Characterization and Simulation of Three-Dimensional Solid-State Solar Cells

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Summary

Introduction

During the last decade, the photovoltaic industry has been growing exponentially, resulting in a world production of 1 GWp per year in 2004. This extraordinary growth is mainly driven by market incentives; large scale application of photovoltaic energy generation still can not compete economically with the classical way of electricity generation. The main photovoltaic technology, based on silicon, requires energy and cost consuming deposition methods and material purifying techniques. Moreover, a large amount of material is used due to the absorption properties of silicon. In the beginning, the left-overs of the micro-industry were enough to supply the photovoltaic industry, but nowadays, the PV industry uses half of the total amount of available silicon. This of course will not help to lower the prices.

New PV technologies need to be developed that use less material, as well as cheaper materials and deposition methods. Thin film technology in particular has succeeded in the first aim, reducing the cell thickness from 30 to 3 µm, introducing copper indium gallium diselenide (Cu(In,Ga)Se$_2$), amorphous silicon (a-Si) and cadmium telluride (CdTe) as material candidates. When reducing the thickness of the light absorbing layer even further, the domain of extremely thin absorber or ETA-layers is entered. To ensure sufficient light absorption, such ETA-layers need to be applied to a nano-structured substrate. Both the substrate and the absorber layer have an additional high low cost potential due to the required non-vacuum deposition techniques.

Dye sensitized solar cells (DSSC’s) fully use this potential; they consist of a nanoporous oxide electrode, that is covered with a monolayer of organic dye and immersed in a liquid electrolyte. However, due to the organic nature of the absorbing dye and the fluidity of the electrolyte, a lot of long-term stability problems are encountered. In the cells studied in this thesis, both the organic absorber dye and the liquid electrolyte are replaced by a solid-state semiconductor; they are called 3D-cells. The nanostructured substrate however, is the same: nanoporous titanium dioxide (TiO$_2$).

Objective

Due to the inherent interpenetrating nature of the nanostructured cell, charge carrier generation due to light absorption and the transport of these carriers to the contacts, is separated in these devices. Since, from the moment the charge carriers are separated, they are less sensitive to defects, this seems to be an advantage with respect to the one-dimensional standard and thin film technology, where charge generation and transport take place in the same materials (thus requiring high diffusion lengths of the charge carriers). Considered the very good short-term performance of DSSC’s (10% efficiency), these cells indeed are able to benefit from this three-dimensional feature. Our and other’s nanostructured solid-state cells however, do not (except for the enhanced quantum response yield from long wavelengths with respect to short ones for nanostructured devices with respect to flat ones). The question is why?
Interface recombination

In order to find an answer to this question, different kind of nano- and microstructured solid-state solar cells are characterized and analyzed. For the analysis, different models are developed and compared. In particular a dynamic model is presented which enables us to quantify the influence of recombination in these cells. Recombination, in particular interface recombination, turns out to be a crucial element in the determination of the final performance of a nanostructured solid-state solar cell.

The reason for this is as follows. With the increase of effective absorber thickness upon applying an absorber to a nanostructured substrate, a huge increase of interface area is gained (up to 1000 times with respect to a flat configuration). Since at an interface, two materials are interacting, is it very likely that the interface, instead of the bulk material, becomes the main source for defects in nanostructured solar cells and hence for efficiency limiting recombination.

Diffusion models

To allow us to determine recombination related parameters like diffusion coefficient and carrier lifetime, detailed effective medium models are set up which describe both steady-state and dynamic response of the cells. In one of the models, the cell is treated as an infinite network of flat band unit cells (i.e. there is no electric field on a microscopic level). In the other, an analytic diffusion model is set up with boundary conditions specific for the treated cell. Both models assume diffusion as the main driving force for electron transport; charge separation occurs due to the difference in electron negativity of the materials.

Results

The diffusion coefficients that are found are in the same range as those found for DSSC’s. The main difference is in the lifetime of the electrons which is $10^4$ times smaller for 3d-cells than for DSSC’s. Both analytic approximations of and full simulations with the analytic diffusion model revealed that the diffusion length is much smaller than the cell thickness, and also than the absorption depth of the light. In that case, the characteristic time constant associated with the break frequency of the optoelectronic photocurrent transfer function is equal to half the electron life time, the characteristic time constant associated with the break frequency of the optoelectronic photovoltage transfer function is equal to the electron life time. The quantum response is equal to the product of the electron diffusion length and the absorption coefficient, which in our case indeed yields a quantum response that is much smaller than one.

At last, the analytic diffusion model turned out to represent the nanostructured solar cell in the same way as the proposed infinite network of flat-band unit cells.

Outlook

With respect to an optimization strategy of our cells, the following result is obtained. Insertion of intermediate buffer and tunnel layers at the active interface enhanced device performance significantly. It is shown that this effect can be ascribed mainly to a decrease of interface recombination due to a more favorable position of the Fermi levels at the interface, with respect to the band edges. Of course, chemical materials interactions like prevention of material diffusion also still play an important role.

Practice has already overtaken theory by demonstrating high efficiency 3d-cells based on the improvements suggested as a result from the theory presented in this thesis.
Samenvatting

Introductie

In de laatste 10 jaar is de fotovoltaïsche industrie exponentieel gegroeid, hetgeen in 2004 leidde tot een geproduceerd vermogen op jaarbasis van meer dan 1 GWp. Deze buitengewone groei is hoofdzakelijk te danken aan markt stimulansen; grootschalige opwekking van fotovoltaïsche energie kan, economisch gezien, nog steeds niet concurreren met de klassieke manieren van energie opwekking. De belangrijkste fotovoltaïsche technologie, gebaseerd op silicium, vraagt om energie en geld verslindende depositie methoden en materiaal zuiveringstechnieken. Bovendien is er een grote hoeveelheid materiaal nodig vanwege de absorptie eigenschappen van silicium. In het begin was het afval van de micro-industrie voldoende om aan de vraag van de fotovoltaïsche industrie te voldoen, maar tegenwoordig gebruikt de PV industrie de helft van al het beschikbare silicium. Dit staat natuurlijk een gunstige prijsontwikkeling van zonnecellen in de weg.

Daarom moeten er nieuwe fotovoltaïsche technieken ontwikkeld worden die toekunnen met minder en materiaal en die gebruik maken van goedkopere depositie methodes en materialen. In het bijzonder dunne-film technologieën zijn geslaagd in de eerste opzet, namelijk het terugbrengen van de celdikte van 30 tot 3 µm; ze gebruiken koper indium gallium diselenide (Cu(In,Ga)Se₂), amorf silicium (α-Si) en cadmium telluride (CdTe). Indien de dikte van de licht absorberende laag nog verder afneemt wordt het gebied van de extreem dunne absorberende (extremely thin absorber, of ETA) lagen betreden. Om toch nog voldoende licht te kunnen absorberen, dient deze ETA-laag aangebracht te worden op een nano-gestructureerde onderlaag. Aangezien voor de productie van zowel deze onderlaag als de absorberende laag geen vacuüm nodig zijn, is er een extra kosten besparing mogelijk.

Kleurstof gesensibiliseerde zonnecellen (dye sensitized solar cells, of DSSC’s) maken maximaal gebruik van dit potentieel. Ze bestaan uit een nanoporeuze elektrode van een oxide van welk ieder deeltje bedekt is met een mono-moleculaire laag van een organische kleurstof. Het geheel is ondergedompeld in een vloeibaar elektrolyt. Echter, de organische afkomst van de kleurstof en de vloeibaarheid van de elektrolyt zorgen voor problemen met de lange termijn stabiliteit van de cel. In de cellen die bestudeerd worden in deze thesis zijn zowel de organische kleurstof als de vloeibare elektrolyt vervangen door vaste-stof halfgeleiders; ze worden 3D-cellen genoemd. De nanogestructureerde onderlagen van beide cellen is hetzelfde: nanoporeus titanium dioxide.

Doel

Als gevolg van de drie-dimensionale morfologie van de nanogestructureerde cellen is de generatie van ladingsdragers door absorptie van licht, en het transport van deze ladingsdragers naar de contacten, gescheiden. Omdat de ladingsdragers nadat ze gescheiden zijn minder ge-
voelig zijn voor de aanwezigheid van defecten, lijkt dit een voordeel te zijn ten opzichte van een-dimensionale standaard en dunne-film technologie, waar de generatie van lading en het transport van diezelfde lading in hetzelfde materiaal plaatsvindt; in het laatste geval dienen de ladingsdragers een lange diffusie lengte te hebben. Gezien de zeer goede korte-termijn prestatie van DSSC’s (10% efficiëntie), zijn deze cellen inderdaad in staat gebruik te maken van deze drie-dimensionale eigenschap. Onze en andere nanogestructureerde vaste-stof cellen kunnen dat echter niet, behalve misschien een verhoogde bijdrage aan de fotostroom van ladingsdragers die gegenereerd zijn door licht met langere golflengtes. De vraag is, waarom?

**Grensvlak recombinatie**

Om een antwoord te kunnen geven op deze vraag zijn er verschillende soorten nano- en microgestructureerde vaste-stof zonnecellen gekarakteriseerd en geanalyseerd. Voor de analyse zijn verschillende modellen ontwikkeld en vergeleken. In het bijzonder wordt er een dynamisch model voorgesteld dat het mogelijk maakt om de invloed van recombinatie te kwantificeren. Deze recombinatie, met name grensvlak recombinatie, blijkt een cruciale rol te spelen ten aanzien van de uiteindelijke prestatie van een driedimensionale vaste-stof zonnecel.

Dit is als volgt te verklaren. De toename van effectieve absorber dikte als gevolg van het aanbrengen van de absorber op een nanogestructureerde onderlaag leidt tevens tot een grote verhoging van het grensvlak oppervlak (tot wel 1000 keer ten opzichte van een vlakke configuratie).

Aangezien aan zulke grensvlakken twee materialen op elkaar inwerken is het niet ondenkbaar dat dit grensvlak in plaats van het bulk materiaal, de belangrijkste bron voor defecten wordt, en daarmee ook voor opbrengst beperkende recombinatie.

**Diffusie modellen**

Om nu aan recombinatie gerelateerde parameters als diffusie coëfficiënt en levensduur van de ladingsdragers te kunnen bepalen, zijn er gedetailleerde effectief-medium modellen opgesteld die zowel de steady-state als de dynamische respons van de cel beschrijven. In een van de modellen wordt de cel benaderd als een oneindig netwerk van vlakke-band eenheidscellen (dat wil zeggen, er is geen elektrisch veld op microscopische schaal). Het andere is een analytisch diffusie model met specifieke randvoorwaarden voor de besproken cel. Beide modellen gaan ervan uit dat het ladingstransport bepaald wordt door diffusie; ladingsscheiding treedt op door een verschil in elektronegativiteit van de materialen.

**Resultaten**

De diffusie coëfficiënten die gevonden zijn, zijn in dezelfde orde van grootte als die, die gevonden zijn voor DSSC’s. Het verschil blijkt hem te zitten in de levensduur van de elektronen, die $10^4$ keer kleiner is voor 3d-cellen dan voor DSSC’s. Zowel analytische benaderingen van, als ook volledige simulaties met het analytische diffusiemodel lieten zien dat de diffusie lengte veel kleiner is dan de cel dikte, en ook de absorptie diepte van het licht. In dit geval is de karakteristieke tijdsconstante die geassocieerd wordt met de breekfrequentie van de opto-elektronische transfer functie van de fotostroom gelijk aan de helft van de levensduur, de tijdsconstante behorende bij de transfer functie van de fotospanning is gelijk aan de levensduur. De quantum respons is dan gelijk aan het product van de diffusie lengte en de absorptie coëfficiënt, wat in het geval van onze cellen inderdaad een quantum respons oplevert die minder is dan 1.
Tot slot blijkt dat het analytische diffusie model de nanogestructureerde cel op precies dezelfde manier beschrijft als het oneindige netwerk model van vlakke-band zonnecellen.

**Vooruitzicht**

Wat betreft een strategie die zou leiden tot een verbetering van onze cellen kan het volgende gezegd worden. Het invoegen van een buffer of tunnel laag op het actieve grensvlak leidt tot een significante verbetering van de cel opbrengst. Het is aangetoond dat dit effect voornamelijk kan worden toegeschreven aan een afname van grensvlak recombinatie door een verbeterde positie van het Fermi niveau aan het grensvlak ten opzichte van de band randen. Natuurlijk spelen ook chemische materiaal interacties zoals het voorkomen van materiaal diffusie nog altijd een belangrijke rol.

De praktijk heeft ondertussen ook al de theorie ingehaald door verbeterde 3D-cellens op te leveren die gebaseerd zijn op de theorie zoals die gepresenteerd is in deze thesis.
Chapter 1

Introduction

1.1 Objective

The main objective of my research is to gain insight in the physical mechanisms underlying the photovoltaic performance of three-dimensional solid-state solar cells using different device characterization and simulation techniques. The main reasons for the development of such cells are their projected low production costs and high stability as compared to crystalline semiconductor and photoelectrochemical photovoltaic devices respectively.

1.2 Background

This objective also serves a more specific goal which is the investigation of the feasibility of the ETA-solar cell concept, for this was the main objective of the EU-project in which our group participated. The full title of this project was ‘A Challenging Solar Cell Concept – The Skillful Intercalation of a Nanostructured Semiconductor by an Extremely Thin Copper(indium)sulphide Absorber’, or in short ‘The ETA-Solar Cell’. It was concluded between the European Commission and 7 institutes and universities\(^{(1)}\) from the EU and associate countries on 1 September 2000 for 48 months (project number HPRN-CT-2000-00141). It was a Research Training Network (RTN) funded by the European Commission’s 5\(^{th}\) Framework Improving Human Potential Programme. The primary objective of a RTN is to promote training-through-research, especially of young researchers, both pre- and postdoctoral level, within the frame of high quality transnational collaborative research projects. The training of the young researchers in the ETA-solar cell project was taken very well care of; it not only concerned the development of their scientific skills but also of their personal skills. For this reason it was decided that a consultant from Kern Konsult\(^{(2)}\) accompanied in particular the young researchers, focusing on creative project management.

The contribution of our research group to the achievement of the project’s goal led to this PhD-thesis. Given the experimental facilities and theoretical device knowledge of our solar cell group, I directed my attention to device characterization and simulation of the characterization results. However, the three-dimensional nature of the cell under investigation directed the attention beyond the thin film experience of the group. Here, the cooperation with other network partners proved very helpful and beneficial once the initiation efforts were over. Be-

\(^{(1)}\) Energy Research Centre of the Netherlands (ECN), Petten (coordinator); Hahn-Meitner Institute (HMI), Berlin, Germany; Tallinn Technical University (TTU), Estonia; University of Uppsala (UU), Sweden; Delft University of Technology (TUD), the Netherlands; Weizmann Institute of Science (WIS), Rehovot, Israel; Ghent University.

\(^{(2)}\) www.kernkonsult.com
sides the samples themselves\(^{(3)}\), new characterization methods, effective medium models and chemistry were introduced into the vocabulary, knowledge and experience of the group and joint publications were written. Even a special ETA-web site has been designed by the author: www.elis.ugent.be/~grasso/eta_solar_cell/.

1.3 Outline

In this thesis, I describe how the different three-dimensional solid-state solar cells of the project partners have been characterized and modelled; the final goal is to find the main efficiency limiting factors of the present generation of these solar cells.

To begin with, the following chapter gives a detailed introduction on the status of renewable energy sources with respect to the classical, non-renewable energy sources, and the role of solar energy in this. Also, the different solar cell technologies are discussed; Chapter 3 is dedicated to the description of one of these cell technologies, i.e. that of the three-dimensional solar cells among which are also the 3D- and ETA-cells that are investigated in this thesis.

Chapter 4 provides theoretical and practical information on the characterization techniques used, Chapter 5 describes the infinite network and effective medium models that are used to analyze the measurement results.

Chapter 6 focusses on interfaces in heterojunction solar cells, their role in the performance of three-dimensional solar cells, and the influence of an extra intermediate layer on the performance. In Chapter 7, an attempt is made at obtaining more insight in the charge carrier dynamics by investigating the electronic and opto-electronic dynamic response of 3D-cells with EIS, and IMPS and IMVS respectively. At last, a few ETA-cell realizations are more closely studied in Chapter 8.

The results are summarized in the last chapter, Chapter 9.

\(^{(3)}\)All the cell fabrication was done by other ETA-project partners; technical details are to be found only in references.
Chapter 2

Solar energy

2.1 Introduction

2.1.1 Energy production and consumption

The fossil fuels coal, oil and natural gas, are non-renewable sources of energy. They are found in deposits beneath the earth, formed from plants and animals that lived up to 300 million years ago. The fuels are burned to release the chemical energy that is stored within the atomic bonds of the hydrocarbons that they are made of; about 90% of the world wide energy demand are met by the combustion of fossil fuels [1]. In energy terms, oil, at 40%, makes the single largest contribution to world energy supply, followed by coal at 26% and natural gas at about 24%.

Since it takes millions of years for them to form, they are finite for all intents and purposes and thus exhaustible energy resources. Still, mankind is using them at a high rate; when nothing changes the fossil fuels will be used up within the duration of one lifetime. Even the most optimistic forecasts concerning the world oil production suggest that world oil peaking will occur in less than 25 years [2]. Natural gas resources are about as limited as petroleum. Moreover, the consumption of petroleum products and natural gas will grow at 1.5% per year [3]. The total recoverable reserves\(^{(1)}\) of coal around the world are estimated at 1 Tton which is enough to last approximately 190 years at current consumption levels. However, assuming that world coal consumption continues to increase at the same rate as is projected for the years 2015 through 2025 (1.3 percent per year), current estimated world coal reserves would last for only about 90 years [3].

Although fossil fuels are just storage forms of harmless (and renewable) radiation energy from the sun, large quantities of dangerous byproducts are formed when these sources are burned to produce power. This makes them not only non-renewable, but also interfering with a sustainable way of life. The release of the byproducts have considerable negative effect on the natural environment (like sulphur dioxide (SO\(_2\)), nitrogen oxides (NO\(_x\)), acid rain) and even on the earth’s climate (carbon dioxide (CO\(_2\))). Therefore, fossil fuels might be called ‘grey’ energy sources, of which natural gas has the brightest shade of grey at least in terms of acidic pollution.

Nuclear energy is the other ‘grey’ source of energy, although it is a virtually endless one. This is because the byproducts only effect their environment when accidents happen during storage, but then the consequences are also almost virtually endless. The same holds when accidents happen during the production, because both the energy source material and the waste material are very dangerous for people and the environment, even in small amounts.

\(^{(1)}\) Recoverable reserves are those quantities of coal which geological and engineering information indicates with reasonable certainty can be extracted in the future under existing economic and operating conditions.
2.1.2 Green energy sources and their market

A change towards the use of renewable, clean and safe energy resources is therefore required in order to prevent the exhaustion of the natural energy resources, destruction of the environment and a crisis in world economy since it happens to be the case that whole nations have built their economy on it... Unfortunately, the generation of electrical power from often free and abundantly available ‘green’ energy resources is a costly matter. This holds especially for solar energy, in particular when it is offered as an alternative to the classical ‘grey’ energy. I will use the recently liberalized Dutch electricity market to elucidate this; the Dutch electricity law\(^{(2)}\) offers a definition of ‘green’ power thus providing a tool for detailed comparison of the different Dutch electricity companies.

In the Netherlands, ‘green electricity’ is defined in the energy law as:

*Electricity that is generated with a hydro-electric power-station with a capacity of less than 15 MW, an installation for the generation of electricity by means of wind energy or solar energy, or an installation in which biomass is thermally worked up without extra stoking or mixing of synthetics in order to produce electricity.*

Nowadays, electricity producers in the Netherlands are able to offer this green energy roughly at the same price as grey energy, but only when the respective taxes are included in the prices. The reason for this is, that the the green energy generation in itself is more expensive but is compensated by lower energy taxes for green power as compared to grey power. Another reason for the equal prices can be seen in Fig. 2.1, namely that only a very small part of the green energy on offer is actually solar energy, nor in the ESSENT\(^{(3)}\) green power, nor in the 100% green ECHTE ENERGIE\(^{(4)}\) green power. Moreover, the latter company does offer solar energy, but at a fairly higher price, see Fig. 2.2; the prices in this figure are bare prices without energy taxes. From these figures it even can be concluded that biomass is likely to be the cheapest renewable energy source of the four green ones (solar, hydro, wind and biomass), assuming that private companies strive after the highest possible profit margin. Moreover, ECHTE ENERGIE, which is able to offer the lowest prices, uses 50% more biomass generated energy than ESSENT.

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\(^{(2)}\)Elektriciteitswet 1998
\(^{(3)}\)www.essent.nl
\(^{(4)}\)www.echte-energie.nl
2.1 Introduction

2.1.3 The solar energy market

Until about halfway the 70s, solar cells were used in the first place for space applications. Since then the solar cells have found applications in customer electronics, small scale remote residential power systems, as well as in communication and signaling. Only 10 years ago, grid connected photovoltaic (PV) systems entered the market with significant contribution as a result of intensive roof programs in Japan, Germany and US.

In 2004, the world production of solar cells rose up to nearly 1.2 GWp\(^5\), a jump of 60% in one year [4], see Fig. 2.3. According to this past forecast, a cumulative installed capacity of all solar energy systems around the world of 3.6 GWp should have been established by the end of 2004. Again, this extraordinary growth is only driven to some degree by improvements in materials and technology, but primarily it is the effect of market introduction programs and government incentives [5].

So, without any subsidization and given the apparent abundance of traditional energy sources and a country where the distribution network reaches nearly each and every remote corner, large scale generation of electricity from the sun’s radiation can not yet compete economically with the classical methods of generating electricity, nor with generation from other green sources.

However, besides this context of future large scale grid-connected energy supply by solar energy, the indispensability of solar energy becomes immediately clear when it is offered as a source of power for so called stand-alone systems: from watches and hand-held calculators to refrigerators or personal computers in remote areas and developing countries, and mountain huts or even space activities. This can be seen in more detail in Fig. 2.4; it shows that off-grid systems form 44% of the total present-day use of solar energy.

A specific future application is the use of solar energy in information and communication technology (ICT). It is expected that in the future the world will be characterized by a large number of electronic devices distributed over the environment ('ambient intelligence') [8]. Most of these devices contain a sensing part associated with data processing capability as well as radio frequency features for data communication. Within this vision, it is a crucial task to ensure

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\(^5\) As a reference: the electric power production of a typical natural gas-fired power plant is about 500 MW.
the energy autonomy of freestanding and portable circuits, actually small scale versions of the stand-alone systems. There are numerous possibilities to extract energy from the environment e.g. temperature differences or mechanical vibration. However, it turns out that, even at low illumination levels of typically 1–10% of standard sunlight, photovoltaic cells are the most obvious means to ensure this required energy autonomy with the lowest area or volume requirements. For this purpose high-efficiency backside-contacted silicon solar cells and flexible organic solar cells represent attractive solutions.

In all these cases, solar energy is a clean and quiet alternative to toxic batteries, hard to maintain noisy generators, or nothing! In my opinion, these applications justify all the research that is done on solar energy, even if it turns out to be an unsuitable, because expensive, method for large scale generation of electricity. Moreover, solar energy devices are more than other renewable energy sources suitable to be integrated in the daily environment of people, so that it might contribute to people’s consciousness towards man’s dependence on energy delivery.
2.2 Solar cells

In practice, ‘solar energy’ as it is used in the previous sections, is the end product of a series of conversion processes; it concerns the electrical power output of a whole array of parallel and series connected modules, adapted to the ac-nature of the external load if necessary by implementing a dc/ac convertor. All the components other than the modules are called the balance of system (BOS) components and may also include mounting structures, tracking devices, batteries, and power electronics (including the convertor, a charge controller, and a grid interconnection). A module, or solar panel, in its turn, consists of several solar cells connected in series, encapsulated in a frame. In this thesis, it is this physical heart of a solar energy system that is studied; it is a photoelectrical device that converts light, preferably the free sunlight, into electrical energy, and is therefore also called a photovoltaic (PV) cell.

So, also when discussing the costs of solar energy production, it was the end product ‘PV power’ that was referred to. In this view it is not so surprising that also the ‘PV costs’ in fact are to be splitted into two contributions: a module part and a BOS part. In the case of crystalline silicon solar cells, the PV-BOS prices have come down very fast, especially in high volume markets. As a result, module prices now make up 70%–80% of the systems [9]. The same study also states that, next to depreciation, yield losses and labor costs, material costs are the most important part of module costs, i.e. about 50%. The three-dimensional solar cells studied in this thesis are a way to achieve a material cost reduction.

The next sections give an overview of the operating principles of solar cells, solar cell technologies, and solar cell research.

2.2.1 Operating principles

The sun is the most clear example of a renewable energy source; its availability is virtually endless. Moreover, it’s abundant; the amount of the sun’s energy that reaches the surface of the earth every hour is greater than the total amount of energy that the world’s human population uses in a year! In other words, the global energy consumption would be filled with only 0.1% of the desert area covered with solar cells.

More precisely, the average sunlight power that reaches the outer edge of the Earth’s atmosphere, perpendicular to the incident beam, is 1367 W/m$^2$. The atmosphere absorbs and reflects some of this radiation, including most X- and UV-rays. The rest of the radiation reaches the Earth’s surface directly (beam radiation), is reflected from the ground onto another part of the surface (albedo radiation), or is scattered but in such a way that it still reaches the surface (diffuse radiation). The total radiation consisting of these three components is called global radiation. A standard spectral distribution is assigned to this radiation: the Global AM 1.5 (AM1.5G) solar spectrum, where AM stands for Air Mass and 1.5 indicates that the direct beam of the sun’s rays has to travel through 1.5 times the thickness of the atmosphere in a standard situation. Approximations give an intensity of about 970 W/m$^2$ for the AM1.5G spectrum. However, the standard AM1.5G spectrum is normalized to give 1000 W/m$^2$, because of inherent variations in incident solar radiation. The AM1.5G solar spectrum is the spectrum to be used when testing its performance under standard terrestrial conditions. The standard spectrum outside the Earth’s atmosphere is called AM0, with no light passing through the atmosphere; it is typically used to predict the expected performance of PV cells in space.

A typical solar cell is in principle ‘just’ an illuminated semiconductor diode, but then one with a relatively high surface area. As a result of the pn-junction in the diode, an electric
field is formed in the cell. Light that enters the cell is absorbed by the p-type absorber, upon generating mobile charge carriers (electrons and holes) which are spatially separated by this intrinsic electric field. The electrons recombine with the holes after passing an external load, thus completing the electrical circuit. The conversion of photons into electrons is called the photovoltaic effect. Under illumination, the standard empirical dark diode current-voltage, or $J(V)$ curve shifts with $J_\ell$ resulting in the $J(V)$ curve of a solar cell given by:

\[
J = J_s \left[ \exp\left( \frac{qV}{n_i k T} \right) - 1 \right] - J_\ell,
\]

(2.1)

see also Fig. 2.5a. In this relation, $J_\ell$ is the light generated current and the other part is the dark current, with $J_s$ the saturation current density, $q$ the electron charge, $k$ the Boltzmann constant, $T$ the absolute temperature and $n_i$ the diode ideality factor, which typically has a value between 1 and 2, preferably close to 1. From a $J(V)$ curve, some important solar cell parameters can be found, see Fig. 2.5b:

- short circuit current $J_{sc}$: $-J_{sc}$ is the current at zero voltage
- open circuit voltage $V_{oc}$: voltage at zero current
- maximum power point $P_{max}$: point at which $\partial (J \times V) / \partial V = 0$ giving $V_{mp}$ and $-J_{mp}$
- fill factor $FF$: measure of cell quality, defined as:

\[
FF = \frac{V_{mp} \times J_{mp}}{V_{oc} \times J_{sc}}.
\]

(2.2)

With this we can calculate the solar cell conversion efficiency:

\[
\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}},
\]

(2.3)

in which $P_{in}$ is the power per surface area of the incident light.

Measuring a $J(V)$ curve is the simplest, most widely used and most direct way to characterize solar cells since it immediately reveals their performance in operating circumstances. However, other methods might be needed to explain in detail any uncommon shapes and resulting bad
performances, or in other words, the physical mechanisms lying behind contingent deteriorating series and parallel resistances. Even stronger, in case of three-dimensional solar cells, these methods, in particular time-resolved methods, really are needed to explain why the experimental value of the efficiency so much differs from the theoretical maximum achievable efficiency which theoretically is dependent only on the band gap of the solar cell material [10]. The methods are discussed in Ch. 4, the physical mechanisms in Ch. 6.

Next to electrons and holes, also other mobile particles like excitons and polarons might be created depending on the materials system. Also the origin of photovoltaic action might be different than or complementary to the built-in electrostatic field [10]; effective forces due to a varying electron affinity, band gap or carrier population might as well drive the charge carriers into a specific direction. The more the solar cells under investigation approach the ‘advanced’ region mentioned in the next section, the more important these other driving mechanisms become.

