

Measurements and Modelling of Space-Charge-Limited Current Transport in Organic Single-Carrier Devices

by

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A thesis submitted to Imperial College London for the degree of

Doctor of Philosophy

October 19, 2018

*"It's not what you look at that matters,
it's what you see."*

- H. D. Thoreau

Declarations

Declaration of Originality

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I certify that I appropriately acknowledged and referenced the work of others where needed.

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Jason A. Röhr

Acknowledgements

I would like to thank a number of people whom have directly or indirectly contributed towards the completion of my doctorate and the writing of this thesis. Without your help and support, this would never have been possible.

First of all, I want to thank my supervisor and mentor, Prof. Jenny Nelson. If you had not read your emails on that infamous Saturday in January 2012, and decided to take me on as a visiting masters' student, I would not have been a position to write these words. Thank you for believing in me, putting up with me, and thank you for allowing me to express myself both creatively and scientifically. I have learned so much from you during the past five years, and I hope to continue to learn from you in the many years to come. From my "open heart", thank you.

Secondly, I want to thank my supervisor and mentor, Dr. Saif Haque. Thank you for allowing me to roam freely in your labs and allowing me to pursue my own scientific interests, and thank you for the many exciting discussions about science and politics. Your passion is unrivalled, and I admire you very much for this. I greatly appreciate the advice and supervision you have given me during my studentship in the last four years.

I want to give a special thanks to Prof. Thomas Kirchartz, both for being a great mentor and collaborator, but also for being a great friend. Thank you for always giving great advice on writing scientific papers, how to do proper presentations, and than you for teaching me how to play the academic game. I hope to keep you as a close confidant in the many years to come.

I want to thank Dr. Andrew Telford for always being willing to give a helping hand, whether with scientific problems, with a grant application or with corrections to my CV. I hope to be able to pass on my own experiences one day as you have done for me.

I want to thank Dr. Davide Moia. Thank you for your honesty and sincerity, your passion and your expertise. I have learned more from you in the past five years than you are willing to admit. I hope one day I can teach you a thing or two as well. I highly doubt it, but time will tell.

I want to thank Dr. Sachetan Tuladhar for showing me the ropes in the clean room and for

supporting me during my first year at Imperial when nothing was working, the labs were being refurbished, and I was close to a mental breakdown. You said, "You're in the right place at the wrong time". You were right, and I am very happy that I had the opportunity to stay here for another four years. I am still waiting for that dinner invitation though.

I want to thank Dr. Xingyuan Shi, both for your friendship and for our very close collaborations. I have enjoyed working with you, and I'm looking forward to start a lab with you one day (yes, that is going to happen). We're a good team, and I think we could produce more amazing results together.

I would like to thank the rest of the people in both the Nelson group in physics, the Haque group in chemistry, and all the basement people in the Durrant group in chemistry. You know who you are. You have made the last five years very enjoyable. I would do it all over again.

I want to give a special thanks to my fellow students in Cohort 5. Especially Mr. Iain Andrews, Mr. Nathan Cheetham, Dr. Alex Giovanitti, Mr. Iain Hammilton, Ms. Madeleine Morris and Dr. Gwen Wyatt-Moon. We have forged a very special bond over the past four years, and I am very proud to be your friend. I hope that we can remain close for the many years to come.

I want to thank all my office mates who had to put up with me over the past many years. I especially want to thank Mr. Matthias König, Dr. Michael Nielsen, Dr. Viktoryia Shautsova, Dr. Themis Sidiropoulos, and Dr. Michelle Vezie. You guys have been great both professionally and personally. I wish you all the very best in the future.

I want to thank Ms. Suki Wong for helping me with the maths, the grammar and for your endless compliments on my figures.

I want to thank all my Danish friends, both the people I know all the way back from my time at Sorø Akademi and the people I know from my time at the University of Copenhagen. I especially want to thank Ms. Mette Bergholt Buhl, Mr. Frederik Weidick Fialin, Mr. Toke Wahl Fritzeimer, Dr. Morten Kjærgaard and Mr. Philip Lundbek for being great philosophic, artistic and academic inspirations.

Finally I want to thank my family for their moral and financial support and for their much appreciated love. I especially want to thank my mum, Ms. Tine Mehder Bangst, my dad, Mr. Robert Birger Röhr, my sister, Ms. Jessica-Lee Lönnqvist, my step-mum, Ms. Pernille Boitang Hansen, my grand-mum, Ms. Kirsten Bangst, and my "step"-dad, Mr. Jan Allan Lönnqvist. Without your help, I would not have been able to complete this degree. It has been five turbulent years away from home, and you have been remarkable in your inexhaustible encouragement. I am extremely thankful, and I love you all very much.

Abstract

This thesis discusses the accuracy of a number of analytical models commonly used to analyse current density-voltage curves from space-charge-limited current measurements, such as Ohm's law and the Mott-Gurney law. We studied the accuracy of the models using a numerical drift-diffusion solver which can calculate single-carrier devices containing either an intrinsic semiconductor, a doped semiconductor or a semiconductor with traps. This allowed us to calculate the current density-voltage curves of a single-carrier device using known input values for the mobility and trap characteristics, and subsequent fitting with the analytical models yielded insight into their accuracy. We found that Ohm's law only correctly describes the current when the probed semiconductor is highly doped, in which case the Mott-Gurney law is no longer valid.

Numerical drift-diffusion solvers can also be used for direct fitting of experimental current density-voltage curves, allowing for the inclusion of traps but also injection barriers at the contact interfaces. We used this approach to fit to data obtained from single-carrier devices based on Spiro-OMeTAD. We then compared the charge-carrier mobility and trap characteristics obtained using the numerical approach to characteristics obtained from the analytical models, and we found that charge-transport could be described with a temperature-independent charge-carrier mobility when traps and injection limitation was included explicitly.

Finally, we examined the effect of oxidation of fullerenes on organic solar cell efficiency. We studied charge-transport when a small fraction of oxidized species was added to the film, and we found that the oxidized species act like charge traps. First principle calculations were used to calculate the energetics of the oxidized fullerene species, with results matching those of the charge-transport analysis. With the obtained knowledge we could qualitatively reproduce the observed reduction in solar cell efficiency.

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Part I

INTRODUCTORY CHAPTERS

Chapter 1

Motivation

1.1 Context

The success of recent solution processed optoelectronic technologies, such as solar cells and light-emitting diodes (LEDs), is partly due to improved understanding and improved processing of well established materials, and partly due to the development of new materials with improved optical properties and charge-transport characteristics. A number of charge-transport characterisation methods exist which have helped towards this development, and like all experimental methods, these have their *pros* and *cons*. The space-charge-limited current (SCLC) measurement is one of these methods, and is convenient for charge-transport characterisation of intrinsic, or weakly doped, semiconducting thin films since the measurement is simple to perform. The measurement has for that reason been widely used to probe transport in a variety of solution processed semiconductors such as amorphous silicon thin films[1, 2], organic semiconductors[3, 4, 5, 6, 7] and lead halide perovskites[8, 9].

SCLC measurements are especially powerful since the transport of electrons and holes can be probed separately by an appropriate choice of contact materials. This is important since transport of electrons and holes can differ significantly in a semiconductor and extrinsic factors can have a negative impact on one charge-carrier type and not the other. This makes the SCLC measurement a very helpful tool for the development of opto-electronic devices. When trying to extract charge carriers from a solar cell, for example, it is important to extract the charge carriers quickly (and be able to extract both the electrons and the holes) to limit recombination, since recombination leads to efficiency losses. Similarly, when injecting charge carriers into a LED, it is important to have balanced transport properties for the electrons and holes, to ensure that the light is emitted from the emitting material and not from the interlayer materials. Additionally, it is convenient to be able to study a specific charge carrier type when studying semiconductor

materials which are designed to transport electrons or holes only, such as interlayer materials used for before mentioned technologies.

Besides being a simple measurement to perform, an additional practical aspect of SCLC is that the devices used for the measurements, called single-carrier devices, are of similar architecture to solar cells and LEDs. This allows for the determination of the charge-transport characteristics in the same transport direction as the diode devices, in a device with similar film thickness, similar processing history, and therefore similar film morphology. Furthermore, the electron selective material used in the solar cell or LED, for example, can be used as the electron injecting layers in the single-carrier device (and similarly for the hole selective materials). All of this allows for a direct comparison of the films and contacts used to measure charge transport with the films and contacts used for the optoelectronic components. SCLC measurements can therefore give insight into the injection properties of the selective material along with the transport properties. All of these benefits are not shared with other popular charge transport characterisation techniques, such as time-of-flight mobility measurements which require very thick devices and does not probe the injection properties, and field-effect-transistor mobility measurements which require a horizontal device structure and hence probe charge transport in the wrong direction.

1.2 Goals and challenges

Besides being an excellent method for probing charge transport in semiconductors used for opto-electronics, the SCLC measurement has its downsides. Data from SCLC measurements is prone to misinterpretation, and identifying the correct model for interpreting the measured current density-voltage (J - V) curves is a critical matter[10]. The widely used Mott-Gurney (MG) law[11] has been proposed as a good model for interpreting SCLC of single-carrier devices. However, the use of this model requires that the following conditions are satisfied: the semiconductor must be un-doped and trap free; the interface between the semiconductor and the electrode must be Ohmic, and the diffusion component to the current must be negligible, meaning that enough voltage must be applied across the device to ensure that the current is drift dominated. These conditions can be considered as ideal. Throughtout this thesis, we will distuingish between an ideal material and an ideal device. An ideal material does not contain any traps or doping and an ideal device is not limited by poor injection, not limited by the presence of a built-in voltage, and not limited by a series resistance or a significant shunt current. However, the measured curves from real single-carrier devices are usually affected by non-ideal features, and also by the non-ideality of the single-carrier device itself[12, 13]. The presence of

any of these non-ideal features render the MG law unhelpful for analysis in most cases. For this reason it is important to use models which can account for non-ideal effects when analysing SCLC measurements. However, the MG is still the most widely used model for SCLC analysis even when applied to disordered materials.

If an ideal semiconductor is probed using an ideal device, fitting the MG law to the J - V curve would yield the *band* mobility for the charge-carrier type being probed (with the band referring to the mobility of either the conduction or valence band). However, if the MG law is used to extract a mobility of a non-ideal material, the extracted mobility will not be a band mobility, but rather an *effective* mobility, and will be affected by whatever gives rise to the non-ideal feature of the material, whether that being traps or doping, or injection limitation, or a combination of all of these. It has become common practise to present SCLC analysis, among other charge-transport methods, when presenting solar cell device data from novel materials, with the charge-transport figure of merit usually being the effective charge-carrier mobility. However, the effective mobility is not always a suitable quantity to present. Consider if one was to compare the charge transport properties of a series of materials, using the MG law for the analysis would most likely not yield a value for the mobility which is directly comparable between each of the different materials, since different materials will have different degree of trapping and will form different interfaces with contact materials. Since the effective mobility will not tell you what caused it to be lower than the band mobility, these mobilities are not directly comparable. Similarly, was one to compare the mobility obtained from SCLC measurements with a mobility obtained from analytical analysis of time-of-flight or FET measurements, these values for the mobilities would most likely also not agree, due to the different assumptions made for the different models. This can give rise to significant implications for the validity of the analysis, and measuring mobilities using analytical models can give values which are orders of magnitude lower than the band mobility, and will not yield any direct insight into why they deviate. Still, the most common approach used to analyse SCLC in the organic semiconductor community is to use the MG law without paying much attention to the assumptions put into the model, and then assume that the effective mobility obtained through this analysis is comparable to other effective mobilities.

The consequences of doing wrongful analysis are many. The magnitude of the charge-carrier mobility is often used as a sign of quality of how good a material is or how well it is suited for a certain technology. This is especially the case when a material series is presented. However, in the context of solar cells (and to some extent LEDs) it is just as crucial, if not even more so, to understand how defect states limits transport and, as mentioned above, an effective mobility

will yield limited information regarding the origin of defect states. Utilizing models which can probe the band mobility, directly, is potentially very powerful as it offers a direct comparison between the mobilities obtained from different materials and from different techniques. Some analytical SCLC models which were derived to include the influence of traps, and drift-diffusion solvers which can include all the above mentioned non-ideal features, offer the capability to directly probe the band mobility. Using such models, will yield not only mobilities which are comparable, but also additional information about traps and injection limitation which can help elucidate the reasons for performance loss.

In a number of published studies, attempts have been made to find alternative models to the MG law to fit SCLC data to account for the above mentioned non-ideal behaviour and hence allow for a direct measurement of the band mobility. For example, analytical equations have been derived to give qualitative explanations to the observed effects of traps, such as Rose's and Lampert's equation[14, 15], and the Mark-Helfrich equation which describes current in the Mott-Gurney regime when a shallow exponential distribution of traps is present[12]. Equations have also been derived to explain Poole-Frenkel like effects, such as the Murgatroyd equation[16]. However, since all of the above mentioned equations ignore the diffusion part of the current, which is the part of the current which is most heavily influenced by the presence of traps and disorder, they must be approached with caution when used for analysis[17, 18]. A number of other studies have however utilized a more sophisticated model to analyse SCLC through the use of drift-diffusion simulations[19, 20, 21, 22, 23]. The reason for the community still relying on analytical models can be explained from the fact that fitting with drift-diffusion solvers can no longer be achieved through simple procedures, but must be performed in an iterative manner using either home-written or bought software. In order to achieve a simple but reliable fitting approach, new analytical models must be developed which can account for non-ideality using reasonable assumptions in physically achievable regimes.

Finally, in order to properly test newly developed materials it is important to have an established methodology for the data analysis. For this reason, characterisation tools must be thoroughly tested on well-understood materials before being used for analysis of novel materials. Only a few papers have studied the effect of not using a standardized methodology, such as the work of Blakesley *et al*, where it was found that different scientists tend to get highly different results when measuring the same device using the same model[10]. As mentioned above, most groups tend to use overly simplified analytical models to analyse their data, even though the data clearly shows the presence of non-ideal behaviour. For this reason, it is also important to study the effect on the analysis of using one model over another, whether the model is oversimplified

or within physical reason, and discuss the validity of the obtained material characteristics, such as the charge-carrier mobilities, injection limitation and trap characteristics.

1.3 Thesis overview

The work presented in this thesis will investigate the issues mentioned above. The thesis is divided into two parts. Part I includes the motivation, chapter 1 (the current chapter), along with two introductory chapters, chapters 2 and 3. Part II includes four results chapters, namely chapters 4, 5, 6 and 7, and a chapter summarizing the conclusions from each chapter along with a section about potential future work which can follow directly from the work presented herein.

1.3.1 Part I

Chapter 2, titled "Introduction", gives a short introduction to the general subject of solar cells along with device operation and the current state-of-the-art, how charge transport measurements are used to study solar cell materials, and finally a short introduction into the different techniques used for materials analysis along with the technique that this thesis is mainly concerned with, namely space-charge-limited current measurements. Chapter 3, titled "Theoretical Treatment of Charge Transport in Disordered Semiconductors", gives a description of the theory of disordered semiconductors along with the derivations and discussion of the most commonly used equations for space-charge-limited current analysis. All the derivations are included so that the next student can start their work directly without having to scour the literature for the derivations.

1.3.2 Part II

Chapter 4, titled "Interpretation of SCLC in the low voltage regime" discusses the method of using single-carrier devices to estimate the charge-carrier density of materials used for solar cells. Specifically by comparing the current densities at both low and high voltages. The work specifically studies how the charge-carrier density of a semiconductor in a single-carrier device changes with thickness and doping concentrations. However, the method is mostly based on misconceptions in the literature, and it is shown that the method is rarely valid and will give results which are wrong by up to many orders of magnitude. Chapter 5, titled "Exploring the Validity and Limitations of the Mott-Gurney Law", discusses whether the MG law is, in fact, valid for studying ideal semiconductors in thin devices. The MG law is based on a number of assumptions that are generally not true, one of which is that the semiconductor must be trap

free. However, it is shown that the MG law does not give correct values for the charge-carrier mobility of a trap free semiconductor if the device is thin and/or if the injection barriers are small but non-zero, and extracted mobilities can deviate with orders of magnitude. Chapter 6, titled "Revisiting Charge Transport through Spiro-OMeTAD", discusses the differences in extracted mobilities from single-carrier devices when the current density-voltage curves are analysed using analytical equations compared to numerical methods. It was found that when the data was fitted with analytical equations, the mobility was found to be temperature dependent, whereas when numerical methods were used, the mobility was found to be temperature independent. Chapter 7, titled "The Role of Fullerene Oxidation on the Stability of Organic Solar Cells", discusses the effect of fullerene oxidation on the transport characteristics of polymer:fullerene films and subsequent device performance of polymer:fullerene solar cells. It was found that oxidation primarily leads to degradation of the fullerene component with oxidized species giving rise to electron traps. Chapter 8, titled "Concluding remarks", summarizes the conclusions from the four result chapters and gives a summary of potential future work.

Chapter 2

Introduction

2.1 Renewable energy

With the limited supply of non-renewable fossil fuels, such as coal, oil and natural gas[24], and the raising concern about anthropogenic global warming, the call for efficient renewable energy sources and access to low power lighting appliances has never been higher.

Solar energy is a promising candidate to help meet the World's energy budget by using the vast amount of energy hitting Earth's surface in the form of light[25, 26]. By using suitable materials, this light can be harvested to generate useful energy in the form of electricity. Other renewable energy sources exist such as wind, tides and geothermal heat and the application of these technologies where optimal is important in order to mitigate carbon dioxide emissions[27, 28, 29], to allow countries to be energy self-sufficient, and to supply power to vast numbers of people currently living without access to an electrical grid. The majority of the people not having access to grid electricity are living in Africa (approximately 640 million), Asia (approximately 430 million) Central and in Latin America (approximately 19 million) as shown in figure 2.1[30].

