this, several injection regimes are distinguished [43]:

- Low injection; when the amount of photons is lower than the doping. In this case not all the defects in the sample are ionized and they can contribute to the TRPL re-emission.
- Medium injection; when the amount of photons is about the same as the doping. In that case, there is only part of the defects that contribute to the TRPL re-emission.
- High injection; when the amount of photons is higher than the doping. In that case, all the defects in the sample are ionized and they do not contribute to the TRPL re-emission. They are in a saturated state.

In order to compute the injection regime, D_{ph} must first be computed using the following equation:

$$D_{ph} = \frac{E_{\text{laser}}}{E_{ph}} \cdot \frac{A \cdot r_{\text{laser}}}{r_{\text{beam}}} = \frac{P_{\text{laser}}/f_{\text{laser}}}{hc/\lambda_{ph}} \cdot \frac{A \cdot r_{\text{laser}}}{r_{\text{beam}}} \quad (5.3.1)$$

where $P_{\text{laser}} = 20\text{mW}$ is the power of the laser, $f_{\text{laser}} = 40\text{MHz}$ is the operating frequency of the laser, $\lambda_{ph} = 532\text{nm}$ is the laser wavelength, $A = 1\text{mm}^2$ is the illuminated area of the sample, $r_{\text{laser}} = 10\%$ is the attenuation ratio of the laser and $1/r_{\text{beam}} = 1/20$ is the optical aperture. This leads to:

$$D_{ph} = \frac{20 \cdot 10^{-3}}{3.74 \cdot 10^{-19} \cdot 40 \cdot 10^6} \cdot \frac{10^{-2} \cdot 0.1}{20} = 6.684 \cdot 10^{10} \text{ cm}^{-2} \quad (5.3.2)$$

From there, the volume density of e^-/h^+ pairs D_{eh} is simply computed using the absorption coefficient of CIGS, $\alpha = 4 \cdot 10^5 \text{cm}^{-1}$ with- the following equation:

$$D_{eh} = D_{ph} \cdot \alpha = 2.674 \cdot 10^{16} \text{ cm}^{-3} \quad (5.3.3)$$

This value of D_{eh} needs to be compared to the value of doping, to determine in which injection regime the measurement is performed. The apparent doping of reference 3, that includes the action of defects, can be extracted from CV measurements. This is shown in figure 5.3.5a. The doping seems to be mostly concentrated in the range $[5 \cdot 10^{15} \text{ cm}^{-3}, 5 \cdot 10^{17} \text{ cm}^{-3}]$. This means that the TRPL measurement presented hereabove for reference 3 is done in medium injection.

To understand if the Gaussian behaviour is coming from the action of defects, different injection regimes are considered. To easily change D_{ph} , and thus D_{eh} , two parameters can be tuned: the optical aperture and the attenuation ratio of the laser. By doing so, TRPL measurements under different injection regimes are obtained. They are represented in figure 5.3.5b. This figure clearly shows that the injection regime influences the shape of the TRPL curve. In medium injection (blue and orange curves), the Gaussian behaviour dominates the PL characteristic. In high injection (green and red curves), the TRPL decay becomes exponential again. Even though it is not certain, this is an argument in favour of a defect being responsible for the Gaussian behaviour. Indeed, at high injection

level, its state is fully saturated and it does not contribute to TRPL re-emission anymore. Because the Gaussian shape disappears under these conditions, this is an argument in favour of defects being at its origin.

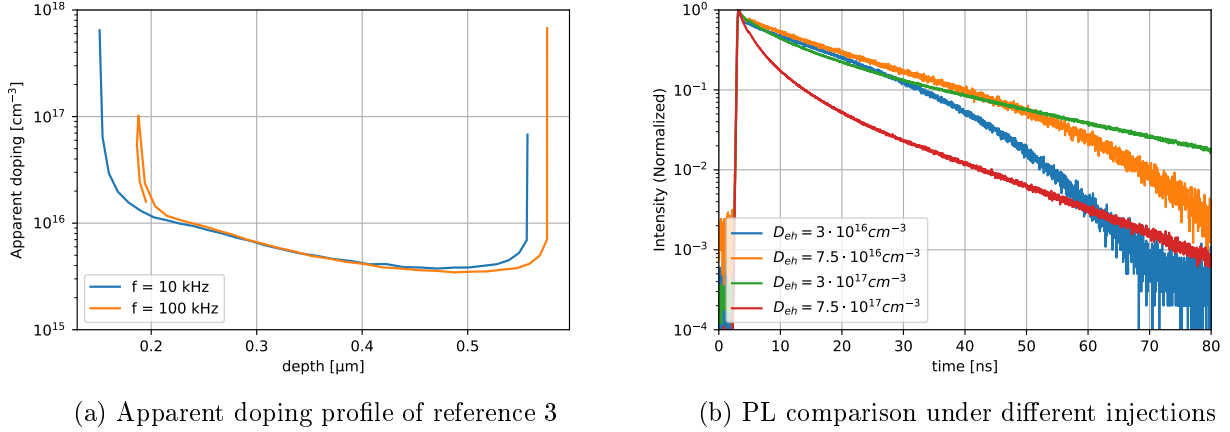


Figure 5.3.5: TRPL of reference 3 under different injection regimes and comparison with the apparent doping profile extracted from CV measurements

5.3.3 Effect of annealing on TRPL measurements

The effect of annealing on the three references is already quite extensively discussed in previous sections of this chapter. This section briefly introduces the effect of annealing on the TRPL measurement. The comparison before and after annealing is presented for reference 2 & 3 in figure 5.3.6.

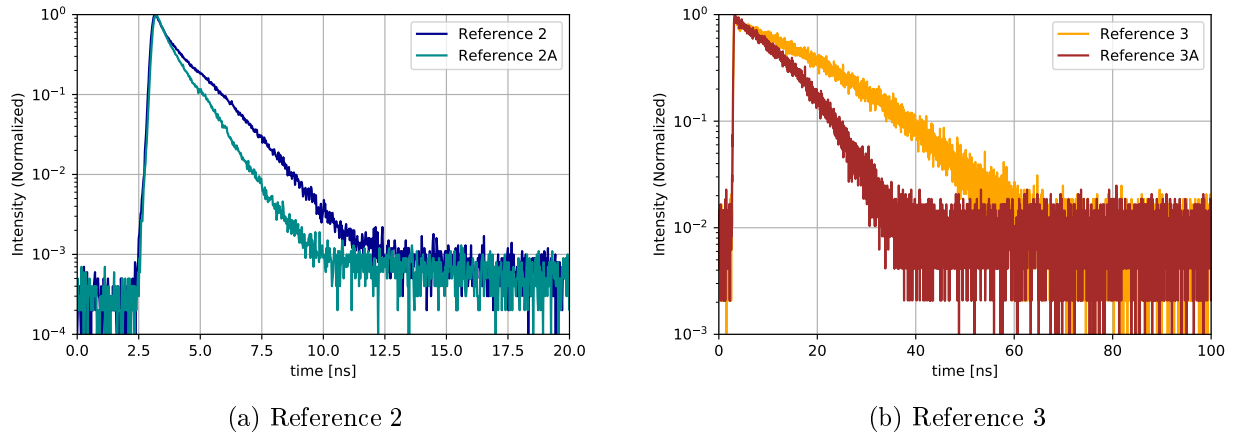


Figure 5.3.6: Comparison before and after annealing for reference 2 & 3

When annealing is introduced, the lifetime of the carriers is reduced for both reference 2 & 3. Normally, as the lifetime is related to the recombination rate inside the cell, this should lead to a reduction in V_{oc} . This is indeed the case of reference 2, which has a small reduction of 25mV, but not of reference 3 where V_{oc} remains almost unchanged. Possibly, there is in the case of reference 3 another effect that boosts V_{oc} in spite of this reduction in the carriers lifetime.

5.4 Conclusion

In this chapter, three reference CIGS solar cells, made with three different absorbers, are studied. They are also compared to their annealed version. In the first section, IV measurements are used to evaluate the performance and the external losses. Some information is given on the accuracy of this technique, and EQE is presented as a way of validating the interpretation of J_{sc} evaluation. In the second section, CVf loss maps are used to characterize defects in the three reference cells. A link is also made between these intrinsic losses and the performance of the solar cells. Finally, PL measurements are used to characterize the carriers lifetime and validate the previous interpretations.

Reference 1 presents poor performance compared to the two other samples, with $\eta = 5.65\%$. This bad performance is, in a first time, attributed to the low shunt resistance inducing a very low FF. The lower value of V_{oc} is interpreted by looking at the CVf loss maps. There, a big signature is visible in the active area of the solar cell, which indicates a charge trapping mechanism, that is likely coming either from a bulk defect or a barrier present at the CIGS/CdS interface. The presence of this important intrinsic loss is also validated when considering the TRPL measurements. There, it appears that the carriers lifetime for reference 1 are quite low, especially compared to the other two references.

Reference 2 presents the best performance of all three samples, with $\eta = 14.09\%$. This comes from the very high V_{oc} and FF, as well as from the low external losses. The high value of V_{oc} is confirmed when looking at the CVf characteristic. There, very few loss mechanisms are visible, which is the sign of very low intrinsic losses. This is also supported by the TRPL measurements where the lifetime of the carriers is rather high.

Reference 3 also presents very good performance, with $\eta = 12.49\%$. This comes from a high V_{oc} , J_{sc} and FF. Its lower performance compared to reference 2 can mainly be attributed to a higher R_s which induces a lower FF. The CVf loss map, confirms that a high R_s is present and is supposedly responsible for performance loss in the device. Low temperature measurements also underline the presence of an interface defect, whose signature merges with the one of the series resistance at room temperature. This can be at the origin of the small V_{oc} decrease. For this sample, the carriers lifetime is much higher than for the other two. This indicates a very good absorber quality. It also presents a Gaussian behaviour which is explained by the action of a defect inside the structure, probably the interface defect characterized with the low temperature measurements.

Annealing has mostly an impact on Reference 1. In that case, performance are significantly improved. This can be attributed to the increased R_{sh} and V_{oc} . The last one comes from the lowered action of intrinsic losses, that is visible on the CVf characteristic. Indeed, the signature in the center of the map moves towards the right, which reduces its impact on the cell performance.

6 Front passivation of CIGS solar cells

In this chapter, an analysis of front passivated CIGS solar cells is performed. The same methodology developed previously is used, but not every step is justified when it is already done in the previous chapter. The obtained results are compared with the ones from the reference cells presented in the previous chapter.

Five different samples are introduced in this chapter (table 6.0.1). They all have the structure of a CIGS standard cell, where a passivation layer is introduced at the CIGS/CdS interface (figure 6.0.1). The passivation layer is 1nm thick and is made either of AlO_x or HfO_x . In a first section, the comparison with references is made on a performance standpoint, with analysis of the IV curves and EQE measurements. After that, the cells are analyzed using the AS method and PL measurements.

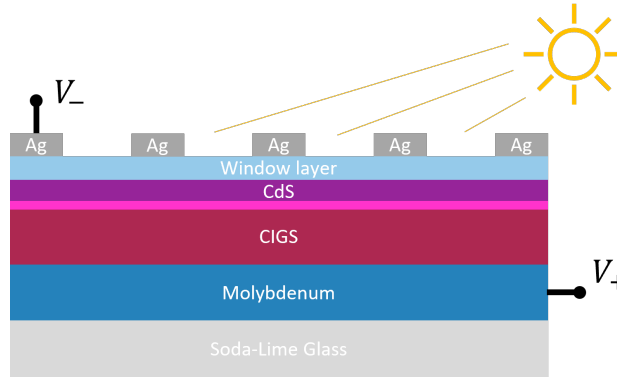


Figure 6.0.1: Schematic representation of the front passivated CIGS cell.