### 2.2.2 Technologies and efficiencies

In Fig. 2.6, the six largest cell technologies are shown as well as their typical module efficiencies and market shares for the capacity installed in the year 2003. It demonstrates that there is not just one kind of solar cell and it is clear that still by far most of the solar cells are made of silicon. This is because silicon is abundantly available in nature, and the semiconductor industry has built-up a lot of useful experience in this field. The crystalline silicon (c-Si) technologies mono c-Si, multi c-Si and ribbon grown on substrate c-Si, are wafer-based manufacturing, i.e. self supporting wafers of $\approx 300 \mu m$ thick are fabricated and then soldered together to form a module.

The other, thin film approaches are module-based; these cells use layers of semiconductor materials of only a few micrometers thick, attached to an inexpensive backing such as glass, flexible plastic, or stainless steel. The entire module substrate is coated with the desired layers and a laser scribe is then used to delineate individual cells. In this way, the materials can be deposited onto large surfaces, which is advantageous for large scale production. The thin film technology is also referred to as the second generation photovoltaic technology, i.e. after the first generation of crystalline silicon technology. From a materials point of view, the thin film cells based on CdTe and the chalcogenide CuInSe$_2$ are related to the cells studied in this thesis, see also Sect. 3.6.1.

Apart from these widely commercially available solar cells, a variety of advanced approaches to solar cells are under investigation. Among them are high-efficiency and expensive devices that use III-V semiconductors like gallium arsenide, and indium gallium phosphide. Other advanced approaches include dye sensitized solar cells, polymer (or plastic) solar cells, and photoelectrochemical cells, which produce hydrogen directly from water in the presence of sunlight. From a morphological point of view, also the last trio is related to the cells studied in this thesis, see next chapter.

### 2.2.3 Research and development

The technical research on solar cells focusses on different, though strongly related topics:

- minimizing the production cost,
- maximizing the efficiency,
Concerning the EPBT of a solar cell, it can be stated that it has been improved very much during the years [6]. In the past, solar cells were not able to ‘pay back’ their energy investment within their expected lifetime which is about 25 years. This is because the energy used, especially during the production of solar cells, is seen to far outweigh the electricity eventually generated. Data from recent studies shows, however, that present-day systems already have an EPBT of 3 to 4 years, well below their expected lifetime. With increased cell efficiency and a decrease in cell thickness, as well as optimized production procedures, it is feasible that the EPBT for grid-connected PV will decrease to two years or less for crystalline silicon modules and to one year or less for thin film modules.

The three-dimensional solid-state solar cell concept under study in this PhD, was designed from the low cost and stability enhancement point of view, as already pointed out in Ch. 1, and further explained in Ch. 3. Still, due to the early stage of development that the solid-state solar cell is in, the full low cost potential of some of the solar cells presented here was not yet reached; the 3D-cells for example were produced with the use of relatively expensive because vacuum deposition techniques. However, the same cell structure has recently also been produced with a low cost spray deposition technique, not to mention other earlier attempts to spray CuInS$_2$ for thin film configurations [11, 12, 13] and ETA- or 3D-cells [14, 15], see also Sect. 8.3.
Chapter 3

Three-dimensional solar cells

3.1 Introduction

In Sect. 2.1, (wafer-based) silicon was introduced as being the most important solar cell technology nowadays. However, silicon solar cells are also very costly because of the required layer thickness of 300 $\mu$m of high purity material, due to the low optical absorption; this makes these technologies less suitable for large scale generation of electricity or small and flexible area solar cell applications.

Therefore, other concepts should be developed. Reducing the layer thickness for example requires less but also less quality material as is explained a little further on; much thinner cells are possible when switching to direct band gap material, improved back reflection, enhanced internal scattering by surface texturing or reducing the crystallinity, and module-based fabrication instead of wafer-based fabrication.

At this point, the thin film solar cell research was born. When driving this concept to its limits, the three-dimensional world is entered, see Fig. 3.1 for the development from the one-dimensional thin film concept towards a three-dimensional extremely thin film solar cell concept. Figure 3.1a schematically depicts a standard pn-junction in which the grey material is the thin film p-type absorber, and the black rectangle represent the contacts. When reducing the absorber thickness more and more, the area of ‘advanced solar cell approaches’ mentioned in Sect. 2.2.2 is entered and a two-dimensional Extremely Thin Absorber layer (ETA-layer) is obtained in b. This layer is so thin (1–100 nm) that not all the light is absorbed by the film, so that more layers are required to ensure sufficient light absorption as shown in c. A structure that enables effective scattering could increase the absorption even more due to an enhanced optical path length (d). In all these pictures, the photogenerated electrons are collected at the front contact where the light enters the cell, and holes at the back contact. More on the optical properties and scattering of porous electrodes in Sect. 3.6.2.

With decreasing absorber thickness, a very important feature concerning the charge transport is introduced as well, see again Fig. 3.1; the effective absorber thickness in a, c and d is the same, but the mean distance for the electrons to cover before reaching their contact has decreased with about a factor $d^{(1)}$ for the stacked and structured configuration. In more physical terms, the projected conceptual advantage of the three-dimensional cell concept over the flat cell concept is that charge separation in the former occurs at a shorter distance scale. The charge carriers are generated within a distance from the junction that is smaller than the diffusion length of the minority carriers. In this way, majority carrier devices are created, i.e. the minority

\footnote{That is, as drawn in this conceptual example.}
carriers become majority carriers once they have crossed the junction that is now very nearby. Therefore the charge carriers are less adversely affected by poor materials quality, so that cheap materials with real low electron and/or hole diffusion length can be used which are worthless otherwise. So, the processes of absorption, charge separation and charge carrier transport don’t take place any longer in the same material.

Unfortunately, the configurations of c and d both also have an 11 times larger interface area than the flat configuration so that it becomes even more important than it already was in thin film cells, due to the enhanced interface/bulk quotient. More on this is found in Ch. 6. Moreover, the problems change from one-dimensional into three-dimensional.

In the preceding pages, what could be called the thin film approach towards the ETA-cell is described (using thinner and thinner absorber layers to allow, or to account for the use of cheap and low quality absorbers). Another one is the stability approach that describes the development of unstable photoelectrochemical (PEC) cells into more and more stable cell configurations. This line can be traced back to the first reported studies of photovoltaic action by Becquerel in 1839. He used an electrolyte-solid configuration. These cells are also called surface-barrier solar cells, due to the common feature that only one semiconductor, in one doping type, is employed and the principle source of photovoltaic action is a depleted barrier region at the surface of this semiconductor [10, Ch. 6]. The other surface-barrier type cell is the all-solid-state cell that uses a metal-semiconductor (M-S) or metal-insulator-semiconductor (M-I-S) configuration; these are often referred to as Schottky-barrier type cells. Investigation of the solid-state surface-barrier cells begins with the Cu|Cu$_2$O structure which was shown to be photosensitive by Hallwachs in 1904.

The electrolyte-solid surface barrier cells consist of a semiconductor electrode and a counter-electrode immersed in the same electrolyte solution that contains both the oxidized and the reduced form of a redox couple; they are also referred to as photoelectrochemical (PEC) cells. Barrier formation in such devices is much easier as opposed to the formation of any solid-state junction which is a expensive time-consuming, high-temperature operation requiring controlled
deposition of several layers in vacuum conditions. Moreover, they are easier to illuminate, namely through the electrolyte because it is transparent.

However, during the early 1950’s, surface-barrier photovoltaic structures were quickly overshadowed by the emerging \(pn\)-homojunction solar cell technology, due to the higher efficiencies of the latter; PEC cells for example were unstable devices with efficiencies which had yet to reach 1\% under terrestrial sunlight \[10\]. The cause of the poor stability and extremely low conversion efficiencies was simply that the oxidation-reduction couple solvent systems used to form the barrier in the semiconductor and used to collect the photocurrent were not serving as an efficient sink for photogenerated minority carriers swept to the liquid-semiconductor interface. Since the photocarriers were not being effectively removed from the semiconductor surface, they were recombining, back-diffusing away, or participating in photodecomposition of the semiconductor electrode, resulting in the very poor conversion efficiencies and instability observed.

In other words, in order to make any progress in this field, one or more of the following efforts should be made with respect to the choice of the materials (only the processes that take place in operating conditions are considered):

- Favorable energy location of electrolyte energy level with respect to the surface positions of the semiconductor band edges in order to ensure effective electron transfer.
- Thermodynamic stability of \(n\)-type electrode towards photoelectrochemical decomposition due to oxidation of electrode (photo-corrosion).
- Suppression of photo-corrosion of \(n\)-type electrode by addition of stabilizing reagent in the electrolyte that favors the oxidation of the electrolyte due to kinetic aspects or replacement by solid-state conductor.
- Avoiding \(p\)-type electrodes because of undesirable conversion of large part of absorbed photon energy into heat due to interface recombination.
- Band gap as close to 1.3–1.4 eV as possible to ensure most efficient solar energy conversion, taken into account the solar spectrum, current gain versus voltage loss upon lowering \(E_g\) due to balance of absorption enhancement versus thermalization of ‘overqualified’ photons.

Indeed the turning point in the development of liquid-semiconductor surface-barrier solar cells was the report in 1976 that a liquid–\(n\)-type CdS device had been stabilized and conversion efficiencies in the 1–2\% range had been achieved by using a polychalcogenide electrolyte \[10\]. By the end of the 1970’s, liquid-semiconductor surface-barrier solar cells had achieved efficiencies as high as 12\% (polyselenide electrolyte–\(n\)-type GaAs) by choosing redox-couples favorably located in energy with respect to the surface positions of the semiconductor band edges, or by modifying the kinetics governing electron transfer between the semiconductor and redox couple, or by doing both.

They disappeared from the scene though. Only at the end of the eighties, PEC solar cells came into business again by solving the problem of low efficiencies of oxide based PEC cells; oxides might just be stable towards photo-corrosion\(^\text{(2)}\), but they also have too large band gaps to yield respectable efficiencies (e.g. TiO\(_2\) and SrTiO\(_3\) 3.2 \[16\] and > 3 eV \[17\] respectively). This problem was solved by adsorption of a layer of light sensitive and efficient charge injecting

\(^{\text{(2)}}\)... and easy to produce and to handle, abundantly available, cheap and non-toxic.
Three-dimensional solar cells

Figure 3.2: Overview of nanostructured oxide based three-dimensional solar cells. In a DSSC, the oxide particle is covered by a monolayer of organic dye and emersed in a liquid electrolyte, in a DSH, this electrolyte is replaced by a solid-state material, in an ETA-cell, also the dye is replaced by a solid-state material, and in a 3D-cell, the same solid-state absorber material replaces both absorber layer and electrolyte.

organic dye that takes over the task of absorbing the light from the large band gap semiconductor. Moreover, the dye, that often contains Ru$^{3+}$ ions, suppresses interface recombination that turns out to be a problem for this kind of cells (for example Os$^{3+}$ ions can do the same). Since the organic absorber has no conductive properties at all, only a monolayer is adsorbed, thus requiring a three-dimensional electrode structure to ensure efficient light absorption. Here the thin film and the stability approach come together.

These cells are called dye sensitized solar cells (DSSC’s), or Grätzel cells after one of its inventors [18]. In the next sections, the DSSC is described in more detail, as well as three other types of three-dimensional solar cells based on porous oxide electrodes that contain no electrolyte at all anymore; they are pictured in Fig. 3.2. Three-dimensional bulk heterojunction solar cells are not discussed since their treatment is beyond the scope of this thesis.

3.2 Dye sensitized solar cell

Next to the already mentioned advantages of PEC-cells that still hold for the DSSC, the DSSC has the following additional more specific advantages over e.g. silicon solar cells:

- performance increases with temperature,
- bifacial configuration - advantage for diffuse light,
- efficiency less sensitive to angle of incidence due to scattering properties of nanostructured electrode,
- high application potential in building integration (BI) due to transparency e.g. for power windows,
- color can be varied by selection of the dye, even invisible PV-cells based on near-IR sensitizers are feasible, again leading to high application potential in BI, and
- energy payback time is only a few months as compared to years for silicon.
Moreover, the confirmed record efficiencies achieved are nowadays quite reasonable, i.e. 8.2% class record\(^{(3)}\) and 11.0% not class record cell efficiency at 0.25 cm\(^2\) aperture area \([19]\). However, there still some problems to overcome that stand in the way of large scale outdoor applications. This is also the reason that they are not found in Fig. 2.6. Next to market demand, the factor of most importance in this is the long-term stability \([20]\). The overall stability of this cell is controlled by two factors, namely physical and chemical stability. Physical stability is related to the possible evaporation of the liquid electrolyte at elevated temperatures. This is a technological problem, for which solutions can be found by using suitable sealing materials and techniques. The intrinsic chemical stability is related to irreversible (photo-) electrochemical and thermal degradation of the dye or electrolyte components, which might occur during operation of the cell. Note that the semiconductor stability of PEC devices with respect to corrosion already was solved by using wide-band-gap oxide semiconductors such as TiO\(_2\) rather than the more covalent semiconductors used in PV such as Si and CdTe. It can be improved further by better understanding of the degradation mechanisms and chemical balancing of the electrolyte components \([20]\).

Next to extensive studies on the present DSSC system, also other routes are being followed replacing the instability causing materials with more stable ones. In the dye sensitized heterojunction for example, the aqueous iodide/tri-iodide solution is replaced with a stable solid phase such as a \(p\)-type semiconductor CuSCN or phase such as a redox polymer or a conducting polymer.

In the ETA- and 3D-cell, even the organic dye is replaced with a stable solid-state semiconductor. In this way, the problems concerning physical instability related to solvent containment are solved, as well as those concerning the chemical instability. These cells are discussed in Sect. 3.3 to 3.5.

### 3.2.1 Cell structure

A typical DSSC consists of a porous nanocrystalline TiO\(_2\) electrode, deposited on a TCO-coated glass substrate with the TCO-coating acting as a front contact. A typical TiO\(_2\) electrode is 10 μm thick, with an average particle and pore size in the order of 20 nm. It has an internal or microscopic surface area which is at least 1000 times larger than the geometrical or macroscopic electrode area. The oxide particles are covered with a monolayer of light absorbing dye molecules; the pores are filled with a liquid electrolyte containing a redox-couple, for example \(I^–/I^3–\). The back contact consists of a Pt catalyst coated glass substrate as counter electrode. The cell is illuminated through the front contact.

### 3.2.2 Operating principles

Figure 3.3 shows the working mechanism of a DSSC, including the relative energy levels of a working cell. In this, a microscopic approach (i.e. the flat-band approach of Sect. 5.3) is used for representation of the electrolyte|dye|oxide system, while a macroscopic approach is used to connect this flat-band inner to the outer circuit according to refs. \([21, 22, 23]\). The dye in ground state \(\overset{\circ}{D}\) has a redox Fermi level\(^{(4)}\) \(E_{\text{F,\text{redox}(D^+D)}}\) within the band gap of the oxide, while

\(^{(3)}\)The requirements to be recognized as a class record comprise that the total, aperture, or designated illumination area is larger than 1 cm\(^2\), and that the results are measured under the AM1.5G spectrum (1000 W/m\(^2\)) at 25°C by a recognized test center.

\(^{(4)}\)Energy level at which the chance that the energy level is occupied is 1/2, depending on concentration of oxidant and reductant.
the redox Fermi level of its excited state $D^*$, $E_{F, redox(D^+D^*)}$, lies above the conduction band of the oxide. When the system is illuminated, photons with energy larger than the difference between the two redox Fermi levels of the dye are absorbed (1), thus bringing the dye molecule in its excited state $D^*$; this photo-excited state of the dye is quenched by electron transfer to the oxide (2), leaving the dye in its oxidized state $D^+$. The injected electron is transported through the oxide electrode towards the front contact; the electrode therefore is sometimes also called ‘electron conductor’. Simultaneously, the oxidized dye molecule returns to its original state $D$ by accepting electrons from iodide ions (3). The electrolyte is reduced at the counter-electrode which provides the electrons that are transferred to tri-iodide $I_3^-$, thus yielding iodide ions (4). Since these latter reactions can be viewed as the transport of a hole from the dye to the counter-electrode, the electrolyte is also called the ‘hole conductor’. It is generally accepted that in DSSC’s the electron transport through the oxide is predominantly governed by diffusion, because the highly conductive electrolyte screens the interior of the cell from any applied electric field. Recombination in the DSSC can be the back reaction of electrons either with the oxidized dye or with $I_3^-$; the electron recombination in the TiO$_2$ is assumed to be very low due to the extremely low hole concentration in the TiO$_2$ owing to its wide band gap (3.2 eV).

Still, the exact detailed working mechanisms are not fully clear and therefore the subject of many publications. For example, somewhere between the electrodes, a photovoltage should be built up. According to [24], it is the potential difference between the conduction band edge of TiO$_2$ and the redox Fermi level of the $I^-/I_3^-$ couple that determines the maximum theoretical value, but other estimates for the maximum $V_{oc}$ are proposed as well. A related controversy concerns the driving force for charge separation under short circuit conditions [25], or the presence and shape of the electrostatic field at the TCO|oxide interface [26].

**Kinetics** There are a large number of localized electronic states in the band gap of the TiO$_2$ and at its surface. Therefore, the electric current in the TiO$_2$ can be carried by electrons and holes in delocalized as well as localized states [10]. The motion of an electron in localized states must be viewed as hopping from one localized site to another. That is, the electron tunnels from one localized state to another. In all probability these sites are not at the same energy.
Consequently, hopping is a phonon-assisted tunnelling process. This makes hopping a thermally activated process, with a hopping mobility that is expected to be of the form:

\[ \mu(E) = \mu_0(E) \exp\left(-\frac{W(E)}{kT}\right), \]

where \( W \) is the activation energy. Since the mobilities of the delocalized states are expected to be orders of magnitude larger than those of localized states, and since among the localized states mobilities can vary by orders of magnitude due to the exponential in Eq. (3.1), the conductivity \( \sigma \) of the material can be tremendously affected by shifts in populations. For example, if light appreciably shifts the carrier population into localized states with large hopping mobilities or into band states, then large changes in the conductivity will result. Therefore, the occupancy of all electron states under illumination can only be derived using a kinetic model [25].

The success of the final conversion is depending of the kinetics of electron generation, trapping, detrapping and recombination. The electron injection from the dye into the TiO\(_2\) for example is very efficient because of the fast kinetics (sub-picosecond scale) involved [20]. The resulting internal quantum efficiency is close to unity. It is also stated that, in the standard electrolytes, electron diffusion in TiO\(_2\) is the limiting charge transport rate, as opposed to ion diffusion in the electrolyte.

Due to the increased importance of the kinetics in nanostructured three-dimensional devices, other characterization methods than the standard steady-state methods like \( J(V) \) and IPCE might be needed to study these devices; these dynamic characterization methods are discussed in Sect. 4.1.

### 3.3 Dye sensitized heterojunction solar cell

As in DSSC’s, the basis is a \( \approx 10 \mu\text{m} \) thick layer of nanosized oxide particles (\( \approx 20 \text{ nm} \)), wherein all the internal surface is coated with a dye. However, the pores are not filled with a liquid electrolyte but with a solid, transparent, hole conductor; it is a kind of solid-state dye sensitized cell. This nanocomposite has been referred to as ‘interpenetrating (network) heterojunction’ (i-het), ‘bulk heterojunction’, or ‘dye sensitized heterojunction’ (DSH) [27] and is conceptually pictured in Fig. 3.2.

### 3.4 ETA-solar cell

The ETA-cell concept was designed to find a way to use cheap, but stable poor quality materials in solar cells. These materials often exhibit too low diffusion lengths in comparison to the transport length required in thin film cells. To be precise, the ETA-project defined the following goals to achieve:

- Study the use of cheap, low quality, inorganic semiconductor material as optical absorber.
- Replace the liquid electrolyte that is used in a classical DSSC by a transparent solid-state \( p \)-type semiconductor, to be able to guarantee the long term stability of solar cells.
- Obtain a better fundamental insight in nanostructured interfaces, which are responsible for the charge carrier separation.

The result is a completely inorganic, three-dimensionally structured heterojunction solar cell, in which charge generation and charge transport are spatially separated like in the DSSC.
Its microscopic layer thickness is in the order of the diffusion length. In this way, the concept combines the best of the DSSC (cheap), with the best of inorganic all solid-state thin film solar cells (stable), see Fig. 3.2.

Two kinds of porous electrodes are used: microstructured and nanostructured electrodes, see Sect. 8.2 and 8.3 respectively. Table 3.1 lists the realized ETA-cells, as well as ‘first-stage’ ETA-cells, or 3D-cells, as described in the next section. Since the 3D- and ETA-cells are so often compared with the DSSC in this thesis, also the features of a DSSC is included for comparison.

3.5 3D-solar cell

The 3D-solar cell is in fact an ETA-cell but with the absorber and hole conductor functions combined in one material. Therefore it is no ETA-cell in the sense that its absorber is just not extremely thin, but merely a fill-up of the pores of the structured electrode. However, due to the three-dimensional structure, it still is a ‘majority carrier cell’, i.e. in the absorber only the majority carriers are transported because the minority carriers are very fast removed due to the all-over presence of the junction. And the majority carriers are less sensitive for recombination.

It is pictured schematically in Fig. 3.2 with respect to its precedents. Whether the cell is ‘just’ an intermediate step on the way towards a ‘real’ ETA-cell, or a cell on itself, might not even be clear yet; the fact is, that is a stable and relatively simple study-object since the relevant material’s system of the 3D-cell contains one material less than the ETA-cell. In this thesis, I have made a distinction between the studied cells (both those that I have worked on, and those that have been reported in literature) based on what they are, and not how they are called in literature; if a cell lacks a separate hole conductor, be it a p-type semiconductor or a metal, it is being called a 3D-cell and no ETA-cell.

3.6 Materials used in ETA- and 3D-cells

3.6.1 Semiconductor absorbers

Up to now, several absorber materials have been studied, among them CdTe [28, 29], PbS [14], CuInS$_2$[16], CdS [30], and a-Si [31].

CuInS$_2$ CuInS$_2$ appears to be a particularly promising choice, because it is a well investigated absorber material in solar energy conversion and has proven to be an excellent candidate in thin film solar cell designs other than ETA solar cells; calibrated efficiencies of over 11% on CuInS$_2$ based thin film cells are reported [32]. Other chalcogenide thin film cells have reached an even higher efficiency (copper indium gallium diselenide (CIGS) for example has reached confirmed laboratory efficiencies of 18.4% [19]) and shown excellent stability, but they also contain with toxicity associated selenium.

Next to the low cost Ion Layer GaS Reaction (ILGAR)-deposition of CuInS$_2$ for ETA-cells [33, 16], also Atomic Layer Deposition (ALD) is used to deposit CuInS$_2$ for 3D-cells [34]. These 3D-cells produced in the group of ETA-partner TUD (Delft, the Netherlands) are studied in Ch. 7.

CdTe Cadmium telluride is a material with a nearly optimal band gap and is easily deposited with thin film techniques. Over 16% laboratory efficiencies have been demonstrated for thin film cells [35]. An often discussed issue of the CdTe technology is the cadmium content of the
3.6 Materials used in ETA- and 3D-cells

While this question is likely to be solved by recycling the Cd and taking special security precautions during the production, the public acceptance of the technology is a somewhat trickier question. However, in particular due to the suitability of CdTe deposition methods for infiltrating the nanostructured electrodes, CdTe is used in ETA-cells [29, 36, 37, 38] including those studied in this thesis.

3.6.2 Oxide electrodes

The basis of all the three-dimensional cells described before as well as studied in the rest of this thesis, are oxide electrodes. They provide an electrochemically stable three-dimensional structure necessary for sufficient light absorption in case the absorber layer has decreased into the nanometer range. Moreover, most of them are relatively inexpensive. This offers the potential to significantly cut the cost of solar cells. Several materials have been tried for the structured n-type layer (a.o. ZnO [39, 37, 38]), but the material that is most widely used, both for DSSC’s and ETA- and 3D-cells, is TiO₂.

Due to this three-dimensional character, the electrical properties for most transition metal oxides cannot be described by conduction via electrons and holes in conduction or valence bands. Parameters as optical or thermal energy gaps and carrier mobilities do not characterize the materials. Influences to be considered involve hopping processes, plasma effects, polaron coupling etc. Furthermore, many properties of the transition metal oxides depend very sensitively on deviations from the stoichiometry.

Optical properties  Intuitively, as well as scientifically funded [40], it can be understood that using nanostructured oxide electrodes is beneficial for efficient light absorption, due to the enhancement of macroscopic optical thickness due to scattering.

Ferber et al. applied the Mie theory to coated spheres to account for single scattering by the individual TiO₂ particles, and the radiative transport equation to handle multiple scattering between the different TiO₂ particles [41]. However, the use of the transport equation requires independent scattering (volume fraction of the scatterers should not exceed 10–30%) which in practice is valid only approximately (volume fraction is 50%). It turned out that a mixture of small particles (20 nm diameter) which result in a large effective surface, and of larger particles (250-300 nm) which are effective light scatterers, have the potential to enhance solar absorption significantly. Vargas et al. used the same approach and found the same optima, together with a maximum in intrinsic solar absorption coefficient at a mean particle size of 60 nm [42]. The general trends observed in some of the parameters are said to be in agreement with previous analysis including optical measurements of nano-crystalline solar cells.

In practice however, any enhancement of optical path length due to effective light scattering is only obtained if the absorber layer is not too thick. This is demonstrated by measurements on one of the first ETA-cells, a TiO₂|CdTe cell that is also discussed in Sect. 8.2. It turned out that the enhancement of optical path length with macroscopic CdTe thickness shrinks from almost 5 at films of 80 nm, to just 1 at films of macroscopic thickness 1 µm [43]. It seems that in case of thicker films, already at the first passage so much is absorbed, that scattering only plays a minor role.

To account for all the optical phenomena in the cells studied in this thesis, the effective medium approach is chosen. All optical phenomena are thus included in effective absorption parameters (e.g. absorption coefficient and absorption depth).

\( ^{(5)} \text{a.o. Ti}_{x}O_{2x-1}, V_{y}O_y, Mn_{x}O_y, Fe_{y}O_y, Co_{y}O_y \)
3.6.3 Solid-state hole conductors

The solid phase hole conductors that replace the aqueous electrolyte solution are p-type semiconductors like CuSCN [27] or CuI [44], thus yielding the DSH and the ETA-cell of Fig. 3.2, or an amorphous organic hole-transport material like OMeTAD\(^{(5)}\) [45]. If the basis for these last cells is still formed by dye sensitized oxides, they are also referred to as hybrid cells.

3.6.4 Intermediate layers

At last, but not less important as will be shown in Ch. 6, different buffer and tunnel layers are introduced between the n-type oxide and the p-type absorber. Buffer layers are conducting semiconductors, tunnel layers are wide gap insulating layers like those used in metal-insulator-semiconductor (M-I-S) cells and semiconductor-insulator-semiconductor (S-I-S) cells [46, 10, 47].

Because some of the buffer layers used in thin film configurations to form the pn-junction turn out to have a passivating influence on the buffer|absorber interface [48], these buffer layers are also applied in nanostructured solar cells. Since their role is now limited to interface engineering, they need to be only 10–50 nm. Indeed, also in a TiO\(_2\)|CuInS\(_2\) ETA-system, improvement of cell characteristics is reported upon applying a CdS buffer layer, see Sect. 6.4.1. Also indium (hydroxy) sulphide In\(_x\)(OH)\(_y\)S\(_z\) is proposed as a buffer layer at the TiO\(_2\)|absorber interface to suppress recombination [14].

Insertion of extremely thin insulating oxide coatings at the active interface of DSSC’s has already led to significant improvement of solar cell characteristics [49, 50, 51]. Again, applying such a layer in solid-state nanostructured solar cells turns out to be beneficial as well [52]. Efficiencies of \(\approx 4\%\) are even reported upon inserting both Al\(_2\)O\(_3\) and In\(_2\)S\(_3\) layers [53].

\(^{(5)}\)2,2’,7,7’-tetrakis(N,N-di-p-methoxynaphthalenyl-amine)9,9’-spirobifluorene)
<table>
<thead>
<tr>
<th>structure</th>
<th>n-type</th>
<th>IL</th>
<th>absorber</th>
<th>p-type contact</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
<th>ETA&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>[ref] or discussion</th>
</tr>
</thead>
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<tr>
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<td>CuInS$_2$</td>
<td>CuInS$_2$</td>
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</tr>
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<td>0.03</td>
<td>$\approx$ 300</td>
<td>$\approx$ 25</td>
<td>$\approx$ 0.4</td>
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</tr>
<tr>
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<td>Au</td>
<td>9</td>
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<td>20</td>
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<td>CdHgTe</td>
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<td>Au</td>
<td>15</td>
<td>?</td>
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<td>24</td>
<td>2.1</td>
<td>yes</td>
</tr>
<tr>
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<td>CdTe</td>
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<td>Au</td>
<td>0.85&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>?</td>
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<td>25</td>
<td>0.1&lt;sup&gt;(b)&lt;/sup&gt;</td>
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<td>CuSCN</td>
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<td>1</td>
<td>590</td>
<td>44</td>
<td>1.7</td>
<td>no</td>
</tr>
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<td>57</td>
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<td>71</td>
<td>11</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 3.1: List of published and unpublished ETA- and 3D-cell device realizations, developed inside and outside the EU's ETA-project; DSSC features are shown for comparison.

<sup>(a)</sup>Results are obtained within the framework of the EU's ETA-project.