The energy coming from the Sun is vast (approximately 1000 W/m^2 at the surface of the Earth with the Sun over head) and can be harvested in a number of different ways: Many modern houses are built in order to maximize the amount of heat collected from the sun, either through passive solar house design or through active solar heating, to minimize the need to burn fossil fuels for heating (and cooling) and to minimize the need for grid electricity[31, 32]. Solar energy can be concentrated and used to heat up water reservoirs to drive a turbine in order to generate electricity[33, 34], and the light from the Sun can be harvested by solar cells for direct generation of electricity using photovoltaic solar panels[25]. In 2008 the total world electricity energy production was 20,261 TWh[35], yielding a total power output of 2.31 TW (composed of coal, oil, gas, nuclear, hydro, geothermal, solar, etc.). If an area the size of Texas (696,241

km²) was to be covered in solar cells and assuming that all the sunlight could be harvested, solar panels could produce 696 TW of solar power, 301 times more than what is currently being produced. From this back-of-the-envelope calculation, it is apparent that harvesting solar power has the potential to fully power all, and future, applications on Earth. However, in order for this to become a realisation, cheap and efficient solar cells must be invented and produced.

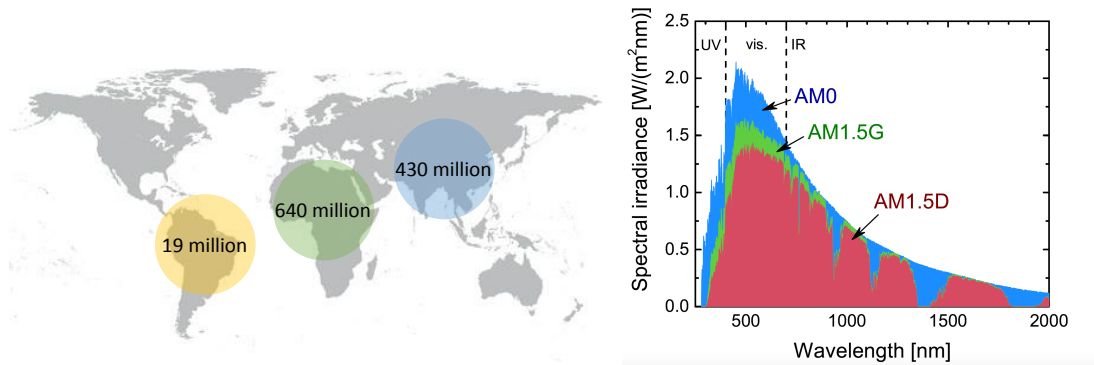


Figure 2.1: Number of people living off the electrical grid in South America, Africa and Asia out of a world population of 7.347 billion (as of 2015); and the solar irradiance spectrum without (AM0, blue curve) and with atmospheric absorption (AM1.5G, green curve, and AM1.5D, red curve).

2.2 Solar cells

Even though the photovoltaic effect, which is the generation of a current or voltage in a material when exposed to light, was first discovered by Alexandre-Edmond Becquerel in 1839, it was Willoughby Smith who first publicly described the effect, when he discovered the semiconducting properties of selenium in 1871[36]. However, it would be many years before an efficient solar harvesting device would be invented.

2.2.1 Early solar cell technologies

The modern solar cell was invented in Bell Laboratories in 1954 by Daryl Chapin, Calvin Souther Fuller and Gerald Pearson, which was a silicon p-n junction with a remarkable efficiency of roughly 6%[37]. The silicon solar cell is by far the most common solar cell (and is usually the type adorning roof tops), but it is not the best suited to the solar spectrum coming from the Sun, due to its relatively low, and indirect, band gap (≈ 1.1 eV)[38]. Silicon is however highly abundant in the Earth's crust, cheap to produce and highly studied due to the massive silicon industry. The current efficiency record for a crystalline silicon heterojunction solar cell

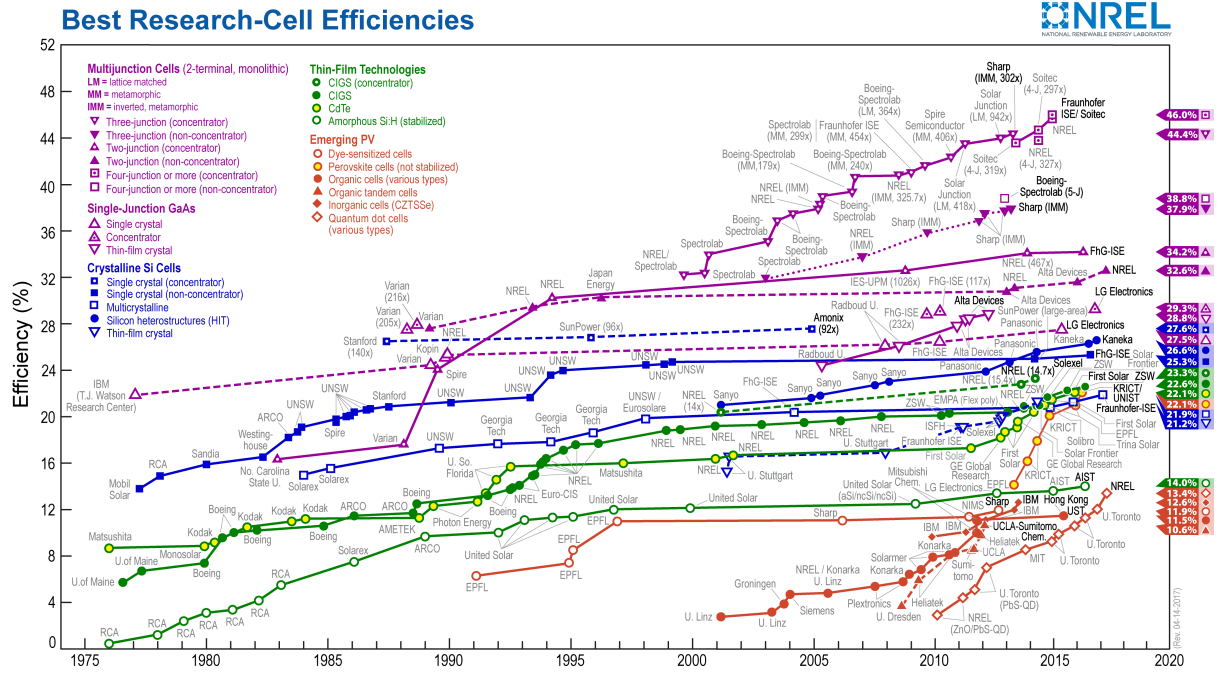


Figure 2.2: National Renewable Energy Laboratory solar cell certified efficiency chart. Record efficiency values for emerging PV technologies (Dye cells, Perovskites, OPV, CZTS and quantum dot solar cells) are shown in orange (from www.nrel.gov).

measured under global AM1.5 solar spectrum is around 26.6% as shown in fig. 2.2[39][40].

A III-V semiconducting material such as gallium arsenide (GaAs) has a better suited band gap than silicon (≈ 1.43 eV)[41, 38], but the means of processing is expensive, resulting in such solar cells only being used in situations where cost is not an issue, such as for space exploration. The current efficiency record for a crystalline single-junction gallium arsenide solar cell measured under AM1.5 is 28.8% as shown in fig. 2.2[40, 42, 43].

Alternative materials to crystalline silicon and GaAs are the highly absorbant and non-crystalline materials, amorphous silicon (a-Si), copper-indium-gallium-selenide (CIGS) and cadmium telluride (CdTe), which all saw early emergence with reasonable efficiencies reported as far back as 1976. Solar cells made from one of these alternative materials are commonly referred to as thin-film solar cells, and are currently being sold commercially as cheaper, flexible and low weight options to the bulkier Si and GaAs solar cells. Solar cells made from copper zinc tin sulphide/selenide (CZTS) are promising candidates for competition, with a crystal structure similar to CIGS, with the indium replaced by zinc and the gallium replaced by tin, making it free of toxic and non-abundant materials (unlike CIGS and CdTe). Like the other thin film technologies, CZTS has a very strong absorption coefficient making it useful for thin film solar

cell applications.

2.2.2 Solution processable solar cells

The older Si and GaAs technologies are based on highly crystalline materials which are grown using very elaborate and expensive techniques. A new generation of emerging solar cell technologies is based on the vision of utilizing cheap materials which are easily processed into solar cells, by either roll-to-roll processesing or other fast, low cost, low temperature and vacuum free manufacturing techniques. A great deal of scientific effort has been put into developing new solution processed organic and inorganic semiconducting and conducting materials in order for this vision to come true. Dye sensitized solar cells[44, 45, 46], quantum dot solar cells[47], all-organic solution processed solar cells[48] and organic/inorganic hybrid cells (such as lead-halide perovskite cells) have all shown great promise[49]. Out of this list, the technologies receiving the most attention to date are organic and lead-halide perovskite solar cells. However, before discussing the basic principles of organic such solar cells (in the next section), we briefly discuss the basic device operation of a solar cell in general.

2.2.3 Simplified model of device operation

Semiconductors can absorb light particles (photons), including the light coming from the Sun, in order to generate electricity. As discussed above, many types of solar cells, using a large variety of semiconducting materials, have been presented in the literature. Regardless of the choice of semiconductor material, the operating principles are very similar; the energy from light can promote an electron from a filled state to an empty state within the material, forming a quasi-particle called an exciton. This exciton, which consists of a bound pair of an electron in the normally empty band and the hole left behind in the normally filled band, can then either recombine radiatively (generating light), recombine non-radiatively (generating heat), or be dissociated into free charge-carriers which can move to their respective electrodes, generating a current (see fig. 2.3a). Whether an exciton will dissociate spontaneously depends on the electric field strength, F , between the electron and hole. The force due to this field strength, $\mathcal{F}_{e-h}$, is given by,

$$\mathcal{F}_{e-h} = \frac{1}{4\pi\epsilon_r\epsilon_0} \frac{q_e q_h}{r^2} \quad (2.1)$$

where ϵ_r is the dielectric constant, ϵ_0 is the permittivity of free space, q_e and q_h are the elementary charges of the electron and hole, respectively, and r is the distance between the two

charge carriers. The force is inversely proportional to the dielectric constant, and with the dielectric constant of inorganic materials being very large ($\epsilon_r > 10$), the binding energy between the electron and hole is very weak, and excitons will usually dissociate spontaneously[37, 41]. However, as will be discussed in more detail below, since ϵ_r is very small for organic materials, an additional driving force is required to dissociate the excitons[50, 51].

A semiconductor is usually described using a number of different energies: The band gap energy, E_g , and the conduction and valence band edge energies, E_C and E_V , respectively (these quantities will be discussed in more detail in the next chapter). E_g denotes the minimum energy required to promote an electron from the valence band to the conduction band, $E_g = E_V - E_C$, meaning that light particles with an energy larger than the band gap, $E_{\text{light}} > E_g$, can be absorbed, forming excitons. One of the simplest and most intuitive solar cell designs consists of a semiconductor sandwiched between two selective metal contacts. Such solar cells are called metal-insulator(semiconductor)-metal (MIM) solar cells, an example of which is shown in fig. 2.3, with electrons wanting to move downwards in energy and holes upwards in energy.

A solar cell can be operated under different applied voltages. When no voltage is applied across the solar cell, but it is being illuminated, the solar cell is said to be in short circuit (fig. 2.3a shows a schematic of a MIM solar cell at short circuit). If the energy of the sun light exceeds the band gap, and given that the generated excitons can dissociate, a photo-current is observed. The photo-current at $V = 0$ V is called the short-circuit current, I_{SC} . Note that we usually speak of the short-circuit current density, J_{SC} , in order to normalize for the area of the cell. If a voltage is applied across the solar cell, depending on the polarity of this voltage it is either called a forward or reverse bias voltage. The application of a reverse bias to the solar cell is shown in fig. 2.3b. Since no additional charge carriers can be injected from the contacts, the effect is simply to tilt the energy landscape and no additional current is achieved. If the voltage is applied in the opposite direction, in forward bias, under illumination, charge carriers are injected from the contacts into the semiconductor as the same time as the energy levels are flattened (see fig. 2.3c). This causes more charge carrier to recombine, and the photo-current decreases as a consequence. When a large enough forward bias voltage is applied, all photo-generated charge-carriers recombine, and the photo-current is zero. This applied voltage is called the open-circuit voltage, V_{OC} (see fig. 2.3c). A J - V curve from an idealised solar cell is shown in fig. 2.4, showing the position of the J_{SC} , V_{OC} , and the point where recombination begins to dominates over the photo-current and the injected current.

Since the power provided by a cell is given as the product of the current and the voltage ($P = IV$), the power will be zero at both short circuit ($V = 0$ V) and at open circuit ($J = 0$ at

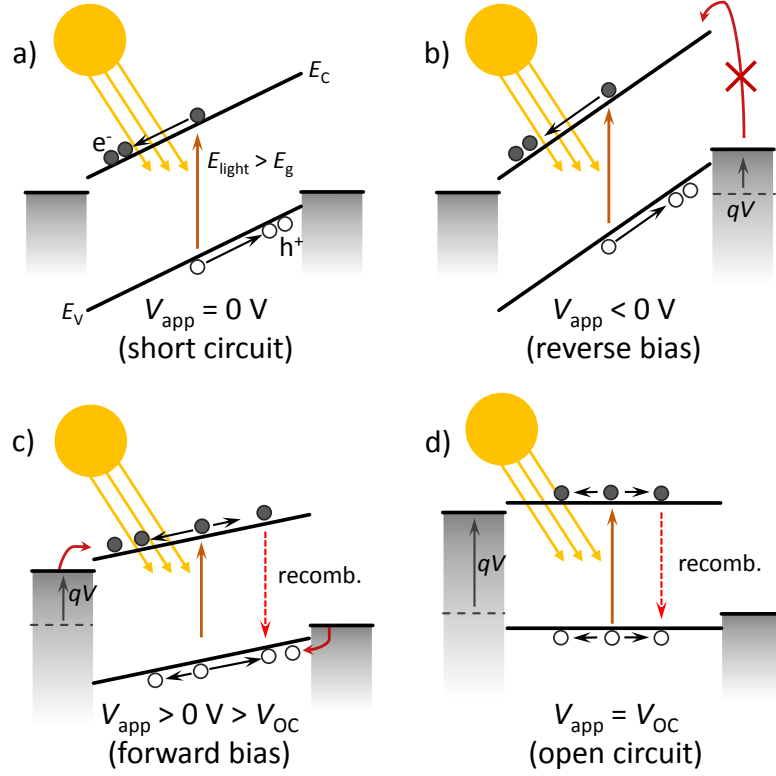


Figure 2.3: Schematic of basic device operation of a solar cells. a) The energetics of a basic MIM solar cell when no voltage is applied across the cell (short circuit). Light is absorbed when the energy of the light is larger than the band gap. Electrons (e^-) and holes (h^+) can drift to their respective contacts. b) The same solar cell in reverse bias. No additional charge carriers are injected into the cell, resulting in no change in the current. c) The cell under a small forward bias. d) The cell when a large enough voltage is applied in forward that the generated charge-carriers will all recombine, since the electrons and holes will diffuse around in the semiconductor (open circuit).

$V = V_{OC}$). So even though the maximum current provided by the cell is at short circuit (or in reverse bias), the power is either zero or negative, respectively. In order to produce power from the solar cell, the voltage is increased beyond short circuit until the maximum power point is reached, (P_{max}), which is defined by the voltage, V_{max} , and current, I_{max} (see fig. 2.3c) at this point. In order to achieve a high power output I_{max} and V_{max} must be maximised.

The power conversion efficiency (PCE), which is the efficiency of the solar cell to generate useful power from a light source, is given by the ratio of P_{max} to the power from the incoming light, which, in the case of solar cells, is the power from the Sun, P_{sun} (with the AM1.5G power

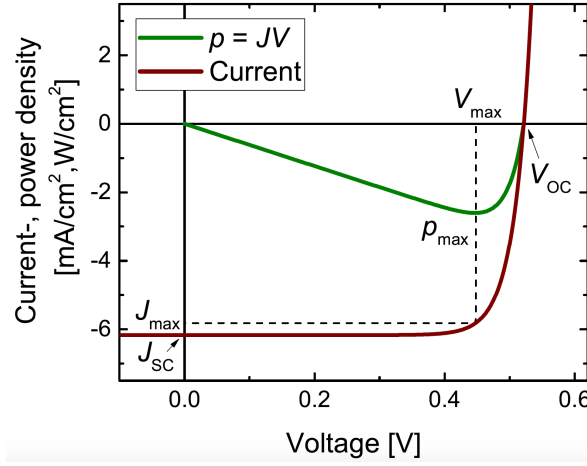


Figure 2.4: Current density-voltage (J - V) curve depicting the short-circuit current density, J_{SC} , the open-circuit voltage, V_{OC} , and the maximum power density ($p = JV$) point (denoted with dashed lines). The current density, J , and the power density, p , are the area normalized values equivalent to the current, I and the power, P .

density, which terrestrial solar cells are usually characterised with, being equal to 1000 W/m^2),

$$\text{PCE} = \frac{P_{\max}}{P_{\text{sun}}}. \quad (2.2)$$

Instead of considering the maximum power point we can describe a solar cell by the I_{SC} and the V_{OC} . To do this we need to define another quantity, namely the squareness, or the fill factor (FF) of the current-voltage curve when the voltage is swept under illumination. The FF defines the response of the current when a voltage is applied, and the maximum power will be highest if the current-voltage curve is a perfect square, in which case $V_{\max} = V_{OC}$ and $I_{\max} = I_{SC}$ when $\text{FF} = 100\%$. This is however not achievable even theoretically, so in order to define the maximum power output one has to give the FF along with the I_{SC} and the V_{OC} . Given the definitions of the I_{SC} , V_{OC} and the FF , we can define the maximum power generated by the solar cell as, $P_{\max} = I_{SC}V_{OC}FF$, and hence the PCE as,

$$\text{PCE} = \frac{I_{SC}V_{OC}FF}{P_{\text{sun}}}. \quad (2.3)$$

Since charge carriers are generated through absorption of a photon, the I_{SC} is mainly governed by the E_g of the semiconductor. For this reason, the optimal solar cell must be made from a

material where the band gap fits nicely with the solar spectrum in order to absorb as many photons as possible, as the intensity of the solar spectrum is not constant with energy (see fig. 2.1). It is important to note that the energy of a photon, once the band gap is surpassed, does not usually play an important role for the current as the excited electron will quickly relax to the lowest level in the conduction band through thermal dissipation. So the key to achieving a high photo-current is the number of photons (intensity of light) rather than the energy of the photons and by assuring that most of these generated charge carriers are transported to the contacts. The maximum obtainable voltage is given from the magnitude of the band gap $qV_{OC} \leq E_g$. It is very important to point out that in order to absorb a large amount of photons coming from the visible part of the solar spectrum, a low band gap must be used (usually less than 1.7 eV). However a low band gap reduces the highest obtainable V_{OC} . For a single-junction solar cell, which is usually the type of cells employed in inorganic solar cells, the optimal E_g (allowing for a large current and a large voltage) is approximately 1.4 eV (which is very close to the band gap of GaAs, with $E_g = 1.43$ eV).