Absorber	Sample name	Type of cell	Annealing temperature [°C]	Passivation layer
1	FP1	Front passivation	150	AlO_x
2	FP2- AlO_x	Front passivation	150	AlO_x
2	FP2- HfO_x	Front passivation	300	HfO_x
3	FP3- AlO_x	Front passivation	150	AlO_x
3	FP3- HfO_x	Front passivation	300	HfO_x

Table 6.0.1: Samples used in this chapter

6.1 Performance evaluation

In this section, the performance of the front passivated cells are presented and analyzed. They are compared to the performance of the reference cells presented before. First, the performance of the cells made with absorber 1 (FP1) are presented. Secondly, the same is done for the cells made with absorber 3 (FP3).

6.1.1 FP1 performance analysis

IV curves The IV curve in the dark and under light for the champion cell of FP1 compared to reference 1 are represented in figure 6.1.1.

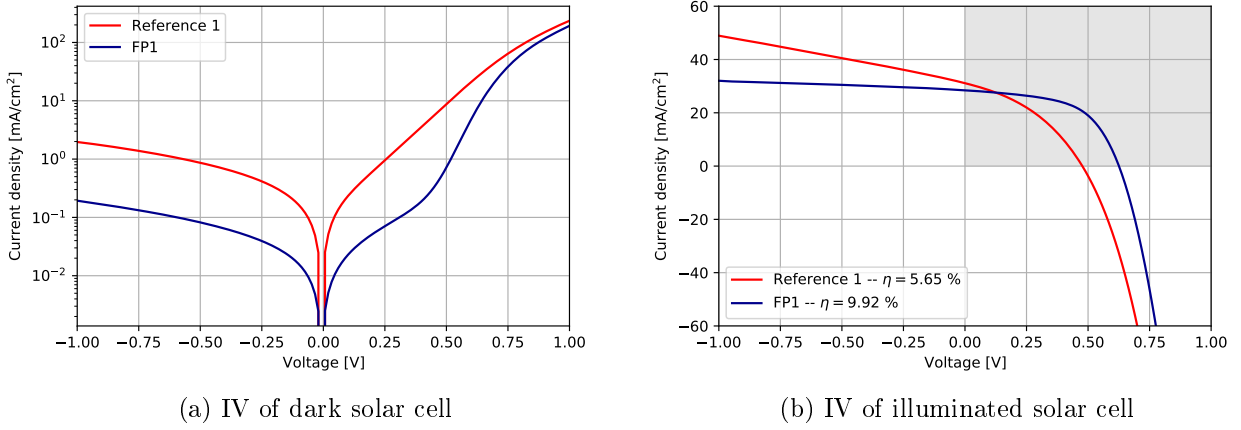


Figure 6.1.1: IV curve in the dark and under light of reference 1 and FP1

When analyzing the IV curve in the dark (figure 6.1.1a), it appears that the front passivation has a significant effect on the low voltage and reverse voltage characteristics of the solar cell, with a current density that is reduced by one order of magnitude. This suggests that the shunt resistance is notably higher for FP1 compared to reference 1. In the same figure, the IV curves seem to both have the same slope at higher bias voltages. From previous analysis, this leads to the interpretation that R_s remains unchanged from one sample to the other.

This trend is confirmed when looking at the IV curves under light (figure 6.1.1b). There, the slope in reverse bias is significantly improved for FP1 compared to the reference, leading to a much better FF, but to a lower J_{sc} . On the same figure, the slope in forward bias is similar for the two cells, which tends to confirm that R_s is almost the same for the two cells. Overall, due to a much better FF and an increased V_{oc} , the efficiency of FP1 is greatly improved compared to reference 1.

Figures of merit The figures of merit extracted from the IV curves are presented in table 6.1.1. All the parameters are improved for the passivated sample, with the exception of J_{sc} that is a little reduced and R_s that is a little increased. Corrected values of η_c and FF_c are also better for FP1, which suggests that there is a positive intrinsic change to the cell that impacts the performance. This

is sustained by the higher value of V_{oc} , whose value is linked to the action of defects and intrinsic losses of the cell.

Parameter	Reference 1	FP1
J_{sc} [mA/cm ²]	31.28	28.47
V_{oc} [mV]	476.8	625.5
η [%]	5.65	9.92
FF [%]	37.9	55.7
R_{sh} [$\Omega \cdot \text{cm}^2$]	558.49	5718.06
R_s [$\Omega \cdot \text{cm}^2$]	0.42	0.63
η_c [%]	8.15	11.22
FF _c [%]	47.92	61.8

Table 6.1.1: Table of performance, including the external losses and the correction of the IV curve.

Interpretation From the figures of merit and using the knowledge of the previous chapters, it is already possible to make some educated guesses about the origin of the differences between reference 1 and FP1. The lower current density that is observed can originate from two phenomena: a lower absorption due to the presence of the dielectric passivation layer, or the higher shunt resistance that limits the current at low bias voltage. The lower absorption could be confirmed or not using EQE measurements, but they are not available for these samples. Furthermore, it is very unlikely that a dielectric layer with a bandgap around 6eV is at the origin of an absorption reduction. In the previous chapter, it is underlined that V_{oc} is lower for reference 1 due to the action of a charge trap. The improvement in V_{oc} in this case could be the sign of a reduced action of this charge trap on the cell. This hypothesis needs to be confirmed using AS measurements, which is done further in this chapter. The improved FF is clearly coming from the increased R_{sh} . An hypothesis for the improvement of this last one may be the action of the passivation layer, that could act as a protective layer between the CIGS and the CdS to reduce the reverse leakage current. Finally, the higher R_s is probably a consequence of the passivation layer which is made of resistive dielectric material.

Even though this interpretation seems plausible, another reading of this data is possible. Indeed, when comparing the results of FP1 with the results of reference 1A, the annealed version of reference 1, it appears that the trends are very similar. This is underlined in table 6.1.2. Almost all the figures of merit of reference 1A and of FP1 evolve in the same way: V_{oc} , η , FF and R_{sh} ¹ increase (in green), while J_{sc} decreases (in red). The only figure of merit that does not change in the same direction for reference 1A and FP1 is R_s (in blue).

¹As a reminder, even though it looks like R_{sh} is worse in the case of reference 1A, it is previously established that this is not the case when considering the value under illumination which is responsible for the performance increase (see section 5.1.5).

Parameter	Reference 1	Reference 1A	FP1
J_{sc} [mA/cm ²]	31.28	28.84	28.47
V_{oc} [mV]	476.8	527.5	625.5
η [%]	5.65	6.83	9.92
FF [%]	37.9	44.9	55.7
R_{sh} [$\Omega \cdot \text{cm}^2$]	558.49	256.54	5718.06
R_s [$\Omega \cdot \text{cm}^2$]	0.42	0.34	0.63
η_c [%]	8.15	8.37	11.22
FF _c [%]	47.92	52.12	61.8

Table 6.1.2: Table of performance, including the external losses and the correction of the IV curve.

Because the passivation layer is deposited at high temperature, the same as the annealing of reference 1A, it is possible that the improved performance of FP1 does not only come from the passivation layer itself, but also from the effect of its high processing temperature. There would be in that case a combined action of the passivation layer and the annealing which would explain the higher efficiency. Another argument in favour of the annealing being at least partly responsible for the good performance is that AlO_x does not hold well the CdS deposition process [49]. It is thus completely conceivable that there is actually few material of the passivation layer remaining at the end of FP1's processing. This alternative explanation, combining the effect of passivation and annealing, needs to be investigated using other characterization techniques, which is done further in this chapter.

6.1.2 FP3 performance analysis

IV curves For the cells realized with absorber 3, two different materials are used for the passivation layer: AlO_x and HfO_x . These two materials have very close electronic properties (see section 2.4.4), but HfO_x is supposedly more resistant to the CdS deposition process. The IV curve in the dark and under light for the champion cells of FP3 compared to reference 3 are represented in figure 6.1.2.

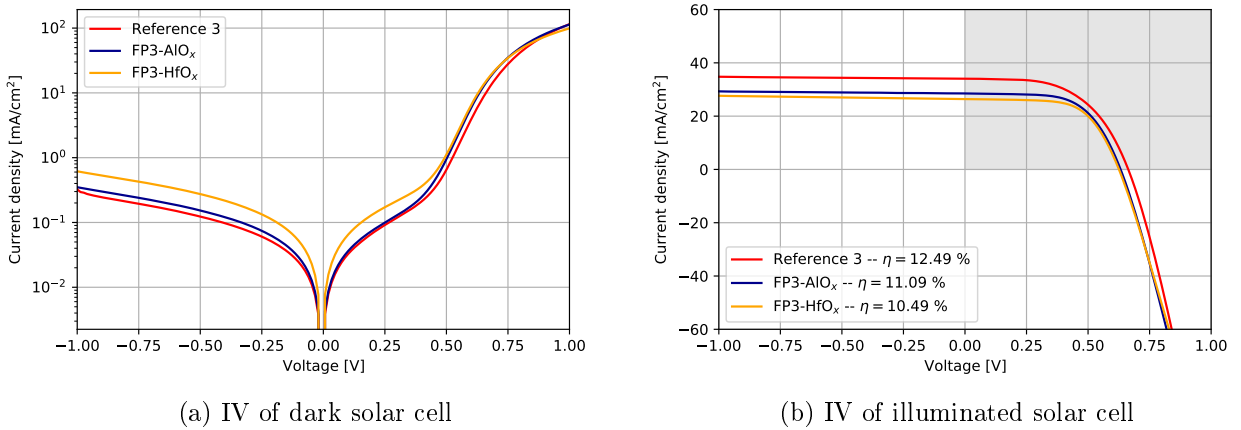


Figure 6.1.2: IV curve in the dark and under light of reference 3 and FP3

From the IV measurements in the dark (figure 6.1.2a), it emerges that all three samples have a very close IV characteristic, with the HfO_x sample behaviour being slightly further away. The reverse bias current deteriorates marginally for both FP3 samples compared to the reference, which indicates a lower R_{sh} . In forward bias, it looks like FP3- HfO_x presents a higher saturation, which is the sign of a higher R_s .

This higher R_s for the HfO_x passivated sample is confirmed when looking at the IV curve under light (figure 6.1.2b), even though all samples are again very close one to another. The slope in forward bias is slightly reduced for both FP3 samples. In reverse bias, all three sample seem to have a similar slope. It is expected that FF is reduced for the FP3 samples, because the external losses have deteriorated a little compared to the reference. Concerning the other figures of merit, J_{sc} and V_{oc} , they are clearly degraded in the case of the passivated sample.

Figures of merit Looking at the extracted figures of merit in table 6.1.3, the observations seem to be overall confirmed. As expected, the changes in performance are much smaller than for the samples made with absorber 1. Most of the performance has degraded when going from reference 3 to FP3, such as J_{sc} , V_{oc} , R_{sh} and R_s . Nevertheless, FF has improved for the passivated samples. Because the external losses are worse, this suggests that there is an intrinsic reason for the FF increase. This needs to be confirmed using AS characterization and PL measurements.

Parameter	Reference 3	FP3- AlO_x	FP3- HfO_x
J_{sc} [mA/cm^2]	34.1	28.53	26.42
V_{oc} [mV]	663.3	632.2	625.5
η [%]	12.49	11.09	10.49
FF [%]	55.2	61.5	63.5
R_{sh} [$\Omega \cdot \text{cm}^2$]	3717	3189	1775
R_s [$\Omega \cdot \text{cm}^2$]	2.06	2.93	4.26
η_c [%]	13.99	12.92	12.92
FF_c [%]	70.07	71.86	77.78

Table 6.1.3: Table of performance, including the external losses and the correction of the IV curve.