<sup>(b)</sup>at 1/2 sun
Chapter 4

Device characterization

To be able to describe the physical working mechanisms of a solar cell, two kinds of characterization methods are available. The first one characterizes the solar cell as electrical or photo-electrical device, from which material parameters can be determined, provided the underlying physical mechanisms that give rise to the measured characteristics are known. Since complicated mathematics is often involved, simulation programs can be helpful in this, see Ch. 5. The second one characterizes the material that is used in the solar cell an sich, preferably in the same form as it appears in the final solar cell structure. Since the material characterization, if done, was done by others than me, I will only mention the method and use the results directly.

When characterizing the solar cell as a device, the solar cell under investigation is subjected to a perturbation and its response is recorded. In general, such perturbation-response methods may be classified according to the time dependence of the perturbation (steady state versus time-resolved) or to the nature of the perturbation and the response [55, p63] and [56].

4.1 Steady state versus time-resolved

Steady state methods use a perturbation $x$ which is time independent, and thus record a time-independent response $y(x)$. This process may be repeated for different levels of perturbation; no information will be obtained though on the dynamic properties of the system, except for responses with very long time constants like Cu-migration and aging phenomena.

Time-resolved measurements on the contrary, can reveal the system dynamics. This can be done in two ways. One way is to record the response from the moment the perturbation is applied to obtain so called transient behavior of the system under study. The other way is to apply a harmonically modulated perturbation and record the response for different levels/frequencies of the modulation. Since the latter is/are intuitively more difficult to understand, the next part of this section will explain this technique in more detail.

Harmonically modulated perturbation

Modulated perturbation techniques are far less sensitive to noise than the transient methods. Therefore they even might be used to enhance the low signal-to-noise ratio of steady state measurements, for example the application of the lock-in technique in quantum efficiency measurements. In such cases it is very important though to keep the modulation frequency low enough to ensure steady state conditions, see also section 4.3.1.
To make the interpretation of the results as easy as possible, it is necessary to find a region in which the system is behaving linear. This is achieved as follows.

**Linear systems**

Using a sinusoidally varying perturbation \( x(t) = \text{Re}[\bar{X}(\omega)\exp(i\omega t)] \), a harmonically perturbed linear system has a response that is, after a certain transition time, also harmonic, differing from the perturbation only by its amplitude and phase \( y(t) = \text{Re}[\bar{Y}(\omega)\exp(i\omega t)] \). Here, the complex representation is used which means that \( \bar{X}(\omega) \) contains the amplitude and phase information of the signal, and \( \exp(i\omega t) \) expresses the time dependence.

**Linearization of non-linear systems**

Using ‘small-signal’ perturbation superimposed on a time-independent bias perturbation, linear dependence of the response on perturbation can be achieved if the level of perturbation is sufficiently small. Examples are impedance spectroscopy and photocurrent spectroscopy, see below.

In both cases, all information on the dynamics of the system is contained in the transfer function \( H(\omega) \), which is a complex function of angular frequency:

\[
H(\omega) = \frac{\bar{Y}(\omega)}{\bar{X}(\omega)}. \tag{4.1}
\]

The transfer function may be represented in many ways, e.g. in Nyquist representation, Bode-plots, or equivalent electrical circuit having the same response as the system under study. In general, measuring the transfer function of a system under study using harmonic modulation techniques is straightforward, interpretation of experimental data however is not.

In the next sections, the characterization methods that are used for the studies in this thesis are described.

### 4.2 Electrical characterization

#### 4.2.1 Current–voltage

The use of steady state current voltage measurements is explained in section 2.2.1. However, the \( J(V) \)-equation (2.1) is often too ideal to analyze the measurements. Therefore, a more general equation usually holds, including also the different resistivities in the device:

\[
J = J_s \left[ \exp \left( \frac{q(V - J R_s)}{n_i k T} \right) - 1 \right] + \frac{V - J R_s}{R_||} - J_t, \tag{4.2}
\]

where \( R_s \) and \( R_|| \) represent a constant series and parallel resistance respectively. Figure 4.1 shows the influence of the two resistivities in the \( J(V) \) characteristic.

In general, a low \( J_t \) hence \( J_{sc} \) indicates low photon to current conversion efficiency \([57]\), which can be studied in detail by spectral response measurements, see section 4.3.1. According to the following equation (i.e. Eq. (2.1) for \( J_t \gg J_s \) and \( R_|| \) not too small), a low value of \( V_{oc} \) can be ascribed to a dark saturation current \( J_s \) that is too high:

\[
V_{oc} = \frac{n_i k T}{q} \ln \left( \frac{J_t}{J_s} \right). \tag{4.3}
\]
4.2 Electrical characterization

Figure 4.1: Influence of parasitic series and shunt resistivities $R_s$ and $R_\|\|$ on a typical $J(V)$ characteristic with $J_s=0.1$ nA, $n=1.3$, and $J_f=10$ mA/cm$^2$ (solid line). Dotted lines: no influence of shunt resistance ($R_\|\| = \infty$), variable $R_s$; dashed lines: no influence of series resistance ($R_s = 0$), variable $R_\|\|$.

Measurement set-up

Four-point probe measurements are performed to avoid the influence of parasitic contact and spreading resistances due to the metal probe-semiconductor contact and the effect of a current flowing from a small probe into the cell, respectively; these are non-negligible when only two probes are used. In case of four probes, two are current-carrying and two sense the voltage. Therefore, especially the voltage is monitored more accurately since no voltage drops are present across the resistances. The measurements are done with a KEITHLY Source Measure Unit 236.

The samples are illuminated with the light from an ORIEL 81160 solar simulator, using an ozone free Xe arc lamp of 300 W and the proper filters; the simulator creates a homogeneous spot of 5 cm $\times$ 5 cm AM1.5G at about 100 mW/cm$^2$.

All $J(V)$ measurements are carried out at room temperature.

4.2.2 Admittance spectroscopy

Admittance spectroscopy records the capacitive behavior of the system when perturbed with a modulated voltage. For this, a harmonically modulated voltage signal is superimposed on a bias voltage. The exciting ac-voltage is generally a few tens of millivolts in amplitude and is superimposed on a chosen dc-bias. The measurements are carried out as a function of the bias voltage (also called Mott-Schottky measurements) or as a function of the frequency of the modulation. This latter form is very often used in electrochemistry, and therefore also called Electrochemical Impedance Spectroscopy (EIS), with impedance being just the inverse of admittance, see below. It makes the dynamics of various (photo)electrochemical processes experimentally accessible. It is used for example to determine the energetics of the semiconductor surface like oxide and interface trapped charge in semiconductor-based photoelectrochemical systems.

In solid-state semiconductor physics, it is used to determine carrier and doping concentrations and (thermal activation energies of) deep level impurities. It is complementary to Deep Level Transient Spectroscopy (DLTS) which also yields the thermal activation energy but normally uses large voltage pulses to excite a sample with the observation being made in the time domain.
The measurement itself is essentially of the (complex) electrical admittance $Y(\omega)$, which is the system transfer function determined by the quotient of the current $I$ and the voltage $V$. Its inverse is the impedance $Z(\omega)$, which resembles the different resistances of network components. Since any electrical circuit can be represented as the parallel connection of a frequency dependent conductance $G(\omega)$ and a capacity $C(\omega)$ like in Fig. 4.2, the following equation holds:

$$Y(\omega) = G(\omega) + i\omega C(\omega).$$

From this relation, the capacitive behavior of the system $C(\omega)$ is then determined as $\text{Im}[Y(\omega)]/\omega$. It should be clear that this also means that the (indirectly) measured $C(\omega)$ may contain much more capacitances than just the junction capacitance as well as several more other electrical components. Several fitting programs exist to do the job of finding an equivalent circuit that has the same response as the cell. The main objective is however, to find an equivalent circuit that also has a physical meaning. Sometimes for example, hard to interpret elements like Warburg elements are introduced. It is not always straightforward to translate its meaning in physical terms. This is discussed in detail in Sect. 5.3.

Mott-Schottky measurements on the other hand can be analyzed with the Mott-Schottky equation:

$$\frac{1}{C^2} = \frac{2}{qN_B \varepsilon s \varepsilon_0} (V_{bi} - V),$$

where $N_B$ is the uniform background doping of a one-sided junction, and $V_{bi}$ the built-in voltage. It is derived from $C(V) = \varepsilon s \varepsilon_0 / W(V)$, which holds if we consider the space charge region as a parallel plate capacitor. The doping density thus can be obtained from the slope of the $1/C^2$ versus $V$ plot, or Mott-Schottky plot. When the Mott-Schottky plot does not yield a straight line, the background doping is non-uniform, and the doping profile $N_B(x)$ is obtained from the local slope of the Mott-Schottky plot [56].

**Measurement set-up**

The measurements are carried out using a four-point probe set-up, like the one used for the $J(V)$ characterization. A HP 4192A LF Impedance Analyzer provided the applied ac and dc bias voltages and collected the response signal. The small signal amplitude is held between 30 and 50 mV. For the Mott-Schottky measurements, a modulation frequency is used for which the phase difference between the response and the perturbation is close to $-90^\circ$. At this point, the contribution of the parallel conductance $G(\omega)$ to the admittance $Y(\omega)$ is approaching 0 and the measured admittance $Y(\omega)$ is equal to $i\omega C(\omega)$. No bias voltage is applied in the EIS measurements. All measurements are carried out at room temperature.

### 4.3 Opto-electrical characterization

#### 4.3.1 Spectral response

With spectral response or quantum efficiency measurements the steady state photocurrent response is unravelled into its separate responses to light of different wavelengths. Normally this is done at short circuit, but with this method also complete $J(V)$-curves for different wavelengths can be determined. Quantum efficiency data provide more insight in the cause of efficiency losses; they show in which part of the solar spectrum the solar cell fails to convert the light into current, which then can be related to the geometry, and energy barriers.
When no reflection losses are taken into account, the quantity that is measured is an external quantum efficiency, also called Incident Photon to Current conversion Efficiency (IPCE). When reflection losses are known though, internal quantum efficiencies, or Absorbed Photon to Current conversion Efficiency (APCE) can be determined. Here, we measure the IPCE, which can be expressed as:

\[
\text{IPCE}(\lambda) = \text{LHE}(\lambda) \Phi_{\text{inj}} \eta_c,
\]

in which \( \text{LHE}(\lambda) \) is the light harvesting efficiency, or generation efficiency, of the absorber, \( \Phi_{\text{inj}} \) the quantum yield for charge carrier injection, and \( \eta_c \) the charge collection efficiency at the back contact [57]. Unfortunately, there is no direct way to determine all these separate efficiencies; \( \text{LHE}(\lambda) \) and \( \Phi_{\text{inj}} \) can be determined though by surface photovoltage spectroscopy (SPS). This method is based on the surface photovoltaic effect which comprises an illumination induced change in the equilibrium potential distribution and is typically the result of some charge transfer followed by charge redistribution within the device due to the incident illumination [58, 59]. The charge collection efficiency \( \eta_c \) is determined by the transit time of the electrons to the back contact and the recombination rate. For example, a slow transport rate can lead to more recombination, e.g. back transfer of electrons into electrolyte in a DSSC.

**Measurement set-up**

Light of a 100 W halogen lamp is being splitted into its separate wavelengths with a BENTHAM M300 monochromator. A diffraction grating of 1200 grooves per mm and blaze wavelength of 500 nm is used, resulting in a usable wavelength range from 300 to 1100 nm.

In and output windows of the monochromator are 5 mm wide which results in a homogeneously illuminated cell, both in terms of intensity and of wavelength\(^{(1)}\). At 30 cm from the output window of the monochromator, the light intensity is around 0.5 W/m\(^2\). Since this is quite low, the lock-in technique is used to overcome the difficulties of the resulting low signal-to-noise ratio. To make the actual photocurrent more recognizable for the measuring unit, it is given a non-linear character by turning the constant intensity of the lamp into a block wave intensity by passing the light through a chopper wheel. The frequency \( f \) of the block wave signal is 277 Hz, in order that \( f / f_0 \), with \( f_0 \) the utility grid frequency of 50 Hz, is an irrational number. Though the cells under study are TiO\(_2\) based cells that could be very slow [60, 61], Fig. 4.3 shows clearly

\(^{(1)}\)Intensity was homogeneous for a region with a diameter of at least 10 times the cell diameter, the bandwidth of the illumination was 13 nm for a region with a diameter of 20 times the cell diameter; the cell was always positioned in the middle of the highest intensity region.
that the cell signal is able to follow the applied signal very well at 277 Hz; no alarming distortion of the cell signal is measured like for example a signal without a clear maximum within the given period of $1/f$. The little delay is caused by the measuring system itself due to the position of chopper wheel, since the chopper wheel has no fixed position; its open and closed states do not necessarily have to be in phase with the signal from the frequency generator. Because the lock-in system is able to find the maxima of both signals, this does not affect the measurement. All this is confirmed by the IMPS results which show very fast response times.

The precise incident photon spectrum from the monochromator is measured with a (not recently) calibrated Si photodiode/detector. The photocurrent that comes from the cell is converted and amplified by a current/voltage amplifier (P-9209-5, GIGAHERTZ-OPTIK) before feded into a lock-in amplifier (EG&G PRINCETON APPLIED RESEARCH, model 5210). The lock-in then compares the incoming signal with the reference signal which comes directly from the frequency generator to determine the part of the incoming photocurrent that is due to the incident photons from the monochromator. For this, the response signal $V_1 \sin(\omega_1 t)$ is multiplied with the reference signal $V_2 \sin(\omega_2 t + \vartheta)$, resulting in a goniometric function which, has a maximum only if $\omega_1 = \omega_2$. Then, all ac-signals are filtered out and $V_1$ can be determined from the output of the lock-in which is the remaining constant dc component (provided $\vartheta$ is set to 0 or 180°). Both the reference signal and the converted photocurrent signal are monitored by a digital phosphor oscilloscope (TEKTRONIX TDS 3052).

White background light (BGL) is provided by a 100 W halogen lamp (OSRAM HLX 64625) passed through a water filter to get rid of the IR light to ensure a constant temperature of the cell under study. The light is directed as parallel as possible to the incoming light from the monochromator, using a mirror. The power of the BGL is 240 W/m², determined with a silicon power detector, see section 4.2.1. The lamp that provided this particular BGL was implemented after the original lamp broke down. The original BGL intensity however had to be estimated to be 360 W/m², since no direct power measurement was done for this lamp.

### 4.3.2 Intensity modulated photocurrent spectroscopy

The time-resolved approach to study the photocurrent response is to measure photocurrent transient measurements (time-of-flight), or to subject the cell to an harmonically modulated incident light flux imposed on a bias. The last method is called Intensity Modulated Photocurrent Spectroscopy (IMPS). IMPS is sensitive to small variations in the charge carrier dynamics, and relies on small amplitude modulation of the irradiation intensity to achieve a linear response. For this, laser light with sinusoidal modulated intensity is superimposed on a steady-state white background light (BGL) of varying intensity. The photocurrent response of the cell at short
circuit as a function of modulation frequency is measured as the opto-electrical transfer function \( H_{\text{IMPS}} \) of the system in its complex representation:

\[
H_{\text{IMPS}}(\omega) = \frac{\tilde{I}(\omega)}{e^{\Phi(\omega)}} = |H_{\text{IMPS}}(\omega)| \exp[i\theta(\omega)],
\]

(4.7)

in which \( \tilde{\Phi}(\omega) \) is the modulated photon flux, and \( \tilde{I}(\omega) \) the resulting modulated photocurrent. In this thesis, the opto-electrical transfer function is always presented graphically by its real and imaginary part as a function of frequency, or in so called Nyquist, or Cole-Cole plots, which is the real versus the imaginary part; this is the way commonly used in electrochemistry. The value of the real part of \( H_{\text{IMPS}} \) at low frequencies corresponds to the IPCE value at the wavelength of the IMPS laser light.

Figure 4.4 shows these representations for the simple standard transfer function\(^{(2)}\):

\[
H(\omega) = \frac{1}{1+i\omega \tau}.
\]

(4.8)

The frequency \( f_\tau = 1/2\pi \tau \) is the break frequency of this function; at this frequency, the amplitude of the transfer function 'breaks' from a constant value into a decreasing straight line with slope -1, i.e. in a log-log diagram. The imaginary part of the transfer function has its minimum at that point. Since in our measurements also clear minima in the imaginary part of the respective transfer functions are observed at frequency \( f_{\text{min}} \), the following time constants are introduced:

\[\tau_x = 1/2\pi f_{\text{min}} \text{ with } x = \text{IMPS, IMVS, or } Z.\]

However, at least some dispersion of time constants is expected for the measured transfer functions (IMPS, IMVS and impedance \( Z \)); this is reflected in particular in the Nyquist representation of the transfer functions by a distortion of the semicircles. Therefore, a detailed analysis of the interpretation of the \( \tau_x \) constants occurring in our measurements is given in Ch. 7.

IMPS enables the study of electronic transport under steady-state conditions for photocurrent flow and occupation of electronic states. This is important when trapping of charge carriers plays a role; it gives information on charge recombination and collection/transport dynamics. The collection/transport time constant should be the fastest in order to obtain high charge collection efficiency, but also to allow a transport-related interpretation of \( \tau_{\text{IMPS}} \).

Measurement set-up

The IMPS measurements have been carried out at the Inorganic Chemistry department of Delft University of Technology. The samples are illuminated through the glass substrate with 635 nm light of a 15 mW diode COHERENT lablaser, being within the absorption spectrum of the CuInS\(_2\). About 45% of the laser light is modulated by an opto-acoustic modulator (ISOMET 1205C-2), which is driven by a frequency response analyzer (FRA, SOLARTRON model 1255), see Fig. 4.5. A small fraction of the modulated beam is reflected by a beam splitter and detected by a fast reference photodiode from which the reference phase is derived. The remainder of the laser beam is expanded to a spot of 0.5 cm radius with uniform intensity. The constant component of the laser light has an intensity of 54 W/m\(^2\) and the modulated component an amplitude of 20 W/m\(^2\) as is measured with a NOVA PD300-SH photodiode. Since the reference diode turned out to be not that fast in the highest frequency range, its deviation was determined with respect to a HAMAMATSU S5971 Si PIN photodiode of which the frequency response is guaranteed constant up to 12 MHz; the phase deviation of the reference diode exceeded 1 degree at 50 kHz up to 15 kHz.

\(^{(2)}\)The impedance of a resistance \( R \) parallel with a capacity \( C \) is for example of this form with \( \tau = RC \).
Figure 4.4: Imaginary (a), real (b) and Nyquist (c) representation of transfer function (4.8) with break frequency $f_\tau = 1$ Hz.
degrees at 1 MHz. All measured data were corrected for this deviation since the availability of the Hamamatsu photodiode was far from guaranteed during the measurement periods.

Additionally, constant broad-band white illumination is applied to investigate the cells under operating conditions. The light intensity is varied from 5 to 705 W/m² with neutral density filters. A water filter prevented infrared photons to heat the sample, and a 395 nm long pass filter was used to prevent generation of charge carriers in TiO₂. The illumination is uniform over an area even larger than the sample size in the case of sample S1. However for sample S7, it was necessary to stick the glass/front side of the sample to the copper plate that is used to heat the sample; a hole with a diameter of 2 mm was made in the plate in order to be able to illuminate the sample.

The photocurrent is detected as a voltage drop over a 27 Ω load or measuring resistance $R_{load}$ connected to the cell as shown in Fig. 4.5. The voltage signals of both the reference photodiode and the solar cell are detected by the FRA, which also calculates the opto-electrical transfer function. $R_{load}$ is taken as small as possible with respect to the detection level of the measuring FRA to ensure that the measurement is done as close to short circuit as possible. The analysis was done from 10 Hz to 1 MHz. Figure 4.5 also shows the assumed series resistance $R_s$ between the cell and the measuring unit.

A bias voltage $V_{bias}$ is supplied by a simple 9 V battery and a resistive voltage divider because a sophisticated, programmable Keithley 2400 Current/Voltage Source and Measure Unit appeared to greatly distort the measurements on the 3D-cell. Since no influence was found when the response of the fast Hamamatsu photodiode was measured instead of a 3D-cell, it was concluded that the complicated internal circuit of the Keithley Unit was likely to interfere with the processes in the 3D-cell. Therefore, the dc-stability of a simple battery was preferred. In case a voltage is applied, it is divided over the cell and the measuring resistance. Since the resistance of the 3D-cell is estimated from $V_{oc}/I_{sc}$ to be at least 500 Ω, the part of the applied voltage that drops over the measuring resistance is less than 5%. In case of full BGL illumination, this was indeed the case (additional multi-meter measurement), but without BGL, there was a significant deviation from -0.2 V at $V_{bias} = -1.0$ V to 0 V at $V_{bias} = 0.4$ V, the point at which the dark and light curves cross.

At last, a scaling factor $SF$ should be determined in order to obtain real physical values for in particular the real part of $H_{IMPS}$ which represents the IPCE. How this is done is explained in Appendix A. However, due to uncertainties in the determination of some experimental conditions (including the fact that the measurements were done without a mask), the IMPS and IMVS results presented in this thesis are not scaled with the scaling factor. To ensure that the obtained values for the simulation parameters do have physical value, the scaling factor is used though; in this, a uniform scaling factor for all measurements is assumed.

### 4.3.3 Intensity modulated photovoltage spectroscopy

Instead of the photocurrent, also the modulated photovoltage can be measured as a function of modulated photon flux, now at open circuit. It is called Intensity Modulated photoVoltage Spectroscopy (IMVS) and is measured with the IMPS set-up leaving out $V_{bias}$ and $R_{load}$. In general it is assumed that, since at open circuit there is no net charge transport, IMVS gives information on charge recombination. The characteristic time constant $\tau_{IMVS} = 1/\omega_{min}$ is associated with the graphical minimum of the imaginary part of the IMVS transfer function, as is $\tau_{IMPS}$ in case of the IMPS transfer function. Again, this issue will be discussed in detail in Ch. 7.
4.4 Optical characterization

The transmission $T$ of the cells is determined using a Newport 818-SL Si low power detector, in combination with a Newport 883-SL OD3 attenuator when necessary. It is calculated from the measured photocurrent together with the detectors absolute spectral responsivity found in the instruments specs data file.

4.5 Discussion

Since the low frequency limit of $\text{Re}[H_{\text{IMPS}}(\omega)]$ and the IPCE value at the wavelength of the IMPS laser light should yield the same value, it is interesting to compare the results of both studies. However, the intensity of the dc-part of the laser light was rather high as compared to the maximum of the chopped IPCE signal (50 versus 0.5 W/m$^2$). Since this creates slightly other reference conditions, exact correspondence is not to be expected. Moreover, other IMPS references also use a much lower constant laser light intensity, e.g. 0.7 W/m$^2$ [62]. It also means that even at the ‘no white background light’ condition, there is a 50 W/m$^2$ red light interacting with the cell; the parameter ‘BGL’ only means common white background illumination.

For the $J(V)$ and IPCE measurements, a mask is used with an open surface area equal to that of the Au contact, i.e. 0.035 cm$^2$. The mask was applied to the glass substrate through which the cell is illuminated. However, due to the fact that the monochromatic light and the BGL in the IPCE set-up are not impinging at the same angle, it was not possible to ensure that the IPCE light and the BGL illuminated the same surface area, see Fig. 4.6. This resulted in a shifted background lighted area with respect to the Au contact; the area of illumination due to the monochromatic light and the illuminated area due to the BGL are only overlapping for about 50%.

Detailed optics, toxicity and stability of the studied cells were not explored, nor in this research nor somewhere else inside the ETA-project. What could be noticed though was that the 3D-cells turned out to be giving the same $J(V)$ results even after two years of storage in air filled...
Figure 4.6: Detail of cell in IPCE measurement set-up showing influence of mask on illuminated area of cell under study. Layer thicknesses not to scale but enough to demonstrate the problem of oblique falling background light.

boxes (in dark and in open circuit). Let’s regard this as a stability test in the first order.
Chapter 5

Device simulations

5.1 Introduction

According to WordNet(1), a computer simulation is the technique of representing the real world by a computer program, with the remark that ‘a simulation should imitate the internal processes and not merely the results of the thing being simulated’. This is also my point of view. I think that in this stage of the research on the 3D-cell it is more important to use computer simulations to develop a feeling for the physical phenomena that determine its behavior than that we find the precise values for the parameters that are in the model. Therefore we will focus more on the assumptions behind each model and less on the exact values of some, though obviously very important, material or cell parameters. The question is: which assumptions should be made in case of solid-state nanostructured solar cells?

5.2 Modelling of nanostructured solar cells

Since the experimental breakthrough in the 90’s, a number of theoretical aspects of the DSSC concept have been presented [63, 64]. From initial effective medium approaches [65, 66, 67, 68], sophisticated transport and device models [68, 69] including descriptions of the nanoporous structure have been developed. Recently, Cass et al. presented a model including a description of the nanoporous structure, a distribution of traps and a coupling between transport at fine and coarse scale to study the overall electron transport.

However, theoretical studies of DSSC’s are far from being completed. A bit simplified, the reason is two-fold. First, the dynamics at the semiconductor|dye|electrolyte interface is not completely understood, which resulted in modelling of recombination, kinetic and transport related mechanisms as effective processes. Additionally, a computational difficulty exists to couple these highly detailed mechanisms in a macroscopic sense. That is, to relate the mechanisms in three dimensions to effective, one-dimensional processes.

The only serious modelling paper on ETA-cells apart those from our group, is from Taretto [70]. The model considers an ETA-cell as being a pin junction, with tunnelling-assisted defect recombination. High electrical fields are assumed in the absorber as opposed to the flat-band situation in our model, see Sect. 5.3.

In the next sections of this chapter, our point of view on the applicability is discussed of (some of) these models as well as others to describe the physical phenomena in three-dimensional solid-state solar cells.

(1)http://wordnet.princeton.edu/
5.3 Equivalent network model

In this approach the opto-electrical properties of a solar cell device are described using equivalent circuit theory. In this, every possible part or phenomenon of the device is represented by an electrical circuit element. To solve a network problem in dc-regime, the current and voltage laws of Kirchhoff are needed, together with the Volt-Ampere or constitutive laws (these express of which elements the branches are composed and which relations the elements impose on the currents and voltages). In a linear network, any ratio of a current or voltage and the source value is called the transfer function of the source to the particular current or voltage. When time dependent sources are concerned that evolve sinusoidally in time, the ac-regime is entered; the network problems become differential equations and the solutions may be complex. Solutions can be found as a function of time (transient analysis) as well as of frequency of the sinusoidal source. Again, transfer functions can be deduced.

Equivalent networks can be very useful in the study of solar cells and panels. Examples of specific solar cell ‘circuiting’, i.e. the application of equivalent circuit theory to solar cell structures, are integrated, series connected cells in panels, cells with a small contact dot [71], admittance spectroscopy (numerous references) and nanostructured solar cells as is explained below.

In Figure 5.1, it is demonstrated how this is done for the 3D-cell. First, we simplify the three-dimensional structure by projecting it onto a two-dimensional plane. Then, a bit of reordering is carried out. At last, the materials and the interfaces are represented by electric circuit elements. A one-dimensional network connection of unit cells is thus obtained to simulate the macroscopic cell. A unit cell is formed by a diode and a parallel connected current source, the resistors $R_{sn}$ and $R_{sp}$ stand for the percolation of the $p$-network (left), and the $n$-network (right). Nor the particle|particle interfaces in the $n$-network nor the grain boundaries in the $p$-network are regarded as separate contributions in this. In that case, it depends on the characteristic lengths of the cell with respect to the particle size whether the distance $\Delta x$ between the unit cells is ‘only’ a discretization parameter without a physical meaning, or has the physical value of the particle size. This is because the discretization parameter $\Delta x$ can have any value as long as it is much smaller than the characteristic lengths of the cell like diffusion or Debye lengths, or absorption depths (and particle size in case the particle|particle interfaces are decided to have a separate resistor representing them). However, as we will see in Ch. 7 and more particular in Table 7.1, the characteristic lengths in our cell are in the order of the particle size, thus leaving us no possibility to attribute a physical value to $\Delta x$.

Two contact diodes describe possible Schottky barriers at the electrodes. Depending on the specific characteristic that is to be described with it, the network can be developed towards a manageable problem in different ways.

5.3.1 Infinite diffusion network

The first way is to develop the network of Fig. 5.1 towards an electrical, ‘dark’, dynamic representation. In this, the current sources are omitted and the diodes are approximated by a parallel connection of an incremental conductance and a depletion capacitance, see Fig. 5.2. Despite the result of the flat-band unit cell approach concerning the influence of resistance in the $p$-subnetwork, it is assumed here that the transport of holes in the valence band of the $p$-type network is not limiting or determining the cell’s behavior. In the network model this is expressed by taking $R_{sp} = 0$. The contact diodes are neglected because the characteristic lengths of our cells are assumed to be much smaller than the cell thickness $\ell$ which indeed turns out
to be the case for the cells under study. The resulting infinite network accounts for drift and diffusion of electrons in the \textit{n}-type semiconductor (grey box on the left), and recombination at interfaces (grey box on the right). The cell’s behavior is therefore assumed to be determined by the electrons in the \textit{n}-type network. This is expressed by the presence of the $R_{sn}$ resistors.