The J - V curve shown in fig. 2.4 is highly ideal, with a FF close to the theoretical maximum. As will become more apparent in a later section, the current density, hence the J_{SC} , V_{OC} and the FF, is highly sensitive to the electrical characteristics of the semiconductor, defects, and the ideality of the contacts.

2.3 Organic solar cells

As mentioned in the previous section, a large variety of solution processable semiconductors have been developed for solar cell application, but none has achieved the amount of attention in the past three to four decades as organic semiconductors. One of the powers of using organic materials for electronics lies in the almost endless possibilities of combination of chemical constituents for fine tuning to match application, ease of processing, and solubility.

2.3.1 Discovery of organic semiconductors

One of the earliest articles reporting photo-physical effects and band-like structures of an organic material was published in 1946 by Szent-Györgyi, where he showed that the conductivity of coloured protein films increased upon illumination[52]. In 1948 it was proposed that π -stacking (overlap of π -orbitals) between neighboring molecules form crystals which would give rise to band-like electronic behaviour[53], much like is seen for inorganic semiconductors. In 1954 it was shown that it was possible to dope conjugated polymers, and that the polymer conjugation length is paramount for good conduction[54]. The discovery that polymers could be doped to

an extent that they behaved like conductors, in 1977, accelerated the field of organic electronics. Heeger, Shirakawa and MacDiarmid were awarded the Nobel prize in chemistry in 2000 for their discovery[55, 56].

2.3.2 From discrete energy levels to band-like structures

The semiconducting properties of organic materials arise from the hybridization of atomic p-orbitals into molecular π -orbitals.

From a quantum mechanical perspective, electrons in atoms can be considered to exist in discrete energy levels called atomic orbitals. As atoms are combined into molecules, the energy levels split, forming molecular orbitals. Considering two similar atoms combining, as in the case of a hydrogen molecule (H_2), the molecular orbital, formed from two 1s orbitals will form two new energy levels, a level which is slightly higher in energy than the atomic orbital energy, the anti-bonding molecular orbital (which in this case is a σ^* -bond), and a level which is slightly lower in energy, the bonding molecular orbital (a σ -bond)(see fig. 2.5a). Several atoms can be combined to form molecules of higher complexity, such as organic crystals, and so, the number of energy levels formed can reach a very high number (see fig. 2.5b). In this case, the discrete energy levels are no longer distinguishable, and rather form a continuous spectrum of energy levels. The energy levels can then be regarded as energy bands[80].

Due to electrons being Fermions, it is only possible for two electrons of opposite spin to occupy a single energy level, and for that reason (and assuming all the electrons are in the ground state, i.e., $T = 0$ K), half of the energy levels are filled up until the highest occupied molecular orbital (HOMO). The rest of the energy levels are empty, starting from the lowest unoccupied molecular orbital (LUMO). The difference between the HOMO and the LUMO is referred to as the optical gap, as this is the energy required to excite an electron from the HOMO to the LUMO. Due to its similarity to the inorganic counterpart, the optical gap is usually called the band gap.

Hybridization of s-orbitals into σ -orbitals does not usually lead to semiconducting properties. In order for an organic compound to be a semiconductor, the molecule must be made by alternating π -bonded (formed from p orbitals) and σ -bonded building blocks, which is also known as conjugation. Conjugation allows for de-localisation of the electrons over the conjugated sections of the molecule, which greatly reduces the band gap of the molecule or crystal (to a few electron volts) and enhances charge-transport by allowing for π -stacking (attractive, non-covalent interactions between conjugated segments on neighbouring molecules), which allows for efficient electron transfer between neighbouring molecules (see fig. 2.5c).

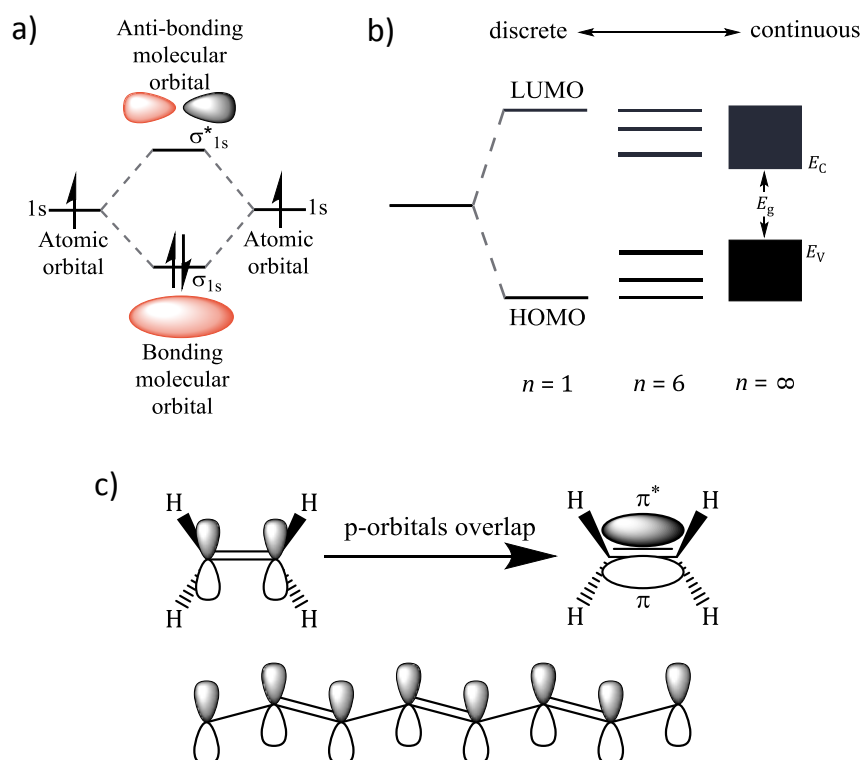


Figure 2.5: a) Schematic of energy level splitting when combining two atomic orbitals into a molecular orbital (here shown for hydrogen, H_2). b) Energy levels going from discrete states to a continuous band in the limit of an infinite crystal, showing the reduction in the band gap and that the LUMO and HOMO levels can be regarded as the conduction and valence band edge energies, and that the optical gap can be regarded as the band gap, in the infinite limit. c) Overlap of two p orbitals to form a π -bond, and a long conjugated segment of alternating π - and σ -bonds.

At $T = 0$ K and in the absence of light to excite an electron across the gap, the lowest energy band is completely filled with electrons, and this band is called the valence band, E_V . The organic semiconductor quantity corresponding to the valence band is the HOMO. On the other side of the band gap, the band is completely empty, and this band is called the conduction band, E_C . The organic semiconductor quantity corresponding to the valence band is the LUMO. The difference between the conduction and valence band edges is called the band gap, E_g .

Metals are materials where the conduction and valence bands overlap ($E_g < 0$ eV), so that the energy bands are not completely empty or completely full, and the charge carriers are free to move within these bands. It is therefore the well-defined E_g that grants the semiconductor its unique properties. Electrons follow Fermi-Dirac statistics, and at room temperature, some

charge carriers will be thermally excited across E_g , giving rise to a low but measurable charge-carrier density and hence electrical conductivity (if measured using a non-contact technique). These thermally excited charge-carriers are called the intrinsic charge-carriers. Materials with large band gaps (usually larger than 2 eV) will have a low concentration of intrinsic charge-carriers, and they are normally referred to as insulators (non-conducting materials). Materials with band gaps lower than 2 eV (but larger than a few $k_B T$) are commonly referred to as semiconductors. This is a somewhat arbitrary definition, but is utilized by many in the research community. The band gap is the quantity giving rise to absorption of photons of visible light. If a photon with an energy equal to or above the band gap energy is incident on the semiconductor, the photon will be absorbed, promoting an electron from the valence band into the conduction band. Such excited charge-carriers can be utilized for photo conduction in solar cells.

Another unique aspect of semiconductors is the possibility to introduce helpful impurities into the semiconductor to increase its electrical abilities. Impurities introduced in this way is called doping. Similarly, during the synthesis process of semiconductors, impurities might be present due to the lack of control. Such unintentional impurities are usually not beneficial for the material application, as they can act as charge-carrier traps. One can normally distinguish between the two by the fact that doping impurities are purposely so low in ionization energy, that charge carriers being trapped there are quickly released, because the position of the trap level is only a few $k_B T$ away from the carrier band. Deeper impurity levels will on the other hand usually act as traps.

2.3.3 Highly studied organic semiconductors

Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a commonly studied semiconducting polymer used as a absorbing material in organic solar cells. Up until around 2006, much work on organic solar cells was put into optimization of the morphology of P3HT based solar cells to increase the efficiency[57, 58, 59]. However, a lot of the work in recent times have been on developing new materials with better absorption and charge transport properties[60, 61], developing better interlayers and optimizing device architecture[62], and making tandem devices (stacked devices for optimised solar spectrum absorption) to increase the efficiency[63, 64]. Developing donor and acceptor materials with optimal band gaps, optimal energy levels for charge separation, and proper processing abilities is paramount for the commercial success of organic photovoltaics. PCDTBT, DPP-TTT and PTB7 are such materials (see fig. 2.6).

PCDTBT shows a relative high efficiency due to, among other reasons, high fill factors and high quantum efficiencies (ratio of charge-carriers collected compared to the charge-carriers

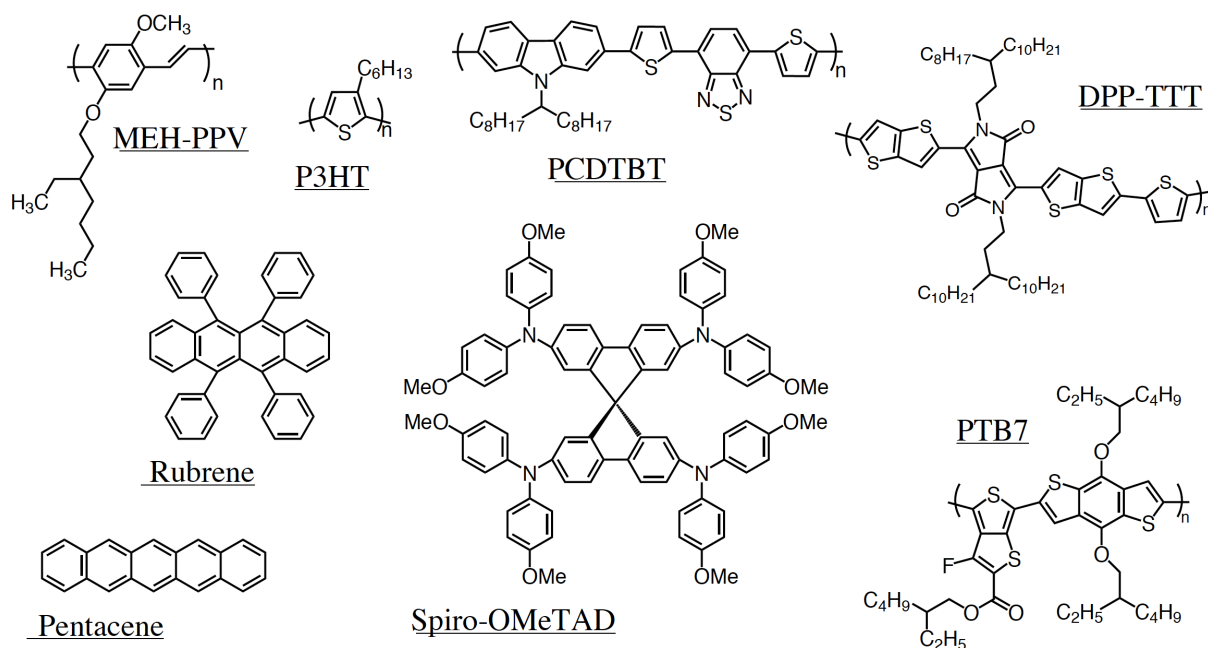


Figure 2.6: Some of the most commonly studied organic semiconductors. Used for Solar cells: MEH-PPV, P3HT, PCDTBT, PTB7 and DPP-TTT. Organic light-emitting diodes: MEH-PPV. Organic field effect transistors: Pentacene. Interlayer material: Spiro-OMeTAD.

generated). This is an indication of a very high collection rate at the contacts, which has been reported to be due to high and balanced charge transport[50, 65]. PTB7 has also been studied extensively with efficiencies exceeding 8%[61, 66]. PTB7-Th, a derivative of PTB7, was the first organic polymer to exceed the benchmark 10% device efficiency, owing it the alternate name PCE10[67].

The group of Prof. He Yan, at Hong Kong UST, currently holds the NREL certified efficiency record for a lab scale single junction polymerfullerene solar cell with a power conversion efficiency of 10.8%[68, 69]. Mitsubishi currently holds the efficiency record for polymer:fullerene solar cells with a power conversion efficiency of 11.0%[70]. Heliatek currently holds the unofficial efficiency record for OPV solar cells with a device efficiency of 13.2% using unknown organic materials.

Besides solar cells, organic materials have also been used to make other thin film technologies, namely organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). An OLED uses an organic semiconductor for the emissive electroluminescent layer. An OLED works in the opposite regime than a solar cell. Instead of generating electricity from light absorption, light is generated from the semiconducting layer from injected charge carriers. MEH-PPV is used as an emissive layer in OLEDs. OLEDs are used to make digital displays for TV screens, computer monitors, mobile phones and hand-held gaming consoles. An OFET uses an

organic semiconductor as the channel material. OFETs have been developed as low-cost and flexible alternative to conventional FET devices. As will be mentioned below, much of the same requirements are needed for efficient OLEDs and OFETs, as for solar cells, regarding charge transport characteristics.

2.3.4 Organic bulkheterojunction solar cells

P3HT, PCDTBT, DPP-TTT and PTB7 are all used as absorbing polymers in organic solar cells. However, these polymers by themselves can not generate a high photo-current due to their low dielectric constants.

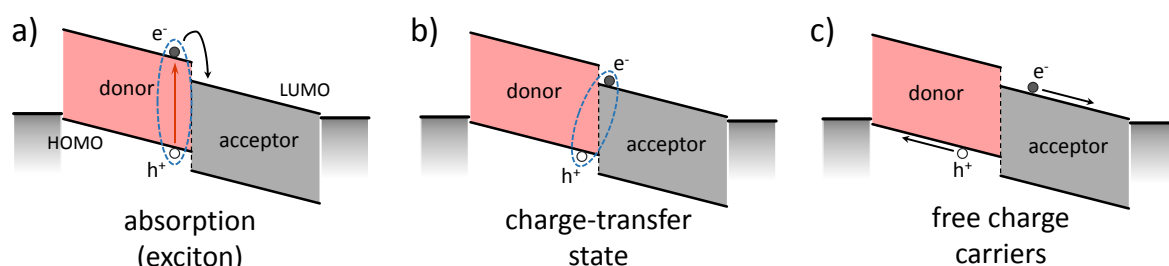


Figure 2.7: Schematic showing exciton separation using a donor/acceptor approach: a) Absorption and formation of the bound exciton, b) charge transfer of the electron to the acceptor, forming a charge-transfer state, and c) dissociation of the charge-transfer state to free charge carriers.

It was mentioned in a previous section that the exciton binding strength is determined by the magnitude of the dielectric constant, ϵ_r . For inorganic materials, where ϵ_r is very large (> 10), excitons dissociate spontaneously. However, in organic materials, where ϵ_r is very small (< 4), excitons are tightly bound. This means that most excitons will diffuse around in the semiconductor until they eventually recombine, resulting in a very low photo-current generation. For this reason, an alternative approach is usually employed to separate the excitons, namely by introducing an electron acceptor in a heterojunction interface with the absorbing (donor) semiconductor (see fig. 2.7a). By choosing an acceptor with an energy offset compared to the donor semiconductors, the electron can transfer from the donor to the acceptor, forming a charge transfer state (see fig. 2.7b), and it is usually easier to separate the charge transfer state than the exciton to form free charge carriers (see fig. 2.7c).