Interpretation The lower value of J_{sc} could be justified by the presence of the passivation layer but, as explained in the previous section, this is not very likely. EQE measurements are thus used to understand if this lower value of J_{sc} is indeed confirmed (figure 6.1.3). These measurements show that the values of J_{sc} in the passivated case are under-evaluated. There is in fact a slight improvement in J_{sc} going from reference 3 to FP3 samples. Concerning V_{oc} , the loss maps should be able to explain its lower value, further in this chapter. Indeed, an interface defect is identified in reference 3 in the previous chapter, and it could be affected negatively by the passivation layer and lead to a reduction in V_{oc} . In the same register, the increased FF seems to indicate that internal losses are improved, but this is in direct contradiction with the reasoning on V_{oc} . The reduction in shunt resistance is not very significant, and it is possibly related to process variations, especially in the AlO_x case. The

higher series resistance is, certainly in the case of FP3-HfO_x, related to the additional dielectric layer introduced in the cell.

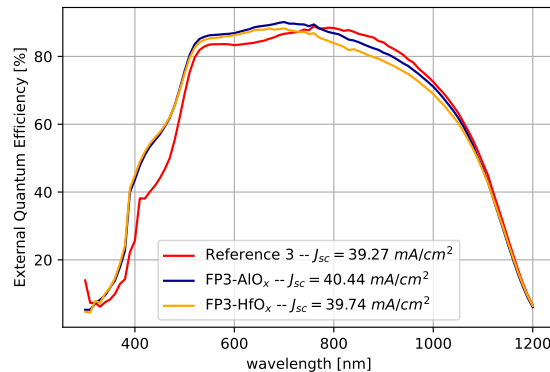


Figure 6.1.3: EQE comparison between the FP3 samples and reference 3

In the same way as for the cells made with absorber 1, it is very likely that the AlO_x layer of FP3-AlO_x is also partly degraded by the CdS deposition process. This interpretation is motivated by the IV curves in the dark (figure 6.1.2a) where the AlO_x passivated cell is very close to the reference cell. Moreover, there is in terms of performance very few differences between the two cells that could be coming from process variation only. On the contrary, there seems to be more impact on the performance when using a HfO_x layer, even though this impact is mostly detrimental.

6.1.3 FP2 samples

In the same way as for the other two absorbers, front-passivated structure with absorber 2 were also realized. They present very similar characteristics to FP3 samples, which is why they are not integrated in the main part of this work. Overall, performance is not improved when comparing the passivated samples to reference 2, and it is even degraded for the most part of it. A complete table of performance for these cells, along with the corresponding IV curves, is presented for the reader's perfect information in appendix C.

6.2 CV measurements

In this section, CV measurements and loss maps are used to characterize defects inside the front passivated cells. These measurements are compared to the ones obtained for the reference cells in the previous chapter. In a first section, room temperature CV measurements are presented and analyzed for FP1 and FP3 samples. In a second section, low temperature CV measurements are used to fully characterize the defects inside the FP3 samples.

6.2.1 Room temperature measurements

FP1 sample In figure 6.2.1, the comparison is made between FP1, reference 1 and reference 1A. This choice of comparison comes from the suspicion that FP1 is not only affected by its passivation layer but also by the annealing happening during its fabrication process.

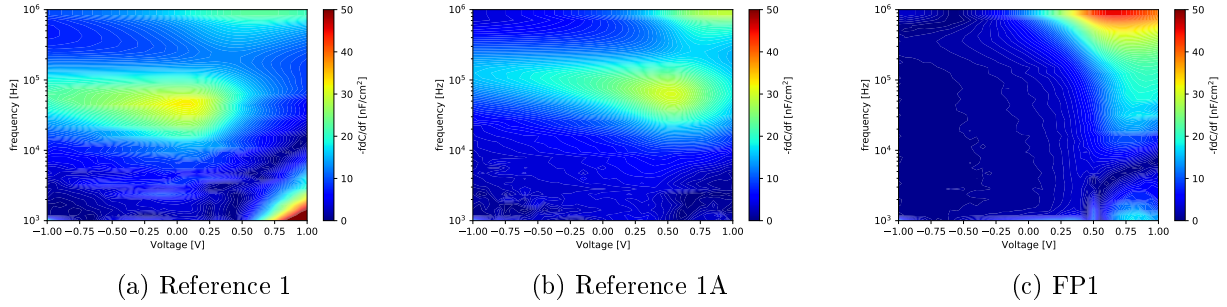


Figure 6.2.1: CV characteristics of FP1 compared to Reference 1 & Reference 1A

The first observation that can be made from the FP1 loss map (figure 6.2.1c) compared to the reference (figure 6.2.1a) is that the big defect-like signature in the center of the map has disappeared and that there is a new one in the top right corner. A plausible hypothesis is that it is the same signature that has moved in frequency and voltage bias. The disappearing of the signature in the center is clearly at the origin of FP1's performance improvement, as the active region of the solar cell is, there, mostly unaffected by defects. This constitutes a very plausible explanation for the V_{oc} increase that is observed in the previous section. The signature in the corner of the map does not have the same shape as for the reference case. When looking at the SCAPS simulations to try to identify the nature of this response, it appears that there is not one phenomenon that would fit to this shape. It is more likely that this is a combination of two different responses, one of which could be a series resistance that is also visible in the upper part of the maps of reference 1 and reference 1A, and the other one that could be a defect.

It is possible that this supposed defect would be the previously observed bulk defect whose signature has moved to the right and up in frequency. Indeed, reference 1A (figure 6.2.1b) compared to reference 1 already shows that trend, and it is possible that FP1 is a continuation of this signature moving right and up in frequency. It would then have merged with the series resistance and present this corner-like shape in figure 6.2.1c. This could be an argument in favour of the role played by annealing here.

A remaining question is to know why this signature moves in this way. From the theory and the SCAPS simulations, a defect's characteristic frequency changes when either its activation energy or its capture cross-section is modified. This means that the defect signature moving up could be linked either to a lower E_A or to a higher σ . This last possibility does not physically make much sense, since a defect with a higher σ attracts more charges and thus contributes more to intrinsic losses therefore reducing V_{oc} . If the hypothesis of annealing being partly responsible for this change is considered, it is possible that E_A has changed. In fact, because annealing has an impact on the internal structure of the CIGS, it is possible that the bulk defect is completely altered. This could also explain the shift in voltage bias. This last one can happen when the defect level is modified and therefore the Fermi level crosses it at a different range of voltage biases.

FP3 samples In figure 6.2.2, FP3-AlO_x and FP3-HfO_x are compared to reference 3.

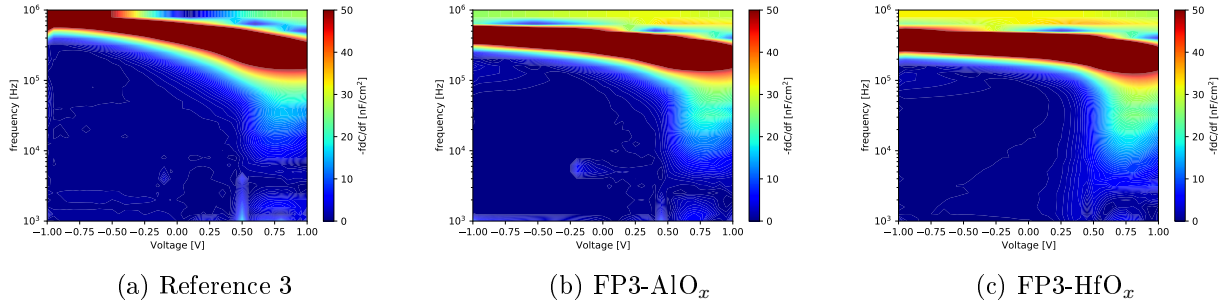


Figure 6.2.2: CV characteristics of both FP3 samples compared to Reference 3

As expected from the performance evaluation of the previous section, the loss maps of the FP3 samples (figure 6.2.2b & 6.2.2c) are not better than the one of the reference (figure 6.2.2a). The response of the series resistance is still very much visible on the top of the map, and even degrades for the FP3 samples. The part of the response that is associated to the interface defect previously identified for reference 3 (see section 5.2.3) is also more significant for the passivated samples. Both these changes in the passivated maps are slightly more significant for FP3-HfO_x compared to FP3-AlO_x. This is also reflected in the V_{oc} , which is the best for reference 3, and the worse for FP3-HfO_x.

Overall, when comparing figure 6.2.2b with figure 6.2.2c, it seems like the mechanism is the same for the two structures. Knowing that one is made with an AlO_x layer and the other one with a HfO_x layer, two hypothesis can be formulated. First, it is possible that the action of the HfO_x layer is stronger. This would be caused by a difference of Q_f or D_{it} between the two materials. Secondly, it is also possible that only part of the AlO_x layer is still present in FP3-AlO_x, due to the CdS deposition process. Indeed, knowing the important surface roughness of CIGS layers generally observed, the non-uniform deposition of the CdS layer might also etch the AlO_x in a non-uniform fashion. In that case, it would be normal that the action of the HfO_x layer is stronger. The most probable is that there is a combination of these two hypothesis happening. Either way, it is clear that the presence of

this layer is not beneficial and that it does not provide the expected passivation effect.

At this stage, the origin of the improved FF for the FP3 samples compared to reference 3 remains unclear. It is possible that a reduced action of the interface defect visible on the map is responsible for this improvement. To investigate this, low temperature measurements are used in the next section.

Apparent doping profile Before moving to low temperature measurements, it is also interesting to look at the apparent doping profile of the different samples presented here, as they also provide information about the action of defects in the structure. They can be used to have an additional quantitative confirmation that defect mechanisms are more active in one case or the other. These doping profiles are represented in figure 6.2.3.

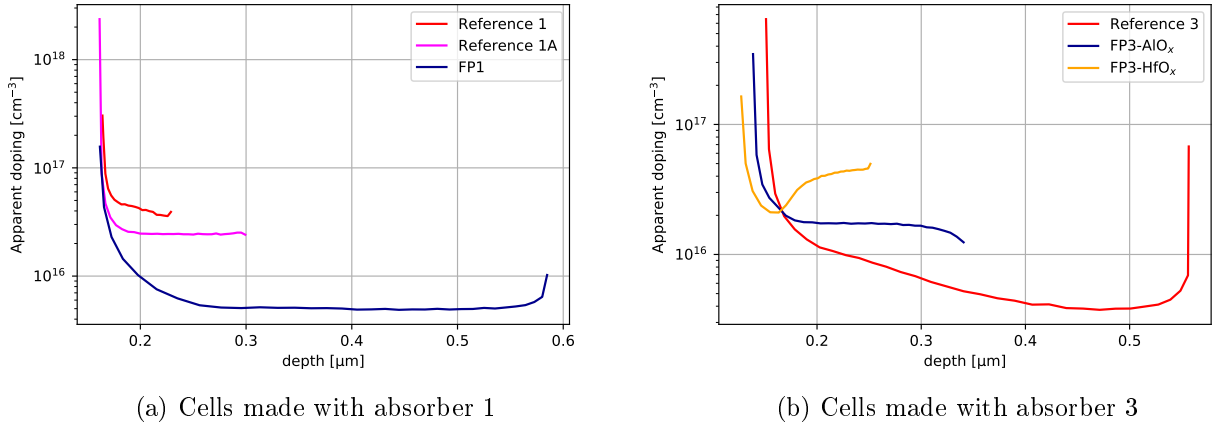


Figure 6.2.3: Apparent doping profile of the cells made with absorber 1 & 3, extracted from 10kHz CV measurements

In the case of FP1 compared to reference 1 & 1A (figure 6.2.3a), the apparent doping is lower for the passivated cell. Because all the cells use the same absorber, their real CIGS doping profile should be the same. Every difference in the apparent doping is thus caused by the action of loss mechanisms in the device, or by the annealing that affects grain size in the CIGS and thus also possibly the doping. Here, it makes sense that it is lower for FP1 compared to reference 1, because it has less defects visible on the loss map. The apparent doping profile in this case thus confirms the reduced action of defects in the case of FP1.

For FP3 compared to reference 3 (figure 6.2.3b), the opposite trend is visible. There, the passivated structures have an overall higher apparent doping. This confirms that the action of intrinsic losses is higher in that case compared to the reference.