The complex impedance for this infinite network is:

$$Z(\omega) = \frac{R_{sn}}{2} \left[ 1 + \sqrt{1 + \frac{4}{R_{sn}(1 + i\omega R_{||} C)}} \right]$$  \hspace{1cm} (5.1)

Since any circuit can be represented by a parallel circuit with frequency dependent $G(\omega)$ and $C(\omega)$, the latter is obtained from $Y(\omega) = 1/Z(\omega)$ and $C(\omega) = \text{Im}[Y(\omega)]/\omega$. The latter expression is used to simulate EIS measurements. When $R_{||} \gg R_{sn}$, this expression comprises:

$$C(\omega) = C_0 \quad \text{for } \omega \ll \frac{1}{R_{||} C}$$
$$\sim \frac{1}{\omega^p} \quad \text{for } \omega \gg \frac{1}{R_{sn} C}$$
$$\sim \frac{1}{\sqrt{\omega}} \quad \text{for } \omega \text{ in an intermediate frequency band.}$$  \hspace{1cm} (5.2)

In the intermediate frequency range, the expression is just the relation for a Constant Phase Element (CPE) with exponent $p = \frac{1}{2}$.

### 5.3.2 Flat-band unit cell

A second way is to develop the network of Fig. 5.1 towards an opto-electrical, steady-state representation [72, 73]. In it, the microscopic unit cell which is typically 50 nm thick, is described as a flat-band cell. In a flat-band cell, the total band bending typically is lower than 2 mV, which can be totally neglected. Hence, the conduction and valence bands are flat, as well as
both Fermi levels $E_{F_n}$ and $E_{F_p}$, see Fig 5.3. The separation between the Fermi levels equals the ‘applied voltage’ over the unit cell. The position of both Fermi levels, relative to the band edges of the materials, is determined by the requirement that the unit cell cannot carry a net electrical charge. This charge-neutrality condition is easy to calculate, since all bands and Fermi levels are flat. In a $pn^+$ cell for example (Fig. 5.3b), holes in the $n$-type material can be neglected, as well as electrons and holes in the $p$-type material. At high forward bias $V$, $E_{F_p}$ approaches the VB in the $p$-type material and holes can become important. Although the minority carrier Fermi levels ($E_{F_n}$ in the $p$-side and $E_{F_p}$ in the $n$-side) are determined by the illumination intensity, the cells remain flat-band cells under illumination, i.e. the electrostatic potential and the conduction band level remain constant over the cell.

The macroscopic cell is modelled as follows. The voltage at the network nodes of the left branch in Fig. 5.1 represents the hole Fermi level $E_{F_p}$ in the CuInS$_2$ shell of the unit cells, the voltage at the nodes of the right branch represent the electron Fermi level $E_{F_n}$ in the TiO$_2$ core of the unit cells. Again, it should be noted that the distance between the nodes $\Delta x$ is only a discretization parameter with no physical meaning; it can take any value as long as it is much smaller than the characteristic lengths associated with the cells under study.

The difference between the two Fermi levels determines the local voltage difference over a network diode. In the network description, all other physical quantities such as electrostatic potential, electron and hole concentration within the unit cells, are lost, and are lumped in the current voltage law of the diode (here assumed to be purely exponential, however not with the ideal value $n_d = 1$ but with $n_d = 2$, scaled to account for actual light input on each unit cell). All generated currents are added, the open circuit voltages are rather averaged, an essential difference with classical solar cells. Constant resistors stand for transport by drift and diffusion; a voltage drop between node $x$ and node $x + \Delta x$ stands for a Fermi level gradient. The resistances of the two subnetworks add up to a total distributed series resistance $R \cdot A = \rho d / 3(1 - p)$ with $\rho$ the specific resistivity of the layer, $p$ its porosity, and $d$ the distance between the electrodes, the factor 1/3 is because the series resistance is distributed.

Now if $R_{sn} = R_{sp} = 0$, all the cells are forced to be at the same voltage which results in a lower $V_{oc}$ than the $V_{oc}$ of a unit cell, because at open circuit, current flows from the rear cells to the front. The resistances in the networks turn out to be of essential value in this; if present, they
decouple the cells, so that the cells can have the specific open circuit voltage that is determined by their illumination intensity. The result is a higher macroscopic $V_{oc}$ (valid until moderate $R_{sn}$ and cell thickness of $\approx 4 \mu m$). On the other hand however, high losses are occurring if the resistances in the subnetwork that is connected to the back contact (in our solar cells, the $p$-network), are too high. This is, because the highest current, i.e. generated at the front (in our case the hole current) has to be carried through the whole cell thickness to the back. In this regard, electrolyte cells have an advantage over poorer conducting all solid-state cells. Our cells are however only $3 \mu m$ thick which means that the expected resistance in the TiO$_2$ will result in an almost perfect correspondence of local $V_{oc}$ and the cell’s generated voltage (correct for $R_{sp}A = 0$).

The circuit of Fig. 5.1 is also used as a basis to develop a dynamic version of this opto-electrical approach; it is then used to define the assumptions and their implications for a macroscopic analytic diffusion model. All this is explained in the next sections.

### 5.4 Macroscopic effective medium models (EMM)

An effective medium model (EMM) treats the nanostructured part of the solar cell as if it were one material, or effective medium, possessing effective material parameters. The CB level is that of the $n$-type material, the VB level is taken from the $p$-type material. For the dielectric constant, a mean value according to the $n$-type/$p$-type ratio is determined or a value according to more sophisticated models, e.g. those based on the effective medium theory developed by Maxwell-Garnett (1904 en 1906) or Landauer (1952, 1978).

Once an effective medium model is set up, an existing solar cell simulation programme can in principle be used to implement it: both the EMM and the solar cell simulation programmes available to the PV research community are based on the same ‘semiconductor equations’ (Poisson’s equation and the continuity equations for electrons $n$ and holes $p$) and on a number of ‘constitutive relations’, describing specific internal phenomena (e.g. the relation between current $J$, the concentrations $n$ and $p$, and the electric field $E$, in a simple case diffusion and drift - relations describing recombination of carriers, and charge trapped in deep states...). It has to
be checked in each particular case whether the simulation programme describes all phenomena that are esteemed to be important in a particular EMM description of a nano-structured solar cell, since often, the programmer has already made additional assumptions in function of the type of solar cell under study in order to avoid unnecessary complicated programming and interpretation. Fortunately now and then, review articles appear, for example [74] on the criteria for and comparison of thin film device simulation programs.

If a macroscopic effective medium model is used to simulate three-dimensional solar cell structures, the program must be able to handle the following critical issues:

1. one layer (trivial);
2. moderate band gaps (effective band gap always smaller than band gap of largest band gap material);
3. graded band gaps $E_g(x)$ and $n(x), p(x), \alpha(x)$;
4. recombination and charge in deep bulk states (Shockley-Read-Hall);
5. way to represent recombination and charge in deep interface states;
6. simulation of non-routine measurements other than $J(V)$, like $C(V), C(f), IPCE$, all as a function of temperature;
7. fast and easy to use.

Moreover, the simulation of time-resolved measurements is very useful due to the different kinetics of the different processes, see Sect. 4.1.

In the next paragraphs, we give some information of the practical usability of solar cell simulators (in particular SCAPS) to implement an EMM of a nanostructured solar cell.

### 5.4.1 Sophisticated thin film model SCAPS-1D

For the effective medium and unit cell calculations in this thesis, SCAPS-1D is used [75]. SCAPS is an advanced thin film model, that has been and still is developed in our group since 1996 [76]. It should be mentioned however, that it lacks the following, for us important, options/physics:

- graded band-gaps $E_g(x)$;
- two and three dimensions;
- Auger recombination;
- hopping conduction between traps;
- tunnelling;
- simulation of time-resolved measurements (though transient analysis is being implemented [77]).
5.4.2 SLICE

A new implementation of an effective medium model for nanostructured solar cells is SLICE; it has been presented for the first time in 2004 [78], and an article is accepted for publication [79]. It is the result of the cooperation of three young researchers of the ETA-project: Kristofer Fredin (UU), Sven Rühle (WIS) and this author. Nevertheless, I did not use it for this work on ETA and 3D-cells for several reasons: SLICE is not (yet) available as a user program and its development has been simultaneously with my experimental IMPS and IMVS work (see later), so SLICE was not ready when I needed it. Finally, SLICE does, compared to SCAPS and equivalent simulation software, not add new features or facilities for ETA- or 3D-cells due to its strong emphasis on the DSSC with a liquid electrolyte; it is designed to study coupled charge transport within DSSC devices. It uses an effective medium approach that takes electrons in the nanoporous TiO\textsubscript{2} structure as well as ions in the electrolyte into account; in this way, it resembles much other semiconductor diode based simulation programs. However, in contrast to existing models [69], SLICE is able to simulate steady state as well as time dependent measurements, i.e. transient measurements. This feature discerns SLICE from the majority of the available solar cell simulation programmes, including SCAPS.

5.5 Partial EMM models

Implementing an EMM in a solar cell simulator like SCAPS is quite straightforward, easy and fast, once the effective parameters are known, and provided that all physical phenomena which one wants to describe are included in SCAPS. Even when this is the case, it is not easy to gain physical insight from a few SCAPS simulations only. Since a variety of phenomena is included in SCAPS, and since the input parameter set is quite large (typically \( \approx 100 \) parameters) it is not straightforward to uncover if, and to which extent, some aspect of the macroscopic cell behavior (e.g. a minimum in a measured \( \text{Im}[H_{\text{IMPS}}] \) vs. \( \omega \) plot) is determined by a single or a few properties. For this purpose, it is very useful to develop an analytic model which only describes one (or very few) mechanisms. Possibly such a model will be valid only in a part of the solar cell, or only under particular working conditions: then we speak of a ‘partial model’. The advantage of such partial models lies in the fact that they focus to one mechanism, that they require a very limited number of input parameters (compared to a full SCAPS model), and that they often can be treated analytically.

Existing simulation programmes can simulate routine measurements, and sometimes a few more advanced measurements, but often not all measurements which one has carried out and wants to interpret. SCAPS e.g. can handle admittance measurements (or EIS, Electrochemical Impedance Spectroscopy), but not experiments where the intensity of the illumination is modulated (Intensity Modulated Photocurrent and Voltage Spectroscopy, or IMPS and IMVS, see Sect. 4.3.2 and 4.3.3). These IMPS and IMVS measurements are a substantial part of this work (see Ch. 7). In the next section, we therefore will develop a partial effective medium model, based on diffusion, to describe EIS, IMPS and IMVS measurements.

5.6 Analytic diffusion model for EIS, IMPS, IMVS

Applying a macroscopic diffusion model to describe electron transport in nano-structured solar cells is not new, neither in stationary form [80] nor in dynamic form [62]. Our cells have a
strong resemblance with the cells that were the subject of these articles, so I will take these models as a starting point.

Usually, IMPS and IMVS measurements are interpreted by applying some simple rules of thumb. From the measurements, one deduces the characteristic time constants $\tau_{IMPS}$ and $\tau_{IMVS}$ (see Sect. 7.2). The standard interpretation is dealing with two mechanisms only: transport and recombination of electrons in the nano-structured TiO$_2$ layer. The IMVS measurements are carried out in open circuit conditions. One then attributes the measured $\tau_{IMVS}$ to the recombination lifetime $\tau_n$, since there is no net transport in open circuit. The IMPS measurements are carried out in short circuit conditions. One then attributes the measured $\tau_{IMPS}$ to a combination of $\tau_n$ and some characteristic time $\tau_{transport}$ describing the current transport. Comparative measurements are then used to decide whether one of the two time constants $\tau_n$ or $\tau_{transport}$ is dominant and can be associated to the measured $\tau_{IMPS}$. Sometimes, the rules of thumb are further simplified: 'IMVS measures recombination and IMPS measures transport’. It is clear that a more rigid treatment of the IMPS and IMVS measurements is needed.

Our starting point is an existing diffusion model for IMPS measurements in DSSC’s [62]. This model is formally identical to the small signal analysis in semiconductor diodes (study of the ‘diffusion capacitance’ or ‘diffusion admittance $Y(\omega)$’), now known for many decades and documented in all textbooks on semiconductor device physics, e.g. [81, p. 94]. Our aim is:

- to present a unified framework for three small signal measurements: the admittance $Y(\omega)$ and the opto-electronic transfer functions $H_{IMPS}$ and $H_{IMVS}$;
- to establish a relation between the three functions $Y(\omega)$, $H_{IMPS}$ and $H_{IMVS}$;
- to establish relations between the time constants deduced from the measurements, thus $\tau_Y$, $\tau_{IMPS}$ and $\tau_{IMVS}$, and the characteristic times for the underlying physical mechanisms: recombination ($\tau_n$), diffusion ($\tau_{diff}$) and drift ($\tau_{drift}$).

### 5.6.1 Assumptions and model formulation

The effective medium approach of the cell structure of the ETA or 3D-cell under study is shown in Fig. 5.4. An equivalent network representation of the cell is shown in Fig. 5.5 which is based on the general model presented in Sect. 5.3 and pictured in Fig. 5.1; it gives a pictorial view of the arguments used below. The various assumptions and features of the model are enumerated; the numbers between brackets refer to Fig. 5.5.

1. The transport of holes in the valence band of the CuInS$_2$ filling the pores of the TiO$_2$ structure is not limiting or determining the cell’s behavior. In the network model this is expressed by assuming zero resistance in the bottom line (1), in the effective medium model by assuming a constant hole Fermi level $E_{Fp}$ in the effective medium. This has been confirmed many times for DSSC cells where the hole conductor is an electrolyte. From time-of-flight measurements on flat TiO$_2$|CuInS$_2$ systems also was concluded that hole transport through the CuInS$_2$ is faster than electron transport through TiO$_2$ [82]. Therefore, it is assumed here that this is also valid for our ETA cells where CuInS$_2$ is the hole conductor.

2. The cell’s behavior is determined by the electrons in the TiO$_2$ layer. We describe the effective TiO$_2$|CuInS$_2$ medium thus as an ‘electrons only’ medium. The varying electron Fermi level $E_{Fn}$ (or the electron concentration $n$) in the effective medium is thus an unknown
The electron current in the effective TiO$_2$|CuInS$_2$ medium is by diffusion only: we neglect everywhere the electric field $\mathcal{E}$, and we assume flat conduction and valence bands in the structure. It is clear that this assumption cannot hold for the entire cell structure under all bias conditions: we are dealing with a ‘partial model’. This assumption is checked with a full numerical implementation of the effective medium model, e.g. with SCAPS. It turns out that the energy bands indeed are flat over most of the cell thickness under open circuit conditions [73]. Under short circuit conditions, the boundary conditions (thus the work function of the contacts and the electron affinity) impose an appreciable total band bending. However, depending on doping and illumination, this band bending occurs in a small transition region near the contacts, and the bulk of the cells can remain essentially field-free. Again, this is better justified experimentally for DSSC’s than for the ETA cells under study here. We assume here that in the bulk of our cells indeed the drift current is negligible with respect to the diffusion current. The resistances (2) thus describe the diffusion current.

4. The assumption $\mathcal{E} = 0$ implies that a possible charge built-up in our cell is not strong enough to cause an important electric field. Thus we do not have to deal with the charges in trap states, nor with the Poisson equation. As we have also assumed an ‘electron only medium’, the semiconductor equations are reduced to the electron continuity equation. This greatly simplifies the treatment: the problem is reduced to one differential equation,
the time dependent diffusion equation for electrons. Also, the total cell current $I$ (per unit area) is given by the diffusion current through the leftmost of the resistances (2):

$$I = -eD_n \frac{\partial n}{\partial x}(0).$$  (5.3)

This constitutive equation takes account of the conventional reference sense of the solar cell current, and of the fact that the electrons carry a charge $-e$.

5. The cell is illuminated from the TCO|TiO$_2$ interface. The photon flux $\Phi$ incident from the left on the $x = 0$ plane exponentially decays by absorption through the effective medium. The generation rate at each position is thus given by $g(x, \lambda) = \alpha \Phi \exp(-\alpha x)$ where $\alpha = \alpha(\lambda)$ is the effective absorption constant. The current sources (3) in the network model are proportional to $g(x, \lambda)$.

6. The diodes (4) in the network model represent the recombination $u(x)$. We assume here a simple expression $u(x) = (n(x) - n_{eq})/\tau_n$, where $n_{eq}$ is the equilibrium electron concentration (thus in dark ($\Phi = 0$), at zero applied voltage $V = 0$ and in the bulk). In the macroscopic effective medium view, the recombination is bulk recombination. At the microscopic scale, this recombination can be bulk recombination in a TiO$_2$ grain or in the CuInS$_2$ filling, or interface recombination at the TiO$_2$|CuInS$_2$ interface. We think that interface recombination is the dominant contribution to recombination, thought this assumption is not necessary for the model.

7. With these assumptions on generation and recombination, the differential diffusion equation becomes:

$$\frac{\partial n(x, t)}{\partial t} = D_n \frac{\partial^2 n(x, t)}{\partial x^2} + \alpha \Phi \exp(-\alpha x) - \frac{n(x, t) - n_{eq}}{\tau_n}.$$  (5.4)

8. The front TCO|TiO$_2$ contact is not limiting the solar cell behavior. The resistor/diode combination (5) which represents the electrical contact, is replaced by a short circuit. In [62], this is formulated as 'the electron transfer at the TCO|TiO$_2$ interface is infinitely fast'. The consequence of this assumption is that the local diode voltage at position $x = 0$ equals $\nu_d(0) = V$, the applied voltage. This is a very important issue. Since $\nu_d$ is proportional to the local electron concentration, a first boundary condition can be set:

$$n(0) - n_{eq} = n_{eq} \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right].$$  (5.5)

9. Also at the CuInS$_2$-Au contact, we assume that there is no current limitation: possible contact elements (6) are shorted in the model (this assumption is also a necessary condition for Eq. (5.5) above).

10. We assume that there are no direct shorts at the contacts: e.g. at the back contact $x = \ell$, electrons are blocked completely. In the network model, this is expressed by the absence of a connection between the resistor (7) and the contact. In our 3D-cells, this is justified by the presence of a CuInS$_2$ topping layer: there is no direct contact between the gold contact and the TiO$_2$ structure. This leads to the second boundary condition:

$$J(\ell) = 0 \Rightarrow \frac{\partial n}{\partial x}(\ell) = 0.$$  (5.6)
5.6 Analytic diffusion model for EIS, IMPS, IMVS

The model assumptions outlined above lead to the mathematical formulation of the problem: a differential equation for the electron concentration \(n(x)\), together with boundary conditions (5.5) at \(x = 0\) and (5.6) at \(x = \ell\). After this is solved for \(n(x)\), the current can be obtained from the constitutive equation (5.3). This can in principle be done for any excitation (applied voltage \(V\) and/or illumination \(\Phi\)).

5.6.2 The dc-solution

We will solve the problem first in steady-state conditions (that is, a constant \(V\) and \(\Phi\)). Then we will carry out a small signal analysis to find the response to small oscillations of \(V\) and \(\Phi\) around their dc-values.

As the differential equation (5.4) is of only second order, linear, and with constant coefficients, it can be solved by standard mathematics. The solution is:

\[
I = en_{eq} \frac{D_n}{L_n} \tanh \left( \frac{\ell}{L_n} \right) \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right] - e\Phi \frac{a^2 n_e^2}{a^2 L_n^2 - 1} \left[ 1 - \frac{\exp(-\alpha t)}{\cosh \left( \frac{\ell}{L_n} \right)} - \frac{1}{a L_n} \tanh \left( \frac{\ell}{L_n} \right) \right],
\]

where we defined the diffusion length \(L_n\) as \(L_n = \sqrt{D_n \tau_n}\). The first term represents the dark current, and the second the light current. The ideal light current is \(e\Phi\), every photon contributing one electron to the current. The spectral response, or IPCE is thus given by:

\[
\text{IPCE} = \frac{a^2 L_n^2}{a^2 L_n^2 - 1} \left[ 1 - \frac{\exp(-\alpha t)}{\cosh \left( \frac{\ell}{L_n} \right)} - \frac{1}{a L_n} \tanh \left( \frac{\ell}{L_n} \right) \right].
\]

5.6.3 Small signal analysis: formulation and solution

Now we will give a small perturbation to the applied voltage \(V\) and/or to the illumination intensity \(\Phi\), in the form of low amplitude sinusoidal oscillations with angular frequency \(\omega\). When these perturbations are infinitesimally small, the system response to them is linear, and all system properties, including the electron density and the current also will show small oscillations with the same frequency. We take the following notation: the subscript 0, e.g. in \(V_0\), is the dc-bias value; the tilde above a symbol e.g. \(\tilde{v}\) is the complex representation (or phasor) of the ac-small signal perturbation; the bold symbol, e.g. \(V\), is the complex representation of the total property (dc + ac), except for \(\Phi^*\); and finally the symbol without any special make-up, e.g. \(v(t)\), is the total time dependent property. Thus:

\[
\begin{align*}
\Phi^* &= \Phi_0 + \Phi \exp(i\omega t) \quad \text{and} \quad \Phi(t) &= \text{Re}[\Phi(t)] = \Phi_0 + \text{Re}[\Phi \exp(i\omega t)] \\
V &= V_0 + \tilde{v} \exp(i\omega t) \quad \text{and} \quad v(t) &= \text{Re}[V(t)] = V_0 + \text{Re}[\tilde{v} \exp(i\omega t)] \\
n &= n_0 + \tilde{n} \exp(i\omega t) \quad \text{and} \quad n(x, t) = \text{Re}[n(x, t)] = n_0(x) + \text{Re}[\tilde{n}(x) \exp(i\omega t)] \\
I &= I_0 + \tilde{i} \exp(i\omega t) \quad \text{and} \quad i(t) &= \text{Re}[I(t)] = I_0 + \text{Re}[\tilde{i} \exp(i\omega t)].
\end{align*}
\]

In the mathematical formulation of the problem, i.e. equations (5.3) to (5.6), \(\Phi\) has to be substituted by \(\Phi^*\) and so on, and in (5.4), the time derivative in the left hand member is substituted by a multiplication with \(i\omega\). By doing so, the problem can be split in a set of equations for the dc-variables \(\Phi_0, V_0, \ldots\) for which exactly equations (5.3) to (5.6) are obtained, and in a set of
equations for the complex ac-variables $\Phi$, $\tilde{V}$, ... Hence, the ac-form of the differential diffusion equation (5.4) is:

$$i\omega \tilde{n} = \alpha \Phi \exp(-ax) - \frac{\tilde{n}}{\tau_n} + D_n \frac{\partial^2 \tilde{n}}{\partial x^2}.$$  

(5.10)

After rearranging, this ac-differential equation for $\tilde{n}$ is written in exactly the same form as the dc-differential equation for $n_0 - n_{eq}$:

$$\tilde{n} = \alpha \frac{\tau_n}{1 + i\omega \tau_n} \Phi \exp(-ax) + \frac{L_n^2}{1 + i\omega \tau_n} \frac{\partial^2 \tilde{n}}{\partial x^2} + n_{eq}.$$  

(5.11)

Here, we have introduced an effective complex lifetime $\tau_n^*$:

$$\tau_n^* = \frac{\tau_n}{1 + i\omega \tau_n},$$  

(5.12)

and an effective complex diffusion length $L_n^*$:

$$L_n^* = \frac{L_n}{\sqrt{1 + i\omega \tau_n}} \quad \text{with} \quad L_n = \sqrt{D_n \tau_n}.$$  

(5.13)

The boundary condition (5.6), and the constitutive equation (5.3) are identical in dc and in ac. The boundary condition (5.5) needs a little more attention. It can be written in a form equivalent to the dc-form, provided that one can approximate the complex exponential by a two-term Taylor expansion:

$$\exp \left( \frac{qV}{kT} \right) = \exp \left( \frac{qV_0}{kT} \right) \exp \left( \frac{qV_{c} e^{i\omega t}}{kT} \right) \approx \exp \left( \frac{qV_0}{kT} \right) \left[ 1 + \frac{qV}{kT} e^{i\omega t} \right] \quad \text{when} \quad \left| \frac{qV}{kT} \right| \ll 1.$$  

(5.14)

The meaning of the term ‘small signal’ is now clear: the amplitude of the voltage oscillations should be well below the thermal voltage $kT/q$. By separating the dc-part from the ac-part, we obtain:

$$\text{dc :} \quad n_0(0) - n_{eq} = n_{eq} \left[ \exp \left( \frac{qV_0}{kT} \right) - 1 \right]$$  

$$\text{ac :} \quad \tilde{n}(0) = n_{eq} \exp \left( \frac{qV_0}{kT} \right) \frac{qV}{kT}.$$  

(5.15)

We can thus immediately copy the small-signal ac-solution from the dc-solution already obtained, just by substituting the life time $\tau_n$ and the diffusion length $L_n$ by their effective, complex values $\tau_n^*$ and $L_n^*$, and by substituting the right hand member of the dc-part of Eq. (5.15) by that of the ac-part of Eq. (5.15). We obtain:

$$\tilde{i} = Y \tilde{v} - H_{\text{IMPS}} e \Phi,$$  

(5.16)

where we defined the admittance $Y$ as:

$$Y(\omega) = \frac{q}{kT} q n_{eq} \frac{D_n}{L_n^*} \tanh \left( \frac{\ell}{L_n^*} \right) \exp \left( \frac{qV_0}{kT} \right)$$  

(5.17)

and the dimensionless ‘internal opto-electronic transfer function’ or the ideal IMPS-response $H_{\text{IMPS}}$:

$$H_{\text{IMPS}}(\omega) = \frac{a^2 L_n^*}{a^2 L_n^* - 1} \left[ 1 - \exp(-a\ell) \cosh \left( \frac{\ell}{L_n^*} \right) - \frac{1}{a L_n^*} \tanh \left( \frac{\ell}{L_n^*} \right) \right]$$  

(5.18)

The frequency dependence of $Y$ and of $H_{\text{IMPS}}$ only stems from the $\omega$-dependence of the effective diffusion length $L_n^*$. 


5.6.4 Small signal measurements: ideal and real

In an ideal admittance or impedance measurement, the illumination is held constant ($\Phi = 0$), and a small ac-voltage $\tilde{v}$ is superimposed on the dc-bias voltage $V_0$. The response of the current $\tilde{i}$ to $\tilde{v}$ is then measured, usually with a lock-in technique. Equally well, a current perturbation $\tilde{i}$ could be imposed, and the resulting $\tilde{v}$ measured. It is clear that our calculated function $Y(\omega)$ equals the measured admittance. It is also clear that an oscillation $\tilde{\Phi}$ of the illumination (with the same angular frequency $\omega$ as the voltage oscillation $\tilde{v}$) should be avoided.

In an ideal IMPS measurement, the cell is biased in short circuit conditions: the dc-voltage is held constant at $V_0 = 0$ and $\tilde{v} = 0$. The current response $\tilde{i}$ to a sinusoidal intensity variation $\tilde{\Phi}$ of the illumination is then measured. It is clear that our calculated $H_{\text{IMPS}}$ gives a correct description of the measurement, provided that $\tilde{v} = 0$ is guaranteed. In a practical set-up, this is difficult to realize. As explained earlier in Sect. 4.3.2, $\tilde{i}$ is measured as the voltage drop $\tilde{v}_{\text{ext}}$ over a small load resistance $R_{\text{load}}$. The external opto-electronic transfer function (this is, the non ideal measurement of the IMPS response) is then measured as:

$$H_{\text{IMPS,ext}} = \frac{\tilde{i}}{e\Phi} = + \frac{\tilde{v}_{\text{ext}}}{R_{\text{load}} e\Phi}.$$  (5.19)

Since also the presence of a series resistance $R_s$ as a part of the measuring system is unthink-able, see (the inset of) Fig. 4.5, the measured voltage is related to the internal cell voltage by the voltage divider formula:

$$\tilde{v}_{\text{ext}} = \tilde{v} \frac{R_{\text{load}}}{R_{\text{load}} + R_s}.$$  (5.20)

The relation between $\tilde{i}$, $\tilde{v}$ and $\tilde{\Phi}$ is given by Eq. (5.16). Therefore, Eq. (5.19) can be rewritten as follows:

$$H_{\text{IMPS,ext}} = H_{\text{IMPS}} \frac{1}{1 + Y(\omega) (R_{\text{load}} + R_s)}.$$  (5.21)

Since we know from experience that nanostructured electrodes are able to store a large number of electrons, which gives rise to a large capacitance $C$, a cell admittance given by a simple capacitor $C$ is assumed [62]. So, finally one obtains the following relation for the externally measured opto-electronic transfer function:

$$H_{\text{IMPS,ext}} = H_{\text{IMPS}} \frac{1}{1 + i\omega C (R_{\text{load}} + R_s)}.$$  (5.22)

In this way, the external measurement circuit can introduce an extra time constant $\tau_{RC} = (R_{\text{load}} + R_s)C$ which can obscure the interpretation. This second time constant $\tau_{RC}$ expresses itself as the expansion of the ideal semicircle of Fig. 4.4 (representing the simple standard transfer function (4.8) with time constant $\tau$), into the third quadrant. This is shown in Fig. 5.6 which is a plot of the product of two standard transfer functions (4.8) with two different time constants $\tau_1$ and $\tau_2$. However, this only happens if one time constant differs from the other with less than a factor of about 50; for example no expansion occurs if the constants are differing more than a factor 100 (pink line). The maximum expansion is when the time constants are the same, see the blue line.