Sariciftci et al reported that charge transfer from a semiconducting polymer to a buckminsterfullerene (C_{60}) upon excitation of a photon in the polymer was possible[71, 72], and upon the discovery of a synthetic route to phenyl-C61-butyric acid methyl ester (PCBM, which is a solu-

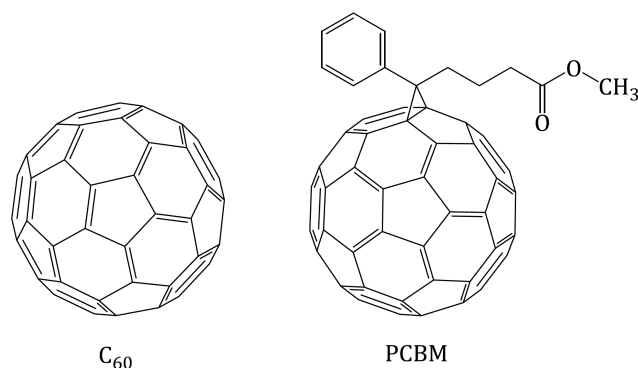


Figure 2.8: The Buckminsterfullerene also known as C_{60} and a solution processable variant of C_{60} called phenyl-C₆₁-butyric acid methyl ester, also commonly called PCBM. PCBM is the most commonly used acceptor material in BHJ solar cells.

tion processable C_{60} derivative)[73] the polymer:fullerene solar cell was reported in 1995[74] (the polymer:polymer bulk-heterojunction solar cells were reported earlier the same year[75, 76]). P3HT in combination with PCBM is by far the most studied material system for organic solar cells.

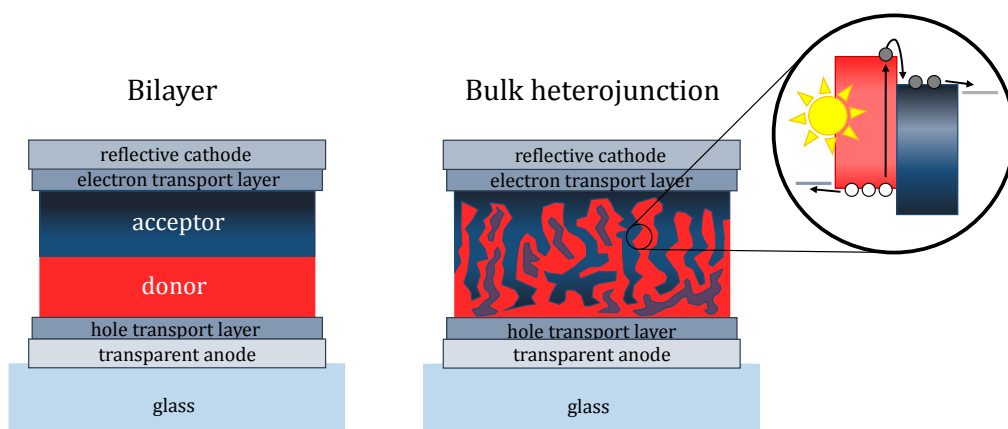


Figure 2.9: Schematic of organic solar cells. Left: Bilayer solar cell employing a donor/acceptor architecture with charge separation happening only at the interface. Right: Bulk heterojunction solar cell with the donor and acceptor phase intermixed to enhance charge-separation.

The simplest organic solar cell design, employing a heterojunction, is the bilayer design (see fig. 2.9), where a flat interface between the donor and acceptor is fabricated, and upon charge dissociation at this interface, the charge carriers can travel to their respective contacts[77]. Such a bilayer structure is however limited by the small exciton diffusion lengths in polymers (approx

10 nm)[77] along with the very small interface between the two materials. For this reason, in order to achieve good charge separation, the thickness of the device must be very small to ensure that most of the excitons reach the donor/acceptor interface, which in turn lowers the absorption (leading to a lower efficiency).

An alternative device structure was achieved by blending the donor and acceptor molecules in the same solution, and upon film processing, a bulkheterojunction could be obtained with the donor and acceptor molecules forming an inter-penetrating network (see fig. 2.9). The bulkheterojunction allows for a very large donor/acceptor interface, allowing for free charge carrier generation and hence more efficient devices. However, as will be discussed below, with this large interface which extends throughout the device, recombination is also made more likely. For this reason, it is extremely important to extract the free charge carriers as quickly as possible to achieve a high device efficiency.

2.4 The role of the charge-carrier mobility

All organic opto-electronic devices share a common trait. Whether the device being a solar cell, an OLED, or an OFET, performance critically depends on the efficiency with which electrons and holes move within the semiconducting material. In a solar cell charge carriers are generated within the materials via photon-induced charge separation at the interface between the donor and acceptor components, and these charge carriers need to be extracted at the contacts to drive a load. Furthermore, fast extraction of charge carriers leads to a reduced power loss and avoidance of excessive heating[78]. In an OLED charge carriers are injected into the organic semiconductors from metal or conducting oxide electrodes, and it is important to have balanced charge transport to ensure that photons are emitted from the right place inside the device (from the emissive layer and not from the interlayers).

2.4.1 The charge-carrier mobility

The charge carrier mobility can be defined in the following way. In the absence of any external potential, transport is purely diffusive and is generally described by a simple diffusion equation. The mean-square displacement, $\langle x^2 \rangle$, due to random motion inside the material, can be described by

$$\langle x^2 \rangle = nDt \tag{2.4}$$

where, n is an integer number equal to 2, 4 or 6 depending on the dimensionality of the system, D is the Einstein-Smoluchowski diffusion coefficient, and t is time. The key quantity characterizing charge transport is the charge-carrier mobility, μ . The charge mobility is related to D , and hence $\langle x^2 \rangle$, via the Einstein-Smoluchowski equation

$$\mu = \frac{qD}{k_B T} \quad (2.5)$$

where q is the elementary charge and $k_B T$ is the thermal energy. Since there is no driving force in the form of an external potential, the average position of the charge carrier will not move and the current across the material will be zero. The dimensions of the charge-carrier mobility is usually given in cm^2/Vs .

2.4.2 Current density

From the above it is clear that the charge-carrier mobility is part of determining the extent a charge carrier can diffuse within a material due to random fluctuations. However, the charge-carrier mobility also determines the velocity of a charge carrier when accelerated through an electric field, F . Such an application of an electric field induces a drift of the charge carriers. The mobility can then alternatively be defined through the charge-carrier drift velocity, ν , and the amplitude of the applied electric field, F , as

$$\nu = \mu F \quad (2.6)$$

where diffusion, in a flat energy landscape, is a local displacement of the charge carrier around an average position, drift induces a displacement of that average position leading to a current flow. The drift current flow of charge, ρ , can be described through the drift velocity ($J = \rho \nu$) by,

$$J_{\text{drift}} = \rho \mu F. \quad (2.7)$$

In the case where there is a local excess of charge carriers, diffusion of such will also lead to a local current which will depend on the charge carrier mobility through the diffusion coefficient,

$$J_{\text{diffusion}} = -qD \frac{d\rho}{dx} \quad (2.8)$$

and the total current can be written in terms of both drift and diffusion, $J_{\text{drift}} + J_{\text{diffusion}}$ of charge carriers,

$$J = \rho\mu F - qD \frac{d\rho}{dx}. \quad (2.9)$$

Note that it is not only the magnitude of μ which is important, but the magnitude of the charge-carrier density also plays a crucial role for the overall magnitude of the current.

If the semiconductor contains traps or is affected by energetic disorder, and/or if the semiconductor device is affected by poor injection, the charge-carrier density and hence the observed/apparent mobility can be greatly affected. As an example, when the mobility of a semiconductor influenced by traps and/or energetic disorder is estimated using experimental methods which cannot directly account for this, the obtained mobility is usually underestimated compared to its true value (the band mobility) and is commonly referred to as an effective mobility,

$$\mu_{\text{eff}}(n, p, T, F) = \mu\Theta(n, p, T, F) \quad (2.10)$$

where Θ is a function which is usually much smaller than unity and usually depends on the charge-carrier densities (n and p), temperature (T), and electric field (F). Examples of reductions of μ_{eff} due to both traps and energetic disorder will be shown both in later sections in the current chapter and in later chapters.

2.4.3 Relating mobilities, and the presence of traps, to solar cell device performance

Several papers have discussed the effect of the magnitude and imbalance of mobilities on optoelectronic device performance[79, 80, 81, 82, 83]. However, the effect of charge-carrier traps has also been extensively studied since many organic devices utilize disordered materials, as traps can have a huge influence on the transport properties, and hence the device performance[80, 84, 85].

The organic solar cell quantities mostly affected by the magnitude and imbalance of the mobilities are the short-circuit current density, J_{SC} , and the fill factor, FF. The competition between non-geminate recombination and collection of free charge carriers will have a profound impact. For example, if the electron and hole mobilities of the active layer materials are too low,

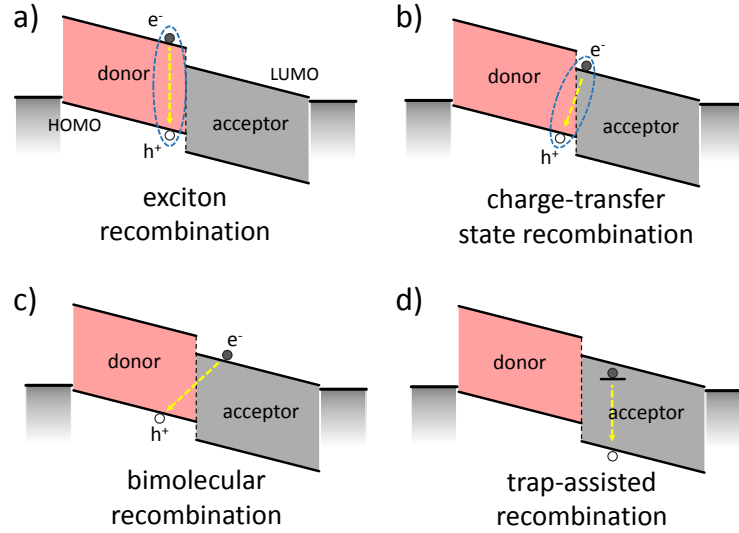


Figure 2.10: Typical recombination pathways in organic solar cells: a) Exciton recombination due to lack of charge separation; b) charge-transfer state recombination; c) bimolecular recombination of free charge carriers; d) trap-assisted recombination between a trapped charge carrier and a free carrier in either the donor or the acceptor.

recombination will dominate over charge collection[81, 82], and if a large imbalance in charge-carrier mobilities is present this will lead to space charge build-up, which will lead to a larger degree of recombination[79, 83]. The J_{SC} and FF are also influenced by the presence of traps and the choice of electrodes[80, 85, 86]. With traps, the overall density of free charge carriers in the device is decreased, and since these trapped charges increase the non-radiative recombination rate this leads to additional losses[85]. So in order to probe these quantities in order to work towards limiting losses it is therefore convenient to use a charge transport method which can probe the charge-carrier mobility, the trap characteristics and in the injection properties.

2.4.4 Mobilities in other thin film technologies

For OLEDs, it is especially important to balance the transport properties[87]. However, this is difficult since most of hole transporting materials used in OLEDs have much higher reported mobilities than the electron transporting materials[88]. For this reason, balance is usually achieved by either increasing the injection barrier for holes or reducing the injection barrier for electrons[88]. Also, similar to solar cells, traps can give rise to unwanted non-radiative recombination leading to losses[89, 90]. OLED device efficiency is also limited by the choice of contacts, especially the magnitude of the injection barriers and unwanted surface recombination[91].

For this reason, it is important to use both a charge-transport method and model which can probe the mobility, traps and injection properties.

2.5 Charge transport in organic semiconductors

The discovery that organic semiconductors behave much like their inorganic counterparts means that a lot of the same theory can be used for their description[52, 53]. The classical semiconductor theory was however developed to understand the crystalline nature of these materials, and since many organic semiconductors are either amorphous or semi-crystalline, some adaptation is required for it to be used to understand charge transport through these materials.

2.5.1 Energetic disorder

Much theory was developed to explain charge transport through disordered inorganic semiconductors, such as amorphous silicon[1, 2], and much of this theory has been used to characterise the disordered behaviour of organic semiconductors. Especially when modelling energetic disorder and traps[20, 21, 22, 85].

Energetic disorder usually arises due to the material's amorphous or semi-crystalline nature. A variation in the degree of the material crystallinity, locally, will give rise to a range of band gaps within the material, since the magnitude of the band gap is affected by the degree of electron localisation (generally, the more delocalised the electrons are, the narrower the band gap, i.e., crystalline materials have narrower band gaps compared to their amorphous counterparts). Similarly, an organic molecule with a large degree of conjugation, i.e., a larger degree of electron delocalisation, will have a small band gap compared to a molecule with no or little conjugation. This range of band gaps will give rise to a varied energy landscape which will affect charge transport.

A large organic molecule, such as a polymer, can have a varied degree of conjugation along the chain due to segments of varied conjugation (see fig. 2.11a). Considering a semiconducting polymer like the ones in fig. 2.8, the polymer will usually not fully crystallise, i.e., will not be straight, but rather twist and bend around the other polymer chains (and fullerene molecules). This gives rise to differences in conjugation length along the chains, which will give rise to variations in the energy levels (see fig. 2.11a). This energetic disorder will affect both the optical properties and the transport properties of the film since the optical gap is no longer described as the difference between discrete states but rather as the difference between two broad distribution of states which can be Gaussian or have some other form such as a superposition between a Gaussian and a discrete level[92, 93, 94, 95](see fig. 2.11b).

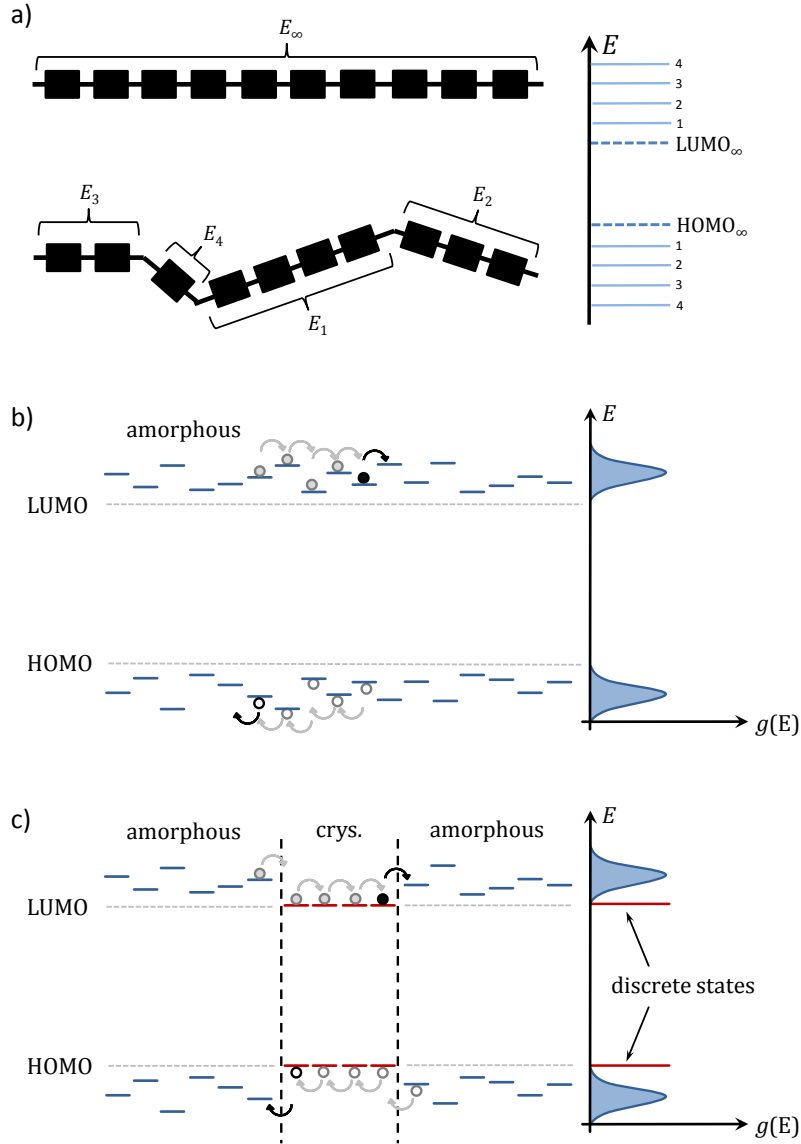


Figure 2.11: Energetic disorder and discrete traps. a) As the chain is segmented (with each segment having a different conjugation length), the wavefunction is interrupted and localized on smaller segments, giving rise to different energy level. b) The density of states is broadened in energy due to varying conjugation lengths. c) Crystalline regions has a lower energy, causing charge-carriers to be trapped. The resulting density of states can be understood as a broad distribution of states from the amorphous phase with a discrete trap level from the crystalline phase.

Since charge carriers will preferentially occupy a low energy state, the transport properties of any semiconducting material will typically decrease with an increase in disorder. In a polymer with a large distribution of energy levels the charge carrier will prefer to occupy the lowest

energy states when travelling down the back-bone. The lowest energy states can therefore be considered as charge neutral trap states from which the charge carrier will have to escape in order to continue moving down the polymer and in order to contribute towards conduction (see fig. 2.11b). The energy landscape as the one seen in fig. 2.11b is usually found in amorphous materials.

2.5.2 Deeper lying traps

As mentioned above, disorder will be decreased, locally, with an increase in the crystallinity of a material (in the case of a polymer, regions of large conjugation segments). However, such local crystalline regions can act as trap sites if the connecting pathway between such domains is amorphous. When mixing crystalline and amorphous phases together, the total density of states will be broad with deeper lying discrete trap states formed by the crystalline phase (see fig. 2.11c). Since electrons prefer to occupy the lowest energy states inside a semiconductor, and since crystalline segments will always have a lower energy compared to the amorphous regions, the electrons will prefer to occupy the states in the crystalline phase. This means that an additional energy is required for the electrons to move from the crystalline phase to the amorphous phase, and transport down the chain is then affected, and decreased, by a combination of the charge carrier preferentially occupying the states in the tails, of the broadened distribution, and the discrete states. Furthermore, deep lying states can be introduced if another chemical species (such as an oxidised species), with a different set of energy levels, is present in the film[96, 97]. This can then be considered as a chemical defect and will usually also be detrimental to charge transport.