6.2.2 Low temperature measurements

As done in the previous chapter, it is possible to use low temperature CV measurements to extract E_A and σ for the defect of the FP3 samples. Because the mechanism is very similar for FP3-AlO_x

and FP3-HfO_x, the loss map at each temperature is only represented for FP3-HfO_x, in figure 6.2.4. They can be compared to the maps of reference 3 presented previously in figure 5.2.6.

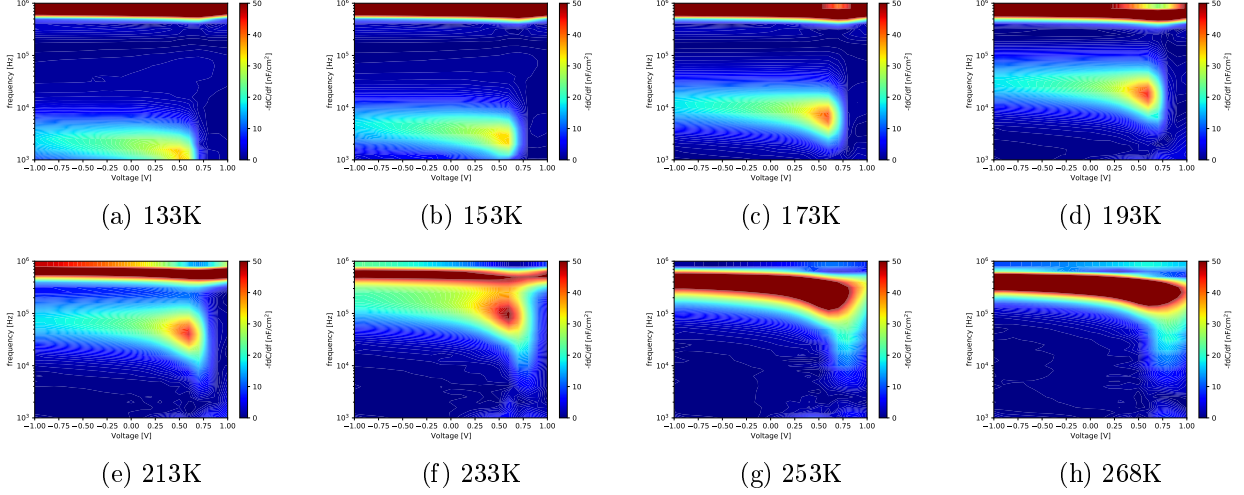


Figure 6.2.4: Loss maps of FP3-HfO_x at different temperatures

The evolution of the signature is quite similar than for reference 3, in which an interface defect was identified. The main difference between the two sets of loss maps is that the tail of the signature is much more pronounced for FP3-HfO_x. Following the theory and SCAPS simulations, two different hypotheses could be formulated.

First, a long tail like the one observed in figure 6.2.4 could be caused by an interface defect with a very high defect density N_t . This generally leads to Fermi level pinning, as previously mentioned in section 4.2.2. This would suggest that the passivation layer contributes to increasing N_t at the CIGS/CdS interface, which can be at the origin of the small V_{oc} decrease that is observed.

Secondly, it is also possible that the passivation layer would have modified the barrier at the CIGS/CdS interface. When looking at the simulation of a barrier in SCAPS, it presents a similar signature than the one visible in figure 6.2.4. If the barrier height is modified, it is moreover probable that the position of the Fermi level changes and that the interface defect characterized in reference 3 is rendered inactive in the passivated samples. This would suggest that the trace visible on the map is the one of the barrier, and that the trace of the interface defect from reference 3 has disappeared. Another possibility is that the barrier signature is superposed on the one of the interface defect.

These hypotheses do not give an explanation for the better FF in the case of the FP3 samples. As FF has many contributions, it is quite tricky to evaluate the exact origin of this change. To study this, other more advanced characterization techniques should be used.

The Arrhenius plot made from the data of figure 6.2.4 is presented in figure 6.2.5a.

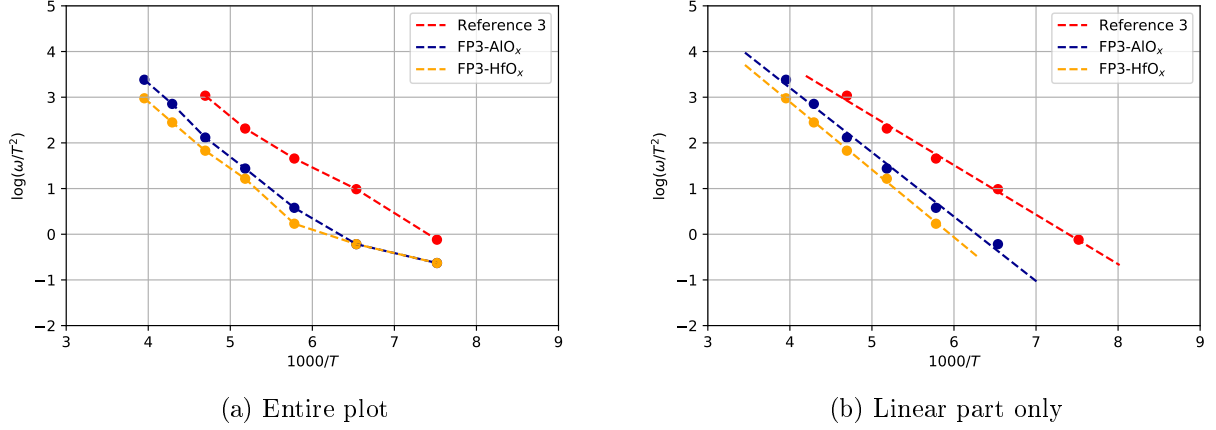


Figure 6.2.5: Arrhenius plot comparing FP3 samples with reference 3. Both the complete plot and a linearized version, where the non-linear values are removed, are shown.

In the case of FP3 samples, the extracted values of characteristic frequency in function of the temperature do not give a linear Arrhenius plot. This is already documented in the literature and corresponds to a certain type of interface defects, typical of CIGS solar cells, generally named "N1-type defect" [17]. This type of defect typically presents this reduced slope in the Arrhenius plot at lower temperature. The explanation behind the reduction in slope, as explained in [50], is that the contribution of this defect is linked to thermally assisted tunnelling. The barrier at the CIGS/CdS interface acts as a reservoir of electrons, which are then captured and re-emitted by the interface defect via tunnelling. This would validate the hypothesis that states that a combined action of the interface barrier and the interface defect is responsible for the signature on the map. Following the theory on N1 defects, it is probable that a change in the barrier height results in more electrons being trapped at the interface which are then exchanged with the interface defect.

When linearizing the Arrhenius plot to try to extract the defect parameters (figure 6.2.5b), the value of table 6.2.1 are obtained. In the passivated case, the value of σ remains mostly unchanged. On the contrary, there is a little change in the value of E_A . This would suggest that the defect at the CIGS/CdS interface in reference 1 is shallower than the one at the CIGS/AlO_x or the CIGS/HfO_x in the passivated case.

Sample	E_A [eV]	σ [cm ⁻³]
Reference 3	0.093	$2.88 \cdot 10^{18}$
FP3-AlO _x	0.121	$6.61 \cdot 10^{18}$
FP3-HfO _x	0.127	$6.45 \cdot 10^{18}$

Table 6.2.1: Extracted values of E_A and σ for FP3 samples compared to reference 3

6.3 TRPL measurements

In this section, the TRPL measurements of front passivated samples are briefly introduced in order to further validate the results and hypothesis presented before. They are presented in figure 6.3.1

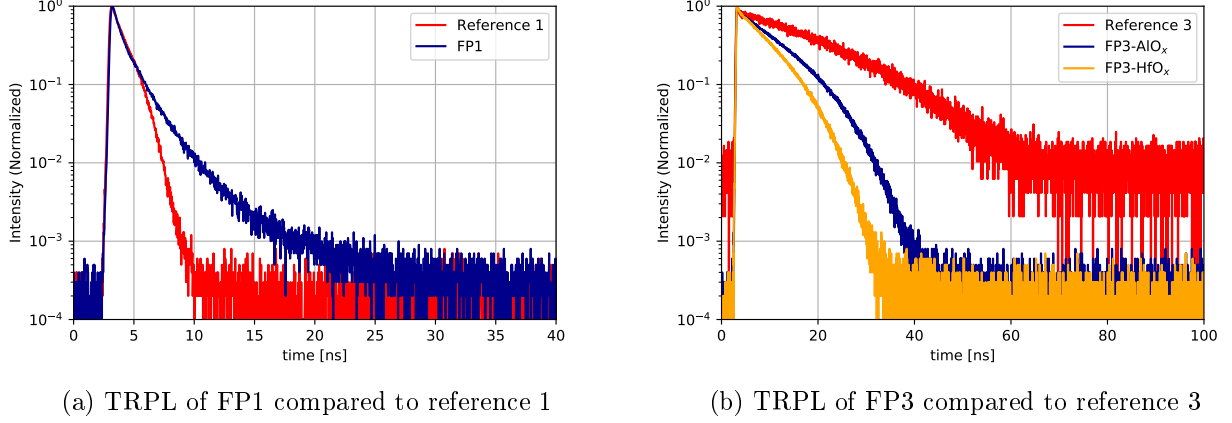


Figure 6.3.1: TRPL measurements of the front passivated samples

FP1 sample The TRPL measurements of FP1 compared to reference 1 are shown in figure 6.3.1a. In this figure, it appears that the total TRPL decay is longer for FP1 than for reference 1. Its first part, related to τ_1 , is the same. This is, as a reminder, linked to the intrinsic time constant of the carriers. It thus makes sense that it is similar in these two structures. The second decay, linked to τ_2 , is longer for FP1. Moreover, contrarily to reference 1, $\tau_2 > \tau_1$. This is the sign, as presented in [43], that there is a reduced action of SRH recombination, and thus probably also of defects, in the case of FP1. This confirms what is presented in the previous sections.

FP3 samples The TRPL measurements of FP3 compared to reference 3 are shown in figure 6.3.1b. In this case, a strong Gaussian behaviour observed previously for reference 3 is still present. It is even stronger for the FP3 samples than for reference 3. As a reminder, an hypothesis is that this Gaussian shape comes from the action of defects. As shown in the loss maps, they are more active for the FP3 samples and the Gaussian shape is also stronger for these samples. This could be another indication in favour of this hypothesis. Furthermore, τ_2 is visibly lower for FP3 samples compared to reference 3, which indicates a lower lifetime and an increased recombination. This is in line with the performance degradation of FP3 samples and the observations made from the CVf maps.

6.4 Conclusion

In this chapter, a front passivated structure for CIGS solar cells is investigated. It is tried on two different absorbers (absorber 1 & 3) and with both AlO_x and HfO_x .

FP1 sample This sample presents improved performance compared to reference 1, η being increased by more than 4%. All the figures of merit are improved, except J_{sc} that is a little lower. An important hypothesis that is formulated is that the improved performance do not only come from the passivation layer itself, but also from the annealing of the sample happening during the deposition process of the layer. Several leads suggest that this hypothesis is indeed valid. First, the trend that is observed in the figures of merit is similar for FP1 and reference 1A. FP1 has even better performance, which probably comes from a combination of passivation and annealing. Secondly, it is likely that the deposited layer, a 1nm AlO_x , is at least partly removed during the deposition process of the CdS. This would suggest that the passivation layer is not the only responsible for the performance improvement.