In an IMVS measurement, the ac-voltage $\tilde{v}$ in response to an ac-intensity variation $\tilde{\Phi}$ is measured. In the measurement circuit of Fig. 4.5, the load resistance is then omitted ($R_{\text{load}} \to \infty$), and of course the voltage source $V_{\text{bias}}$. There are no measurement complications, because it...
Figure 5.6: Influence of supposed capacitive behavior of nanostructured oxide electrodes on Nyquist representation of IMPS results; expansion into negative quadrant if $\tau_{\text{IMPS}}$ and $\tau_{\text{RC}}$ do not differ that much.

is obviously easier to perform an ideal voltage measurement than an ideal current measurement with low resistive samples (the internal impedance of the solar cells is of the order of 1 to 10 $\Omega$): one can safely assume that $i = 0$. Bearing in mind that the experimental circumstances regarding the dc-voltage of IMPS and IMVS measurements are different, one obtains:

$$H_{\text{IMVS}}(\omega, V_0) = Z(\omega, V_0) H_{\text{IMPS}}(\omega, V_0) = \frac{H_{\text{IMPS}}(\omega, V_0)}{Y(\omega, V_0)}.$$  (5.23)

This means that:

$$H_{\text{IMVS}}(\omega, 0) = Z(\omega, 0) H_{\text{IMPS}}(\omega, 0)$$  (5.24)

$$H_{\text{IMVS}}(\omega, V_{\text{oc}}) = Z(\omega, V_{\text{oc}}) H_{\text{IMPS}}(\omega, V_{\text{oc}}).$$

The functions $Z(\omega, 0)$, $H_{\text{IMPS}}(\omega, 0)$, and $H_{\text{IMVS}}(\omega, V_{\text{oc}})$ are the most commonly measured functions; in this work also $H_{\text{IMPS}}(\omega, V_{\text{oc}})$ is measured. In general however, the result of Eq. (5.23) may provide another way for the experimentalist to obtain the $H_{\text{IMPS}}$ function, namely by measuring only $H_{\text{IMVS}}$ and $Z$, which are non-current measurements. This is further illustrated in Fig. 5.7a and b where $H_{\text{IMPS}}$ is represented by the red lines, $H_{\text{IMVS}}$ by the green lines, and $Z$, the reciprocal, by the blue lines; only one positive half of the light amplitude is sketched. This method however can only be used if the $J(V)$ curve deviates from that of an ideal diode, and no cross-over of the light and dark $J(V)$ curves occurs, for in the first case both $H_{\text{IMVS}}(\omega, 0)$ and $Z(\omega, 0)$ go to $\infty$, and in the latter all measurements become hard to determine. What should be mentioned either, is the possibility of a phenomenological light dependence of the transfer functions which is not found in the model, so that Eq. (5.23) should actually be written as:

$$H_{\text{IMVS}}(\omega, V_0, I_0) = Z(\omega, V_0, I_0) H_{\text{IMPS}}(\omega, V_0, I_0).$$  (5.25)

In retrospect, this equation of simple beauty seems self-evident, but I have not encountered it yet in the literature.

5.6.5 Small signal measurements: time constants

Approximations

In one of the next chapters, IMPS, IMVS and EIS measurements are presented. Often, a graph of the real part and of the imaginary part of the measured property versus the frequency will be
given. The most striking feature of these plots is the presence of a minimum in the Im[H(ω)] − ω plot at an angular frequency ω_{min}; here H represents the measured property, which can be the IMPS, IMVS or the EIS measurement. In a ‘zeroth-order’ analysis, we will associate this minimum to a time constant (τ = 1/ω_{min}). The question that we tackle now is how these experimental time constants τ_{IMPS}, τ_{IMVS} and τ_Z are related to the physical parameters in our diffusion model. To do so, we will calculate the first-order Taylor expansion of the functions H_{IMPS}, Z = 1/Y and H_{IMVS} in the angular frequency ω: we will thus drop all terms in ω² and higher powers of ω.

Finally, we will end up with an approximation:

\[ H(\omega) \approx A - i\omega B \propto \frac{1}{1 + i\omega\tau} \rightarrow \tau = \frac{B}{A} \quad \text{(when } \omega\tau \ll 1). \]  

(5.26)

When doing so, we need some elementary series expansions:

\[ L_n^* \approx \frac{L_n}{1 + \frac{1}{2}i\omega\tau_n} \approx L_n \left( 1 - \frac{1}{2}i\omega\tau_n \right) \]
\[ \frac{a^2t_n^2}{a^2t_n^2 - 1} \approx \frac{a^2t_n^2}{a^2t_n^2 - 1} \left( 1 + \frac{i\omega\tau_n}{a^2t_n^2 - 1} \right) \]
\[ \cosh \left( \frac{\ell}{L_n} \right) \approx \cosh \left( \frac{\ell}{L_n} \right) \left[ 1 + i\omega\tau_n \frac{\ell}{2L_n} \tanh \left( \frac{\ell}{L_n} \right) \right] \]
\[ \tanh \left( \frac{\ell}{L_n} \right) \approx \tanh \left( \frac{\ell}{L_n} \right) \left[ 1 + i\omega\tau_n \frac{\ell}{L_n} \cosech \left( 2\frac{\ell}{L_n} \right) \right]. \]

(5.27)

After laborious manipulations, we find for the IMPS measurement:

\[ \frac{\tau_{IMPS}}{\tau_n} = \frac{1 - a^2t_n^2}{2at_n \cosh(\ell/L_n)} + \frac{at \exp(-at) \sinh(\ell/L_n) - \ell/L_n - \sinh(\ell/L_n) \cosh(\ell/L_n)}{\exp(-at) + \frac{\ell}{at} \sinh(\ell/L_n) - \cosh(\ell/L_n)} \]  

(5.28)

and for the impedance measurement:

\[ \frac{\tau_Z}{\tau_n} = \frac{1}{2} + \frac{\ell}{L_n \sinh(2\ell/L_n)}. \]

(5.29)

The time constant τ_{IMVS} of the IMVS measurement then follows from (5.23) and from our first-order approximation in ωτ_n (that is, a one pole approximation):

\[ \tau_{IMVS} = \tau_{IMPS} + \tau_Z. \]  

(5.30)
Especially Eq. (5.28) seems repellent for practical use. We will therefore approximate the expressions for the time constants in five limiting cases: for a very long or very short diffusion length, \(L_n \to \infty\) or \(L_n \to 0\), for a very thick cell \(\ell \to \infty\), and for short or long wavelength illumination \((\alpha \to \infty \text{ or } \alpha \to 0)\). After quite some manipulations, we find:

For a very long diffusion length:

\[
L_n \to \infty : \quad \tau_{\text{IMPS}} \to \tau \frac{\ell^2 (\alpha \ell - 1) + (1 - \alpha^2 \ell^2/2) \exp(-a\ell)}{L_n^2 \alpha^2 \ell^2 (1 - \exp(-a\ell))}
\]

\[
L_n \to \infty \text{ and } \alpha \ell \gg 1 : \quad \tau_{\text{IMPS}} \to \tau \frac{\ell}{2aL_n^2} = \frac{\ell}{aD_n}
\]  

(5.31)

For a very short diffusion length:

\[
L_n \to 0 : \quad \tau_{\text{IMPS}} \to \tau \frac{1}{2} \left(1 + \alpha^2 L_n^2\right) \approx \frac{\tau}{2}
\]

\[
L_n \to 0 \text{ for all } \alpha \ell : \quad \tau_{\text{IMPS}} \to \frac{\tau}{2}
\]  

(5.32)

For very thick cells:

\[
\ell \to \infty : \quad \tau_{\text{IMPS}} \to \tau \frac{1}{2 + aL_n}
\]

\[
\ell \to \infty \text{ and } aL_n \ll 1 : \quad \tau_{\text{IMPS}} \to \frac{\tau}{2}
\]

\[
\ell \to \infty \text{ and } aL_n \gg 1 : \quad \tau_{\text{IMPS}} \to \tau \frac{L_n}{2aL_n} = \frac{L_n}{2aD_n}
\]  

(5.33)

For short wavelength illumination \((\alpha \to \infty)\):

\[
\alpha \to \infty : \quad \tau_{\text{IMPS}} \to \tau \frac{2}{2\alpha L_n} \left[\tanh\left(\frac{\ell}{L_n}\right) + \frac{\ell}{L_n} \frac{1}{\cosh^2\left(\frac{\ell}{L_n}\right)}\right]
\]

\[
\alpha \to \infty \text{ and } \frac{\ell}{L_n} \ll 1 : \quad \tau_{\text{IMPS}} \to \tau \frac{\ell}{2\alpha L_n} = \frac{\ell}{aD_n}
\]

\[
\alpha \to \infty \text{ and } \frac{\ell}{L_n} \gg 1 : \quad \tau_{\text{IMPS}} \to \tau \frac{L_n}{2\alpha L_n} = \frac{L_n}{2aD_n}
\]  

(5.34)

For long wavelength illumination \((\alpha \to 0)\):

\[
\alpha \to 0 : \quad \tau_{\text{IMPS}} \to \tau \frac{2}{2} \left[1 - \frac{\ell}{L_n} \frac{1}{\sinh\left(\frac{\ell}{L_n}\right) \cosh\left(\frac{\ell}{L_n}\right)}\right]
\]

\[
\alpha \to 0 \text{ and } \frac{\ell}{L_n} \ll 1 : \quad \tau_{\text{IMPS}} \to \tau \frac{\ell^2}{3L_n^2} = \frac{\ell^2}{3D_n}
\]

\[
\alpha \to 0 \text{ and } \frac{\ell}{L_n} \gg 1 : \quad \tau_{\text{IMPS}} \to \tau \frac{\ell}{2}
\]  

(5.35)
The square root dependence of the frequency, typical for diffusion dominated processes, is encountered here.

It should be noted that the approximate time constants calculated above are based on

$$\omega \tau_n \ll 1$$

Anticipating the experimental results of the next chapter, the conditions where $L_n \gg \ell$ are labelled as relevant for DSSC’s, and the conditions where $L_n \ll \ell$ are labelled as relevant for ETA- or 3D-cells.

These analytic approximations of the time constants are very useful as a guideline in the setup and interpretation of the IMPS, IMVS and EIS measurements; they will be discussed below, in Sect. 5.6.6.

It should be noted that the approximate time constants calculated above are based on the low-frequency approximation (that is, $\omega \tau_n \rightarrow 0$) of the exact analytic formulae (5.28) and (5.29). Fortunately, the high frequency approximation (that is, $\omega \tau_n \rightarrow \infty$) is much easier to carry out. The LF-series expansions of Eq. (5.27) should be replaced by:

$$L_n \approx \frac{l_n}{\sqrt{2kT}} \left(1 - \frac{i}{2}\right)$$

$$\frac{a^2 \ell^2}{d \ell_n^2 - 1} \approx \frac{a^2 \ell^2}{d \ell_n^2} \exp\left(\frac{\omega \tau_n}{2}\right)$$

$$\cosh\left(\frac{\ell}{L_n}\right) \approx \cosh x \cos x + i \sinh x \sin x \rightarrow \frac{\exp(x)}{2} \exp(ix)$$

$$\tanh\left(\frac{\ell}{L_n}\right) \approx \frac{\sinh x \cos x + i \cos x \sin x}{\cos x \cos x + i \sin x \sin x} \rightarrow 1$$

With these approximations we obtain:

$$Y(\omega) = \frac{q}{kT} \exp\left(\frac{qV_0}{kT}\right) qn_{ed} \frac{D_n}{L_n} \sqrt{\frac{\omega \tau_n}{2}} \left(1 + i\right)$$

when $\omega \rightarrow \infty$.

$$H_{\text{IMPS}}(\omega) = \sqrt{\frac{a^2 \ell^2}{2d \ell_n^2}} \left(1 - i\right) - \frac{1}{2} \sqrt{\frac{\omega D}{\ell_n^2}}$$

when $\omega \rightarrow \infty$ and with $\omega_{HF} = \frac{2\tau_n}{a^2 \ell^2} = \frac{2}{\alpha D_n}$.

The square root dependence of the frequency, typical for diffusion dominated processes, is encountered here.

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<th>$\tau_{\text{IMPS}}$</th>
<th>$\tau_{\text{Z}}$</th>
<th>$\tau_{\text{IMVS}}$</th>
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</tbody>
</table>

Table 5.1: First-order approximation of the time constants of the IMPS, IMVS and impedance measurement, and the low frequency limit for $\text{Re}[H_{\text{IMPS}}]$, for the possible relative magnitudes of the characteristic lengths (the diffusion length $L_n$, the cell thickness $\ell$ and the absorption depth $1/\alpha$).
In the low frequency approximation, $|\text{Im} [H_{\text{IMPS}}]| \propto \omega$ (5.26), whereas in the high frequency approximation $|\text{Im} [H_{\text{IMPS}}]| \propto 1/\sqrt{\omega}$ (5.38): in the transition from the LF to the HF region, there should be a minimum in the $|\text{Im}[H_{\text{IMPS}}(\omega)]|$ curve. This is also observed experimentally (see Ch. 7). However, no simple analytic approximations can be found in the transition region. In the next section, we will compare our simple approximations to the numerical results obtained with the full analytic expressions (5.12), (5.13), and (5.18).

**Results**

We therefore calculated the transfer functions $Z(\omega)$ (Eq. (5.17)), $H_{\text{IMPS}}(\omega)$ (Eq. (5.18)), and $H_{\text{IMVS}}(\omega)$ (Eq. (5.23)), plotted their imaginary part against the frequency (logarithmic scale), determined the angular frequency at the minimum, and deduced a ‘numerical’ time constant from it. These numerical time constants are compared to the analytic approximations of Table 5.1 in Fig. 5.8. The results for the IMVS and the EIS measurement are quite good. The results for the IMPS measurements are also quite good for small diffusion lengths (small lifetime), but the behavior at large diffusion lengths (long lifetimes) is a little bit complicated. When both the lifetime $\tau_n$ and the absorption constant $\alpha$ are high, two minima can occur in the $|\text{Im}[H_{\text{IMPS}}]| - \omega$ plot, see Fig. 5.9.

The evolution of the approximated time constant $\tau_{\text{IMPS}}$ according to Table 5.1 is plotted in Fig. 5.10 as a function of the diffusion length $L_n$, for one cell thickness $\ell = 1\, \mu m$, and three values of the absorption constant $\alpha$ ($10^3$, $10^4$ and $10^5\, \text{cm}^{-1}$). It turns out the time constant to be taken in Table 5.1 is, for each set of parameter values $(L_n, \ell, \alpha)$, the smallest of all time constants $\tau_{\text{IMPS}}$ listed in the table. For small diffusion lengths, $\tau_{\text{IMPS}}$ always is dominated by recombination, and equals $\tau_4 = \tau_n/2$. For large diffusion lengths, $\tau_{\text{IMPS}}$ is determined by diffusion: by the diffusion transit time $\tau_2 = \ell^2/3D_n$, or by a similar expression $\tau_1 = \ell/\alpha D_n$ if $\alpha$ is too large.
Figure 5.9: Imaginary part of the opto-electronic transfer function $H_{\text{IMPS}}$, calculated with the same parameters as in Fig. 5.8. Top: a large diffusion length, relevant for a DSSC; bottom: a small diffusion length, relevant for an ETA-cell.
Figure 5.10: Approximate time constant of the IMPS measurement, according to Table 5.1. The time constants $\tau_1$ to $\tau_6$ of this Table are drawn separately (see legends), and the resulting time constant $\tau_{\text{IMPS}}$ for each value of $L_n$ is drawn as open circles. The cell thickness $\ell = 1 \mu m$, and the absorption constant $\alpha$ is $10^5 \text{ cm}^{-1}$ (top), $10^4 \text{ cm}^{-1}$ (middle) and $10^3 \text{ cm}^{-1}$ (bottom).
there is an intermediate $L_n$-region where $\tau_{\text{IMPS}}$ is given by $\tau_6$ of Table 5.1. An experimental way to discern between the different $L_n$-regions would be either the variation of $\alpha$ (if a laser set-up with variable wavelength were available), or the variation of the cell thickness $\ell$ (all other parameters remaining the same: that is of course an essential experimental difficulty).

### 5.6.6 Small signal measurements: discussion

- The $J(V)$, IPCE, IMPS, IMVS and EIS (thus $Z$ or $Y$) measurements are all based on the same model. In an ideal case, it should be possible to explain all these measurements consistently with this single model.

- There is however a problem with the $J(V)$ measurements: they are usually determined by a too high series resistance $R_s$. All other measurements are carried out at much lower illumination levels, thus lower currents, and are thus much less influenced by $R_s$.

- From the definition of $H_{\text{IMPS}}$, it follows that the low frequency limit of the real part of $H_{\text{IMPS}}$ yields the spectral response IPCE:

\[
\text{IPCE}(\lambda) = \lim_{\omega \to 0} \text{Re}[H_{\text{IMPS}}(\lambda)].
\]

The same correspondence is found from the modelling: the low frequency limit of Eq. (5.18) is equal to Eq. (5.8), for then $L_n^* = L_n$. However, this was very difficult to verify experimentally since the circumstances made us using it to (try to) calibrate the IMPS measurement.

- At first sight, the analytic diffusion model gives rise to rather ‘barbarian’ mathematical expressions. Fortunately, suitable approximations have lead to a table with simple and physically meaningful expressions for the time constants.

- One can consider IMVS as a ‘clean’ measurement: the measured time constant $\tau_{\text{IMVS}}$ is in (almost) all circumstances to associate with the electron lifetime $\tau_n$.

- Also the EIS measurement is determined by recombination of electrons: the resulting time constant has to be associated with $\tau_n$ or with $\tau_n/2$, depending on the relative values of the cell thickness and the diffusion length.

- The IMPS measurement on the other hand is complicated to interpret, and various mechanisms can dominate the result: electron recombination (cases 4 and 5 in Table 5.1), diffusion transit time (cases 2 and 3), and other mechanisms which depend on the absorption depth $1/\alpha$ (cases 1 and 6). The difficulty of interpretation is a disadvantage, but the fact that various physical mechanisms can be measured is an interesting aspect.

- Some shortcomings of the model can be noticed already: the calculated admittance $Y$ does not depend on the dc-bias illumination: neither the bias intensity $\Phi$, nor the wavelength of the bias illumination (through $\alpha$) enter in the expression for $Y$ (5.17). The calculated IMPS response does not depend on the bias conditions (neither $\Phi$ nor $V_0$ are present in the equation (5.18)). We will see later that this is in contrast to the experimental findings.

- We will give pragmatic solution to these shortcomings: we will assume that the parameters $D_n$, $\tau_n$, ... depend on the bias conditions (illumination intensity and voltage $V_0$). This is less exotic than it looks at first sight. It is a common practice in these film solar cells.
Device simulations

(including CuInSe$_2$ based cells), where it is accepted that the parameters determining the diode saturation current depend on illumination: one even speaks of ‘the dark current measured under illumination’. These phenomena are referred to as ‘non-linearity of the cell’ or ‘failing of superposition of dark and light situation’. Also, in nano-structured solar cells and in organic polymer solar cells, many materials studies have pointed to the dependence of the transport and recombination parameters on the electron concentration. The causes of the general ‘non-linear’ behavior are almost as manifold as there are materials and cells. A rigorous treatment is beyond the capability of a simple analytic model.

- A short comment on the similarities and differences between this model and the well known ‘diffusion admittance model’ of a one-sided crystalline $n^+p$ diode or solar cells [81] is in order here. Both models are based on exactly the same differential equation (5.4), on the same constitutive equation (5.3) for the diffusion current, and on the same boundary conditions (5.5) and (5.6), when the $n^+p$ diode has a perfectly passivated back contact (i.e. zero surface recombination of electrons at the $p$-contact, $S_n = 0$). There is however a big difference in concept: in an $n^+p$ diode, the description is for electrons, that are minority carriers in the neutral $p$ region, where the neglecting of the electron drift current is well justified. The appearance of the exponential voltage term in the boundary condition (5.5) at the junction side is because both Fermi levels are essentially flat in the depletion layer; also this is well justified. In our cell system, electrons are majority carriers in the TiO$_2$ layer. In the effective CuInS$_2$|TiO$_2$ medium, even both carriers are majority carriers: electrons which move microscopically in the TiO$_2$ constituent of the effective medium, and holes which move microscopically in the CuInS$_2$ constituent. In our model assumptions, there is no drift, and the hole Fermi level is flat, but that needed an own justification (the $n^+p$ diode explanation based on the minority/majority concept cannot be used here). Also the boundary condition (5.5) needed an own justification.

5.7 Discussion

When the analytic diffusion model, a partial EMM, was formulated (Sect. 5.6.1), the network model was used to illustrate the assumptions. Apparently, the two models are complementary. This issue has been addressed more carefully in [83], albeit only for steady state characterization. In this paper, an effective medium representation of the nanostructured cell is offered to SCAPS to calculate its $J(V)$ curve. The results are compared to the characteristics obtained from the opto-electrical steady state approach of the network model referred to in Sect. 5.4. It is shown that a network model and an effective medium model can describe the same physical structure, when they are set-up properly.

Also in the ac-regime, the two models are expressions of the same physics as we will see in Ch. 7. It is however not possible to connect the microscopic parameters from the network model with the macroscopic values of the effective medium model. The main reason for this is, that there are too many unknown parameters, for from the $C(f)$ graph that is used to determine the three network parameters, only two values can be determined (the dc value for $C$ and the breakpoint frequency). If however $R_{sn}$, $R_{||}$ and $C$ could be determined separately (provided that $\Delta x$ would have the physical and fixed value of particle size), the following expressions would define the relations between three microscopic parameters $R_{sn}$, $R_{||}$ and $C$, and four macroscopic parameters $D_n$, $\tau_n$, $\Delta x$ and $n_0$:

$$R_{sn} = \frac{\Delta x}{q\mu_n n_0} = \frac{kT}{q^2 n_0} \frac{\Delta x}{D_n}$$

$$C = \frac{q^2 n_0}{kT} \Delta x = \frac{(\Delta x)^2}{R_{sn} D_n}$$

$$R_{||} = \frac{kT}{q^2 n_0 \Delta x} 4\tau_n = \frac{4\tau_n}{C}.$$  

(5.39)
Chapter 6

Heterojunction interfaces and barrier layers

Since interfaces are likely to play a very important role in three-dimensional solar cell physics, a few theoretical thoughts are spent on this topic here, i.e. a theoretical treatment is given of the mechanisms that are to be considered important at the interfaces in CuInS$_2$-based ETA-solar cells [84]. In particular, the possible benefits of the insertion of an intermediate tunnel barrier (Al$_2$O$_3$, MgO) or buffer layer (CdS) at the active interface are investigated. The results will be used in the explanation of measurement results in the next chapters.

The chapter will start however with a general introduction on donors, acceptors and charges in semiconductors and their relation to recombination. Moreover, some one-dimensional experiments are reported and device simulations are presented, illustrating the theory on the interface layers.

6.1 Donors, acceptors and space charges in semiconductors

The most important loss mechanism in heterojunction solar cells is recombination, the dynamic equilibrium between capture and emission of electrons and holes. It can take place:

- in the quasi neutral region (QNR);
- in the space charge layer (SCL) of the absorber, only in case of short carrier lifetimes;
- at the metal-semiconductor interface (front and back contact);
- at metallurgical interface between two semiconductors: surface recombination due to presence of interface states, the classical recombination then is the sum of the two surface recombination processes at either side of the interface, described by SRH; the Pauwels-Vanhoutte model also takes recombination across the interface into account so that four recombination processes are possible [85]; the dominant np-product determines which of the four dominates which at their turn is determined by the band alignment.

The capture and emission processes are now discussed more in detail, starting from semiconductor physics which tells us that doped, polluted or non-crystalline semi-conductors have accessible energy levels in the forbidden gap $E_g$. The charge in these levels or states contributes to the total electrical charge, and hence can change the band bending.
According to the charge that the atoms associated with the defect levels carry, they are called donors or acceptors; donors are positively charged when empty/ionized, and neutral when filled with an electron; acceptors are negatively charged when filled with an electron/ionized, and neutral when empty, or 'filled with a hole'. A semiconductor with predominantly donors (acceptors) is called an $n$-type ($p$-type) semiconductor.

If a level is within $\approx 3kT$ of a band edge, it is called a shallow level, otherwise it is a deep level. Shallow levels are assumed to be fully ionized at the working temperature and are also called dopants. An impurity with an energy level close to the CB acts as a donor-type dopant, if its energy level is close to the VB, it acts as an acceptor-type dopant. An ionized donor-type dopant has donated its electrons to the CB level so that they contribute to the conductivity of the semiconductor. In that case $n = N_d^+ \gg p, N_a^-$. 

Figure 6.1a shows the energy band diagram of an $n$-type semiconductor with a shallow donor level; b shows how the charges within the semiconductor are distributed. When the semiconductor is brought into contact with a metal, a so called Schottky barrier is formed c. The plus signs indicate the positively charged ionized donors at the donor level, the minus signs indicate the negatively charged electrons in the CB and in a very thin metal sheet; $\chi$ is the electron affinity, $\Phi$ the work function, $W$ the width of the space charge layer or depletion region, and $V_{bi}$ the built-in voltage. Figure d shows the effect of a negative applied bias $V_{bias}$ on the energy levels and charge distribution of the system; since an $n$-type semiconductor is considered, the applied negative bias potential results in a reverse biased semiconductor.
Figure 6.2: Capture and emission processes in $pn$-junction with shallow and deep donor level, and a deep acceptor level (left-hand side, $n$-type), and a shallow and deep acceptor level (right-hand side, $p$-type). Equilibrium (a); forward bias; majority carrier capture by deep traps: electrons are captured by donor atoms making them neutral (A), holes are captured by acceptor atoms making them neutral (B); minority carrier capture by deep traps (D) due to minority carrier injection (C) (b).
Deep donors are not necessarily ionized at working temperature due to their energy level being much more close to midgap; only when their energy level lies above $E_F$, they are empty. They are also called traps because it is very hard for the electrons to come out. Figure 6.2 shows an $n$-type semiconductor with a shallow donor level and deep donor and acceptor levels that is brought into contact with a $p$-type semiconductor with a shallow acceptor level and a deep acceptor level. Figure b shows the system under forward bias; majority carrier capture by deep traps occurs: the donor atoms at A are now filled with an electron (empty in a), the acceptor atoms at B are now filled with a hole (ionized/filled with an electron in a), even minority carrier injection occurs (C), followed by minority carrier capture (D). This last process is not possible in a Schottky barrier junction.

In this way, an applied bias results in the emptying and filling of deep trap states. It changes the amount of charge present in the semiconductor which at its turn changes the capacity. A measurement method that uses this change of charge upon applying a bias voltage to determine the position of the donor and acceptor levels is impedance spectroscopy, see Sect. 4.2.2. Since also illumination changes the occupation of the levels due to disturbing the equilibrium by changing the amount of mobile charge carriers, in a related measurement technique the illumination intensity is given a small-signal ac-perturbation (Ch. 5).

6.2 Band line-up at heterojunction interfaces

When an heterojunction interface is formed, it is very likely that offsets in conduction and/or valence band are established ($\Delta E_c$ and/or $\Delta E_v$ respectively) due to differences in electron affinity $\chi$ and band gap $E_g$ of the two materials. $\Delta E_c$ is defined as $E_{cp} - E_{cn} = \chi_n - \chi_p$, $\Delta E_v$ as $E_{vp} - E_{vn} = (\chi_n - \chi_p) + (E_n - E_p)$, see the grey rectangle in Fig. 6.3. A positive $\Delta E_v$ (VB maximum of $n$-type below VB maximum of $p$-type) is desirable since that decreases the recombination driven by the injection of holes from the $p$-type material into the $n$-side of the junction. On the other hand, a positive $\Delta E_c$ can drastically increase the interface recombination since electrons at the $n$-side can recombine with holes from the $p$-side of the interface via interface states. A negative $\Delta E_c$ can also be harmful since it provides a barrier for the photocurrent of electrons generated in the $p$-type absorber. However, according to simulations by Niemegeers [86, 87], Minemoto [88], Platzer [89] and more recently by Gloeckler [90], a small negative $\Delta E_c$ (-0.4 – 0 eV) is optimal in CIGS based solar cells, for in that case, the barrier prevents interface recombination but still the thermal velocity of the electrons generated in the absorber is high enough to overcome the barrier $\Delta E_c$ without a significant voltage drop. This is explained as follows.