In this thesis, we will show examples of reduced charge-transport characteristics due to both the presence of energetic disorder and due to chemical defects.

2.5.3 Popular models for charge transport

Due to the highly varied nature of organic semiconductors, it is important to apply a model which can describe the features arising from the materials either being crystalline or amorphous (or a combination of both). While films of pentacene are usually crystalline, P3HT is well-known to be semi-crystalline, whilst a polymer like PCDTBT is known to be amorphous (see fig. 2.6). It is expected that the density of states of pentacene would be given by relatively narrow HOMO and LUMO levels, whilst the density of states of PCDTBT and P3HT would resemble that of those schematically shown in figure figs. 2.11b and c, respectively.

Historically, two different approaches have been used for the modelling of organic semi-

conductors: i) an *ad hoc* approach of using models such as Bässler’s Gaussian disorder model (GDM)[95] to explain observed temperature and field dependent data obtained when using simpler models which cannot directly account for disorder or traps[98, 99], or ii) a direct inclusion of energetic disorder and traps such as using a multiple-trapping-release (MTR) model for the analysis of charge transport data[13, 22, 23, 85]. Where the GDM is widely regarded as being the most physically realistic model for describing the DOS of organic semiconductors, the two models have been shown give similar results[100]. Furthermore, the most prevalent models used for analytical analysis, to this date, are based on MTR. Since the majority of the work in thesis is comparing charge-transport data analysis when using analytical models compared to numerical models, the work in this thesis will focus on the MTR model. We will briefly introduce the GDM, whereas details of how to model semiconductor devices with the MTR model will be explained in detail in the next chapter.

The GDM was developed in the late 70’s and early 80’s by Bassler and his co-workers to describe the observed temperature and field-dependent effective mobilities, μ_{eff} , obtained from applying simple analytical models to analyse data from time-of-flight measurements (which are briefly introduced in the next section)[94, 95, 101, 102], and was later used to describe the observed effective mobilities obtained from other charge transport measurements, such as space-charge-limited current measurements[103]. The model assumes that the HOMO and LUMO levels are not described by single discrete states, but rather by Gaussian distributions (as seen in fig. 2.11b). Charge carriers in the HOMO and LUMO levels (either naturally present or injected from either a contact or an excitation pulse) will relax to the lowest energy states. If an electric field is applied across the sample, the charge carriers will hop from one site to another until extracted at a contact. This model predicts that μ_{eff} will be temperature, electric field and charge carrier density dependent while the band mobility, μ , will be invariant[102]. The method was very successful in unifying early experimental work with theoretical Monte-Carlo studies. Several extensive reviews have been published in the literature[95, 104]. The MTR model is discussed in detail in the next chapter.

2.6 Charge-transport measurements

From the above discussion it is obvious that when developing new and improving existing semiconductors, it is important to understand the limiting factors of such materials. Even though solution processed materials are relatively cheap and easy to process (compared to their inorganic counterparts), they are usually disordered, and have charge carrier mobilities of several orders of magnitudes below than that observed for perfectly crystalline inorganic

semiconductors. The imperfectness of organic semiconductors also means that impurities are usually present, which can be detrimental for both solar harvesting and collection, and OLED performance since impurities can trap charge-carriers and act as non-radiative recombination centres[85, 105, 106].

Relatively large charge-carrier mobilities are important in solar cells, as the extraction yield of generated charge-carriers is dependent on the charge-carrier mobility (a low mobility will result in a higher probability of radiative and non-radiative recombination)[107, 108]. In order to correctly diagnose the electrical response of the device, measuring charge transport is important. A number of commonly used charge transport measurement techniques exists. All of these techniques have their pros and cons. Some of these techniques are introduced here.

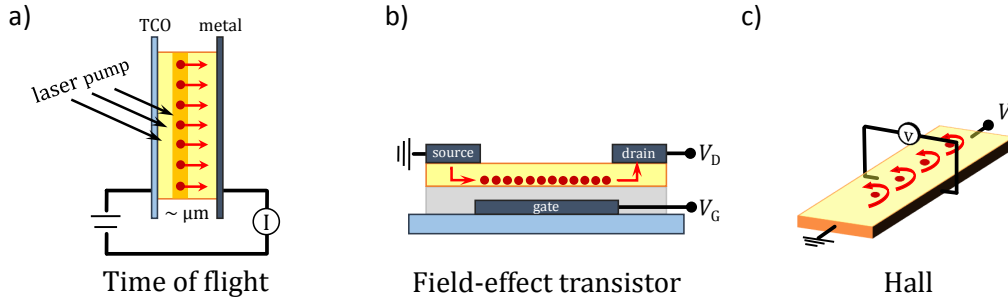


Figure 2.12: Various charge transport measurement techniques: Time of flight (ToF) transient charge transport, field-effect transistors (FETs), and Hall bar measurements.

2.6.1 Time of flight

In time of flight (ToF) measurements, a thick slab of semiconductor is sandwiched between one or more transparent electrodes[109, 110, 111, 112]. A laser pulse with an energy above the semiconductor band gap is used to excite a small concentration of charge carriers in the semiconductor. A high voltage is applied across the device to drive out the photo-generated charge carriers. It is important that the electrodes form blocking contacts to the semiconductor to avoid a current flowing across the device at an applied bias, meaning contacts where charge carriers cannot flow into the device but where charge-carriers are allowed to exit the device. In that way, only current arising from charge carriers excited by the laser pulse are measured. The induced photocurrent at the electrodes is measured as a function of time, and the ToF mobility, μ_{ToF} , is usually determined using,

$$\mu_{\text{ToF}} = \frac{L^2}{Vt} \quad (2.11)$$

where L is the thickness of the probed semiconductor, V is the applied voltage, and t is the average transient time. Despite being relatively simple, there are a few downsides using this technique. To achieve a good temporal resolution, very thick devices must be measured (usually on the order of several microns for low mobility organic semiconductors and even thicker for high mobility semiconductors). Fabrication of thick devices usually require a relatively large amount of material, which is not an option when measuring novel synthetic materials with difficult and inefficient synthetic routes. Furthermore, solution processed thin films often vary in morphology with thickness due to the changes in the processing steps. This means that the film being measured with ToF might not properly reflect the film being used in a solar cell. For the above-mentioned reasons, ToF is usually used to measure charge transport in more established materials or materials whose morphology is rather insensitive to film thickness. On a positive note, charge transport of electrons and holes can be probed separately simply by changing the polarity of the applied voltage. A schematic of a ToF measurement is shown in fig. 2.12a.

2.6.2 Field-effect transistors

Organic field-effect-transistors (OFETs) are a whole class of important devices receiving a lot of scientific attention[113]. An OFET is a type of device in which the semiconductor, called the channel material, does not conduct electricity in its off state, even when a voltage is applied across the semiconductor between the two contact electrodes, called the source and drain (see fig. 2.12b). An OFET can be turned on by applying a voltage to the gate electrode, which induces charge carriers in a channel layer on the other side of an insulating material (called accumulation mode). When the channel is filled with charge carriers, a current can flow from the source to the drain, even under a low applied voltage. Due to the on/off nature of transistors they are used to make amplifiers and logic gates for more complex electronic components. The mobility of a semiconductor can be measured in a FET structure without the ultimate application being a transistor, as is commonly done so in the organic semiconductor community. The analytical models that people use to fit to OFET curves were derived to describe the current through inorganic transistors in the linear and saturation current-voltage regimes. The expression governing the current in the linear regime is given by,

$$I_{SD} = \frac{W}{L} \mu_{FET} C (V_G - V_T) V_{SD} \quad (2.12)$$

and the expression governing the current in the saturation regime is given by,

$$I_{SD} = \frac{W}{2L} \mu_{FET} C (V_G - V_T)^2 \quad (2.13)$$

where I_{SD} and V_{SD} are the source-drain current and voltage, respectively, W is the width of the channel, L is the thickness of the channel, C is the dielectric capacitance, V_G is the gate voltage and V_T is the threshold voltage. OFET charge transport is usually said to be affected by structural defects within the organic layer and at the interface amongst other things. Furthermore, OFETs measure the lateral device structure across large distances (usually tens of microns). The mobility is measured in the accumulation regime where a large gate voltage is applied to electrostatically increase the charge-carrier density to values close to degeneracy. For that reason, the mobility obtained from FET measurements will most likely differ to mobilities obtained from ToF measurements, at least when analytical models are used.

2.6.3 Hall bar measurements

Similar to FET measurements, Hall bar measurements can probe the lateral charge transport of an organic semiconductor[114, 115]. By placing a current carrying semiconductor in a magnetic field, free charge carriers experience a force perpendicular to the flowing current and the magnetic field (the Lorentz force law). The quantity measured in the direction of the force is called the Hall coefficient and will depend on the ratio of the electron and hole mobility along with the electron and hole concentrations. Like ToF measurements, Hall measurements can, in principle, analyse the charge-transport of electrons and holes separately, but require rather sophisticated device structures and the need for a uniform magnetic field.

2.6.4 Space-charge limited current measurements

Solution processed solar cells are often manufactured by adding consecutive layers of material, giving rise to a sandwich type structure (see fig. 2.9). Since the volume mobility, in the vertical transport direction, is the important parameter in a sandwich type structure, techniques that measure either horizontal or surface mobilities (such as FETs and Hall bar measurements) are not ideal. Furthermore, the processing of the devices can lead to anisotropy of the charge transport in the absorbing material, which will influence the measured values (as the horizontal

mobility could easily be larger than the vertical mobility due to the packing of the material or the preferred charge-transport direction). For this reason it is important to utilize a technique which is directly comparable with solar cells if one wants to learn about semiconducting materials used in such devices. The space-charge-limited current (SCLC) measurement is a convenient method to determining the volume charge carrier mobility of a semiconducting (or insulating) thin film, since the devices are easy to fabricate and the measurements are simple to perform. If the experimental equipment is available for the fabrication and characterisation of thin-film electronics, it is then possible to make single-carrier devices and to perform SCLC measurements. The obtained data is however prone to misinterpretation since the current density-voltage (J - V) curves are strongly affected by impurities in the measured films and the choice of contacts[12, 13].

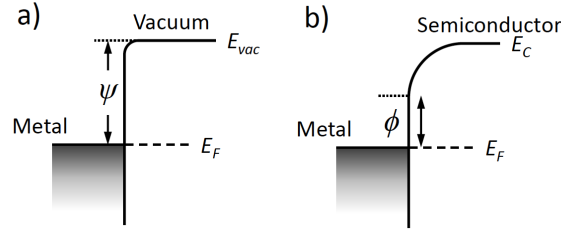


Figure 2.13: Energetic similarity between a) the origin of current flow through vacuum (Child's law) and b) the origin of current flow through a semiconductor.

The idea that high currents can flow through a semiconductor came from the realisation that charge-carrier injection from a metal into a semiconductor is similar to charge emission from an electrode into vacuum (Child's law)(see fig. 2.13a)[116, 117]. Instead of emitting from a metal into the vacuum level, electrons are emitted (injected) from the metal into either the conduction or valence band of the semiconductor (see fig. 2.13b). Based on this concept, Mott and Gurney proposed SCLC in 1940. They proposed that currents far beyond that due to intrinsic charge carriers could be drawn through a semiconductor if appropriate contacts were used[11]. In their 1940 book Mott and Gurney presented their famous square-law equation,

$$J = \frac{9}{8} \mu \varepsilon \frac{V^2}{L^3} \quad (2.14)$$

which is commonly referred to as the Mott-Gurney law. Much later, in 1953, Dacey found that germanium (Ge), which is a low band gap semiconductor ($E_g = 0.67$ eV), exhibited SCLC when a voltage was applied across appropriate contacts. Soon after in 1955, Smith and Rose showed

that reasonably high SCLC could be drawn through crystals of cadmium sulphide (CdS), which was considered as being an insulator ($E_g = 2.42$ eV)[3, 4].

Smith and Rose reported that temperature had a profound effect on the observed current, something which could not simply be explained as being due to the increase of intrinsically present charge carriers with increasing temperature. From this it was concluded that defects inside the crystal was giving rise to trap sites which was hindering the current, releasing charge carriers for conduction with increased temperature (In 1953, Urbach had shown that there are exponential tails extending in from the density of states in the band gap of a semiconductor[118]). Based on the idea of exponential tails by Urbach, Rose developed a simple theory to give a qualitative explanation for the reduction in the current, and proposed that SCLC could be a simple tool to understand and estimate defects in semiconducting thin films[14].

Building on the work by Rose, Mark and Helfrich derived a more detailed equation in 1962 showing that the increase of the characteristic energy of the Urbach tails will have a direct influence on the amount of current that can pass through a semiconductor[12]. Mark and Helfrich also showed that not only the magnitude of the current is affected by traps but also the slope of the J - V curve will be influenced, once more supporting the idea that SCLC measurements can be used to gain information about traps.

SCLC went on to become widely used in the 1980s for determining the density of states within the band gap of amorphous silicon[1, 119], and was also, and is still, used to determine charge carrier mobilities and information about traps in organic thin films made from either polymers[21, 120, 121, 122, 123, 124, 125] or small molecules[23, 126, 127, 128].

Chapter 3

Theoretical Treatment of Charge Transport in Disordered Semiconductors

3.1 Organic semiconductors

To model charge transport in organic semiconductors, some basic semiconductor theory must be discussed. In the following sections, basic theory of intrinsic, disordered and doped organic semiconductors is presented. Most of the theory describing organic semiconductors borrows from the description of amorphous inorganic semiconducting materials, such as amorphous silicon.

3.1.1 Intrinsic semiconductors

By an intrinsic semiconductor is understood a semiconductor which does not contain any impurities and no (or a low degree of) energetic disorder, i.e., a perfect semiconducting crystal. In the absence of injection into the semiconductor from a contact material and in the absence of excitation from a light source, the charge-carrier densities of electrons and holes (the intrinsic charge-carrier densities) in an intrinsic semiconductor are purely governed by the density of states and the temperature of the system. For this to be clear, we first need to discuss the concept of the density of states.

Density of states

The number of states per unit energy is called the density of states (DOS). The DOS is an important quantity in semiconductor physics. A large DOS means that a large number of states can be occupied (if empty) or excited (if occupied), hence, the DOS yields information about transport and optical properties. For an intrinsic semiconductor, the DOS will be zero in the forbidden gap, so one only has to consider the DOS above the conduction band edge and below the valence band edge. For a periodic three-dimensional solid (which are the kinds we will consider in this study), the DOS (including spin degeneracy) above the conduction band, g_C , will be proportional to the square root of the energy (see fig. 3.1),

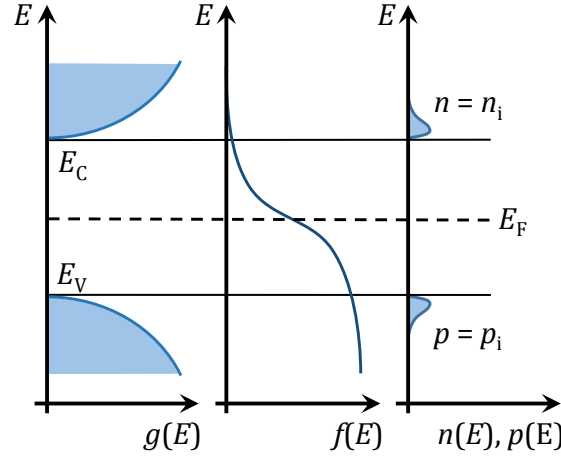


Figure 3.1: Schematic of the 3D-DOS for electrons and holes, the Fermi-Dirac occupation function and the resulting intrinsic charge-carrier densities were one to calculate these numerically.

$$g_C(E) = \frac{8\pi\sqrt{2}}{h^3} (m_e^*)^{3/2} \sqrt{E - E_C} \quad (3.1)$$

where m_e^* is the effective mass of the electrons (the hole effective mass is denoted by m_h^*), and h is Planck's constant. The charge-carrier density can be calculated from the DOS by considering Fermi-Dirac statistics (giving us the probability of finding a free electron, a Fermion, in the conduction band). The electron density can be describes by the DOS and the Fermi-Dirac distribution function, $f = \left\{ 1 + \exp \left(\frac{E - E_F}{k_B T} \right) \right\}^{-1}$, through,

$$n = \int_{E_C}^{\infty} g_C(E) \left\{ 1 + \exp \left(\frac{E - E_F}{k_B T} \right) \right\}^{-1} dE \quad (3.2)$$

where E_F is the Fermi level and $k_B T$ is the thermal energy. As long as E_F is not too close to the conduction band edge (approximately $E_C - E_F > 3k_B T$), Fermi-Dirac statistics can be approximated by Maxwell-Boltzmann statistics, and eq. 3.2 can be written as,

$$n = \int_{E_C}^{\infty} \frac{8\pi\sqrt{2}}{h^3} (m_{e/h}^*)^{3/2} \sqrt{E - E_C} \exp\left(-\frac{E - E_F}{k_B T}\right) dE. \quad (3.3)$$

By using the Maxwell-Boltzmann approximation, the above integral can be solved, and we obtain an expression which depends on the relative position of the Fermi level to the conduction band edge,

The term outside of the exponent is called the effective DOS and is a number density ($[n] = \text{cm}^{-3}$) rather than a distribution. The effective DOS is a convenient quantity to work with since it's a constant.

$$n = 2 \left(\frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \exp\left(-\frac{E_C - E_F}{k_B T}\right). \quad (3.4)$$

Note that the effective density of states for holes can be calculated analogously. Hence, for a perfect three-dimensional crystal, the effective DOS for electrons or holes is given by,

$$N_{C/V} = 2 \left(\frac{2\pi m_{e/h}^* k_B T}{h^2} \right)^{3/2} \quad (3.5)$$

where $m_{e/h}^*$ is the effective mass of either electrons or holes. The effective DOS will be used on numerous occasions throughout this thesis.