FP3 samples These samples present reduced performance compared to reference 3, η is decreased by about 1.5 – 2%. On a performance standpoint, most of the figures of merit are worse for the passivated samples, with the exception of J_{sc} and FF. The series resistance in particular is much higher for the FP3 samples. This is confirmed when looking at the CVf loss maps. There, the trace for the series resistance is higher in the passivated case. Also, the part of the map that is attributed to the interface defect in the previous chapter is more pronounced for the passivated samples, which can be at the origin of the decrease in V_{oc} . Low temperature measurements lead to two different hypotheses. Either there is a greater action of the interface defect, with possible Fermi level pinning for the FP3 samples, or the passivation layer can induce a modification of the CIGS/CdS interface barrier. Using the Arrhenius plot, the signature that is identified on the map is attributed to a N1-type defect, in which the CIGS/CdS interface barrier coupled to an interface defect is responsible for the charge trapping mechanism. Overall, the passivation effect seems to be more pronounced for the samples with the HfO_x layer. This can be due to the partial deterioration of the AlO_x layer during processing, or by the differences in D_{it} and Q_f for these two materials.

7 Window passivation of CIGS solar cells

In this chapter, an analysis of window passivated CIGS solar cells is performed. The same methodology developed in the two previous chapters is used. The obtained results are compared with the ones from the reference cells presented in chapter 5.

Five different samples are introduced in this chapter (table 7.0.1). They all have the structure of a CIGS standard cell, where a passivation layer is introduced at the CdS/Window interface (figure 7.0.1). The passivation layer is 1nm thick and is made either of AlO_x or HfO_x . In a first section, the comparison with references is made on a performance standpoint, with analysis of the IV curves and EQE measurements. After that, the cells are analyzed using the AS method and PL measurements.

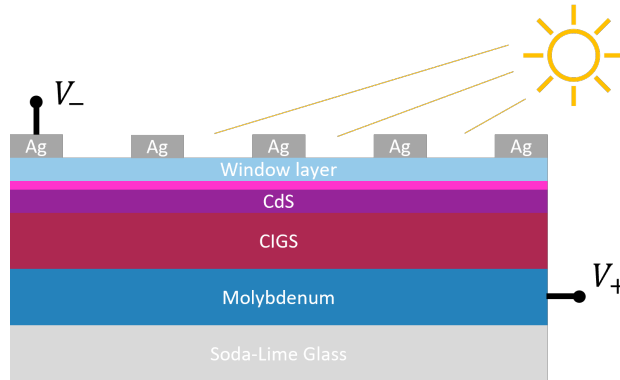


Figure 7.0.1: Schematic representation of the window passivated CIGS cell.

Absorber	Sample name	Type of cell	Annealing temperature [°C]	Passivation layer
1	WP1	Window passivation	150	AlO_x
2	WP2- AlO_x	Window passivation	150	AlO_x
2	WP2- HfO_x	Window passivation	300	HfO_x
3	WP3- AlO_x	Window passivation	150	AlO_x
3	WP3- HfO_x	Window passivation	300	HfO_x

Table 7.0.1: Samples used in this chapter

7.1 Performance evaluation

In this section, the performance of the window passivated cells are presented and analyzed. They are compared to the performance of the reference cells presented before. In a first section, the performance of the cells made with absorber 1 (WP1) are presented. In a second section, the same is done for the cells made with absorber 3 (WP3).

7.1.1 WP1 performance analysis

IV curves The IV curve in the dark and under light for the champion cell of WP1 compared to reference 1 are represented in figure 7.1.1.

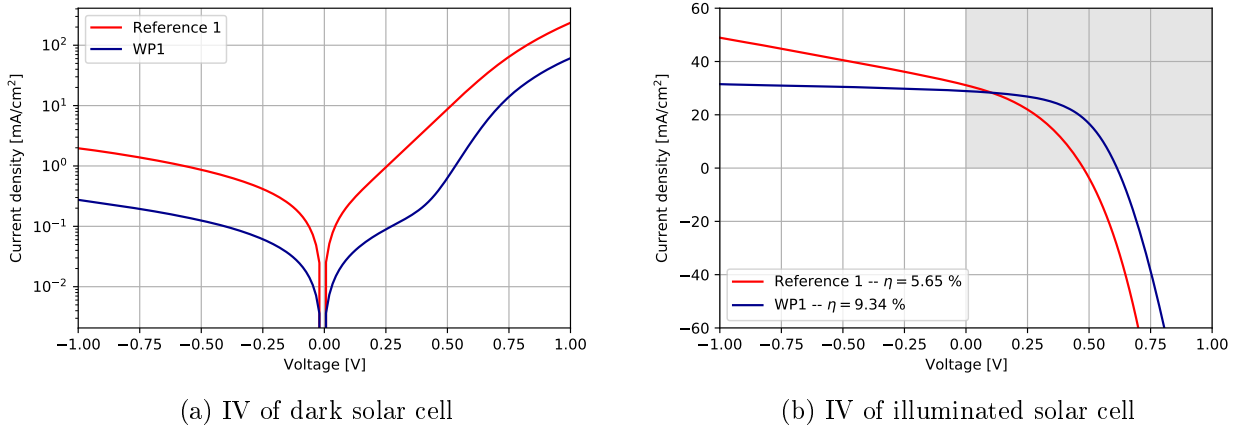


Figure 7.1.1: IV curve in the dark and under light of reference 1 and WP1

When looking at the IV curve in the dark (figure 7.1.1a), it first appears that the reverse leakage current is reduced. This is the sign, as previously mentioned, of a higher R_{sh} . At higher bias voltages, the saturation of the current is higher for WP1. This predicts that the series resistance should be higher for WP1 than for reference 1.

When looking at the IV curve under light (figure 7.1.1b), the reverse bias slope indeed confirms the higher shunt resistance. This leads to an improved higher FF, and to a slightly reduced J_{sc} . A great improvement in V_{oc} is also visible. The slope in forward bias seems to be slightly better for reference 1. Overall, the performance is improved for WP1 compared to reference 1.

Figures of merit The figures of merit extracted from the IV measurements are presented in table 7.1.1. Their values validate the observation made just before. All the figures of merit are improved for the passivated sample, except J_{sc} that is a little lower and R_s that is higher. Corrected values of η_c and FF_c are also improved, which suggests an improvement not only of the external characteristics but also the ones internal to the solar cell. This is supported by the higher V_{oc} value.

Parameter	Reference 1	WP1
J_{sc} [mA/cm ²]	31.28	28.95
V_{oc} [mV]	476.8	613.5
η [%]	5.65	9.34
FF [%]	37.9	52.6
R_{sh} [$\Omega \cdot \text{cm}^2$]	558.49	3804.14
R_s [$\Omega \cdot \text{cm}^2$]	0.42	2.49
η_c [%]	8.15	10.9
FF _c [%]	47.92	60.24

Table 7.1.1: Table of performance, including the external losses and the correction of the IV curve.

Interpretation The improvement to the solar cell that is seen in the case of window passivation is sensibly the same as in the case of front passivation in the previous chapter. This would suggest that for window passivation, there is also a combined action of passivation and annealing that are responsible for the performance improvement. Overall, the same interpretation as before can thus be given. The two samples have undergone the same ALD deposition process with the same 150°C annealing temperature, which is then partly at the origin of improved WP1 compared to reference 1. On top of this, even though the CdS deposition cannot have altered the AlO_x layer in this case, it is possible that the passivation layer is affected by the sputtering deposition process of the window layer. Indeed, as mentioned previously, sputtering is a high energy process that can be very damaging for thin dielectric layers. Concerning the figures of merit, it is probable that the much increased R_s is coming from the additional dielectric layer, but it is more probable that another phenomenon linked to the modification of the barrier at the CdS/window interface is at its origin, as developed further. The improved V_{oc} is probably coming from the same improvement of the intrinsic losses as in FP1. The better FF comes from the higher R_{sh} . Concerning this last parameter, it is again possible that the dielectric layer helps with reducing the shunt losses. Finally, the reduced J_{sc} probably originates from the higher shunt resistance at low voltage bias. More interpretation and detail about the intrinsic mechanisms are given further in this chapter, using the other characterization methods.

7.1.2 WP3 performance analysis

IV curves For the cells realized with absorber 3, two different materials are used for the passivation layer: AlO_x and HfO_x, in the same way as for front passivation in the previous chapter. The IV curve in the dark and under light for the champion cell of WP3 compared to reference 3 are represented in figure 7.1.2.

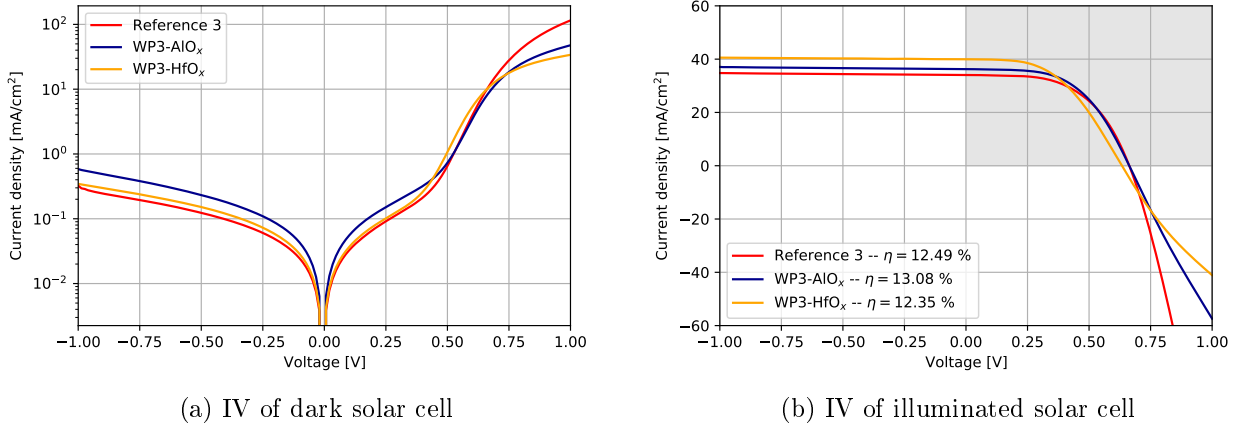


Figure 7.1.2: IV curve in the dark and under light of reference 3 and WP3

From the IV curve in the dark (figure 7.1.2a), it appears that window passivation has a significant impact on the forward bias characteristic of the solar cell, after 0.75V. This tends to indicate that R_s is very high in the device. There is on the contrary not much change in shunt resistance, as deduced from the reverse bias characteristic of the curves.

The supposedly very high series resistance is even more pronounced when looking at the IV curve under light. The slope is much lower for the passivated samples, and WP3-HfO_x even presents roll-over. This mechanism is well documented in references [51, 52]. It appears that it is not caused by R_s , even though it looks similar under dark conditions, but it comes from a modification of the CdS/window interface barrier. Since the passivation layer is added at that interface, it absolutely makes sense that this modification is present. This roll-over has a negative impact on FF, especially for WP3-HfO_x. Concerning the other figures of merit, it looks like J_{sc} is improved for the WP3 samples, and that V_{oc} remains unchanged or is slightly reduced. It does not look like R_{sh} is much affected by passivation, as anticipated from the measurement in the dark.

Figures of merit The figures of merit from the IV curves are presented in table 7.1.2.

Parameter	Reference 3	WP3-AlO _x	WP3-HfO _x
J_{sc} [mA/cm ²]	34.1	36.28	39.95
V_{oc} [mV]	663.3	663.5	633.3
η [%]	12.49	13.08	12.35
FF [%]	55.2	54.33	48.8
R_{sh} [$\Omega \cdot \text{cm}^2$]	3717	2157	3238
R_s [$\Omega \cdot \text{cm}^2$]	2.06		
η_c [%]	13.99		
FF _c [%]	70.07		

Table 7.1.2: Table of performance, including the external losses and the correction of the IV curve.

These figures of merit follow the trend anticipated from the IV curves observations. The efficiency is improved for the AlO_x sample mainly due to the action of the higher J_{sc} . The same increase in J_{sc} is visible in the HfO_x case, but due to much degraded V_{oc} and FF, the performance is not improved for this sample. The shunt resistance is reduced in both cases, but not significantly.