When the electrons cross the barrier due to thermionic emission, it causes a drop in Fermi level of $qV_i$ at the interface given by (in short circuit conditions):

$$J = J_\ell = qv_{th}N_c \exp\left(-\frac{\Delta E_c}{kT}\right) \left[ \exp\left(\frac{qV_i}{kT}\right) - 1 \right].$$  \hspace{1cm} (6.1)

The voltage drop at the interface is thus estimated by:

$$V_i = \frac{kT}{q} \ln \left[ 1 + \frac{J_\ell}{qv_{th}N_c} \exp\left(\frac{\Delta E_c}{kT}\right) \right].$$  \hspace{1cm} (6.2)

With typical values $J_\ell = 30 \text{ mA/cm}^2$, $v_{th} = 10^7 \text{ cm/s}$, $N_c = 10^{19}/\text{cm}^3$, one sees that a barrier $\Delta E_c = 0.4 \text{ eV}$ can be tolerated since the second term between brackets equals 0.017, yielding $V_i \approx 0.017kT/q = 0.4 \text{ mV}$. QED. The interface voltage drop $V_i$ can be regarded as the effect of an effective series resistance at the interface.
Figure 6.3: Definition of band offsets $\Delta E_c$ and $\Delta E_v$ and their influence on interface recombination for three different signs of $\Delta E_c$ ($\Delta E_c > 0$); flat-band cell situation explained in Sect. 5.3, i.e. no built-in electric field hence no space-charge layer and resulting band bending; extrinsic $p^+i$- and $pn^+$-junctions, and intrinsic $pn$-junction; donor type (left) and acceptor type (right) interface states respectively; arrows indicate main IFR paths.
6.3 Intermediate layers in CuInS\textsubscript{2}-based 3D-cells

6.3.1 Introduction

Insertion of extremely thin insulating oxide coatings (MgO, Al\textsubscript{2}O\textsubscript{3}, ZnO, TiO\textsubscript{2}, ZrO\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3}) at the active interface of nanostructured solar cells has led to significant improvement of solar cell characteristics. These coatings are also called tunnel barriers since the insulating nature of the barrier imposes tunnelling on the charge carriers in order to cross the barrier. The improvements hold both for dye sensitized cells [49, 50, 51] and all solid-state ETA-solar cells [52]. Recently also improvement of cell characteristics on applying of intermediate conducting buffer layers of indium (hydroxy) sulphide In\textsubscript{x}(OH)\textsubscript{y}S\textsubscript{z} and In\textsubscript{2}S\textsubscript{3} in TiO\textsubscript{2}|CuInS\textsubscript{2} ETA-systems are reported, [14] and [53] respectively. In general, suggestions for the physical reasons for the observed cell improvement are given, but a quantitative understanding and an insight into the limits of cell improvement to be expected are still largely lacking. In other cell systems though, the action of an intermediate layer (IL) is well studied; we mention a wide gap insulating layer used in metal-insulator-semiconductor cells (M-I-S-cells) and semiconductor-insulator-semiconductor cells (S-I-S-cells) [10, 47, 46]. The remaining part of this chapter is dedicated to study what an IL can do for our nanostructured cells.

6.3.2 Loss factors in 3D- and ETA-cells

In (solid-state) dye sensitized solar cells (DSSC), the light current \( J_\ell \) is more or less acceptable, but the open circuit voltage \( V_{oc} \) is too low; for ETA-solar cells even the light current is not very good.

According to Eq. (4.3), a low value of \( V_{oc} \) can be ascribed to a dark saturation current \( J_s \) which is too high. Therefore, it has to be pointed out how \( J_s \) can be decreased without decreasing the light current \( J_\ell \) at the same time.

In general, the dark current \( J_s \) is caused by recombination, the most important loss mechanism in heterojunction solar cells, see Sect. 6.1. It occurs at the contacts, in both semiconductors (TiO\textsubscript{2} and ETA-layer), and at the interface (TiO\textsubscript{2}|ETA or TiO\textsubscript{2}|ETA|“hole conductor”CuSCN). Since in nanostructured cells, materials interfaces are never further away than \( \approx 25 \) nm and the microscopic surface and interface area is very large, it is assumed that interface recombination (IFR) is dominant instead of ‘normal’ bulk recombination.

Therefore, one can think of three main mechanisms by which the insertion of an IL could improve \( V_{oc} \) without compromising \( J_{sc} \) [10]:

1. the band alignment is such that the dark current is confronted with a higher energy barrier than the light current;
2. interface recombination is diminished;
3. beneficial changes occur in chemical and electrostatic interaction at and through the interface.

These mechanisms are studied below in the context of nanostructured solar cells.

An energy barrier at the interface

An insulating IL at the active interface or junction of a solar cell constitutes an energy barrier, which impedes both the dark current (desired) and the light current (undesired). Current
transport through this IL is limited by tunnelling, a mechanism which is extremely sensitive to (Fig. 6.4, inset) barrier heights $q\phi_1$ and $q\phi_2$ at either side of the barrier, layer thickness $\ell$, and voltage $V_{\text{IL}}$ over the barrier. In the following treatment, tunnelling is iso-energetic, which means that electron states with the same energy left and right from the IL must be available. The final, lower energy state is then attained by relaxation. In Fig. 6.4, the $J(V_{\text{IL}})$ characteristics of an asymmetrical barrier ($\phi_1 = 0.6$ V, $\phi_2 = 1.4$ V) are shown for two values of $\ell$ (2.5 nm and 2.7 nm), as calculated with the formulae given by Simmons [91, Eq. 17–19]. Also shown are the solar cell characteristic $J-V$ in which $V$ stands for junction voltage (an ideal Shockley law is assumed), and the $J(V)$ curves of the series connection of the solar cell with the IL. The latter is calculated by requiring that the solar cell and the IL carry the same current $J$, whilst their voltage is added to give the total cell voltage $V = V_{\text{IL}} + V_j$.

Several features are clearly observed in Fig. 6.4. The voltage $V_{\text{IL}}$ over the IL turns out to be very sensitive to $\ell$ and must remain negligible compared to $V_{\text{oc}}$ otherwise the presence of the IL severely deteriorates the $J(V)$ characteristics of the total cell. For $|V_{\text{IL}}| < \phi_1$, the $J-V_{\text{IL}}$ characteristics of the IL are symmetrical, even if the barrier itself is asymmetrical (i.e. $\phi_1 \neq \phi_2$); the curve is asymmetrical for $|V_{\text{IL}}| > \phi_1$ (if $\phi_2 > \phi_1$) [91]. At the scale of Fig. 6.4, asymmetry is only seen for $\ell = 2.7$ nm. The mere presence of an IL thus affects the light and dark current which move in opposite directions, in precisely the same way, and no improvement of $V_{\text{oc}}$ is to be expected. The above mentioned deterioration of $J(V)$ characteristics goes together with the deterioration of $J_{\text{sc}}$ as is further illustrated in Fig. 6.5, in which $J_{\text{sc}}$ is plotted against the IL thickness $\ell$ for some values of $\phi_1$ and $\phi_2$. Again, the steepness of the curves shows that the thickness of the IL, when beneficial for other reasons, must precisely be controlled not to exceed a critical value, which depends on the barrier heights. We note that the distance $\ell$ itself is roughly inversely proportional to the square root of the effective mass $m^*$ of electrons in the tunnel barrier layer, i.e. $\ell \approx 1/\sqrt{m^*}$, and that the calculations of Fig. 6.4 and 6.5 assume $m^* = m_0$ [91].

**Interface recombination**

**Theory on interface states** All that is mentioned in Sect. 6.1 is also valid for energy levels that are located in the interface band gap $E_{\text{gi}}$, the distance between the lowest of the two conduction
bands and the highest of the two valence bands at the interface, see Fig. 6.3; these energy levels are referred to as interface states (IFS).

Their occupation follows from a dynamic equilibrium between capture and emission from and to the conduction and valence bands of both materials. Interface recombination (IFR) is described by an extension of the Shockley-Read-Hall (SRH) model [85], and is a complicated function of the energetic density of interface states $N_i(E)$, the capture cross sections of electrons and holes $\sigma_n$ and $\sigma_p$, thermal velocities $v_{th1}$, $v_{th2}$, $v_{thn1}$ and $v_{thn2}$, and carrier concentrations at the interface $n_1$, $p_2$, $n_1$ and $n_2$. However, due to the large band gap difference between the two materials, as is always the case when TiO$_2$ is the $n$-type semiconductor, only recombination of electrons in the material with the lowest conduction band with holes in the material with the highest valence band is dominant, and IFR reduces to the familiar SRH expressions. Therefore, a SRH-based expression for the IFR rate can be derived [81] (in the simplest case that $\tau_n=\tau_p=\tau$):

$$U_{IF}(V, \phi, E_t) = n_i \frac{\exp\left(\frac{qV}{kT}\right) - 1}{2\tau \exp\left(\frac{qV}{2kT}\right) \cosh \left(\frac{q\phi}{kT}\right) + \cosh \left(\frac{qE_t}{kT}\right);}$$

(6.3)

it is obtained by applying the SRH-formula to the metallurgical junction of a $pn$-homojunction, see Fig. 6.6a. In it, $n_i$ is the intrinsic carrier density, $V$ the applied voltage, $E_t$ the trap level energy with respect to the intrinsic energy level at the junction (which is assumed to be in the middle between $E_c$ and $E_v$), and $\phi$ the distance between the intrinsic level at the junction and the mean of the Fermi levels $E_{Fp}$ and $E_{Fn}$ at the junction, thus being a measure for the intrinsicality of the junction. In Figure 6.6b, a plot of expression (6.3) is shown. From this figure it becomes clear that for the same density of IS, IFR is much higher at an intrinsic interface ($n \approx p$) than at an extrinsic interface ($n \gg p$ or $n \ll p$). In the case of an extrinsic interface, which is often assumed, one type of carrier dominates at the interface and IFR is only determined by the minority carrier concentration. Let's consider a $p^+n$ interface at which the electrons are the minority carriers. Then their concentration $n$ determines the IFR according to:

$$J_{IFR} = qS_i(n - n_0),$$

(6.4)

with interface recombination velocity $S_i = N_i\sigma_n \nu_{th}$. In a simple case, the electron concentration $n$ exceeds the equilibrium concentration $n_0$ by a factor $\exp(qV/kT)$ where $V$ is the applied voltage, so that:

$$J_{IFR} = qN_i\sigma_p \nu_{th} n_0 \left[ \exp\left(\frac{qV}{kT}\right) - 1 \right].$$

(6.5)
6.3 Intermediate layers in CuInS$_2$-based 3D-cells

The equilibrium concentration $n_0$ is determined by the distance between the equilibrium Fermi level at the interface and the lowest of the two conduction bands. Figure 6.3 shows the main IFR paths for two different extrinsic interfaces. The starting point of the figure is the flat-band model of the unit cell discussed in Sect. 5.3. Only the extrinsic interfaces are shown for this is the reality in most $pn$-heterojunctions. The main interface recombination path is indicated with an arrow. Effective interface states are assumed (large capture cross-section), i.e. donor type IFS in case of a $p^+$-$n$-cell, and acceptor type IFS in case of a $pn^+$ cell.

From the preceding, it can be concluded that interface recombination can be minimized by:

1. creating an extrinsic interface;
2. reducing the interface state density, and thus $S_i$ at either side of the IL compared to the structure without IL;
3. interface band diagram tailoring to minimize minority carrier concentration $p_0$ in Eq. (6.5) (or $n_0$, whatever are the minorities at the interface).

Strategy 1 is obvious from Fig. 6.6, strategy 2 is obvious from Eq. (6.5). Strategy 3 is discussed in detail below.

**Interface band diagram tailoring** If the theory of Sect. 6.3.2, in particular the part pictured in Fig. 6.3, is applied to our flat-band system system, Fig. 6.7 is obtained. In it, the situation is depicted where the insertion of a conducting IL could improve the solar cell by decreasing interface
recombination. It could be a model for an $n$-TiO$_2$|IL-CdS|$p$-CuInS$_2$ cell, but the energy values of Fig. 6.7 are somewhat arbitrarily chosen to illustrate our argument. First, we notice that there is no tunnel barrier which could impede the light current. Without IL (Fig. 6.7a), electrons are minorities at the interface, and the relevant concentration for IFR, $n_0$, is determined by an activation energy of 0.9 eV. With IL (Fig. 6.7b), IFR can occur at two interfaces. At the CdS|CuInS$_2$ interface (left), electrons are minorities, and their concentration $n_0$ is activated with 1.4 eV. At the TiO$_2$|CdS interface, holes are minorities, and their concentration $p_0$ is activated with 1.1 eV; this interface is unfortunately not so pronouncedly extrinsic. Though there is now IFR at two interfaces, where we assume the same high density of IS as without IL, the relevant minority carrier concentrations are now substantially lower, due to the higher activation energies: 1.4 and 1.1 eV instead of 0.9 eV.

It is straightforward to apply these arguments for other values of band gaps, electron affinities (band discontinuities) and doping (position $E_F$). It is clear that improvement (decrease) of IFR can be obtained or not, depending on the precise parameters. Interface band gap tailoring, when combined with control over materials parameters, thus opens a way to improve nanostructured solar cells by insertion of intermediate layers.

Another argument should be mentioned here. The treatment of IFR was given for dark current. The light current can be treated in the same way, but there is an essential difference. When the $p$-type material (or the dye) is the absorbing material, the light current $J_l$ crosses the interface as an electron current. It is thus essential to minimize electron IFR, hole IFR doesn’t matter for $J_l$. For this reason, an $n^+p$-junction is to be preferred over an $np^+$-junction, since this
fills the IS with electrons, and thus minimizes electron capture. This is an accepted and well-
documented property (e.g. [85] and many subsequent reports). It is not unthinkable that an IL
would convert an np+ junction into an n+p-junction, but one depends on the mercy of materials
interactions to realize that (see next section). Therefore, the same picture for an n+p-junction
is shown in Fig. 6.7c and d. In this case, the activation energy of the minority carriers at the
buffer|CuInS2 interface has not changed, but since this interface is expected to have a decreased
IF state density with respect to the TiO2|CuInS2 interface due to a smaller lattice-mismatch, also
in this case the insertion of an IL might reduce IFR.

Chemical and electrostatic interactions at the interface

Even if intermediate layers are so thin that they do not constitute any impediment for tunnel
current, they can sustain a substantial electrostatic voltage drop, which might substantially alter
the interface band diagram (the classical treatment of MS-Schottky barriers, e.g. [81], is an
excellent illustration of this). Such a voltage drop can be caused for example by the charge in
the donor or acceptor-like interface states at both sides of the IL. The band diagram changes may
improve or deteriorate the cell, as is illustrated in the previous sections. Materials interactions
at the interface can influence the cell behavior in several ways. The interface state density at
either side of the IL can be lower than without IL, due to better lattice matching, or by the details
of chemical surface interactions. An IL can act as a chemical buffer layer, stopping unwanted
interdiffusion of species in an eta-cell structure, e.g. Cu into TiO2. In a DSSC, the presence of
an IL can even influence adsorption of the dye at the nano-particles, and hence the solar cell
characteristics, especially the light current [51].

6.4 Experiments and simulations

6.4.1 Influence of CdS buffer on 3D TiO2|CuInS2-cell performance

Structure The structure of the sample under study, produced at TUD, is:

- TCO-glass (SnO2:F);
- TiO2 dense underlayer (spray), layer thickness ≈ 100 nm;
- TiO2 nanoporous pressed P25 film with primary particles between 10 and 50 nm in diam-
eter, porosity before CuInS2 deposition 50%, afterwards 0–10%, layer thickness ≈ 2 μm,
surface area enlargement with respect to flat layer = 600 × (according to measurements
carried out by the group in Delft);
- CdS deposited by Atomic Layer Deposition (ALD), layer thickness = 10–20 nm;
- CuInS2 (ALD), layer thickness = 50 nm – 1 μm depending on the assumption of partly or
total infiltration of the 50% porous TiO2;
- Au contact spots of 0.032 cm2 and work function 5.1 eV.

Also, cells were made with an identical procedure, but for the omission of the CdS deposition.
In this case, Raman spectroscopy reveals a transition of TiO2 anatase crystal structure to the
rutile one\(^{(1)}\) which is known to increase the amount of defects in the TiO\(_2\). This could indicate Cu-diffusion into the TiO\(_2\) layer, which leads to a reaction of the Cu with TiO\(_2\) upon creation of more oxygen vacancies in TiO\(_2\). Also Cu diffusion inside the CuInS\(_2\) is to be expected, which leads to the formation of new bindings so that Cu-rich and Cu-poor areas develop and phases like Cu\(_x\)S occur. Together with the significant lattice mismatch of the TiO\(_2\)\|CuInS\(_2\) system, the basis is set for the very bad cell performance of a TiO\(_2\)\|CuInS\(_2\) based cell without intermediate layer.

When a CdS layer is deposited, a few problems mentioned above might be solved. However, some Cd-diffusion into the TiO\(_2\) layer might occur due to Cu-diffusion into CdS. This might lead to an increase of doping density of TiO\(_2\) but will not influence the conductivity of the TiO\(_2\).

\(J(V)\) Figure 6.8a demonstrates that the insertion of a CdS buffer layer in a cell indeed has a positive influence on cell performance, especially on the current collection which increases with a factor \(\approx 4\). On the same substrate, also a cell with an \(S\)-shaped \(J(V)\)-curve is observed (not shown).

\(IPCE\) The same difference is shown in the IPCE characteristics of the cell (Fig. 6.8b); integration over the spectrum of the IPCE curve seems to result in an increased collection efficiency with a factor \(\approx 4\) as well. A little qualitative difference is observed, namely that the cell without CdS does not absorb/collect very well at longer wavelengths. The IPCE measurements are carried out without bias light or voltage. The IPCE characteristics of the \(S\)-shaped \(J(V)\) cells are not significantly distinguished from those with a ‘normal’ \(J(V)\) curve (not shown).

\(EIS\) Admittance spectroscopy revealed a CPE-like behavior for both samples, with and without CdS buffer layer, see Fig. 6.9.

### 6.5 Discussion and conclusions

From the theoretical treatment of tunnelling, it is clear that even an asymmetric energy barrier at the IL does not decrease the dark recombination current selectively to the light current. In this, the iso-energetic tunnelling picture was used which only holds when tunnelling occurs for example between two conduction bands, where an abundant amount of states is available for the described mechanism. There are however, no indications that this might be otherwise in our system. Literature explanations invoking a tunnel barrier ‘thick enough to decrease \(J_s\), but thin enough to leave \(J_f\) unaffected’ are thus incredible.

It is thus confirmed, here based on theory, that the dark saturation current and hence \(V_{oc}\) are determined by interface recombination, and chemical and electrostatic interactions at the interfaces, as suggested already several times in literature. Improvements in the performance of nanostructured solar cells are then attributed a decrease in interface recombination \([92]\). Our treatment shows that a rearrangement of the band diagram and Fermi levels at the interface is much more effective and probable than a reduction of interface state density to achieve this. Still, also pure materials reasons, such as avoiding interdiffusion of species during deposition, are possible, even probable \([53]\). Simple theory of course cannot give hints as how to realize these strategies.

\(^{(1)}\text{Anatase and rutile, together with brookite, are the three mineral forms in which TiO}_2\text{ is found. Rutile (often used in paint) is the most commonly occurring modification of TiO}_2\text{, and like anatase, it crystallizes in the tetragonal system.}\)
Figure 6.8: $J(V)$- and IPCE-curves of TiO$_2$|$\text{CuInS}_2$ 3D-cells with and without CdS buffer layer.

Figure 6.9: Admittance spectroscopy of TiO$_2$|$\text{CuInS}_2$ 3D-cells with and without CdS buffer layer.
Despite all these theoretical results, the insertion of the CdS IL did not improve the $V_{oc}$, only the $J_{sc}$. This might however only mean that the materials system TiO$_2$|CdS|CuInS$_2$ causes more problematic chemical and electrostatic changes at the interface than beneficial recombination reducing changes, probably due to the often observed ordered defect compound (ODC) layer at the CdS|CuInS$_2$ interface. In the next chapter for example, it will be shown that in case of an In$_2$S$_3$ IL, next to an improvement in $J_{sc}$, also an improvement of $V_{oc}$ is found.
Chapter 7

Charge carrier transport in TiO$_2$|CuInS$_2$ based 3D-cell

After the semi-systematic study on the most important materials system of this thesis, TiO$_2$|CuInS$_2$, and the influence of an intermediate layer on the cell performance, the focus is now on the dynamic properties of alike cells in order to obtain more insight in and/or evidence for the proposed underlying mechanisms. Two samples made by Marius Nanu (TUD) are studied: sample S1, with TiO$_2$ particle size 100 nm, and sample S7 with TiO$_2$ particle size 50 nm and In$_2$S$_3$ buffer layer. In this way, no new buffer layer related nor particle size related study was possible. On the other hand, at the first sample, also regions without porous layer were present, so that a comparison was possible between a flat and a nanostructured configuration of materials from the same deposition step; these regions are referred to as flat-S1 and nanoporous-S1, or np-S1, respectively.

7.1 Cell structures and steady-state performance

7.1.1 Sample S1

A picture of the first sample S1, containing both nanostructured and flat parts of the TiO$_2$|CuInS$_2$ system, is shown in Fig. 7.1. Its microscopic cell structure is built up as follows:

- glass with SnO$_2$:F TCO-coating as front contact layer;
- 80–100 nm flat and dense TiO$_2$ layer deposited by spray pyrolysis;
- 3 µm nanostructured n-type TiO$_2$ layer deposited by doctor blade;
- pore filling p-type CuInS$_2$ as absorber, deposited by ALD;
- 100 nm CuInS$_2$ topping, deposited in the same ALD-run;
- evaporated Au back contact, 2 mm diameter size, $A = 0.035$ cm$^2$.

The cell is pictured in Fig. 7.2. The TiO$_2$ particle size is 100 nm. One of the features of ALD are it's large penetration depth and uniform growth speed of the layers. However, these features are also preventing complete pore filling due to the clogging up of the ‘entrance’ of the pores before they can be completely filled. Some voids are therefore to be expected. The absorber is thin, i.e. 50 nm within the nanostructured network due to the limiting free space in the pores,
but not extremely thin, because the pores are almost totally filled and the cell is even ‘topped’ with a CuInS$_2$ layer of about 100 nm.

The absorption $A$ is determined as being the part that is not transmitted since losses due to reflection are neglected, i.e. $A = 1 - T$ where $T$ is the transmission. For this cell an absorption of 85% at 635 nm is measured and 82% at one sun. Further details of the cell are found in [93].

**$J(V)$** The efficiency of the cell under study is 0.3 %, mainly due to a lower $V_{oc}$ with respect to cells without porous TiO$_2$ layer, see Fig. 7.3a and b respectively. The figure for flat-S1 shows the two extremes that are found on the sample: a cell with diode-like behavior and a cell with higher $J_{sc}$ but with a roll-over effect for $V > V_{oc}$. The cell parameters are summarized in Table 3.1.

**IPCE** The results of the IPCE measurements are shown in Fig. 7.4 to 7.9. Figure 7.4a shows the influence of illuminated surface area on the results; both curves are calculated with the surface area of the mask in order to be able to compare the results with and without mask. Using a mask however, is the only reliable method to obtain reliable quantitative results. It is clear that upon applying a mask, the IPCE decreases drastically.

When carrying out the same experiment with illumination from the back side, i.e. through the Au contact, again a decrease is observed when a mask is applied (Fig. 7.4b); the absolute maximum ‘masked’ IPCE values for front side and back side illumination are in the same order, i.e. $\approx 10\%$, which suggests incomplete coverage of the area around the contact by the mask and a semi-transparent back contact.

All this also indicates that in general there is a significant contribution of carriers generated outside the contact area to the photocurrent, as well as the occurrence of significant scattering phenomena. The fact that in case of back side illumination only the longer wavelengths contribute might be ascribed to the deeper absorption depth of these longer wavelengths, i.e. the shorter wavelengths are absorbed too close to the back contact for the photogenerated electrons to reach the front contact through the TiO$_2$.

The influence of background light (BGL) on the measurements is shown in Fig. 7.5, for front and back side illumination. Since these are measurements without mask, no absolute values can be calculated. However, due to reasons given in Sect. 4.3.1, the influence of BGL is very
difficult to study when a mask is applied. The results show that BGL decreases cell performance with a factor 4 and 1.3 respectively. The results of the masked measurements are shown for completeness in Fig. 7.6; it shows that upon applying a mask, the influence of BGL becomes much less with respect to the unmasked results, i.e. almost zero.

Another feature of applying a mask that also showed up in Fig. 7.4a when no BGL was applied, is that the shorter wavelengths are cut out for which I don’t have an explanation. Again however, this picture is somewhat distorted.

The same measurements are carried out on flat-S1. For this cell, the influence of a mask at back side illumination without BGL is qualitatively the same though less than for np-S1, compare Fig. 7.4b with 7.7. The influence of BGL on backside illuminated masked cells is also qualitatively the same though more than for np-S1, see Fig. 7.6b and 7.8; for non-masked flat cells it is also quantitatively more than for np-S1, see Fig. 7.5b and 7.9b. Since in the flat configuration there is less TiO₂ to influence, and the TiO₂ is only encountered by the light after passing the CuInS₂, the findings suggest a larger photosensitivity of CuInS₂ with respect to TiO₂. This is confirmed by the fact that the influence of BGL on front side illuminated non-masked flat-S1 is about the same as for np-S1, though no relative decrease of shorter wavelength response is observed, see Fig. 7.5a and 7.9a. Instead, a decrease of longer wavelength response for flat-S1 is observed with respect to np-S1.

### 7.1.2 Sample S7

Since in other nanostructured TiO₂ based solar cells like the DSSC, better performances are obtained upon applying an interface layer (see Ch. 6), also the S1 sample has been given one: 

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Figure 7.2: Image of 3D-solar cell, cell structure from bottom (illuminated front contact) to top (back contact): glass|TCO|TiO₂(dense)|TiO₂(porous)|CuInS₂(fill-up) |CuInS₂(top)|Au.
Figure 7.3: $J(V)$ characteristics of two flat-S1 cells (a) and one np-S1 cell (b); the characteristics of the flat-S1 cells are the two extremes found on the sample: diode like behavior and roll-over behavior.

Figure 7.4: IPCE characteristics of masked and unmasked np-S1 cell at front side (a) and back side illumination (b); no BGL. Unmasked values are calculated as if the active surface area were that of the mask, this overestimates the IPCE; inset shows normalized curves.
Figure 7.5: IPCE characteristics of unmasked np-S1 cell at front side (a) and back side illumination (b); with and without 36 mW/cm² BGL.

Figure 7.6: IPCE characteristics of masked np-S1 cell at front side (a) and back side illumination (b); with and without BGL.

Figure 7.7: IPCE characteristics of masked and unmasked flat-S1 cell at back side illumination. Unmasked values are calculated as if the active surface area were that of the mask, this overestimates the IPCE; inset shows normalized curves.
Figure 7.8: IPCE characteristics of masked flat-S1 cell at back side illumination; with and without 36 mW/cm$^2$ BGL.

Figure 7.9: IPCE characteristics of unmasked flat-S1 cell at front side (a) and back side illumination (b); with and without 36 mW/cm$^2$ BGL.
an In$_2$S$_3$ buffer layer. The 15 nm ALD-In$_2$S$_3$ layer is inserted between the TiO$_2$ and ALD-CuInS$_2$ layer. The thickness of the buffer layer is not very critical, because a part of it will be converted into CuInS$_2$ anyway due to Cu diffusion. The CuInS$_2$ topping is 200 nm. The porous TiO$_2$ layer of the new sample has particle size 50 nm; the new sample is labelled S7.

**J(V)** Indeed an improvement in solar cell parameters is observed, see Fig. 7.10; the efficiency has raised from 0.3 to 1.6%, due to a more than doubled current density and $V_{oc}$. The cell parameters are summarized in Table 3.1.

**IPCE** The IPCE measurements in Fig. 7.11 demonstrate that there is hardly any influence left of applying a mask to front side illuminated samples. Moreover, no influence of BGL (mask or no mask) is observed either, see Fig. 7.12. So, in a way, the lateral conductivity has decreased a lot, in contrast to what is observed for sample np-S1, cf. Fig. 7.4a and 7.5a; the same can be concluded for the the sensitivity for BGL.

To conclude, a figure is included that shows the final performance data of the two 3D-cells under study in this chapter, see Fig. 7.13; a threefold increase is reported upon applying an In$_2$S$_3$ IL, i.e. disregarding the remarkable result that the same quantitative results are found for flat-S1 and np-S1, and that np-S1 and sample S7 differ from each other in TiO$_2$ particle size. Given the poorly defined surface area that actually contributes to the current, in particular among different set-ups, this is in good agreement with the 2.2-fold increase in $J_{sc}$ as shown in Fig. 7.3 and 7.10(a).

### 7.2 Dynamic behavior

The content of this section is the result of a bilateral cooperation between TUD (group of A. Goossens) and UGent, which has started as a part of the ETA-network and continued on an informal base after the expiry of the ETA-project. Since important results already have been gained in the field of DSSC’s from charge transport studies, and also recently the transport of

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(1) See also Table 3.1 for an overview of the cell performances of all the cells reported in this thesis.
Figure 7.11: IPCE characteristics of masked and unmasked S7 cell at front side illumination; no BGL. Unmasked values are calculated as if the active surface area were that of the mask, this overestimates the IPCE; inset shows normalized curves.

Figure 7.12: IPCE characteristics of masked (a) and unmasked S7 cell (b) at front side illumination; with and without 24 mW/cm$^2$ BGL.

Figure 7.13: IPCE characteristics of masked np-S1 and S7 cells at front side illumination with 24 mW/cm$^2$ BGL.
charge carriers in all solid-state DSSC's has been investigated [27], more insight in the 3D-cell was expected to be gained when a transport study would be carried out on this cell.