In order to calculate the values of the effective DOS, one must know the effective masses. The effective masses are however given by the curvature of the band structures, which are not well defined for most organic semiconductors. For the purpose of this study, where the band structures of the semiconductors are not known, the effective masses are not known directly either, and it is hence impossible to calculate the exact value for the electrons and holes effective DOS. For that reason, values for the effective DOS will usually be set between 10^{19} and 10^{20} cm^{-3} (for both electrons and holes). Values in this range have been used to model several organic semiconductors in the past.

Intrinsic charge-carrier densities

With knowledge of the DOS, and with the definitions of N_C/V , we can now calculate the intrinsic charge-carrier concentrations analytically. The charge-carrier densities can be described through the effective DOS as,

$$n = N_C \exp\left(\frac{E_F - E_C}{k_B T}\right) \quad \text{and} \quad p = N_V \exp\left(\frac{E_V - E_F}{k_B T}\right). \quad (3.6)$$

In an intrinsic semiconductor (without any contact with other materials), the electron and hole carrier concentrations will be equal, giving rise to a zero net charge density, or charge neutrality. Furthermore, the law of mass action states that the product of the electron and hole density at equilibrium must be a constant and is related to the intrinsic charge-carrier density, $np = n_i^2$. The square root of the product of the above two equations then yields,

$$n_i = p_i = \sqrt{N_C N_V} \exp\left(-\frac{E_g}{2k_B T}\right). \quad (3.7)$$

Given typical values for the effective DOS of both carrier types of 10^{19} cm^{-3} , a band gap of 1.7 eV and the thermal energy at room temperature, 0.026 eV, the intrinsic carrier concentration is approximately $n_i = 5.26 \cdot 10^4 \text{ cm}^{-3}$ with the intrinsic Fermi level in the middle of the band gap. This charge-carrier density is very small and is usually not detected in a semiconductor device due to charge-carrier injection from the contacts or due to excited charge carriers due to a light source. Note that organic semiconductors usually have a band gap which is larger than 1.7 eV (with many of the commonly used materials having a band gap between 2 and 3 eV), meaning that the intrinsic charge-carrier density is even less than the estimate shown here.

3.1.2 Energetic disorder and traps

As mentioned in the chapter 2, organic semiconductors rarely behave intrinsically, but usually have some degree of energetic disorder and/or trap states limiting their charge-transport characteristics. For that reason, it is common to model the DOS with a Gaussian distribution around the HOMO and LUMO levels (see fig. 3.2a)[92][93][94][95].

However, instead of modelling the DOS of an organic semiconductor using a Gaussian distribution, the DOS can be modelled using a parabolic density of states (as used to describe crystalline inorganic semiconductors) and have a exponential tail extend into the gap (see fig. 3.2b). This is a useful approach since i) an exponential tail can be used to approximate a tail

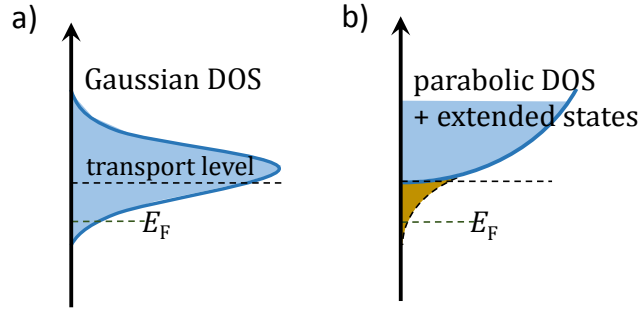


Figure 3.2: a) Schematic of a Gaussian DOS distribution due to energetic disorder showing the approximate position of the transport level and an arbitrary position of the Fermi level during device operation. b) Modelling of energetic disorder using a combination of a parabolic DOS and extended states in the form of exponential tails.

of a Gaussian distribution and ii) since it is easier to perform calculations with exponentials rather than Gaussians.

As mentioned in chapter 2, crystallites and chemical defects can give rise to traps which lies deeper in the gap than the tail of the Gaussian distribution. For this reason it is important to have the possibility to model a density of states which is more complex than just the tail of the Gaussian (see fig. 3.3a). Furthermore, such trap levels are usually not entirely discrete, but will have some width, and are usually modelled by adding a Gaussian distribution of traps somewhere in the gap (see fig. 3.3b). Within the DOS model used in this thesis, the total DOS can then be modelled using a parabolic distribution of transport states, with an exponential tail extending into the gap along with allowing for a Gaussian distribution of additional defects.

In the results chapters we will show that some organic semiconducting materials can be modelled simply by using exponential tails while other materials must be modelled using a deeper distribution of trap states. Modelling of trap states, both exponential tails and Gaussian distributions, will be discussed in greater detail later in this chapter.

3.1.3 Doping

If impurities are introduced into semiconductor, either through intentional incorporation during or after the synthesis or growth, or through unintentional incorporation due to lack of control, charge carriers in the form of free electrons and/or holes can be introduced, far beyond the intrinsic charge-carrier density level, if the impurity energy level is shallow compared to $k_B T$. Most semiconductors cannot be synthesised/grown as single crystals with high purity levels, especially not solution processed organic semiconductors, and even gallium arsenide (a semi-

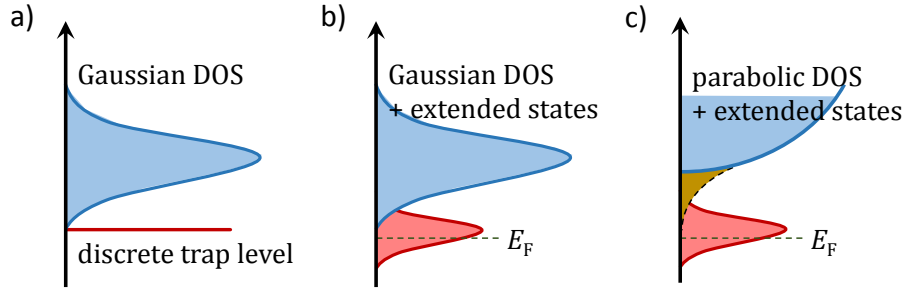


Figure 3.3: a) Schematic of a combination of a Gaussian DOS distribution due to energetic disorder and a discrete trap level due to local crystallisation of the material. b) A combination of a Gaussian DOS distribution and a broadened discrete trap level (Gaussian distribution) due to various degree of crystallisation. c) Modelling of both energetic disorder and discrete trap using a combination of a parabolic DOS and extended states in the form of exponential tails and a Gaussian distribution.

conductor used for record solar cell efficiencies), in its purest commercially available form, will have a carrier density greater by more than nine orders of magnitude from what would be expected from an intrinsic material with a band gap of 1.43 eV.

n- and p-type semiconductors

A semiconductor can be doped in two ways: In the case where electrons are introduced to the semiconductor from the impurity levels, the doping is called donor type, since electrons are donated from the impurity to the conduction band. In the case where holes are introduced, the doping is called acceptor type, since electrons are accepted from the valence band to the impurity level, leaving a vacant hole behind. Ionized donor states provide electrons to the conduction band, and the resulting semiconductor is called n-type. Likewise, ionized acceptor states provide holes to the valence band, and the resulting semiconductor is called p-type.

In fig. 3.4, examples of doping in silicon are shown (silicon was chosen as an example since it is a simple system). Figure 3.4a is showing an intrinsic semiconductor crystal, where all four valence electrons for all atoms are fulfilling the octet rule (the crystal shown is highly simplified, and an actual silicon crystal will form a diamond cubic structure). If a phosphorus atom is introduced into the crystal (fig. 3.4b), the fifth valence electron will not be required for bonding and is therefore free to move around in the crystal. Each incorporated phosphorus atom will then yield a free electron, if ionized, and the semiconductor is now called n-type. Similarly, if a boron atom is introduced, an additional electron is required for bonding, leaving

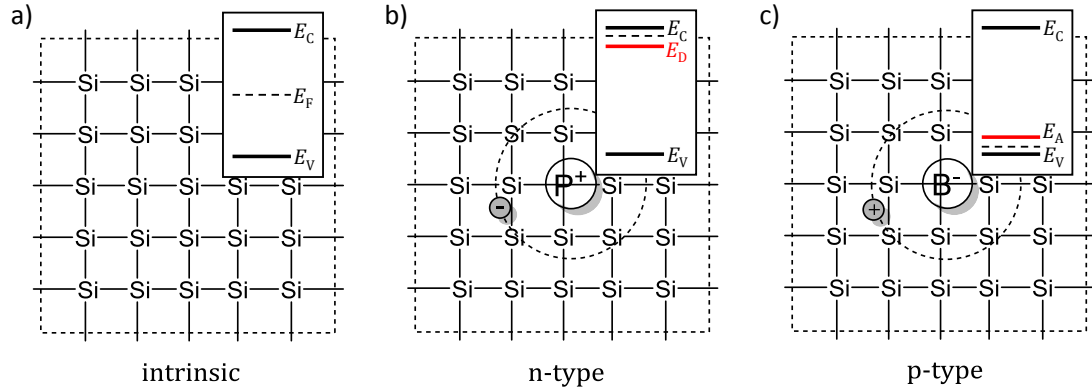


Figure 3.4: Schematic showing the effect of doping crystalline silicon. a) Intrinsic silicon with the Fermi level in the middle of the band gap, b) n-type silicon, where electrons from the donor level is introduced to the conduction band by the phosphorus atom in the crystal, and c) p-type silicon, where electrons from the valence band are introduced to the acceptor level due to the boron atom in the crystal, leaving behind a large density of holes.

behind a hole. Each incorporated boron atom will then add a hole, and the semiconductor is now called p-type (fig. 3.4c).

Impurity ionization

Whether or not the impurities are ionized depends on the thermal energy, $k_B T$, and the position of the impurity energy level within the band gap, E_g .

In fig. 3.4b and c, the introduced charge-carriers are shown to be bound to the dopant atoms due to the Coloumbic force between them (meaning that they are not available for conduction). These charge-carriers can be made free for conduction if the impurity is ionized, which can be achieved at room temperature is the impurity energy level is sufficiently close the band edge. Provided that the impurity levels are very shallow shallow (for example, $E_C - E_D \ll k_B T$), it can be assumed that all the introduced impurity states are ionized at room temperature,

$$N_D^+ = N_D \quad \text{and} \quad N_A^- = N_A \quad (3.8)$$

where N_D^+ and N_A^- are the concentrations of ionized donors and acceptors respectively, and N_D and N_A are the impurity concentrations of donors and acceptors atoms, respectively. If $N_D^+ = N_A^-$, in the same sample, the net charge-carrier density due to inonized dopants will be zero since the carriers resulting from the ionization will compensate each other. However, if the

the ionization concentrations are imbalanced, the electron and hole carrier concentrations will be given by,

$$n \cong N_D^+ - N_A^- \quad \text{if} \quad N_D^+ - N_A^- \gg n_i \quad (3.9)$$

$$p \cong N_A^- - N_D^+ \quad \text{if} \quad N_A^- - N_D^+ \gg n_i. \quad (3.10)$$

The intrinsic charge-carrier density for a 1.43 eV band gap semiconductor was calculated in a previous section to be around $5.26 \cdot 10^4 \text{ cm}^{-3}$. So given the net doping concentration of shallow dopants is orders of magnitudes higher than this value, the charge-carrier density will be fully governed by doping.

Doping organic semiconductors

The basic principle of doping organic semiconductors is similar to that of inorganic materials, in that, one has to add impurities which either transfer an electron to the LUMO states (n-type doping) or remove an electron from the HOMO states to generate a free hole (p-type doping)(see fig. 3.5a and b).

If conjugated organic semiconductors are oxidized, some of the delocalised electrons are removed from the p-orbitals, and all the other electrons are now able to move in the partially empty orbitals. This can be achieved in a number of ways: Strong oxidizing gases, such as chlorine, iodine or bromine, are commonly used to make p-type materials[55]; large aromatic molecules with strong donor or acceptor characteristics can also be used to either reduce or oxidise semiconductors[129].

A number of doped organic semiconductors are used within the field of OPV and for OLEDs. The commonly used doped polymer, poly(3,4-ethylenedioxythiophene), often abbreviated to PEDOT, is a highly transparent and conductive ($\approx 300 \text{ S/cm}$) p-type polymer synthesised to be a transparent electrode (see fig. 3.5c). However, PEDOT is not soluble, making it difficult to process. This solubility problem can be circumvented by using a water-soluble electrolyte called poly(styrene sulfonic-acid) which is abbreviated to PSS. PSS acts as a charge-balancing ion during polymerization yielding PEDOT:PSS in an aqueous dispersion, which can easily be cast into thin films. Even though PEDOT:PSS is not as transparent or as conductive as PEDOT, it is still an excellent transparent contact ($\approx 10 \text{ S/cm}$) which can be processed from a water solution, making it an ideal contact material for both organic solar cells and organic light-emitting diodes[130].

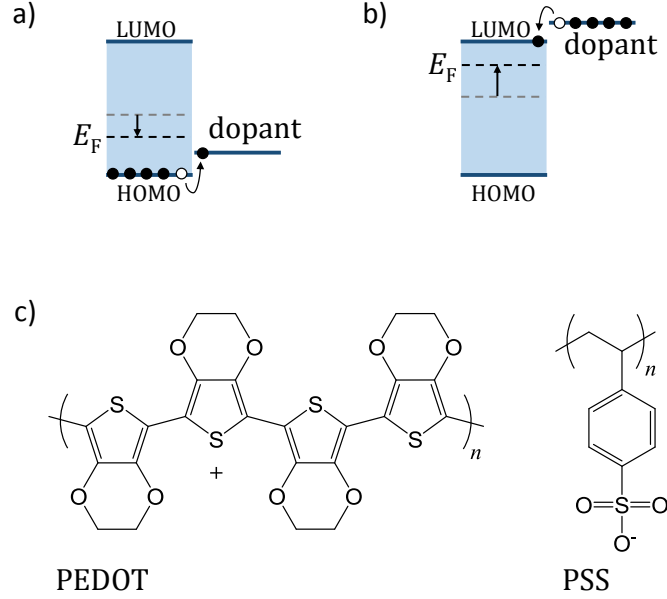


Figure 3.5: a) p-type doping of an organic semiconductor by using an acceptor like dopant (or an oxidation agent). b) n-type doping using a donor like dopant (or reduction agent). c) The two components used in the commonly used transparent and conductive p-type semiconductor, PEDOT:PSS.

3.2 Single-carrier devices

As mentioned in the previous chapter, SCLC measurements are performed on single-carrier devices, i.e., devices containing only one charge carrier type (electrons or holes). In order to understand how single-carrier devices respond to an applied voltage, metal/semiconductor interfaces must first be discussed to some detail.

3.2.1 Metal/intrinsic semiconductor interface

The amount of energy needed to release an electron from a metal to vacuum is called the work function, χ_m . It is defined as the energy difference between the metal Fermi level, E_F , and the vacuum level, E_{vac} ($E_{vac} - E_{F,m} = \chi_m$) (see fig. 3.6a). The work function is a material dependent parameter which varies over many electron volts between different materials. Low work function materials include (amongst many) calcium (2.9 eV), caesium (2.1 eV) and lithium (2.9 eV) and high work function materials include gold (5.1 eV), silver (4.7 eV) and platinum (> 5 eV). Since the work function is a measure of how easy it is to extract an electron from the metal, it is also a measure of how easily the metal will react. For example, both calcium and caesium are highly reactive metals and will readily form oxides. Silver is less reactive but will oxidize, where gold and platinum on the other hand are inert. Generally, the larger the work

function, the less reactive the metal.

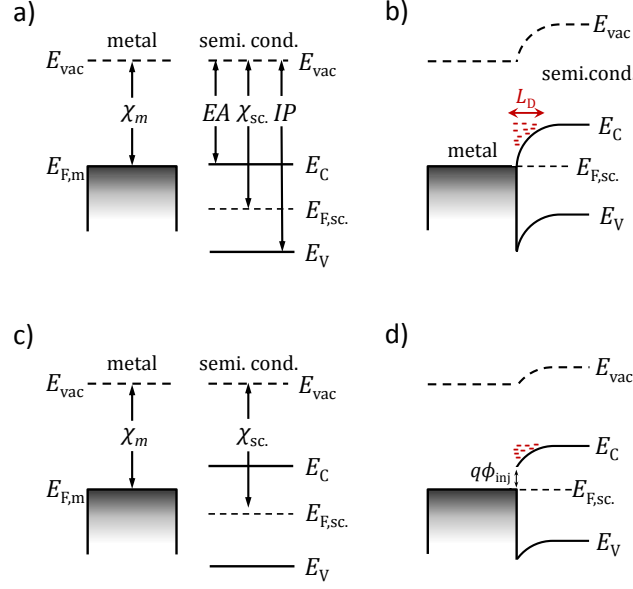


Figure 3.6: a) Metal and a semiconductor (with $E_{F,m} = E_C$) prior to contact and Fermi level equilibration. b) Metal/semiconductor interface (Ohmic contact) where a large number of electrons have been injected into the semiconductor near the interface (the depth of the space-charge region formed at the interface is roughly given by the Debye length, L_D). c) Metal and a semiconductor (with $E_{F,m} < E_C$) prior to contact and Fermi level equilibration. d) Non-Ohmic contact, showing an injection barrier, $q\phi_{inj}$, formed at the interface.

Where a metal is defined by its work function in the context of metal/semiconductor interfaces, a semiconductor is defined by a number of quantities such as the electron affinity, $EA = E_{vac} - E_C$, the ionization potential, $IP = E_{vac} - E_V$, the band gap, $E_g = E_V - E_C$, and the work function, $\chi_{sc} = E_{vac} - E_{F,sc}$, where $E_{F,sc}$ is the Fermi level of the semiconductor (see fig. 3.6a). Since the majority of electrons will reside in the valence band (when the semiconductor is in its neutral state) the amount of energy needed to ionize the semiconductor, by extracting an electron from the valence band to vacuum, is governed by the IP . The affinity for the semiconductor to accept an electron is, however, given by the EA . Different from the metal Fermi level, the semiconductor Fermi level governs the relative concentration between electrons and holes.