Missing figures of merit Due to the roll-over mechanism identified hereabove, some figures of merit cannot be extracted properly, starting from the series resistance. The plot used for the extraction of R_s is represented in figure 7.1.3. In this figure, an unusual U-shape is visible for the passivated samples, which leads to a wrong linear interpolation and extraction of R_s . Because roll-over happens for the same voltage biases as the ones at which R_s is extracted, the two phenomena cannot be easily uncorrelated. There is indeed no simple way of quantifying the effect of the roll-over on R_s . Because there is no correct evaluation of R_s , it is also impossible to obtain the corrected IV characteristic, hence also the values of η_c and FF_c .

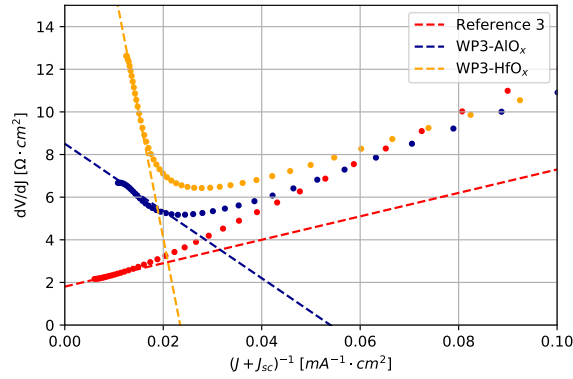


Figure 7.1.3: Extraction of R_s

Interpretation Most of the changes between the reference and the passivated structures come in this case from the passivation layer. It is clear that the reduction in FF is coming from the barrier-induced roll-over. This roll-over is visibly stronger for WP3- HfO_x , which would suggest that the modification to the barrier is stronger in that case. This could be due to a higher fixed charge Q_f in the layer which would add on the electron extraction at the front. This could also be due to a mismatch in the layers, adding a higher barrier at the interface. More likely, as suggested in [49], the sputtering process after ALD deposition damaged significantly the AlO_x layer, while leaving the HfO_x layer mostly untouched. This would be at the origin of the higher roll-over in the case of the HfO_x sample. Another effect of the roll-over is the reduction in V_{oc} . Concerning J_{sc} , an EQE measurement is performed to validate the improvement for the passivated structures, which is shown in figure 7.1.4. This confirms that J_{sc} is indeed improved for the passivated structures, but probably not as much as shown in the IV measurements. In this case as well the values of J_{sc} are higher when extracted from the EQE measurements. This could possibly be coming from a wrong calibration of the solar simulator.

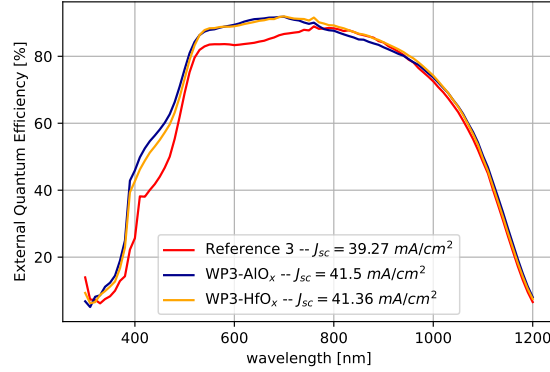


Figure 7.1.4: EQE comparison between the WP3 samples and reference 3

Overall, even though the impact of window passivation in this case is mostly not beneficent, it still enables to put into evidence a mechanism not studied until here; the roll-over. It is interesting to go one step further also in this case, to see how this phenomenon impacts the internal physics of the cell. This is done further in this chapter.

7.1.3 FP2 samples

Similarly to the previous chapter, the WP2 samples performance is not analyzed. A complete table of performance for these cells, along with the corresponding IV curves, is presented in appendix C. They do not present the same roll-over phenomenon as the WP3 samples. Passivation in this case does not improve the performance either.

7.2 CV measurements

In this section, CV measurements and the AS method are used to characterize defects inside the window passivated cells. These measurements are compared to the ones obtained for the reference cells in chapter 5. In a first section, room temperature CV measurements are presented and analyzed for WP1 and WP3 samples. In a second section, low temperature CV measurements are used to fully characterize the defects inside the WP3 samples.

7.2.1 Room temperature measurements

WP1 sample In figure 7.2.1, the comparison is made between WP1, reference 1 and FP1

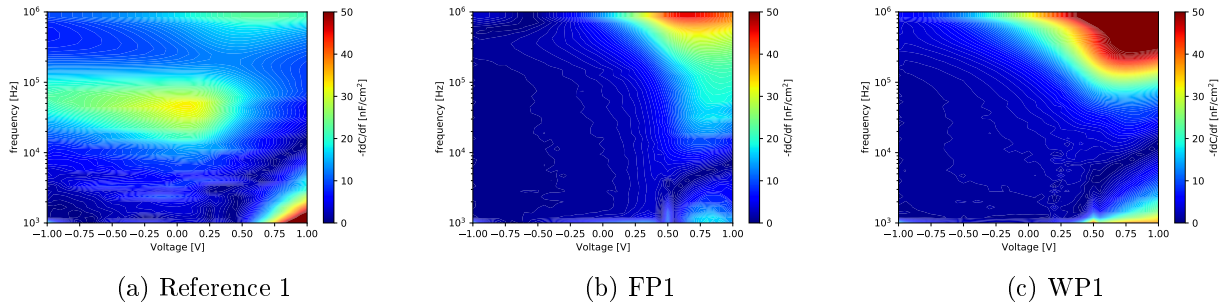


Figure 7.2.1: CV characteristics of WP1 compared to Reference 1 & Reference 1A

The observations made on the basis of this comparison are very similar to the one of the front passivation case. First, the big defect-like signature in the center of reference 1 is not present in the case of WP1. It is probable that it has shifted to the right and towards higher frequencies, and merged with the series resistance. The positive impact on V_{oc} observed in the performance evaluation also comes from the absence of loss mechanisms in the active area of the solar cell.

In terms of interpretations, the situation is also very similar to what is concluded for FP1 in the previous chapter. Again, the intrinsic changes to the structure probably come partly from the annealing of the sample during processing. In fact, the map of FP1 and WP1 are very similar, which naturally leads to the conclusion that a similar mechanism happens in the two cells. This would suggest that the effect of the passivation layer is quite negligible compared to this other mechanism. The difference in signature between the two cells then possibly comes from the passivation layers, but it is minor as also sustained by the performance which are very similar for FP1 and WP1. Such as for FP1, it would be interesting to further investigate the low temperature CV measurements to validate the hypothesis of a defect combined with the series resistance.

WP3 samples In figure 7.2.2, WP3- AlO_x and WP3- HfO_x are compared to reference 3.

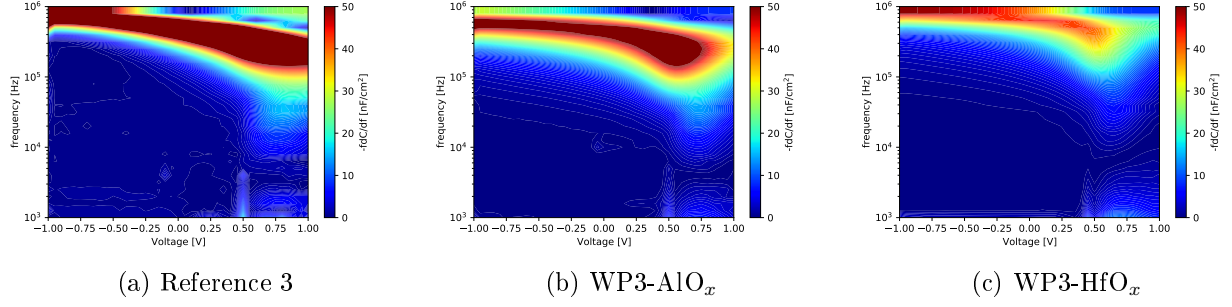


Figure 7.2.2: CV characteristics of both WP3 samples compared to Reference 3

In this figure, and contrarily to what is obtained in the front passivation case, it seems like window passivation has actually improved the solar cell CVf characteristic compared to the reference. In the passivated samples, there is a reduced action of both the series resistance and the interface defect. Such a reduction in the defect signature would suggest, considering the SCAPS simulations done previously, a reduction in the defect density N_t .

Looking at the performance evaluation of the previous section, it appears that window passivation induces roll-over which has a negative impact on the figures of merit. When considering intrinsic losses, it looks like window passivation is, on the contrary, beneficial. Indeed, by considering the loss map and especially for WP3-HfO_x, it looks like the action of intrinsic losses is reduced for the passivated samples compared to the reference. There would thus be a double effect of this passivation layer: first, it induces roll-over which negatively impacts the performance of the device, and secondly, it improves the internal characteristics of the device.

Ultimately, it is not possible to consider that the passivation layer has a positive impact on the cell in this case, because of the roll-over, but it is interesting to see that there is still an improvement in the CVf characteristic. To further understand the impact of the passivation layer on the interface defect, low temperature measurements are undergone in the next section.

Apparent doping profile Similarly to what is done in the previous chapter, the apparent doping profile for the different cells presented hereabove is represented in figure 7.2.3. This should yield quantitative information on the impact of defects on the structure.

For the samples made with absorber 1, the conclusions are again similar to the one made in the previous chapter. There is a clear reduction in the overall apparent doping of WP1 compared to the two references, which indicates a lower action of intrinsic losses in the device.

For the samples made with absorber 3, the conclusions are a little bit less straightforward, as anticipated hereabove. For WP3-HfO_x, the apparent doping profile is overall lower than the one of reference 3. This validates the interpretation made before that the action of intrinsic losses is reduced for this passivated sample. It is less obvious in the case of WP3-AlO_x when compared to the reference, but

it still presents a lower maximum in its apparent doping profile.

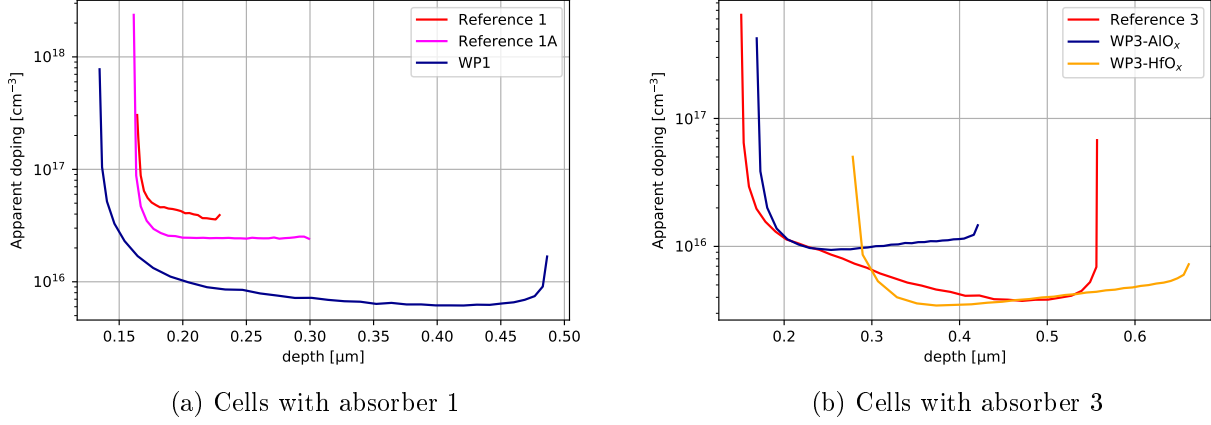


Figure 7.2.3: Apparent doping profile of the cells made with absorber 1 & 3, extracted from 10kHz CV measurements

7.2.2 Low temperature measurements

As done in the previous chapter, it is possible to use low temperature CV measurements to extract E_A and σ for the defect of the FP3 samples. Because the mechanism is very similar for WP3-AlO_x and WP3-HfO_x, the loss map at each temperature is only represented for WP3-HfO_x, in figure 7.2.4. They can be compared to the maps of reference 3 presented previously in figure 5.2.6.