The cells under study here were not yet produced with the cheap deposition methods that the eta-project aimed at, but they were in any case reproducible and stable. A part of the results on the TiO$_2$|CuInS$_2$ system np-S1 presented here is also published in [94] and a part of those on the TiO$_2$|In$_2$S$_3$|CuInS$_2$ system S7 in [95].

7.2.1 Introduction

As already been explained, the 3D-cells S1 and S7 are interpenetrating networks of nanostructured TiO$_2$ and CuInS$_2$. A large density of traps in the 3D-TiO$_2$ is assumed, all of them higher in energy than the Fermi level thus empty in the dark. Under illumination, CuInS$_2$ absorbs the visible light, generating electron-hole pairs (phenomenon (1) in Fig. 7.14). The electrons are injected into the TiO$_2$ (2) and trapped, and the Fermi level in the TiO$_2$ moves up, thus increasing the concentration of conduction band electrons, until equilibrium is reached. The holes on the other hand move through the CuInS$_2$ towards the back contact, in absence of recombination (3). Recombination of electrons can occur though, by bulk recombination before injection with holes in deep defect levels in the CuInS$_2$ (4') or direct with valence band holes (4), or by interface recombination after injection of electrons from the TiO$_2$ with holes in the CuInS$_2$ (5) ([84] and Ch. 6).

To investigate the nature of electron and hole transport in 3D-cells, Intensity Modulated Photovoltage Spectroscopy (IMVS) and Intensity Modulated Photocurrent Spectroscopy (IMPS) has been used. The measurements are carried out at a range of bias voltages and background illumination intensities. Analysis is done by determination of the characteristic time constants $\tau_{\text{IMVS}}$ and $\tau_{\text{IMPS}}$, as well as simulation of the total characteristics, presented in Sect. 5.6. It is shown that 3D-cells exhibit a much faster photocurrent response than DSSC's; differences up to four orders of magnitude are measured. Since the same type of TiO$_2$ is used for 3D-cells and DSSC's, this is very surprising and strongly suggests completely different charge carrier dynamics.

7.2.2 Device characterization and simulation results

To begin with, it should be mentioned again that the real and imaginary values presented in the figures that follow, are not scaled and therefore can not be interpreted as real physical values.
Figure 7.15: Real part (o) and imaginary part (●) of opto-electrical IMVS transfer function $H_{\text{IMVS}}$ as a function of BGL illumination (increasing in the direction of the arrow), for a flat-S1 cell (a) and a np-S1 cell (b).

Figure 7.16: Characteristic time constant $\tau_{\text{IMVS}}$ as a function of BGL intensity and temperature, for all the samples studied in this chapter; $T = 293$ K if not stated otherwise.

See also Sect. 4.3.2 and App. A.

Sample S1

IMVS Figure 7.15 shows the IMVS-spectra of sample S1, represented by the real and imaginary components of the opto-electrical transfer function of the system. The characteristic time constant $\tau_{\text{IMVS}}$ is determined for all cases and plotted in Fig. 7.16, together with the values for sample S7 which will be discussed on page 93. For the highest illumination intensity, 705 W/m$^2$, it is $\approx 5$ $\mu$s.

IMPS - influence of BGL Figure 7.17 shows the IMPS-spectra of sample S1 as a function of BGL illumination intensity for different bias voltages; the Nyquist representation for np-S1 without bias voltage is shown in Fig. 7.18. Again, the characteristic time constants are determined; they are shown in Fig. 7.19. For BGL 705 W/m$^2$ and without bias voltage, $\tau_{\text{IMPS}}$ is 4.8 $\mu$s for flat-S1 which is a factor 1.3 smaller than $\tau_{\text{IMVS}}$ which is 6.5 $\mu$s. For np-S1, $\tau_{\text{IMPS}}$ is 3.6 while $\tau_{\text{IMVS}}$ is 4.8 $\mu$s, again a factor 1.3. In general, these values are more than a factor 1000 smaller than for DSSC’s.
7.2 Dynamic behavior

Figure 7.17: Real part (open symbols) and imaginary part (filled symbols) of opto-electrical IMPS transfer function $H_{\text{IMPS}}$ as a function of BGL illumination (increasing in the direction of the arrow) for a flat-S1 (a) and np-S1 cell (b–d), variable bias voltage.

**IMPS - influence of applied bias voltage** Figure 7.20 shows the spectra as a function of applied bias voltage for the two extreme BGL intensities. For the lowest intensity, i.e. 5 W/m², a significant voltage dependency is measured for the flat sample, which is not the case for 705 W/m², see also Fig. 7.21; this plot again includes ‘future’ values for sample S7 as well.

**Simulations** Although in Ch. 5, relations are deduced that connect the IMPS and IMVS time constants with some physical parameters (summarized in Table 5.1), the results are also simulated directly in order to obtain all parameters, thus providing a check as well. For this, Eq. (5.18) is used, with $H_{\text{IMPS}}$ given by Eq. (5.22).

During the simulations, the effective absorption coefficient $\alpha$ has been given a fixed value, $6.5 \times 10^3$/cm. At this value, a layer of bulk CuInS$_2$ absorbs 85% of 635 nm light, like our sample does (Sect. 7.1). Also the cell thickness $\ell$ has been kept at a fixed value, 3.2 $\mu$m, determined from the TUD-data concerning the cell structure. The variables are therefore the effective diffusion coefficient $D_n$, the effective lifetime of injected electrons $\tau_n$ and the RC-time of the external measuring circuit. During the simulations, most attention was given to the reproduction of the minimum of the imaginary part, i.e. the characteristic time constant. Then, the real part for $\omega \to 0$ was taken care of. At last, the influence of the RC-time was checked, represented by the expansion of the Nyquist curve into the negative real quadrant.

Figure 7.22 shows the result for np-S1. For 705 W/m² for example, the parameters were $D_n = 2.3 \times 10^{-6}$ cm$^2$/s, $\tau_n = 7 \mu$s, and RC-time = 0.4 $\mu$s, which gives a diffusion length $L_n$ of 40 nm. Figure 7.29 summarizes the evolution of the model parameters upon illumination, including already those of sample S7. A striking feature is the overall decrease of both electron life time and diffusion coefficient upon increase of illumination, which is just the opposite as
Figure 7.18: Nyquist representation of opto-electrical IMPS transfer function $H_{\text{IMPS}}$ of np-S1 cell, no bias voltage, variable BGL illumination.

Figure 7.19: Characteristic time constant $\tau_{\text{IMPS}}$ as a function of BGL intensity for all the samples studied in this chapter; variable temperature ($T = 293$ K if not stated otherwise); variable bias voltage (-0.4 V (a), 0 V (b), 0.7 V (c)).
Figure 7.20: Real part (⊙) and imaginary part (●) of opto-electrical IMPS transfer function $H_{\text{IMPS}}$ as a function of bias voltage (increasing in the direction of the arrow) for a flat-S1 cell (a,b) and a np-S1 cell (c,d), variable BGL illumination.
Figure 7.21: Characteristic time constant $\tau_{\text{IMPS}}$ as a function of bias voltage for all the samples studied in this chapter; variable temperature ($T = 293 \text{ K}$ if not stated otherwise); variable BGL intensity (5 W/m$^2$ (top), 705 W/m$^2$ (bottom)).
Figure 7.22: Measurements (o) and simulations (line) of imaginary part (top) and Nyquist representation (bottom) of opto-electrical IMPS transfer function $H_{\text{IMPS}}$ as a function of BGL illumination (increasing in the direction of the arrow) for a np-S1 cell, no bias voltage.

reported for DSSC’s.

Figure 7.23 shows the simulation results as a function of applied bias, see also Fig. 7.30. As for the characteristic time constant $\tau_{\text{IMPS}}$, also now no significant influence of bias voltage is found for the electron lifetime $\tau_n$. The diffusion coefficient however, decreases from reverse to forward bias voltage, as it did for increasing BGL.
Figure 7.23: Measurements (○) and simulations (line) of imaginary part (top) and Nyquist representation (bottom) of opto-electrical IMPS transfer function \( H_{\text{IMPS}} \) as a function of bias voltage (increasing in the direction of the arrow) for a np-S1 cell, 705 W/m\(^2\) BGL illumination.
7.2 Dynamic behavior

Figure 7.24: Real part (♦) and imaginary part (●) of opto-electrical IMVS transfer function $H_{\text{IMVS}}$ of $S7$ cell, 0 V bias voltage, variable BGL illumination (increasing in the direction of the arrow) and temperature.

Sample S7

All measurements are carried out at two different temperatures: 293 and 330 K.

IMVS Figure 7.24 shows the IMVS-spectra of sample S7. The characteristic time constant $\tau_{\text{IMVS}}$ for 705 W/m$^2$ is now 8.7 $\mu$s, an increase of almost a factor 2 with respect to sample np-S1. The values for all $\tau_{\text{IMVS}}$ time constants are pictured in Fig. 7.16.

IMPS - influence of BGL Figure 7.25 shows the influence of illumination for sample S7. The characteristic time constant $\tau_{\text{IMPS}}$ for BGL 705 W/m$^2$ and without bias voltage has increased with a factor 3 to 10 $\mu$s with respect to sample S1. Hence, $\tau_{\text{IMPS}}$ is larger than $\tau_{\text{IMVS}}$ for S7 (factor 1.1), whereas $\tau_{\text{IMPS}}$ was smaller than $\tau_{\text{IMVS}}$ for S1 (factor 1.3). Moreover, the illumination dependence disappears with increasing temperature. All values for $\tau_{\text{IMPS}}$ are summarized in Fig. 7.19.

IMPS - influence of applied bias voltage Fig. 7.26 shows the influence of bias voltage, the values for $\tau_{\text{IMPS}}$ are presented in Fig. 7.21. For 705 W/m$^2$, a much more significant voltage dependency is observed than for sample S1. Moreover for 5 W/m$^2$, a decrease in characteristic time constant is observed for increasing reverse bias as was for flat-S1.

Simulations Figure 7.27 shows the simulation results for the case without bias voltage. In particular the negative slopes of the imaginary curve for low intensities and high temperature were difficult to represent. This goes together with a large error in the correspondence of the real part for $\omega \rightarrow 0$. Figure 7.28 shows the simulation results for applied bias voltage. Also here it is clear that, in case of far reverse bias, the model is not sufficient to describe the measurements. The already introduced figures 7.29 and 7.30 demonstrate the evolution of the parameters upon illumination and bias voltage, for both sample S1 and S7. In general, they show a decrease of diffusion coefficient and electron life time with increasing illumination intensity and higher forward bias.
Figure 7.25: Real part (♦) and imaginary part (⋄) of opto-electrical IMPS transfer function $H_{\text{IMPS}}$ of $S7$ cell; variable bias voltage (a–c); variable BGL illumination (increasing in the direction of the arrow) and temperature (filled symbols 293 K, open symbols 330 K).

Figure 7.26: Real part (♦) and imaginary (○) of opto-electrical IMPS transfer function $H_{\text{IMPS}}$ of $S7$ cell; variable bias voltage (increasing in the direction of the arrow) and BGL illumination (a,b), and temperature (filled symbols 293 K, open symbols 330 K).
Figure 7.27: Measurements (open symbols) and simulations (lines) of imaginary part (top) and Nyquist representation (bottom) of opto-electrical IMPS transfer function $H_{\text{IMPS}}$ as a function of BGL illumination for a S7 cell; variable temperature, no bias voltage.
Figure 7.28: Measurements (open symbols) and simulations (lines) of imaginary part (top) and Nyquist representation (bottom) of opto-electrical IMPS transfer function $H_{\text{IMPS}}$ as a function of bias voltage for a S7 cell, 705 W/m² BGL illumination.
Figure 7.29: Evolution of diffusion model parameters $D_n$, $\tau_n$ and $RC$-time as a function of BGL illumination intensity for np-S1 and S7, $T = 293$ K if not stated otherwise, no bias voltage.
Figure 7.30: Evolution of diffusion model parameters $D_n$, $\tau_n$ and $RC$-time as a function of bias voltage for np-S1 and S7, $T = 293$ K if not stated otherwise, 705 W/m² BGL.
7.2 Dynamic behavior

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<th>α (10⁴/cm)</th>
<th>Dₑ (10⁻⁶ cm²/s)</th>
<th>τᵣ (µs)</th>
<th>RC-time</th>
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<td>0.4 ms</td>
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<td>5.9</td>
<td>6.0</td>
<td>30 µs</td>
<td>0.4 ms</td>
<td></td>
<td></td>
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<td>2.8</td>
<td>4.1</td>
<td>1.4 s</td>
<td>1.6 s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.1: Upper part: Diffusion model parameters for several three-dimensional solar cells, of which ℓ, and α in case of np-S1 and S7 are fixed values (F), determined from other measurements, the other parameters are obtained by fitting (DSSC [62]) and simulating (other [this work]); the values for S7 are interpolated values. Lower part: calculations using diffusion model parameters from upper part; diffusion length Lₑ calculated according to \( \sqrt{Dₑτₑ} \), the IMPS and IMVS time constants according to the first order approximation for case 4,5,6 of Table 5.1.

7.2.3 Discussion

**Time constants** From the measurements of the opto-electrical transfer function, it becomes clear that our solid-state version of the DSSC shows a more than 1000 times faster response than its organic liquid counterpart [62]. Despite the fact that the 3D-cells S1 and S7 are only 3 µm thick and the DSSC typically 10 µm, this is a remarkable result; this difference only could account for a response that is about 5 times faster. Also the difference in TiO₂ particle size (50–100 nm instead of 25 nm in a DSSC) does not provide the missing link.

This link might be deduced from Table 7.1, in which the results are summarized for the diffusion model parameters. The values that are shown are for moderate illumination intensities in order to be able to compare with the DSSC of which no data were found for higher illumination intensities.

First, we see that the diffusion coefficient is the same for all the samples, which can be interpreted as a confirmation for the TiO₂ being the same type in all samples. The main difference is found in the electron lifetime; a 10⁴-fold decrease of electron lifetime is found for the 3D-cells S1 and S7. This strongly indicates a much higher recombination rate.

Similar results for dye sensitized heterojunction are found by O'Regan et al. [27]. Transient photocurrent and photovoltage measurements cells revealed that the charge transport was similar to that in dye sensitized electrolyte cells. Recombination at short circuit however is 100 times faster. Moreover, the charge transport and recombination rates are of the same order, resulting in a low fill factor and photocurrent losses.

**Influence of illumination** Another remarkable result is that a (slight but significant) decrease of diffusion coefficient is observed with increasing illumination intensity, which is just the opposite of what is found for DSSC’s.

This observed inverse relationship with respect to the illumination intensity is also observed for the real part for low frequency. The decrease of IPCE value was also found in the IPCE measurements, which is also just the opposite as reported for DSSC’s [96].

In combination with the very small electron lifetime, I would say that the electrons do not
get the chance to fill the traps upon higher illumination as they do in DSSC’s, for they recombine immediately. This is also reflected in the small $RC$-time which represents the inability of the TiO$_2$ to store charge. Because there is no charge to store.

**Influence of applied bias voltage** A voltage dependence of the characteristic time constant is observed for sample S7. Therefore, a macroscopic electric field might thought to be present, providing an additional driving force for charge transport. Moreover, a macroscopic electric field should make the response faster upon applying a reverse bias voltage, which is exactly the case. The fact that the diffusion model also does not seem to be suitable to describe the measurements (width of imaginary dip has become too broad to simulate with the model), is another indication. For the S1 cell, this effect is not observed.

In general however, the driving force for transport in the cells has to be sought in the selectivity of contacts, resulting in a gradient in the majority carrier density at the contacts, and in general concentration gradients of $n$ and $p$ through-out the cell, in other words, diffusion. The driving force for charge carrier injection has therefore to be sought in:

- an effective force that drives generated electrons to the TiO$_2$, this is caused by a difference in electron affinity resulting in a conduction band discontinuity $\Delta E_c = q\Delta \chi$ which is $> 0$;

- a dipole layer at the interface resulting in a conduction band discontinuity as well, $\Delta E_c$ is now $q(\Delta \chi + \delta)$ with $\delta$ the potential drop over the dipole layer.

In the 3D-sample, requirement (i) is surely met, thus establishing a driving force for charge carrier injection: $\Delta E_c = 0.3$ eV

The question of electron or hole transport could be addressed by carrying out the experiment with laser light of shorter wavelengths and to illuminate through the back contact. Due to time restrictions, this has not been done.

### 7.3 Electrical behavior

The electrical behavior of the S7 system is studied by means of its capacitive response in the dark to a modulated voltage by the EIS technique; the data are plotted as circles in Fig. 7.31. A first look teaches that the absolute values for the capacity are very large; there seems to be a significant influence on the capacitive behavior of the supposed enlargement of the interface area with respect to flat cells. In the effective medium approach that is used for further analysis, the enlargement of surface area is reflected in the effective materials parameters.

The measurements are analyzed in different ways. First, the same analytic diffusion model is used that was used for the analysis of the IMVS and IMPS spectra. Figure 7.31 shows the data as well as the simulation results. Two curves are drawn in the figure. The grey solid line is calculated from Eq. (5.17) with the same parameters that were determined from the IMPS spectra (no bias voltage, lowest illumination intensity), the black solid line is calculated using $D_n = 2.9 \times 10^{-6} \text{ cm}^2/\text{s}$ instead of $D_n = 6.9 \times 10^{-6} \text{ cm}^2/\text{s}$, and $\tau_n = 200 \mu\text{s}$ instead of $29 \mu\text{s}$. In both cases, $7 \times 10^{15} \text{ /cm}^3$ is used for $n_{eq}$.

Then, the diffusion model deduced from infinite network theory is used to analyze the $Y$-from-IMPS-curve and the data-curve. For this, Eq. (5.1) on page 43 is used together with $Y(\omega) = 1/Z(\omega)$ and $C(\omega) = \text{Im}[Y(\omega)]/\omega$. $R_{sn}$ is taken to be 0.23 and 0.19 $\Omega$, $R_{||} = 12.6 \text{ k}\Omega$ and $52.3 \text{ k}\Omega$, and $C = 2.8 \text{ nF}$ and $3.4 \text{ nF}$. 

7.4 Discussion

Determination of diffusion coefficient

Some remarks should be made on the values of $D_n$ obtained from the simulations. The value of $D_n$ is depending for a great deal on the Re[$H_{\text{IMPS}}$] value of the measured data. There can however, be a significant error in this value, because although the scaling factor $\mathcal{SF}$ that is needed to relate the measured data to real physical values, is determined with great care, an uncertainty of at least 10% is expected. As explained in Appendix A, this is the very reason for the fact that all IMPS and IMVS data presented in this thesis are not corrected for this scaling factor. Of course it was taken into account during the simulations, by multiplying the simulation formula with $1/\mathcal{SF}$. The value of $D_n$ is also depending for a great deal on the assumed value for $\alpha$; in the model, a change with a factor $F$ of the fixed parameter $\alpha$ can be totally cancelled out by multiplication of $D_n$ (simulation parameter) with $1/F^2$.

Discussion

It is clear that both diffusion models describe exactly the same physical situation. However, they are only correct for $f > \frac{1}{2\pi R_{\text{eq}} C} = 4.5$ kHz. The same sort of deviation is seen in the IMPS simulations, i.e. the analytic diffusion model fails to describe the features for low illumination and frequencies below 10 kHz. This also reflected in a simulated Re[$H_{\text{IMPS}}$] which is structural too low for low frequency and low illumination.

The fact that a better, though still not perfect, fit is obtained (black solid and dotted lines) upon assuming an almost 10 times larger lifetime indicates again the strange behavior of a better performance in the dark. This argument holds in particular when the difference in EIS and IMPS background light conditions is recalled; the EIS measurements are carried out in total darkness, whereas ‘dark’ in the case of IMPS means 50 W/m$^2$ illumination intensity (see Sect. 4.5).

A last remark concerns the adjustment of $D_n$ (assumed to be more than two times smaller for a correct fit). The same fit also could have been obtained with keeping $D_n$ fixed and change $n_{\text{eq}}$ with the same factor that was needed for $D_n$. 

Figure 7.31: EIS spectra: measurement on sample S7 and simulated infinite diffusion network.
The reason for both dependencies is found in Table 5.1. We already have found that our cells are representing case 4 and 5 of this table, i.e. the diffusion length is very small compared to both the absorption depth and the cell thickness. In that case, it follow right from the table itself that Re[$H_{\text{IMPS}}(\omega \to 0)$] = $\alpha \sqrt{2D_n \tau_{\text{IMPS}}}$. This means that the final obtained value of $D_n$ by simulation strongly depends on the assumption or determination of $\alpha$ and the scaling of $H_{\text{IMPS}}$. Therefore only conclusions in terms of order of magnitude of $D_n$ (and hence $L_n$) can be drawn.

**Illumination dependence of model parameters**

During the simulations, an illumination and even voltage dependence of the simulation parameters has been allowed. The question might arise if this is right.

First, a distinct cross-over of light and dark $J(V)$ curves is measured which normally is ascribed to illumination dependence of electronic properties [75, 97]. This makes for example that for $V_{\text{bias}} > V_{\text{cross-over}}$, negative values for the real part are found. Moreover, the illumination dependence of diffusion coefficients as well as IPCE values is found also in DSSC’s, albeit an the inverse relationship as is found here.

### 7.5 Conclusions

- From the simulations, it can be concluded that the diffusion model of an effective medium cell describes the cell rather well.

- Moreover, the partial EMM approach as well as the infinite network approach to the diffusion model represent the effective medium in the same way, i.e. they deviate from practice in the same way.

- So, the infinite network model very well represents both time-resolved electrical phenomena and the steady state phenomena of nanostructured solar cells [73, 83].

- A similar model with two free parameters describes the IPCE (i.e. low frequency limit of IMPS), and IMPS.

- The analytic approximations revealed that the cell is in the condition $L_n \ll (\ell, 1/\alpha)$. Then, $\tau_{\text{IMPS}} = \tau_n / 2$, $\tau_{\text{IMVS}} = \tau_n$ (a factor 1.3 is reported), and IPCE = Re[$H_{\text{IMPS}}$] | $\omega \to 0$ = $\frac{aL_n}{aL_n + 1} \approx \alpha L_n < 1$. On the contrary, for DSSC’s it is found that $L_n \gg (\ell, 1/\alpha)$, and IMPS is determined by diffusion transport.

- The huge difference in electron lifetime, i.e. $\tau_{3D} = 10^{-5} \tau_{\text{DSSC}}$, results in $L_{3D} = L_{\text{DSSC}}/500$, which makes indeed the difference between $aL_n \ll 1$ and $aL_n \gg 1$. If $J_s \sim 1/\tau$ is assumed, then a difference of $V_{oc}$ for a 3D-cell with respect to a DSSC is estimated to be $\Delta V_{oc} = -kT/q \ln 10^3 = -175$ mV. If $J_s \sim 1/\sqrt{\tau}$ is assumed, then the difference is estimated to be $\Delta V_{oc} = -kT/q \ln 500 = -150$ mV. Moreover, IPCE | $\text{DSSC} \approx 1$, and IPCE | $\text{3D} \approx aL_n \approx 0.25$. Indeed this is measured for the 3D-cell.

- Interface engineering is absolutely necessary to limit the recombination in 3D-cells.
Chapter 8

ETA-cell

8.1 Materials and cell structures

As has been pointed out in Sect. 3.4, the ETA-solar cell is designed according to a concept that applies an Extremely Thin inorganic Absorber layer at the interface of a transparent nano- or microstructured \textit{pn}-heterojunction, \textit{e.g.} \textit{n}-\textit{TiO}_2 | \textit{p}-CuSCN. The first ETA-solar cell was developed at the Hahn-Meitner Institute (HMI) in Berlin, an ETA-partner, and is pictured as in Fig. 8.1a [16]; it is based on a microstructured \textit{TiO}_2 substrate. As can be seen in b, also nanostructured based ETA-cells exist. Of both varieties, one is studied in this chapter.

8.2 Microstructured \textit{TiO}_2 | \textit{Cd(Hg)Te} based ETA-cell

8.2.1 Introduction

The work discussed in the first part of this chapter deals with microporous ETA-cells that were fabricated at the HMI [98], and is based on ref. [28]. The cells consist of a \textit{p}-type \textit{CdTe} ETA-layer on a microporous \textit{n}-type \textit{TiO}_2 substrate, see Fig. 8.2. The transparent hole conductor and back contact are replaced by only one metal contact, \textit{i.e.} Au. The \textit{TiO}_2 is deposited with spray pyrolysis and the \textit{CdTe} absorber with electrodeposition. The \textit{J}(\textit{V}) and IPCE characteristics of these cells show some typical features; its illuminated \textit{J}(\textit{V}) curves for example are \textit{S}-shaped. IPCE(\textit{\lambda}) curves were measured under forward and reverse voltage bias, and under front or back side illumination. Here, we investigate whether the particularities of these characteristics can be attributed to the materials properties of \textit{CdTe} and \textit{TiO}_2, or that they are caused by

Figure 8.1: Schematic drawing of the ETA-solar cell, based on a microporous (a), and a nanoporous (b) \textit{n}-type electrode [98].
the complicated three-dimensional geometrical structure of the ETA-cells. To that purpose, the photovoltaic properties of the cells are measured and analyzed using SCAPS-1D, the quantitative simulation model that is being explained in Sect. 5.4.1. Although this is intended for one-dimensional modelling of planar thin film (µm-range) solar cells, it does simulate the typical features of the \( J(V) \) and IPCE(\( \lambda \)) curves rather well. A fair simulation of the experimentally measured S-shaped \( J(V) \) curves is obtained, as well as a qualitative simulation of the measured IPCE(\( \lambda \)) curves, by the assumption of a rather large conduction band offset (conduction band of CdTe 0.7 eV higher than of TiO\(_2\)) together with tuning of CdTe material parameters doping concentration and electron lifetime.

### 8.2.2 Experimental observations

A cell with promising cell parameters consisting of porous TiO\(_2\) as transparent \( n \)-type layer and CdTe as \( p \)-type absorber was recently reported \[98, 36\]. The porosity of the TiO\(_2\) layer was in the micrometer range rather in the nanometer range, resulting in an enhancement of surface area with a factor 10. The film consists of crystals of 5–15 nm. The local, or microscopic, CdTe thickness of the best cells is 130 nm.

The measured \( J(V) \) characteristics of this cell are shown in Fig. 8.3 (grey and black ●). The light curves show a voltage dependent collection, and are S-shaped; with \( V_{oc} = 0.67 \) V, \( J_{sc} = 9 \) mA/cm\(^2\) and \( FF = 0.20 \). Also there is a slight cross-over of the dark and light \( J(V) \) curves, a feature typical for thin film CdTe and Cu(In,Ga)Se\(_2\) solar cells \[75, 97\].

### 8.2.3 Model and discussion

The one-dimensional simulation program SCAPS is used for simulation of the \( J(V) \) and IPCE characteristics. For this, the ETA-cell under study is represented by a planar stack of semiconductor layers, hence inherently neglecting the complex morphological and optical structure of the cell. Therefore, the value of several physical parameters are regarded as effective values. For the effective absorber thickness in the planar model, we take the optical thickness of the ETA-layer, which is 1.3 µm (surface area enhancement × microscopic thickness). The values taken for the other parameters are summarized in Table 8.1.

### \( J(V) \)

The result of the \( J(V) \) simulations are presented in Fig. 8.3 (solid lines), together with the data. The material parameters which actually had the strongest influence on the shape of the \( J(V) \) curves are the electron affinity of TiO\(_2\) (giving rise to a conduction band offset between
Figure 8.3: Measured dark and light $J(V)$ curves of a TiO$_2$|CdTe ETA-cell [36] under 100 mW/cm$^2$ AM1.5 illumination (●), simulated dark and light $J(V)$ curves of a planar TiO$_2$|CdTe-heterojunction under 65 mW/cm$^2$ AM1 illumination; simulation parameters are found in Table 8.1.

<table>
<thead>
<tr>
<th>parameter</th>
<th>TiO$_2$</th>
<th>reference</th>
<th>CdTe</th>
<th>reference</th>
</tr>
</thead>
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<tr>
<td>$\phi$ (eV)</td>
<td>flat-band</td>
<td>0–0.5 arb.</td>
<td>1.3 opt. thin. [43]</td>
<td></td>
</tr>
<tr>
<td>$d$ (µm)</td>
<td>0.5 [43]</td>
<td>1.5 [99]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
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<td>4.3 [43]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi$ (eV)</td>
<td>5.0 var.</td>
<td>10$^{-4}$ mean lit.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\epsilon/\epsilon_0$</td>
<td>40</td>
<td>10 $([99]+[43])/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CB eff DOS (/cm$^3$)</td>
<td>10$^{20}$ [43]</td>
<td>10$^{18}$ $([99]+[43])/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VB eff DOS (/cm$^3$)</td>
<td>10$^{17}$–20 arb.</td>
<td>10$^{19}$ $([99]+[43])/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_{th}$ (cm/s)</td>
<td>10$^7$ [99] (ZnO)</td>
<td>10$^7$ [99]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_e$ (cm$^2$/V$s$)</td>
<td>10$^{-4}$ var.</td>
<td>100 $[43]&lt;\mu_e&lt;[99]$</td>
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<td></td>
</tr>
<tr>
<td>$N_e$ (/cm$^3$)</td>
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<td>2$\times10^{14}$–16 arb.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_i$ (/cm$^3$)</td>
<td>10$^{15}$–16 arb.</td>
<td>2$\times10^{16}$ var.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>defect type</td>
<td>acc [43] but arb.</td>
<td>donor [99]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_n$ (cm$^2$)</td>
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<td>10$^{-11}$ var.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma_p$ (cm$^2$)</td>
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<td>5$\times10^{(10–14)}$ arb.</td>
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</tr>
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<td>gauss</td>
<td>gauss [99]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_i$ (from VB)</td>
<td>2/3 of $E_g$</td>
<td>mid-gap [99]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{bat}$ (eV)</td>
<td>0.2</td>
<td>0.1 [99]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>spatial distribution</td>
<td>constant</td>
<td>constant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_r$ left (/cm$^3$eV)</td>
<td>$10^{15}$</td>
<td>$5\times10^{15}$ var.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L_n$ from defect (nm)</td>
<td>54 calc.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L_p$ from defect (nm)</td>
<td>540 calc.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.1: Simulation parameters for the TiO$_2$|CdTe ETA-cell, based on, but slightly modified from [28]; ‘arbitrary’ means no influence in the range given, ‘variable’ means influence on final performance but not on the S-shape, ‘variable’ means influence on final performance and on the S-shape, influence shown in other pictures; in addition, a neutral density filter with ND = 0.19 is used.
the CdTe and TiO$_2$), and the doping concentration in CdTe (both labelled with variable in the table).