When a metal is brought into a contact with a semiconductor, charge carriers will be injected from the metal to the semiconductor until the interface reaches thermodynamic equilibrium

(constant metal and semiconductor Fermi level across the interface). These injected charge carriers will greatly increase the charge-carrier density in the vicinity of the interface to a value many orders of magnitude higher than the intrinsic charge-carrier population, forming a space-charge layer. The depth of the space-charge layer, from the metal contact, will be roughly equal to the Debye screening length,

$$L_D = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{q^2 n_\gamma}} \quad (3.11)$$

where n_γ is the concentration of the carrier type present in the device (the subscript, γ , is merely to help distinguish between the different charge-carrier densities) and $k_B T$ is the thermal energy. Since the majority of the injected charge carriers reside near the interface, the charge-carrier density will be highly non-uniform.

If the work function of the metal is equal to the conduction band edge of the semiconductor, an Ohmic contact will be formed as shown in fig. 3.6b. If the work function of the metal larger than $E_{\text{vac}} - E_C$ of the semiconductor, but smaller than the Fermi level of the semiconductor, as shown in fig. 3.6c, a non-Ohmic contact is formed (see fig. 3.6d).

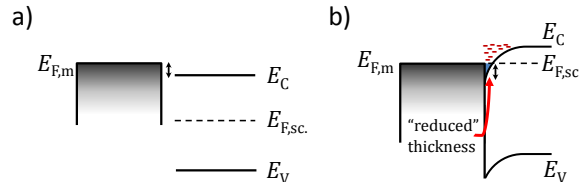


Figure 3.7: Schematic of Ohmic contact formation when $E_C < E_{F,m}$ (indicated by the small black arrow). a) Prior to thermal equilibrium, and b) after thermal equilibrium. The small highly doped region effectively reduces the thickness of the semiconductor layer by a small amount.

In the case that the Fermi level of the metal is shallower than the conduction band ($E_C < E_{F,m}$)(see fig. 3.7a), upon interface formation, charge carriers will be injected from the metal into the conduction band of the semiconductor until the Fermi level is aligned across the interface. The semiconductor will in this case be highly doped at the interface and will behave as a metal (see fig. 3.7b). This will cause the effective thickness of the semiconductor to be reduced but with the metal/semiconductor interface forming an Ohmic contact. Using metals with very small work functions, such as calcium, for making excellent contacts to semiconductors, is very common.

3.2.2 Metal/doped semiconductor interface

In the case of the intrinsic semiconductor it was shown that by varying the work function of the metal between the conduction band and the Fermi level of the semiconductor, either an Ohmic contact or a non-Ohmic contact is achieved.

The Fermi level in a semiconductor is highly dependent on the doping levels in the material, with n-type materials having the Fermi level close to the conduction band and p-type materials having a Fermi level close to the valence band. Depending on the position of the doped semiconductor energy levels relative to the metal work function, three types of contacts can be formed.

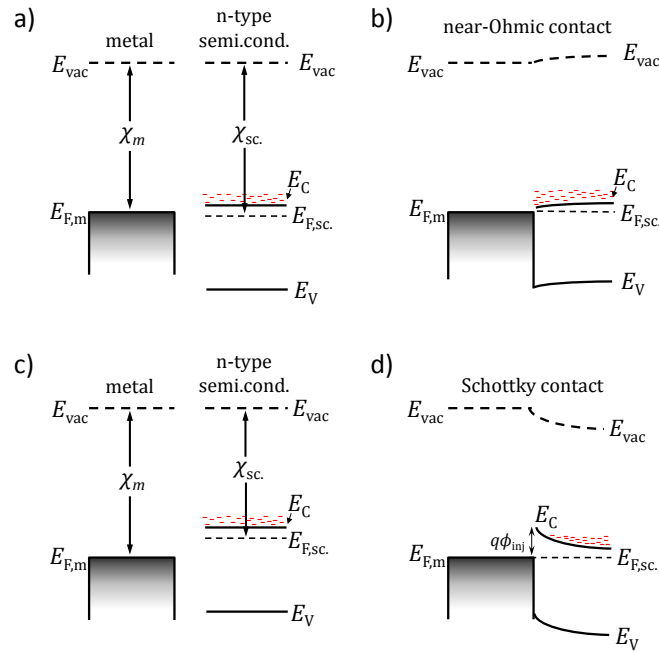


Figure 3.8: a) Metal and an n-type semiconductor prior to contact and Fermi level equilibration (with $\chi_m \leq \chi_{sc}$). b) Metal/semiconductor interface forming a near-Ohmic contact with a very small injection barrier height ($q\phi_{inj} = E_C - E_{F,m}$ which in this case is very small). c) Metal and an n-type semiconductor prior to contact and Fermi level equilibration (with $\chi_m > \chi_{sc}$). d) Metal/semiconductor interface forming a Schottky contact, with a depletion region with a low density of electrons near the interface, and with a very large injection barrier height from the metal to semiconductor. Interface formation between a metal and a p-type semiconductor is analogous.

Since the energy difference between the conduction band and the Fermi level in an n-type semiconductor is small, varying the metal work function by a small amount will have larger

consequences. Similar to the case of the intrinsic semiconductor/metal interface, if the metal work function is equal to the conduction band edge of the n-type semiconductor, an Ohmic contact is formed. If the metal work function is slightly larger than $E_{\text{vac}} - E_C$ but smaller than the work function of the semiconductor, a non-Ohmic contact will be formed. Note that the injection barrier is usually very small in such a contact, and can be regarded as a near-Ohmic contact. If the metal work function is larger than the work function of the semiconductor, the band bending will cause a Schottky contact to form (see fig. 3.8c and d), which is a very different contact than the Ohmic and non-Ohmic contact due to its rectifying behaviour.

In order to achieve a good Ohmic contact to a doped semiconductor, it is important to try and match the metal work functions as close to the conduction band as possible, since a small deviation could lead to a Schottky barrier to form.

3.2.3 Double-junction device

So far we have shown a single interface between a metal and a semiconductor. However, single-carrier devices consist of a semiconductor sandwiched between two selective electrodes, i.e., two interfaces like the ones shown in fig. 3.6.

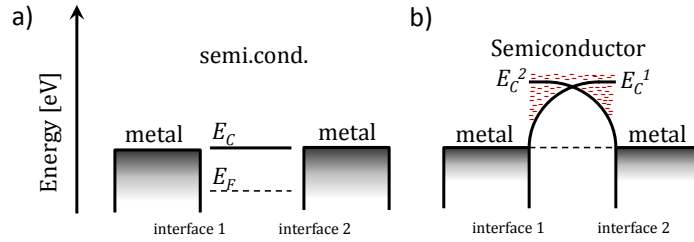


Figure 3.9: Metal/semiconductor/metal interface prior to and after equilibrium. E_C^1 and E_C^2 represents the conduction band edges arising from interface 1 and 2, respectively.

In a metal/semiconductor/metal device where the metal work functions have been selected to form Ohmic or non-Ohmic contacts to the semiconductor, and where the semiconductor layer is thinner than twice the space-charge layer thickness (a situation which is also called overlapping contacts[131, 132]), charge carriers are injected from both electrodes in excess of the intrinsic carrier density across the length of the device. Such a device, as shown in fig. 3.9a and b, is completely governed by electrons, and the device is called an electron-only device. Since injection of further charge carriers, when applying a bias voltage across the device, is of the same type as those already present in the device, the current flowing through the device is space-charge-limited and does not depend on intrinsic charge carriers ($n \gg n_i$ across the entire

device).

By choosing metals with work function values close to the value for the semiconductor IP, upon thermal equilibrium holes would flow into the valence band, and the resulting device would be a hole-only device. Since electron- and hole-only devices are completely analogous, we focus the theoretical descriptions on electron-only devices throughout this thesis.

Single-carrier devices, and how the equilibrium and injected charge carriers respond to an applied voltage, will be explained in more detail later in this chapter.

3.2.4 Injection into a disordered semiconductor

In the framework of the GDM, it has been shown that injection from a metal into a disordered semiconductor is affected by the density of available states present between the transport levels at the metal/semiconductor interface[133, 134]. This is especially the case if the density of available states is large or extends far into the band gap[135]. By ignoring this effect, as is done in this thesis (as the MTR model is used), deviations in obtained results for the injection barrier heights might occur due to the differences in the used interface statistics, even though disorder is accounted for in the model. However, since the degree of energetic disorder in the investigated molecule films is fairly low, we expect that this deviation is small.

3.3 Numerical description of single-carrier devices

The simulations of the current density-voltage profiles of the single-carrier devices were performed using a commercially available device simulator called *Advanced Semiconductor Analysis* (ASA). ASA is a one-dimensional, steady-state device simulator, which provides the means for analysis, and hence optimization, of a variety of semiconductor devices including single-carrier devices. The current section deals with the equations necessary to form a physical description of the single-carrier devices along with models for the density of states in the band gap. Note that this section will not deal with the process of actually solving the equations, but will rather simply present the equations required to understand the physics. For a detailed description of the numerical methods used by ASA, the reader is referred to the software manual[136].

3.3.1 Device model equations

Basic set of semiconductor equations

The following basic set of semiconductor equations forms a mathematical description of the semiconductor device operation under non-equilibrium conditions (for example under an applied

bias). ASA solves Poisson's equation and the drift-diffusion equations for electrons and holes (in one dimension),

$$\nabla^2\psi = -\frac{\rho}{\varepsilon_r\varepsilon_0} \quad (3.12)$$

$$-\frac{1}{q}J_n = -D_n\frac{dn}{dx} + n\mu_n\frac{d\psi}{dx} \quad (3.13)$$

$$\frac{1}{q}J_p = -D_p\frac{dp}{dx} - p\mu_p\frac{d\psi}{dx} \quad (3.14)$$

where ψ is the electric potential, ρ is the total space-charge density, $\varepsilon_r\varepsilon_0$ is the permittivity, q is the elementary charge, J_n and J_p are the current densities for electrons and holes respectively, D_n and D_p are the diffusion coefficients, n and p are the free charge-carrier densities, and μ_n and μ_p are the charge-carrier mobilities. The electric field, F , is given by $-d\psi/dx$, i.e., the first terms of the eqs. 3.13 and 3.14 are the diffusion terms and the last to terms are the drift terms.

The total space-charge density is given by the sum of all charge-carriers present in the device,

$$\rho = q(p_{\text{free}} - n_{\text{free}} + p_{\text{loc}} - n_{\text{loc}} + N_{\text{acc}} - N_{\text{don}}) \quad (3.15)$$

where p_{loc} and n_{loc} are the localised charge-carrier density in trap states, and N_{don} and N_{acc} are the free charge carriers due to ionised donor and acceptor states. Where the total space-charge density contributes to the total electrostatic potential, only free charge carriers, p_{free} , n_{free} , N_{acc} and N_{don} , contribute to the current density, i.e., $n = n_{\text{free}} + N_{\text{don}}$ and $p = p_{\text{free}} + N_{\text{acc}}$.

Energetics

In a semiconductor, E_C represents the minimum energy of the conduction band, i.e., the conduction band edge. In an organic semiconductor, E_C is equivalent to the lowest unoccupied molecular orbital (LUMO). For simplicity, we will only refer to E_C . E_C can be related to the vacuum energy, E_{vac} by,

$$E_C = E_{\text{vac}} - \chi \quad (3.16)$$

where χ is the electron affinity of the semiconductor. E_V represents the maximum energy of

the valence band, which is equivalent to the highest occupied molecular orbital (HOMO) in an organic semiconductor. E_V can be related to the vacuum level by,

$$E_V = E_{\text{vac}} - \chi - E_g \quad (3.17)$$

where E_g is the band gap of the semiconductor. The relative concentration of electrons and holes in a semiconductor device is given by their respective quasi Fermi levels, $E_{F,n}$ and $E_{F,p}$. In thermal equilibrium, where no bias voltage has been applied, the quasi Fermi levels are flat and exactly equal across the device,

$$E_{F,n} = E_{F,p} \quad (3.18)$$

and

$$\frac{dE_{F,n}}{dx} = \frac{dE_{F,p}}{dx} = 0. \quad (3.19)$$

With the derivatives of the quasi Fermi levels equal to zero, there is no net current flow across the semiconductor, since drift flow is being cancelled by an opposite diffusion flow.

Charge-carrier statistics

The free electron and hole concentrations are calculated in ASA using Maxwell-Boltzmann statistics (the occupation of traps are calculated using Shockley-Read-Hall statistics), which is an appropriate level of theory when the quasi Fermi levels are more than a few $k_B T$ away from the band gap edges, E_C and E_V . Bear in mind that for some of the calculations performed in this thesis, this condition will be violated. However, a significant deviation between Fermi-Dirac and Maxwell-Boltzmann statistics is not observed even when the quasi Fermi levels coincide with the band edges. It is not until the quasi Fermi levels are moved into the conduction band and valence band, i.e., at degeneration, that a significant error is introduced. This will be discussed later. Using Maxwell-Boltzmann statistics, the free electron and hole densities are given by,

$$n = N_C \exp\left(\frac{E_{F,n} - E_C}{k_B T}\right) = N_C \exp\left(\frac{E_{F,n} + E_{\text{vac}} + \chi}{k_B T}\right) \quad (3.20)$$

$$p = N_V \exp\left(\frac{E_V - E_{F,p}}{k_B T}\right) = N_V \exp\left(\frac{E_{\text{vac}} - \chi - E_g - E_{F,p}}{k_B T}\right). \quad (3.21)$$

The quasi Fermi levels can now be written as,

$$E_{F,n} = E_{\text{vac}} - \chi + k_B T \ln \left(\frac{n}{N_C} \right) \quad (3.22)$$

$$E_{F,p} = E_{\text{vac}} - \chi - E_g - k_B T \ln \left(\frac{p}{N_V} \right). \quad (3.23)$$

Boundary conditions

For ASA to solve the one-dimensional drift-diffusion simulations along with the Poisson equation, appropriate boundary conditions must be specified. The boundary conditions for the simulations are set at the two metal/semiconductor device boundaries through the injection and extraction barrier heights, $q\phi_{\text{inj}}$ and $q\phi_{\text{ext}}$,

$$n_{\text{eq}} = N_C \exp \left(-\frac{q\phi_{\text{inj/ext}}}{k_B T} \right) \quad (3.24)$$

and

$$p_{\text{eq}} = \frac{n_i^2}{n_{\text{eq}}} \quad (3.25)$$

where n_i is the intrinsic charge-carrier concentration. Equation 3.25 is due to the law of mass action, since the total concentration of charge carriers must be a constant at thermodynamic equilibrium (note that this is not only valid at the interface, but across the entire device, $p(x) = n_i^2/n(x)$). The values of the injection and extraction barrier heights defines the built-in voltage, V_{bi} , through,

$$qV_{\text{bi}} = q\phi_{\text{ext}} - q\phi_{\text{inj}}. \quad (3.26)$$

The following conditions are introduced for the electrostatic potential and quasi Fermi levels at the device boundaries ($x = 0$ and $x = L$) under an applied voltage,

$$\psi(x = 0) = \psi_0(x = 0) + V \quad (3.27)$$

$$\psi(x = L) = \psi_0(x = L) \quad (3.28)$$

$$E_{F,n}(x=0) = E_{F,p}(x=0) = qV \quad (3.29)$$

$$E_{F,n}(x=L) = E_{F,p}(x=L) \quad (3.30)$$

where ψ_0 is the thermodynamic electrostatic potential prior to the applied bias voltage. Even though the quasi Fermi levels for electrons and holes are the same at the device boundaries, they are allowed to be different (and will be different) across the device when a voltage is applied according to eqs. 3.22 and 3.23. The current over the interfacial injection barrier is governed by thermionic emission,

$$J_n = qS_n N_C \exp\left(\frac{q\phi_{n,\text{inj}}}{k_B T}\right) \left[\exp\left(\frac{qV}{k_B T}\right) - 1 \right] \quad (3.31)$$

$$J_p = qS_p N_V \exp\left(\frac{q\phi_{p,\text{inj}}}{k_B T}\right) \left[\exp\left(\frac{qV}{k_B T}\right) - 1 \right] \quad (3.32)$$

for electrons and holes, respectively, where $\phi_{n,\text{inj}} + \phi_{p,\text{inj}} = E_g$ and where S_n and S_p are the surface recombination velocities at the device boundaries for electrons and holes, respectively. Note that injection properties can now be varied by changing either or both $S_{n/p}$ and the injection barrier heights. As long as the contact current densities are greater than the current density across the device, the current will not be injection limited. However, when the contact current is lower, due to a high injection barrier or a low surface recombination velocity, the current across the device will be injection limited.

For the majority of the simulations we will keep the recombination velocities fixed where we allow the injection barrier heights to vary to account for the mismatch between the metal contact work function and the transport levels of the semiconductor.

3.3.2 DOS models

In order to accurately simulate organic semiconductor thin films, the density of defect states present in the band gap must be included into the description (see fig. 3.10a). We normally distinguish between two types of traps, namely acceptor-like and donor-like traps, irrespective of the nature of these traps. Where transport through an electron-only device will be hindered by the presence of acceptor-like traps, transport through a hole-only device will be hindered by donor-like traps.

Two types of sub-band models can be included in ASA, namely exponential tail states (see fig. 3.10b) and Gaussian distributions (see fig. 3.10c). Where energetic disorder is usually modelled by exponential tail states, and are almost always present in disordered organic semiconductors, such as polymers, Gaussian distributions are usually present due to chemical defects or small concentrations of another chemical species, either wanted or unwanted, in the probed films, or due to local crystalline phases.