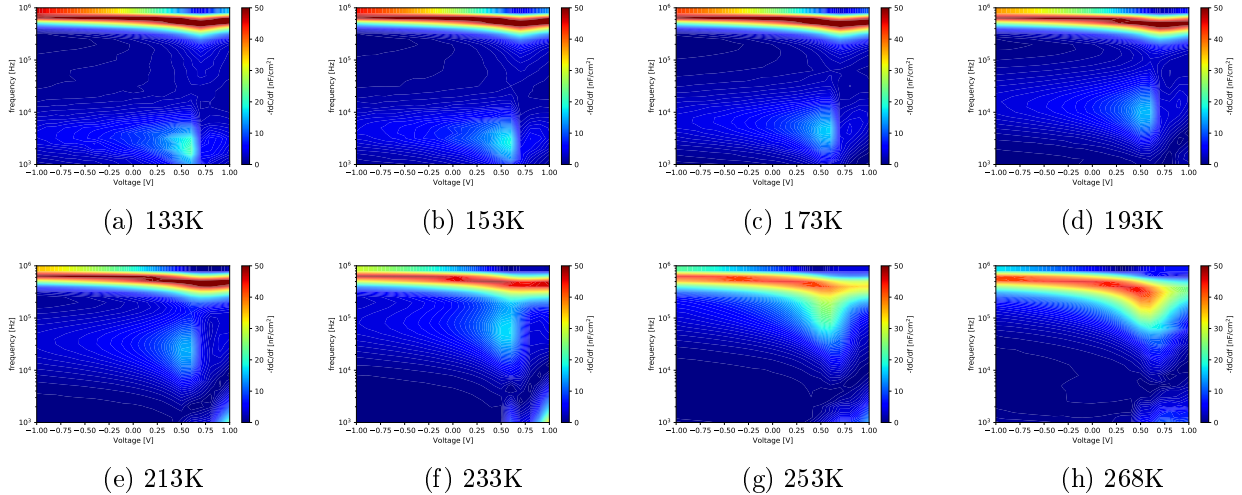


Figure 7.2.4: Loss maps of FP3-HfO_x at different temperatures

The evolution of the defect signature with temperature is quite similar to the one observed for reference 3 and FP3. The main difference here is that the defect density is visibly much smaller, which is deduced from the lower response visible on the maps. This would suggest, contrarily to front passivation, that the passivation layer at the window interface contributes to decreasing the action of this interface defect. This is a quite interesting hypothesis, because this defect is identified in the previous

chapter as a N1-type defect and because these defects are present at the CIGS/CdS interface [17, 50]. An hypothesis would then be that the passivation layer has a remote impact on the N1 defect. This is of course not real passivation, but it is still possible through the modification of the CdS/window interface barrier. Further investigation of this mechanism would be needed, but this is beyond the scope of this work.

The Arrhenius plot made from the data of figure 7.2.4 is presented in figure 7.2.5a.

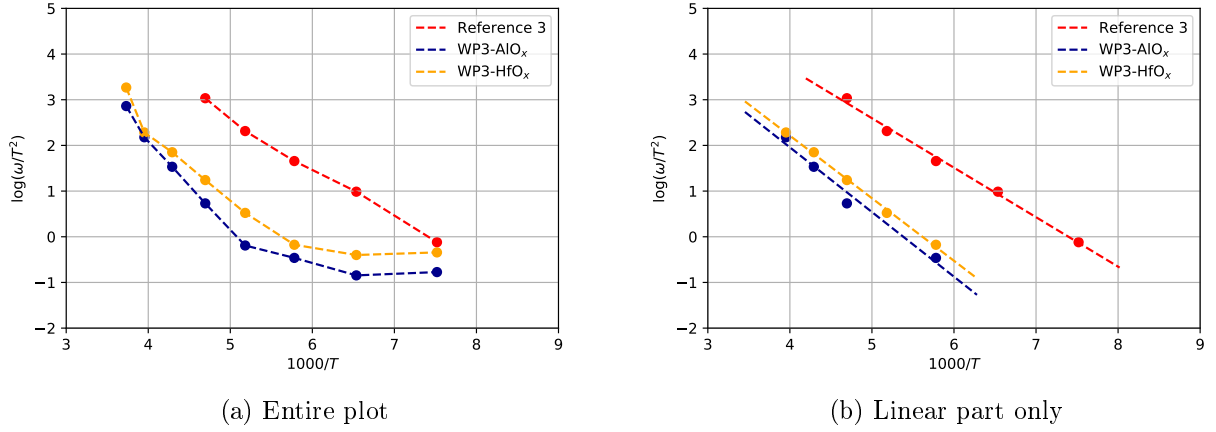


Figure 7.2.5: Arrhenius plot comparing WP3 samples with reference 3. Both the complete plot and a linearized version, where the non-linear values are removed, are shown.

In this case also the Arrhenius plot is not linear, confirming the presence of a similar N1-type defect than identified previously. When linearizing the Arrhenius plot (figure 7.2.5b), the values of table 7.2.1 are obtained.

Sample	E_A [eV]	σ [cm ⁻³]
Reference 3	0.093	$2.88 \cdot 10^{18}$
FP3-AlO _x	0.122	$2.74 \cdot 10^{18}$
FP3-HfO _x	0.118	$2.09 \cdot 10^{18}$

Table 7.2.1: Extracted values of E_A and σ for FP3 samples compared to reference 3

These values are quite close to the one obtained for the FP3 samples, where σ is mostly unchanged and E_A is a little increased. Of course, the reduction of the defect density is not visible when using this technique. In order to be able to extract the defect density, capacitance profiling should be used, such as in reference [53], but this is beyond the scope of this work.

7.3 TRPL measurements

In this section, the TRPL measurements of window passivated samples are briefly introduced in order to further validate the results and hypothesis presented before. They are presented in figure 7.3.1

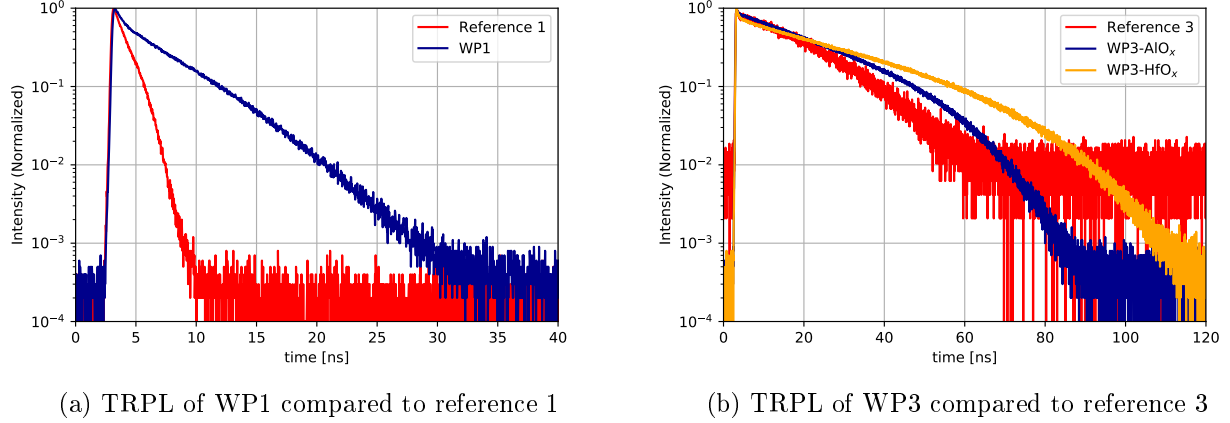


Figure 7.3.1: TRPL measurements of the window passivated samples

WP1 sample The TRPL measurements of WP1 compared to reference 1 are shown in figure 7.3.1a. There, it appears that the τ_2 lifetime is much higher for WP1 than for reference 1. This is in line with the observations made for front passivation, but even higher. This would suggest that window passivation has an even stronger effect on carrier lifetime than front passivation in this case. More precisely, when considering that the effect mainly comes from annealing for FP1 samples, it is probable that in the case of WP1 there is a combined effect of annealing and window passivation on the carrier lifetime. This is not particularly in line with performance analysis, as WP1 shows slightly lower V_{oc} , FF and η compared to FP1. Because of the complexity and amount of phenomena influencing TRPL, it is complicated to conclude further on this.

FP3 samples The TRPL measurements of WP3 compared to reference 3 are shown in figure 7.3.1b. These are again completely in line with the observations made in the previous sections of this chapter. TRPL decay is a little better for WP3 samples than for reference 3, contrarily to FP3 samples. This is also observed in CVf measurements where the action of defects is reduced in the case of the window passivated samples.

7.4 Conclusion

In this chapter, a front passivated structure for CIGS solar cells is investigated. This is tried on two different absorbers (absorber 1 & 3) and with both AlO_x and HfO_x .

WP1 sample Similarly to FP1 in the previous chapter, the performance is much improved for WP1 compared to reference 1, with about a 4% efficiency increase. Since the evolution of performance and the CVf loss map are very similar for the FP1 and WP1 samples, it is very likely that the same phenomenon is at the origin of the change compared to reference 1. This is an argument in favour of annealing being mostly responsible for the performance improvement for both front and window passivation.

WP3 samples In the case of these samples, the performance is not improved compared to the reference, with about 0.7% efficiency loss. Most of the figures of merit are decreased in this case and the main reason for this appears to be the roll-over that is visible on the IV characteristic. This can come from the modification of the CdS/Window interface and is responsible for a decrease of V_{oc} and FF. It also prevents the correct extraction of R_s . Contrarily to this detrimental effect on performance, it seems that the passivation layer has a positive effect on the intrinsic losses. Indeed, the loss map indicates a reduced impact of the interface defect and the series resistance. This is confirmed by the low temperature CVf measurements, where it looks like N_t is reduced for the N1-type defect. Nevertheless, this improvement in the intrinsic characteristic of the solar cell is not sufficient to counteract the roll-over induced by the passivation layer.

8 Conclusion

8.1 Summary

The three first chapters of this work are dedicated to establishing the background and the theoretical knowledge that is necessary to fully apprehend CIGS solar cells, the characterization of defects and passivation. In the **first introductory chapter**, a general presentation about the context in which this work finds its place is given. It is shown that solar PV and new technologies of solar cells are essential for a transition towards sustainable energy. To this regard, CIGS solar cells constitute a very promising lead, if the remaining performance limitations such as the high concentration in defects are tackled. In the **second chapter**, the general theory about solar cells is first briefly developed. The principle of charges generation and recombination is presented and a link is established with the main figures of merit as well as with the main loss mechanisms present in these solar cells, both extrinsic and intrinsic. After that, the peculiarities of CIGS solar cells are presented, with the CIGS/CdS heterojunction and the bandgap grading. The emphasis is put on the defects and their mitigation, which is a critical challenge in CIGS technology. This precedes a very important section on admittance spectroscopy, a technique that is used to characterize loss mechanisms in CIGS solar cells. The theory behind AS is extensively developed in that section, taking a novel graphical approach called loss map that enables an easier representation of defects and other loss mechanisms. Low temperature measurements are also introduced as a way of extracting the defects parameters. The final section of chapter 2 highlights different strategies that can be used for mitigating performance losses in CIGS solar cells. Post-deposition annealing, bandgap grading, interface barrier modification and finally interface passivation are developed in this section. In **chapter 3**, the work methodology and the experimental setup used in this work are presented. SCAPS simulations are introduced as a way of predicting experimental trends and interpreting experimental observations. The samples processing is developed, along with the ALD technique that is used to deposit the passivation layers. Finally, the 4 characterization techniques used in the rest of this work (IV, CV, PL and EQE) are presented in detail.