This is illustrated in Fig. 8.4, where these crucial parameters are varied over a wide range around the values listed in Table 8.1. The influence of the conduction band offset $\Delta E_c = \Delta \chi = \chi_n - \chi_p$ on the $J(V)$ curves is shown in Fig. 8.4a. It is seen that an increase of $\Delta E_c$ results in a more pronounced S-shape, and the occurrence of a flat plateau in the $J(V)$ curves near open circuit. $\Delta E_c$ was modified by changing the electron affinity $\chi_n$ of TiO$_2$ whilst keeping the electron affinity $\chi_p$ of CdTe at a constant value of 4.3 eV. We did so because CdTe is perhaps the best characterized material of the two. However, varying $\chi_p$ and keeping $\chi_n$ constant yields the same result, for SCAPS deals with $\Delta \chi$, and simulations at this particular cell set-up show that the back contact barrier for holes is not significantly influenced by this alternative approach. The influence of the acceptor concentration $N_a$ in CdTe is shown in Fig. 8.4b. A low CdTe doping gives rise to a more pronounced S-shape, and a softer bend in the $J(V)$ curve around the maximum power point.

The following parameters have no such direct relationship with the S-shape but they seriously influence the device performance (all labelled with ‘variable’ in Table 8.1). When taking $N_{a,\text{TiO}_2}$ 10 times lower for example, the S-shape disappears but also the current ($J_{sc}$ is halved), as does a 10 times decrease of $\mu_{e,\text{TiO}_2}$. Increasing the electron lifetime $\tau_n$ in CdTe by a reduction of $\sigma_n$ or $N_p$ improves the cell and in particular the current; the S-shape does not change however. The defect in the TiO$_2$ which is found in the literature by [43], turns out to be totally unimportant (‘arbitrary’ in the table), as is the often reported barrier $\phi$ at the back contact. A neutral density filter of ND = 0.19 is inserted in front of the cell to account for all possible current losses related to the large internal surface area of the cell which is not present in the planar model. The cross-over of light and dark $J(V)$ curves at a voltage higher than $V_{oc}$ is not taken care of in the simulations. No specific effort was made either to simulate the measured $V_{oc}$. This deviation is ascribed to all possible voltage losses inherent to the three-dimensional nature of the cell that might influence the voltage, in particular those connected with the large internal surface area.

Figure 8.5 demonstrates in detail how a conduction band offset results in an S-shaped $J(V)$ curve. In it, the calculated band diagram of a TiO$_2$/CdTe structure is shown for various values of the applied voltage (only the conduction band is shown). The offset value $\Delta E_c = 0.7$ eV is assumed here. At a forward bias voltage of 0.5 V, the band bending disappears and a barrier occurs for the electrons which are generated in CdTe to reach the junction and contribute to the current. This barrier reduces the collection of electrons for no electric field is present anymore in the space charge layer. This is the reason why the simulated light $J(V)$ curve flattens at 0.5 V, giving rise to the S-shape.

Spectral response The spectral response of the ETA-cell of Fig. 8.3 was measured with monochromatic illumination incident on the TiO$_2$ front side or on the CdTe back side without BGL. The bias voltage was varied from 0.4 V reverse to 1 V forward. The measurements were carried out at and by the HMI.

It is a touchstone for the planar cell model presented in the foregoing section to simulate the IPCE$(\lambda, V)$ characteristics with the same model and parameters. The front side IPCE$(\lambda, V)$ curves are shown in Fig. 8.6a (measured) and b (simulated). The back side IPCE$(\lambda, V)$ curves are shown in Fig. 8.7a (measured) and b (simulated). The figures show that the general form of the front and back IPCE$(\lambda, V)$ curves actually is simulated in a qualitative way, i.e. the gross features of the measurement also appear in the simulation. These are in particular the regular decrease of IPCE with increasing forward bias voltage, and even some minor effects such as the occurrence of a small peak at $\lambda \approx 400$ nm under front side illumination and high forward
Figure 8.4: Influence of conduction band offset $\Delta E_c$ (a) and doping concentration in CdTe (b) on the $J(V)$ curves presented in Fig. 8.3 (framed values); all other parameters are found in Table 8.1.

Figure 8.5: Conduction band energy at a distance $x$ from the back contact as a function of applied voltage, normalized to the energy at the interface; conduction band offset $\Delta E_c = 0.7$ eV. Note the barrier for the electrons in the CdTe at the junction, i.e. at $x_{\text{interface}}$, when $V > 0.5$ V.
bias (0.8 V). The negative value for the measured IPCE for \(V = 0.8\) V is not simulated by the model. Not unexpectedly, because it comes from the cross-over of light and dark \(J(V)\) curves for a higher voltage, and this very phenomenon has not been simulated in the \(J(V)\) characteristics either.

However, the agreement between measured and simulated curves is worse for the spectral response than it was for the \(J(V)\) curves. This is now discussed further.

Under front side illumination, there is a large drop in IPCE at forward bias, which is also observed in the simulations (compare Fig. 8.6a with b, curves 0–0.6 V). Under back side illumination though, there is a large drop when the bias voltage passes from \(-0.1\) V (slightly reverse) to 0 V (no bias) which does not appear in the simulations (compare Fig. 8.7a with b). Moreover, the slope in the 400–800 nm range of the measured IPCE(\(\lambda, V\)) curves at front side illumination clearly is less steep than the modelled result. Also, the measured back side characteristics give a measurable IPCE value for \(\lambda < 500\) nm while the simulated IPCE yields zero. The latter two discrepancies can be attributed to differences between the actual microporous structure and the simulated planar structure in terms of morphology.

The absorption depth (= \(1/\alpha\)) in CdTe varies from \(\approx 40\) nm at a short wavelength \(\lambda = 400\) nm, to \(\approx 400\) nm for a long wavelength \(\lambda = 800\) nm [100] (note that SCAPS uses experimental values for \(\alpha\)). Long wavelength light is thus absorbed relatively far from the surface. In a planar configuration this also means far from the junction, with resulting low collection. In the microporous configuration, the light has the possibility to travel not only perpendicularly, but also laterally with respect to the plane of incidence, so that even the longer wavelengths are absorbed near to the front contact. This is an advantage if the cell’s behavior is assumed to be determined by the transport of electrons in the TiO\(_2\) and not by the transport of holes in the CdTe (as is done before, number 1 and 2 on page 48). In this way, a higher collection efficiency for the longer wavelengths is possible, represented by a less steep decrease of the IPCE in the measured IPCE(\(\lambda, V\)) compared with the simulated ones.

Short wavelength light on the other hand, is absorbed immediately at the surface. In a planar configuration, at back side illumination, this region is too far from the junction for the electrons to get collected; they are the minority carrier in the absorber. In an extremely thin absorber layer, the collection of the electrons generated by short wavelength light benefits therefore from the fact that the junction is much more close to the illuminated surface. This explains the better performance at short wavelengths (\(\lambda < 500\) nm) of the measured IPCE curves with back side illumination compared with the simulated curves.

### 8.2.4 New results on CdHgTe (HMI)

Based on the above reported results, the HMI group added Hg to the CdTe absorber films in order to obtain Cd\(_x\)Hg\(_{1-x}\)Te (CMT), an absorber with a smaller band gap than CdTe [101]. In the CdTe and (Cd,Hg)Te lattices, the Te-ion sublattice is the same. As a rule of thumb, one often assumes that the VB edge of both materials is at the same level with respect to the vacuum level, and that the difference in band gap \(\Delta E_g\) is completely taken up as a difference in conduction band edge level, \(\Delta E_c = \Delta E_g\). This is the so called ‘common anion rule’. Hence, if Hg is added to CdTe, one expects a decrease of the conduction band edge resulting in particular in an improvement in \(FF\), based on the above discussed findings.

Figure 8.8a shows the \(J(V)\) curves of a CMT cell of which the band gap is determined to be 1.3 eV [101]. For this particular cell, the \(FF\) enhances indeed, \(i.e.\) from 20 to 30%. According to a figure of the \(J(V)\) curves in [101] however, no significant change is observed for the CMT cell with respect to the CdTe cell discussed earlier. This is explained by the fact that not all CMT
Figure 8.6: Measured (a) and modelled (b) IPCE(λ, V) curves without light bias under different voltages; illumination through front contact (TiO$_2$ side).
Figure 8.7: Measured (a) and modelled (b) IPCE(\(\lambda, V\)) curves without light bias under different voltages; illumination through back contact (CdTe side).
cells show improvement; mapping of all the cells on the sample substrate shows that only a few cells display a better FF, or diminished S-shape, see Fig. 8.9.

A simulation based on the parameter set for the CdTe cell (but with $E_{g,CMT} = 1.3 \text{ eV}$ and $\Delta E_c = 0.5 \text{ eV}$) revealed that $N_{a,CMT}$ needed to be lowered with an order of magnitude (now $2\times10^{15} / \text{cm}^3$), and that the electron lifetime $\tau_n$ in the CMT needed to be increased with a factor 25; the simulation is shown in Fig. 8.8b. This result confirms again the negative influence of a conduction band offset and a low absorber doping density on cell performance of Cd$_x$Hg$_{1-x}$Te|TiO$_2$ based ETA-cells.

8.2.5 Discussion

The investigations of the wavelength and voltage dependencies of the photocurrent reveal, that in particular the spectral behavior can not be fully explained by a simple planar cell structure. This confirms the need of descriptions of the cell with effective parameters, like those presented
in Ch. 5. However, it can be stated that both the CdTe-based cell and the CMT-based cell are satisfactorily modelled by the assumption of a conduction band offset, together with specific doping concentrations. In previous work at the HMI, the conduction band offset $\Delta E_c$ of a porous TiO$_2$|CdTe configuration was measured with Ultraviolet Photoelectron Spectroscopy (UPS), and a value of $\approx 0.6$ eV was found [43]. The correspondence between two independent results for $\Delta E_c$ should give confidence on this, otherwise surprisingly high, value.

An explanation of the way in which the CB offset influences cell performance is given in terms of a barrier for electrons at higher voltages. It should be remarked, that this explanation is justified only by the fact that the cells considered in this chapter were microporous instead of nanoporous. This is, because a unit cell in a microporous network does not necessarily have to be a flat-band cell in which any barrier of the proposed type is unlikely to occur.

Still, a third possible reason for the reported S-shape should be mentioned. This is related to the back contact as often in CdTe cells, an effect that is commonly known [102, 103]. When the barrier height at the back contact, $\phi_b$, increases, the $J(V)$ curves start to roll-over in the first quadrant, then the FF decreases, and finally an S-shaped $J(V)$ curve in the active quadrant develops. Figure 8.10a shows the network representation of a solar cell with a back contact barrier: two opposite biased diodes and an additional current source. The calculations on this network show the S-shape inducing effect of the reverse biased contact diode (b,c). In one way or another however, the assumption of such a back contact barrier in our planar thin film model, described by the specific parameter set of Table 8.1, has no influence on the $J(V)$ characteristics. This is remarkable since the effect is of great importance in real CdTe based thin film cells.

Due to the irreproducibility of the S-shape for both CdTe- and CdHgTe-based ETA-cells even on the same sample substrate, it can not be concluded which of the three possibilities is the most likely to occur. Favorite candidates however, are the conduction band offset and the low doping concentration in the absorber.

8.3 Nanostructured TiO$_2$|CuInS$_2$ based ETA-cell

The research group from Tallinn has done a lot of work on the CuInS$_2$ absorber; it resulted in cells with spray-deposited CuInS$_2$ absorbers [104] on nanostructured as well as on flat TiO$_2$ layers [105]. The flat layer interfaces were used as model system, which helps to receive insight into the interface energetics, based purely on the materials properties and not obscured by effects from nanotechnological problems (such as the penetration depth of the absorber into the nanostructured film). Solar cell devices of these structures were fabricated with and without the addition of p-type CuSCN layers and investigated by recording their $J(V)$ response and IPCE-spectra. Surface photovoltage spectra, that have already been used to detect electron injection in dye and PbS sensitized nanocrystalline TiO$_2$ [59, 106], confirmed the ability of the CuInS$_2$ absorber material to inject electrons into the TiO$_2$. Reasonable cell efficiencies are not reported though.

8.4 Conclusion

It was shown that the S-shaped light $J(V)$ curves of Cd$_x$Hg$_{1-x}$Te based ETA-cells can be attributed to a positive conduction band offset that is too high; at a certain forward voltage, an energy barrier for the electrons rises, causing a plateau in the photocurrent. This negative influence of a conduction band offset can be partly cancelled out however, by a doping concentration in the absorber that is very high. An advantage of a microstructured configuration over a flat one due to purely morphological reasons, seems to be the enhanced contribution to the photocurrent of generation due to long wavelength light.
Figure 8.10: Possible explanation of S-shape $J(V)$: cell junction diode in series with back contact reverse diode junction (a); separated contributions of the two diodes in light (b), dark and light curves for the total current (c).
Chapter 9

Conclusions

In three-dimensional solar cells, an advantage of the structured configuration over a flat one is the enhanced contribution to the photocurrent of carrier generation due to long wavelength light. However, the overall device performance of solid-state nano- and microstructured solar cells is far from sufficient. In case of CdTe|TiO$_2$-based microstructured cells, this can be ascribed to a conduction band offset which is so high that it forms a barrier for the electrons at higher voltages. However, there is more going on.

**Problem**  In general, it is assumed that in 3D-solar cells, the importance of a large minority carrier diffusion length with respect to cell performance has decreased. This happens, because charge separation takes place on a very small scale so that smaller minority carrier diffusion lengths ought to be good enough. When this is assumed, only the distance from the generation spot to the separating junction is concerned (roughly spoken half of the TiO$_2$ particle size), since after the separation (i.e. injection of electrons into the oxide electron conductor, in case of a real ETA-cell also the injection of holes into the hole conductor), the charge carriers have become majority carriers. In principle, this makes them less sensitive to recombination. However, the charge carriers are not ‘safe’ at all after the separation; before reaching the contact, a lot of hindrances have to be taken which are associated with the overall presence of interfaces throughout the cell. Therefore, also the majority carrier diffusion length should exceed a critical value: it should be comparable to the cell thickness $\ell$ or to the absorption depth $1/\alpha$, whatever the smaller. In DSSC’s, this is indeed the case, in 3D-cells, not.

**Modelling and quantification of the problem**  Three different models are set-up in order to be able to quantify the recombination and transport properties of the three-dimensional solar cell: an analytic partial effective medium model based on diffusion, a macroscopic effective medium model, and an equivalent network model. They are used to analyze steady-state $J(V)$ and IPCE curves, and dynamic photocurrent, photovoltage and electrical impedance measurements (IMPS, IMVS and EIS).

In the analytic diffusion model, the cell’s behavior is determined by the electrons in the TiO$_2$ layer. Both the analytic approximations and the full simulations with the diffusion model revealed that the electron diffusion length $L_n$ in a 3D-cell unfortunately is much smaller than both the cell thickness $\ell$ and the absorption depth $1/\alpha$. In that case, the characteristic IMPS time constant $\tau_{\text{IMPS}}$ is equal to $\tau_n/2$, and the characteristic IMVS time constant $\tau_{\text{IMVS}}$ is equal to $\tau_n$. The IPCE, which is the real part of the optoelectronic IMPS transfer function $H_{\text{IMPS}}$ for $\omega \to 0$, is equal to $\frac{\alpha L_n}{\alpha L_n + 1} \approx \alpha L_n$ which unfortunately is much smaller than 1.
There can be several reasons for the high recombination, represented by the small diffusion length, in CuInS$_2$|TiO$_2$-based 3D-cells. One possibility is that the electrons recombine with holes in the interface states. Another is that they recombine with holes from the valence band of CuInS$_2$. They also can recombine with holes in deep states in the CuInS$_2$, that tend to act like surface states due to the nano-scale and three-dimensional character of the cells.

Another typical feature is observed. It is known that in general, TiO$_2$ which is the main oxide electrode material concerned in this thesis and the most widely used, is a strong photoconductor. In DSSC’s, this leads to an increase of electron diffusion coefficient upon higher illumination. In 3D-cells however, a small and even inverse relationship is reported. Also a decrease of electron lifetime upon illumination is found. At last, it is shown that a very small RC-time of the system (which is in the order of the electron lifetime $\tau_n$) is found due to the decreased ability of the TiO$_2$ to store electrons.

Both the equivalent network model and the macroscopic effective medium model which also takes the holes in the absorber into account, yielded that in particular the resistance in the $p$-type side is important for especially the $V_{oc}$. Since a cell is illuminated from the $n$-type-side, a generation profile is expected with its maximum at this $n$-type-side; after charge separation, the holes that have to be transported to the back contact have a maximum density at the front side. Therefore, a high resistance in the $p$-type network limit the cell’s performance. Moreover, the models turned out to represent the nanostructured solar cell in the same way as the proposed analytic diffusion model.

The qualitative outcome of the analysis with the analytic macroscopic diffusion model (i.e. very small electron lifetime) might not have been such a surprise. The model however, relates easily-to-measure opto-electric and electric transfer functions with macroscopic material parameters. This makes it a strong tool in the analysis of complicated solid-state nanostructured solar cells.

**Solution** The key answer to all the efficiency limiting recombination in three-dimensional solar cells is interface engineering, for example by the introduction of an appropriate buffer and/or tunnel barrier layer. The insertion of such an intermediate layer at the active interface of a nanostructured solar cell can give rise to complicated changes in the cell operation. Some of these changes are solely due to chemical material interactions. Such mechanisms have to be studied specifically in each case, and are beyond the scope of this thesis. An insulating barrier layer by itself will not form a selective barrier for light and dark current without severely decreasing cell performance, because a tunnel barrier is always an impediment for current, and therefore can never cause an increase in $J_l$.

Improvements in $V_{oc}$ can be achieved though, because IL’s, even non-insulating ones, can effectively decrease interface recombination. In such systems, reduction of the interface state density might not be as important as the reduction of their effect due to a more favorable position of the Fermi levels at the interface, with respect to the band edges.
Appendix A

Scaling factor for IMPS and IMVS

To obtain true physical values, some actual measurement values need to be corrected or scaled for measurement set-up or sample related circumstances. Most of the time, an appropriate correction factor is easy to determine, like for example the phase correction for the failing reference photodiode in the highest frequency range used for the IMPS measurements. However, in the case of the scaling factor $SF$, needed to relate the IMPS and IMVS output to real physical values, some problems were met. Therefore, in this Appendix, the scaling factor is determined but it is not used to scale the IMPS and IMVS results presented in the rest of the thesis. To ensure that the obtained values for the simulation parameters do have physical value, a scaling factor is used though, which is assumed to be uniform for all measurements.

The scaling factor $SF$ is determined according to the following expression:

$$SF = \frac{P_{\text{ref}}A_{\text{ref}}R_{\text{ref}}}{P_{\text{cell}}A_{\text{cell}}R_{\text{cell}}} \frac{hc}{\lambda e}$$

(A.1)

in which $P$ is the power of the laser light, $A$ the surface area of the cell ($\text{ref/cell} = 0.09/0.035$), $R$ the measuring resistance (50/27), $S_{\text{ref}}$ the sensitivity of the reference cell (0.35 A/W), and the last factor the energy of the laser light in J divided by the electron charge. Using in addition 0.1 as the quotient of $P_{\text{ref}}/P_{\text{cell}}$, $SF$ is determined to be 0.34.
### Abbreviations and acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>ac</td>
<td>alternating current</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>AM1.5G</td>
<td>Air Mass 1.5 Global solar spectrum</td>
</tr>
<tr>
<td>APCE</td>
<td>Absorbed Photon to Current conversion Efficiency, cf. IPCE</td>
</tr>
<tr>
<td>BGL</td>
<td>broad-band (white) background light</td>
</tr>
<tr>
<td>BI</td>
<td>building integration</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CIGS</td>
<td>chalcogenide, or Cu(In$<em>{x}$Ga$</em>{1-x}$)(S$<em>{y}$Se$</em>{1-y}$)$_{2}$</td>
</tr>
<tr>
<td>CMT</td>
<td>Cd$<em>{x}$Hg$</em>{1-x}$Te</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant Phase Element</td>
</tr>
<tr>
<td>dc</td>
<td>direct current</td>
</tr>
<tr>
<td>DSH</td>
<td>Dye Sensitized Heterojunction</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye Sensitized Solar Cell</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>ELIS</td>
<td>department of Electronics and Information Systems (UGENT)</td>
</tr>
<tr>
<td>EMM</td>
<td>effective medium model</td>
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<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>HMI</td>
<td>ETA-partner Hahn-Meitner Institute in Berlin, Germany</td>
</tr>
<tr>
<td>IFR</td>
<td>interface recombination</td>
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<td>IFS</td>
<td>interface states</td>
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<td>IL</td>
<td>intermediate layer</td>
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<tr>
<td>IMPS</td>
<td>Intensity Modulated Photocurrent Spectroscopy</td>
</tr>
<tr>
<td>IMVS</td>
<td>Intensity Modulated photoVoltage Spectroscopy</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident Photon to Current conversion Efficiency, cf. APCE</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>M-S</td>
<td>metal-semiconductor</td>
</tr>
<tr>
<td>M-I-S</td>
<td>metal-insulator-semiconductor</td>
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<tr>
<td>ND</td>
<td>neutral density</td>
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<tr>
<td>PEC</td>
<td>photoelectrochemical</td>
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<td>PL</td>
<td>PhotoLuminescence</td>
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<td>PV</td>
<td>photovoltaic</td>
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<td>S1</td>
<td>TiO$_2$</td>
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<tr>
<td>np-S1</td>
<td>nanoporous region of sample S1</td>
</tr>
<tr>
<td>flat-S1</td>
<td>flat region of sample S1 without nanoporous TiO$_2$ layer</td>
</tr>
<tr>
<td>S7</td>
<td>nanoporous TiO$_2$</td>
</tr>
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QNR  quasi neutral region
SRH  Shockley-Read-Hall
SCL  space charge layer
TCO  transparent conducting oxide
TUD  ETA-partner Delft University of Technology in Delft, the Netherlands
UV   ultra-violet
VB   valence band
SCAPS SCAPS-1
SCAPS-1D Solar cell CAPacitance Simulator in 1 Dimension, version 2.4 (December 2003) 2.52 (August 2005)
SLICE EMM currently being developed by K. Fredin (Uppsala University)

Symbols

\(\alpha\)  absorption coefficient (1/cm)
\(\Delta E_c\)  conduction band offset (eV)
\(\Delta E_v\)  valence band offset (eV)
\(\eta\)  efficiency (%)
\(\mu_{n,p}\)  electron, hole mobility (cm\(^2\)/Vs)
\(\vartheta\)  angle (\(^\circ\) or rad)
\(\lambda\)  wavelength (nm)
\(\sigma_{n,p}\)  capture cross section of electrons, holes (cm\(^2\))
\(\tau_{n,p}\)  lifetime of injected electrons, holes (ms)
\(\tau_{\text{IMPS,IMVS}}\)  characteristic IMPS, IMVS time constant (ms)
\(\tau_Z\)  characteristic impedance time constant (ms)
\(\tau_{\text{diff,drift}}\)  characteristic diffusion, drift time constant (ms)
\(\tau_{\text{transport}}\)  current transport time (ms)
\(\tau_{\text{RC}}\)  RC-time (ms)
\(\phi\)  barrier height (eV)
\(\Phi\)  photon flux (photons/cm\(^2\)/s)
\(\Phi_m\)  work function (eV)
\(\chi\)  electron affinity (eV)
\(\omega\)  pulsation small signal measurement (Hz)

\(A\)  area (cm\(^2\))
\(A\)  absorption (%)  
\(C\)  capacitance (nF)
\(D_{n,p}\)  electron, hole diffusion coefficient (cm\(^2\)/s)
\(e, q\)  elementary electrical charge (C)
\(e^-\)  electron
\(\varepsilon\)  electric field (V/cm)
\(E_F\)  Fermi level (eV)
\(E_{\text{Fn,p}}\)  quasi-Fermi level of electrons, holes (eV)
\(E_v\)  valence band maximum (eV)
\(E_c\)  conduction band minimum (eV)
\(E_{\text{vac}}\)  local vacuum level (eV)
\(E_g\)  band gap energy (eV)  
\(E_{gi}\)  interface energy gap (eV)  
\(E_{don}\)  (shallow) donor level (eV)  
\(E_{acc}\)  (shallow) acceptor level (eV)  
\(E_a\)  activation energy (eV)  
\(E_t\)  energy level of defect (above \(E_v\)) (eV)  
\(f\)  frequency small signal measurement (Hz)  
\(f_T\)  exact break frequency of transfer function (Hz)  
\(f_{\text{min}}\)  graphical break frequency of any transfer function \(H\), i.e. frequency where \(\text{Im}[H]\) has a minimum (Hz)  
\(FF\)  fill factor (%)  
\(h^+\)  hole  
\(H_{\text{IMPS,IMVS}}\)  ideal internal opto-electrical transfer function of IMPS, IMVS  
\(H_{\text{IMxS,ext}}\)  externally measured opto-electrical transfer function of IMPS, IMVS  
\(i\)  \(\sqrt{-1}\), imaginary unit  
\(I\)  current (mA)  
\(I_0\)  BGL illumination intensity (sun or mW/cm\(^2\))  
\(I_{sc}\)  short circuit current (mA)  
\(\tilde{i}\)  modulated photocurrent density (mA/cm\(^2\))  
\(J\)  current density (mA/cm\(^2\))  
\(J_l\)  light current density (mA/cm\(^2\))  
\(J_s\)  dark saturation current density (mA/cm\(^2\))  
\(J_{sc}\)  short circuit current density (mA/cm\(^2\))  
\(k\)  Boltzmann constant (eV/K)  
\(\ell\)  thickness of layer, cell, ... (\(\mu\)m)  
\(I_{0,p}\)  diffusion length of injected electrons, holes (nm)  
\(N_i\)  density of interface states (1/cm\(^2\))  
\(N_e\)  effective density of states in CB (1/cm\(^3\))  
\(n, p\)  concentration of free electrons in CB, holes in VB (1/cm\(^3\))  
\(n_{eq}\)  equilibrium electron concentration (1/cm\(^3\))  
\(n_f\)  ideality factor  
\(P_{in}\)  power of incident light (mW/cm\(^2\))  
\(q, e\)  elementary electrical charge (C)  
\(R_{n,p}\)  resistance in \(n\)-type, \(p\)-type part of interpenetrating network (\(\Omega\))  
\(R_{\parallel}\)  parallel, or shunt resistance (\(\Omega\))  
\(R_s\)  series resistance (\(\Omega\))  
\(R_{\text{load}}\)  load resistance used in IMPS measurements (\(\Omega\))  
\(S_i\)  interface recombination velocity (cm/s)  
\(T\)  transmission (%)  
\(T\)  absolute temperature (K)  
\(U_{\text{IFR}}\)  interface recombination rate (1/cm\(^3\)s)  
\(v_{\text{th},n,p}\)  electron, hole thermal velocity (cm/s)  
\(V\)  voltage (V)  
\(V_{\text{bi}}\)  built in voltage (V)  
\(V_{\text{bias}}\)  applied bias voltage (V)  
\(V_{oc}\)  open circuit voltage (V)  
\(W\)  space charge layer width (\(\mu\)m)  
\(Y(\omega)\)  complex admittance
<table>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$Z(\omega)$</td>
<td>complex impedance</td>
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<tr>
<td>$N_d$</td>
<td>total concentration of shallow donors</td>
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<tr>
<td>$N_{d^+}$</td>
<td>concentration of ionized shallow donors</td>
</tr>
<tr>
<td>$N_a$</td>
<td>total concentration of shallow acceptors</td>
</tr>
<tr>
<td>$N_{a^-}$</td>
<td>concentration of ionized shallow acceptors</td>
</tr>
<tr>
<td>$N_t$</td>
<td>total concentration of deep traps</td>
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Bibliography


Publications

International Journals


International Conference Proceedings


Other publications