In **chapter 4**, SCAPS is used as a sensitivity analysis tool for evaluating the impact of different loss mechanisms on the solar cell parameters. In a first section, IV measurements are used to predict the impact of these losses on the main figures of merit. Using the 1-diode model for external losses, it is shown that R_s and R_{sh} both have a significant impact on FF, but no real effect on V_{oc} and J_{sc} . The introduction of bulk and interface defects in the model shows that they mostly affect V_{oc} and marginally J_{sc} . This is due to the strong dependence of J_s in the recombination rate that increases

when defects are present in the structure. On the contrary, defects do not have much impact on FF. In the second section, AS measurements are simulated to identify the various signatures of these losses on the loss map. A series resistance appears as a voltage independent trace, visible only at high frequencies. Bulk defects present a long tail-like signature in the voltage range, and see their frequency response vary in function of E_A and σ , while the intensity of their response varies with N_t . Interface defects, on the other side, have a very narrow response in voltage and a wide response in frequency. Their characteristic frequency also varies with E_A and σ , and for very high N_t , their response is extended in the voltage range due to Fermi level pinning. In the end of this section, it is shown that different losses that are combined in a solar cell simply have their respective trace added one to another in the loss map.

Chapter 5 is dedicated to a base case study of three different reference CIGS solar cells. The methodology introduced in that chapter is then applied to the next two chapters studying passivated CIGS solar cells. In the first section, a performance analysis of the three reference CIGS solar cells is conducted. Differences in terms of figures of merit are highlighted with efficiencies varying in the 5-14% range. The extraction method of external losses, R_s and R_{sh} is presented in that section as being a first step in the performance analysis. It is shown that these external losses indeed have a significant impact on performance, particularly on FF, and that their extraction is not always straightforward. After that, the main limitations to performance analysis using IV measurements are presented, with the J_{sc} artificial variations induced by the processing and the measurement procedure, the R_s variation due to the contacts and the cell-to-cell variations. EQE measurements are identified as a way to correctly evaluate the value of J_{sc} . The final part of this section is dedicated to the effect of post-deposition annealing on the solar cell performance. It has a positive impact on lower performance cells and a limited impact for higher performance cells. In the second section, CV measurements are used to deeply characterize the intrinsic properties of the three reference samples. The CVf loss maps of these cells are presented and used to interpret the variation in performance from the previous section, especially in terms of V_{oc} . It is shown that reference 1, whose V_{oc} is significantly lower, presents a bulk defect in the centre of its loss map, contrarily to the other two references. Low temperature measurements of reference 3 are conducted to extract $E_A \sim 0.1\text{eV}$ and $\sigma \sim 10^{-18}\text{cm}^{-3}$. In the third and last section, PL and TRPL measurements are presented to evaluate the main characteristics of the different absorbers. Moreover, the different injection regimes of TRPL are presented and used to interpret the Gaussian-like TRPL trace of reference 3.

In **chapter 6**, front passivation of CIGS solar cells is investigated. In the first section, significant improvement is highlighted for the front passivated cell made with absorber 1 (FP1), with a 30% V_{oc} improvement and an absolute increase of 4% efficiency compared to the reference. On the contrary, few changes are observed for the front passivated cell made with absorber 3 (FP3), with a slight reduction both in V_{oc} and η . This is at least partly attributed to the positive impact that annealing has on absorber 1 samples compared to absorber 3 samples. In the second section, loss maps are used to confirm the changes in V_{oc} compared to the references. The bulk defect identified in reference 1 is not present in FP1, which is most likely at the origin of the significant V_{oc} increase. Low temperature

measurements for FP3 show that the trace identified before for reference 3 has seen its intensity much increased and extended in the voltage range. This is attributed either to a modification of the CIGS/CdS interface barrier, or to an increase in the interface defect density, possibly leading to Fermi level pinning.

Finally, in **chapter 7**, window passivation of CIGS solar cells is investigated. In the first section, significant improvement is again highlighted for passivated samples made with absorber 1 (WP1), showing very similar results than FP1. This would constitute another argument in favour of annealing being at least partly responsible for the performance improvement. For passivated samples made with absorber 3 (WP3), there is a reduction in performance caused by roll-over, which is probably induced by a modification of the CdS/Window interface. This leads to a significant reduction in FF. In the second section, the loss maps are presented. Similarly to FP1, WP1 also shows that the bulk defect in the centre of the map is not present anymore. Low temperature measurements for WP3 show that there is, contrarily to FP3, an improvement in the interface defect response, with a reduction of the defect density. This positive aspect of window passivation for WP3 is to be put in balance with the negative impact of roll-over. These concurrent mechanisms highlight that there is indeed an interest in window passivation for minimizing the action of defects, but that further investigation is needed, possibly with other materials, in order to minimize the roll-over.

8.2 Future prospects and research

There are some aspects about this work that remain uncertain and that would need further investigation. A first example is that the simulation software used in this work, SCAPS, presents some significant limitations that sometimes affect the ability to conclude on experimental data. More advanced characterization techniques should also be used to gather more insight about the physical mechanisms at play in the structure. In particular, a lot of questions remain about the exact modification of the bandstructure that is induced by interface passivation, which could validate some hypotheses in the case of FP3 loss maps or in the case of WP3 roll-over. All of these challenges regarding CIGS technology are to be also considered on a wider scale. Some materials that constitute CIGS absorbers will be in the near future more and more difficult to obtain. It will thus probably be necessary to adapt the knowledge gathered in CIGS to other more sustainable technologies such as Kesterite. Moreover, while research in PV is certainly essential to a greener electricity production, it is fundamental to also focus on the development of other technologies, such as energy storage, that are critical to the transition towards a completely sustainable world.

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B SCAPS models

B.1 Ideal PN junction

This SCAPS model is the one of an ideal PN junction, which is represented in figure B.1.1. The parameters of the model are given in table B.1.1.

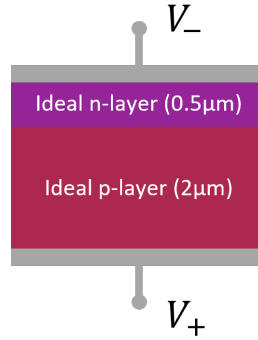


Figure B.1.1: SCAPS model of the ideal PN junction. The contacts are represented in grey and their metal work function is aligned with the Fermi level of the adjacent material (Flat-band parameter in SCAPS).

Parameter	p-layer	n-layer
E_g [eV]	1.2	1.2
χ [eV]	4.5	4.5
thickness [μm]	2	0.5
ε_r [/]	10	10
N_c [cm^{-3}]	10^{19}	10^{19}
N_v [cm^{-3}]	10^{19}	10^{19}
$v_{T,e}$ [cm/s]	10^7	10^7
$v_{T,h}$ [cm/s]	10^7	10^7
μ_e [$\text{cm}^2/\text{V}\cdot\text{s}$]	50	50
μ_h [$\text{cm}^2/\text{V}\cdot\text{s}$]	50	50
N_D [cm^{-3}]	10	10^{17}
N_A [cm^{-3}]	10^{15}	10

Table B.1.1: Parameters from the SCAPS model of the ideal PN junction

B.2 Reference CIGS cell

This SCAPS model is the one of a reference CIGS solar cell, which is represented in figure B.2.1.



Figure B.2.1: SCAPS model of the reference CIGS cell. The back contact represented in grey has its metal work function aligned with the Fermi level of the adjacent CIGS (Flat-band parameter in SCAPS).

The parameters of the model are given in table B.2.1. It has to be noted that, like in real cells, the CIGS layer does have a graded bandgap (non-uniform). In this case, it has an exponential grading with the proportion of CIS and CGS varying in function of the depth in the CIGS layer.

Parameter	CIGS	CdS	ZnO	ZnO:Al
E_g [eV]	1.18 to 1.23	2.42	3.3	3.3
χ [eV]	4.5 to 3.9	4.1	4.1	4.1
thickness [μm]	1.6	0.05	0.2	0.4
ϵ_r [/]	13.6	9	9	9
N_c [cm^{-3}]	$2.2 \cdot 10^{18}$	$2.2 \cdot 10^{18}$	$2.2 \cdot 10^{18}$	$2.2 \cdot 10^{18}$
N_v [cm^{-3}]	$1.8 \cdot 10^{19}$	$1.8 \cdot 10^{19}$	$1.8 \cdot 10^{19}$	$1.8 \cdot 10^{19}$
$v_{T,e}$ [cm/s]	10^7	10^7	10^8	10^8
$v_{T,h}$ [cm/s]	10^7	10^7	10^8	10^8
μ_e [$\text{cm}^2/\text{V}\cdot\text{s}$]	100	350	200	200
μ_h [$\text{cm}^2/\text{V}\cdot\text{s}$]	25	50	50	50
N_D [cm^{-3}]	10^5	10^{17}	10^{17}	10^{20}
N_A [cm^{-3}]	10^{16}	10^5	10^5	10^5

Table B.2.1: Parameters from the SCAPS model of the ideal PN junction

This CIGS reference cell is also sometimes simulated with a bulk defect in the CIGS, with the following properties: it is an acceptor defect with $E_A = 0.35$ eV, $\sigma = 10^{-15} \text{cm}^{-2}$ and $N_t = 10^{16} \text{cm}^{-3}$.

C Performance of FP2 & WP2 cells

The IV curves for the FP2 & WP2 samples compared to reference 2 are presented in figure C.0.1.

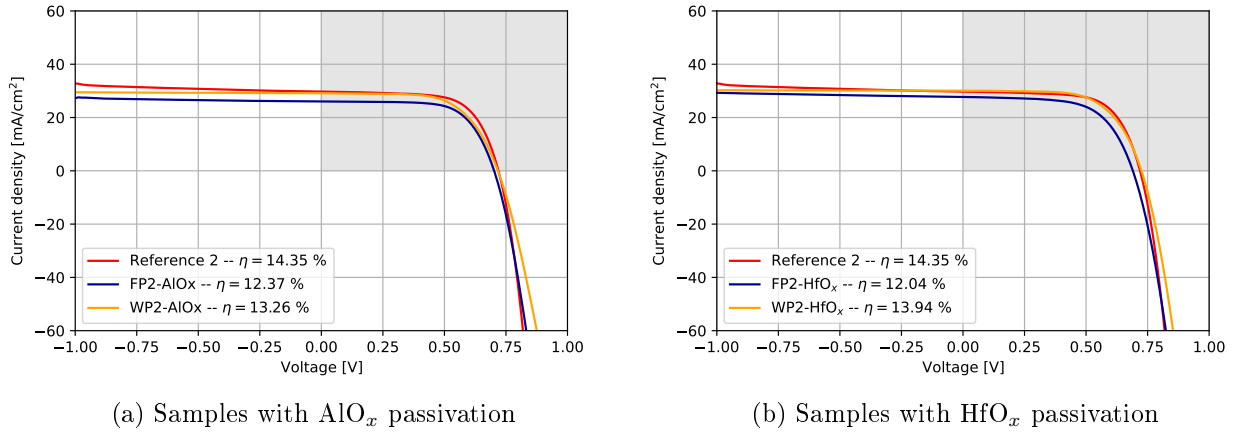


Figure C.0.1: IV curve under light of reference 2 compared to the FP2 & WP2 passivated samples

The figures of merit for sample FP2 & WP2 compared to reference 2 are presented in table C.0.1.

Parameter	Reference 2	FP2- AlO_x	WP2- AlO_x	FP2- HfO_x	FP2- HfO_x
J_{sc} [mA/cm^2]	29.24	26.08	29.06	27.71	30.05
V_{oc} [mV]	720	702	722	690	725
η [%]	14.09	12.37	13.35	12.04	13.94
FF [%]	66	67	63	63	64
R_{sh} [$\Omega \cdot \text{cm}^2$]	10865	5142	10700	1218	12800
R_s [$\Omega \cdot \text{cm}^2$]	0.42	1.29	2.22	0.93	1.07
η_c [%]	14.83	13.17	14.73	13.04	14.73
FF_c [%]	70	72	70	68	68

Table C.0.1: Table of performance, including the external losses and the correction of the IV curve.

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