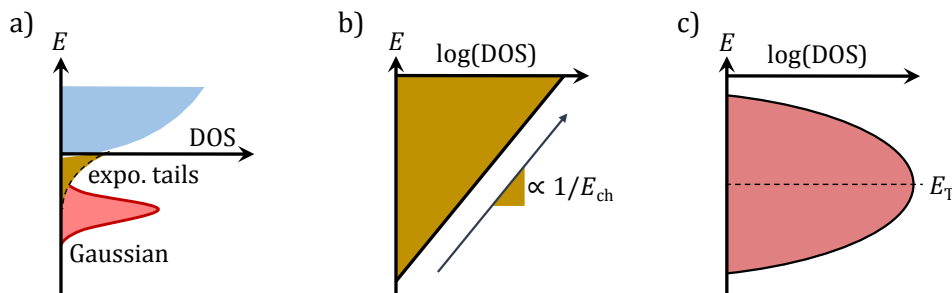


Figure 3.10: a) Schematic representations of: a) An example of the total DOS, with both exponential tails and a Gaussian distribution of trap states; b) Experimental tail states on a $\log(\text{DOS})$ scale, and; c) A Gaussian distribution on a $\log(\text{DOS})$ scale.

We utilize a multiple-trapping-release (MTR) model. When charge-carriers are localised in the sub gap states (exponential or Gaussian), it is assumed that the mobility of these charge carriers is zero. Likewise, when charge-carriers are in the extended states, i.e., the states above the conduction band edge and below the valence band edge, the mobility (the band mobility) is non-zero and equal to the chosen value in the model. We assume non-localised centres, meaning that localised charge carriers can only interact with free charge carriers in the transport bands, i.e., a trapped electron can only recombine with a free hole, and vice versa. This is a good approximation when tail state densities are relatively low.

Exponential tail states

In organic semiconductors, exponential tail states usually extend from both the conduction band and the valence band. Charge carriers can get trapped in these states and in a system where there is a large concentration of both electrons and holes, such as in a solar cell, trapped charge carriers can recombine with a free charge-carrier of opposite polarity, such as a trapped electron and a free hole. In that case the overall free charge-carrier density is decreased, giving rise to a reduction in both the current and voltage.

In a single-carrier device, where direct and free-to-trapped recombination are not dominant

processes, charge carriers will still get trapped in these states and will not contribute to current flow but will rather change the electric field locally and oppose current flow unless they are re-emitted. This both greatly reduces the overall magnitude of the current density and changes the overall shape of the J - V curves.

The exponential conduction and valence band tail state densities per unit volume per unit energy, are given by,

$$N_{\text{CBT}} = N_{\text{C,tail}} \exp\left(-\frac{E_{\text{C}} - E}{E_{\text{n,ch}}}\right) \quad (3.33)$$

$$N_{\text{VBT}} = N_{\text{V,tail}} \exp\left(-\frac{E - E_{\text{V}}}{E_{\text{p,ch}}}\right) \quad (3.34)$$

Within the MTR model, the charge transport is solely governed by the free charge carriers in the extended states but affected by the electric field from all space-charge within the semiconductor, trapped and free.

The density of trapped charge in donor type tail states is calculated using,

$$\rho_{\text{D}} = q \int_{E_{\text{C}}}^{E_{\text{V}}} N_{\text{D}}(E) [1 - f(E)] dE \quad (3.35)$$

where N_{D} is the total number of donor-like trap states per unit energy and $f(E)$ is the occupation function per unit energy. The trapped charge in acceptor-like tail states is calculated using,

$$\rho_{\text{A}} = -q \int_{E_{\text{C}}}^{E_{\text{V}}} N_{\text{A}}(E) f(E) dE \quad (3.36)$$

where N_{A} is the total number of acceptor-like trap states per unit energy.

Shockley-Read-Hall (SRH) statistics describes trapping, de-trapping and recombination processes of a single trap level within the band gap of a semiconductor. Within the SRH picture, conduction band tail states can either be neutral (when empty) or negative (when full), and valence band tail states can either be neutral (when empty) or positive (when full).

There are four possible transitions between a transport level and a discrete trap level, resulting in eight possible processes with both an electron trap level (acceptor-type) and a hole trap level (donor-type)(see fig. 3.11a): i) electron capture in a neutral acceptor-type trap level; ii) electron thermal emission from a negative acceptor-type trap level; iii) recombination between a trapped electron in a negative trap level and a free hole; iv) hole emission from a neutral

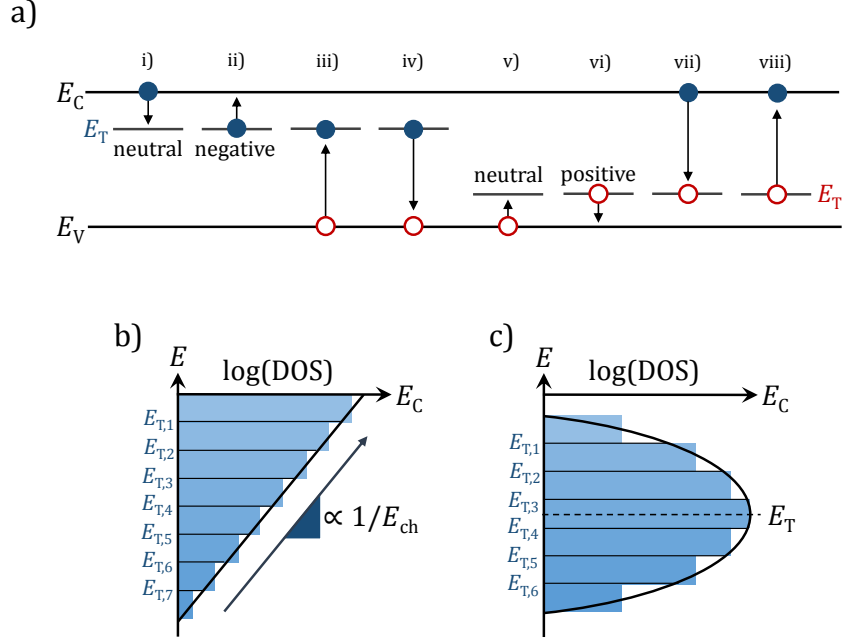


Figure 3.11: Schematic representations of: a) The trapping and emission processes between free and trapped charge carriers in donor and acceptor type states (solid blue circles represent electrons and hollow red circles represent holes); b) discretization of tail states, and; c) discretization of a Gaussian distribution.

acceptor-type trap level; v) hole capture in a neutral donor-type trap level; vi) hole thermal emission from a positive donor-type trap; vii) recombination of a trapped hole in a positive donor-type trap and a free electron; and viii) electron emission from a neutral donor-type trap level. For an electron-only device, where the concentration of holes is orders of magnitude less than electrons, the important processes are i) and ii), whilst in a hole-only device, the important processes are v) and vi).

SRH statistics are applied to exponential tails by modelling the tails as a set of discrete energy levels (see fig. 3.11b). The electron and hole capture rate in an acceptor-type conduction band tail state, processes i) and iii), at every E_T , are given by,

$$r_n^{\text{cap.}} = c_n^0 n N_A (1 - f^-) \quad (3.37)$$

$$r_p^{\text{cap.}} = c_p^- p N_A f^- \quad (3.38)$$

and the electron and hole emission rates, processes ii) and iv), are given by,

$$r_n^{\text{em.}} = e_n^- N_A f^- \quad (3.39)$$

$$r_p^{\text{em.}} = e_p^0 N_A (1 - f^-) \quad (3.40)$$

where e_n^- and e_p^0 , which are the emission coefficients, are given by,

$$e_n^- = c_n^0 N_C \exp\left(\frac{E_T - E_C}{k_B T}\right) \quad (3.41)$$

$$e_p^0 = c_p^- N_V \exp\left(\frac{E_V - E_T}{k_B T}\right). \quad (3.42)$$

c_n^0 and c_p^- are the capture coefficients for electrons and holes. In ASA we only need to set the capture coefficients, as the emission coefficients are calculated from the position of the trap level below the transport level. The steady-state occupation function of acceptor like trap states, f^- , is given by detailed balance ($r_n^{\text{cap.}}/r_n^{\text{em.}} = r_p^{\text{cap.}}/r_p^{\text{em.}}$) by,

$$f^- = \frac{c_n^0 n + e_p^0}{c_n^0 n + e_n^- + c_p^- p + e_p^0}. \quad (3.43)$$

In the case where only electrons dominate the system, such as in the case of an electron-only device, the hole density in the entire device will be orders of magnitude lower, i.e., $n \gg p$ and $c_n^0 n \gg c_p^- p$. In this case we can also ignore the emission coefficient of holes since almost no holes will be trapped and the occupation function can be written as,

$$f^- = \frac{c_n^0 n}{c_n^0 n + e_n^-} = \frac{n}{n + N_C \exp\left(\frac{E_T - E_C}{k_B T}\right)} \quad (3.44)$$

which means that the occupation function does not depend on the capture cross sections, in steady-state, when only one charge-carrier type is being considered. Note that the expression for f^- above could have been achieved by saying that the rate of capture and emission of electrons in the conduction band (eqs. 3.37 and 3.39), when no other processes were present, must be equal in steady-state.

We can now calculate the total concentration (number density) of localised trap states in conduction band tails by replacing the integral in eq. 3.36 with a sum (note that eq. 3.36 gave a charge density, due to q),

$$n_{\text{CB}}^{\text{tot.}} = \sum_{m=1}^M N_A f^- \quad (3.45)$$

where m is the number of discrete levels the continuous exponential tails are separated into. For all simulations presented in this thesis, $M = 30$ ($M = 7$ was shown schematically in fig. 3.11b). The calculations for charge carrier statistics in the valence band tails are completely analogous to the above. For recombination statistics in the case where both electrons and holes are present at appreciative levels, we refer the reader to the ASA manual[136].

Gaussian distribution of trap states

Local crystallinity, chemical defects or the intentional or unintentional presence of a different chemical species within a thin film can lead to a discrete trap level in the band gap. Discrete energy levels will have some energetic broadening due to energetic and/or structural disorder of both the doping material and the host material. Examples of this will be shown later. We model the energetic broadening of a discrete trap level using a Gaussian distribution.

Like in the discussion of trap limited conduction through tail states, we will here discuss trap limited conduction with a Gaussian trap level of an electron-only device, i.e., acceptor-like traps.

The Gaussian distribution of acceptor like traps is given by,

$$N_{\text{acc}} = \frac{N_T^{\text{acc}}}{\sigma\sqrt{2}} \exp \left[-\frac{(E - E_T)^2}{2\sigma^2} \right] \quad (3.46)$$

where N_T^{acc} is the acceptor trap density, σ is the standard deviation of the Gaussian distribution and E_T is the (un-discretized) trap level below the conduction band edge (see fig. 3.11c). The total amount of trapped charge in the Gaussian state can then be calculated from,

$$\rho_{\text{deep}} = -q \int_{E_C}^{E_V} N_{\text{acc}} F^- dE \quad (3.47)$$

where F^- is the occupation function. Similar to the tail states occupation statistics, the Gaussian state statistics are discretized into a number of levels (see fig. 3.11c).

The capture and emission rates from an acceptor like state into the conduction band edge can be written as,

$$r_{n,\text{Gaus.}}^{\text{cap.}} = nC_n^0 N_T^{\text{acc}} (1 - F^-) \quad (3.48)$$

$$r_{n,\text{Gaus.}}^{\text{em.}} = e_{n,\text{Gaus.}}^- N_T^{\text{acc}} F^-. \quad (3.49)$$

where C_n^0 is the capture coefficient, n is the electron density, and $e_{n,\text{Gaus.}}^-$ is the emission coefficient from the Gaussian distribution. Under steady state conditions the charge carrier density occupation does not change with time,

$$nC_n^0 N_T^{\text{acc}} (1 - F^-) = e_{n,\text{Gaus.}}^- N_T^{\text{acc}} F^- \quad (3.50)$$

which yields,

$$F^- = \frac{nC_n^0}{nC_n^0 + e_{n,\text{Gaus.}}^-}. \quad (3.51)$$

The emission coefficient for deep trap states is related to the capture coefficient by,

$$e_{n,\text{Gaus.}}^- = C_n^0 N_C \exp \left[\frac{(E_T + k_B T \ln 2) - E_C}{k_B T} \right] \quad (3.52)$$

which means that the emission coefficient scales with the distance of the trap level from the conduction band edge. We can now write F^- as,

$$F^- = \frac{n}{n + N_C \exp \left[\frac{E_T + k_B T \ln 2 - E_C}{k_B T} \right]}. \quad (3.53)$$

which is a similar result to that which was obtained for the capture and emission statistics of the tail states (except for the extra $k_B T \ln 2$ term), i.e., the capture cross section coefficient does not have an influence on the trap occupation statistics in steady-state when we are only dealing with one charge-carrier type.

The total concentration of localised electrons in the acceptor type states can now be expressed by,

$$n_{\text{Gaus.}}^{\text{tot}} = \sum_{m=1}^M N_T^{\text{acc}} F^- \quad (3.54)$$

where m is the number of discrete levels the continuous Gaussian state is separated into. For all simulations presented in this thesis, $M = 40$. The calculations for charge carrier statistics for the donor type Gaussian states are completely analogous to the above. Once again, for recombination statistics in the case where both electrons and holes are present at appreciative levels, we refer the reader to the ASA manual.

Total localised space-charge

In the case where both exponential tails and a Gaussian distribution of trap levels are present, the total concentration of localised charge, from both electrons and holes, can be written as,

$$q(p_{\text{loc}} - n_{\text{loc}}) = q(p_{\text{VB}}^{\text{tot}} - n_{\text{CB}}^{\text{tot}} + p_{\text{Gaus.}}^{\text{tot}} - n_{\text{Gaus.}}^{\text{tot}}). \quad (3.55)$$

However, in an electron-only device, the relative amount of localised holes compared to electrons is negligible, and we can write,

$$qn_{\text{loc}} = q(n_{\text{CB}}^{\text{tot}} + n_{\text{Gaus.}}^{\text{tot}}). \quad (3.56)$$

3.3.3 Choice of material values

In this section, the range of values of each material quantity is discussed and shown in table 3.1. The electron and hole mobility of organic semiconductors vary over orders of magnitude from as low as $10^{-6} \text{ cm}^2/\text{Vs}$ to as high as $10 \text{ cm}^2/\text{Vs}$. However, most organic semiconductors used for organic bulk heterojunction solar cells have a mobility around $10^{-4} \text{ cm}^2/\text{Vs}$, irrespective of charge carrier type. For this reason, this value for both electron and hole mobility is chosen during any preliminary simulations. The values for the mobilities primarily influence the magnitude of the current density when a single charge-carrier type is dominating the charge transport. In a solar cell device where recombination dominates the charge-carrier density across the device, the value of the mobility will have a larger influence.

Band gaps of organic semiconductors vary from around 1.5 eV to 4 eV. For a single-carrier device where the equilibrium charge-carrier density is much larger than the intrinsic charge-carrier density, the value of the band gap is not that critical. For this reason a somewhat arbitrary value of 2 eV is used for any preliminary simulations.

Table 3.1: Typical drift-diffusion simulation values

Quantity	Symbol	Value	Units
Electron mobility	μ_n	10^{-4}	cm^2/Vs
Hole mobility	μ_p	10^{-4}	cm^2/Vs
Band gap	E_g	2	eV
Thickness	L	100	nm
Effective density of states	N_C	10^{19}	cm^{-3}
-	N_V	10^{19}	cm^{-3}
Relative permittivity	ϵ_r	3	-
Injection barrier	ϕ_{inj}	0.1	eV
Extraction barrier	ϕ_{ext}	0.1	eV
Density of Gaussian states	N_T	10^{17}	cm^{-3}
Gaussian trap level	E_T	-0.3	eV
Standard deviation	σ_T	0.1	eV
Density of tail states	N_t	10^{20}	$\text{cm}^{-3}\text{eV}^{-1}$
Characteristic tail slope	E_{ch}	0.08	eV
Ionized donor states	N_d	variable	cm^{-3}
Ionized acceptor states	N_a	variable	cm^{-3}
Tail capture coefficients	c_n^+	10^{-12}	cm^3/s
-	c_p^0	10^{-10}	cm^3/s
-	c_p^-	10^{-12}	cm^3/s
-	c_n^0	10^{-10}	cm^3/s
Gaussian capture coefficients	C_n^+	10^{-10}	cm^3/s
-	C_p^0	10^{-10}	cm^3/s
-	C_p^-	10^{-10}	cm^3/s
-	C_n^0	10^{-10}	cm^3/s
Surface recombination velocity	S	10^5	cm/s
Series resistance	R_S	0	Ωm^2
Shunt resistance	R_P	∞	Ωm^2
Temperature	T	300	K

Semiconductor thicknesses in organic devices are usually between tens of nanometres to hundreds of nanometres. Organic solar cells usually have a thickness between 80 nm to 120 nm

since there is a trade-off between charge transport, recombination and absorption.

Since organic semiconductors are usually amorphous and have molecular orbital energies which are well defined, an effective density of states is not well defined as one cannot usually assume a parabolic distribution in energy of the density of states. However, models assuming a parabolic density of states have been used with good success in the past, where an effective density of states between 10^{19} and 10^{21} cm^{-3} was assumed. The value of the effective density of states does not have a huge influence on the simulations when the device is trap-free, but the value will influence fitting results when traps are present.

The relative permittivity of organic materials is usually cited to be between 3 and 4. The value of the relative permittivity primarily affects the magnitude of the current density and the magnitude of the electric fields inside the device.

Injection barrier heights between conductive contacts and a semiconductor can vary greatly. This is usually due to a mismatch between the contact work function and the transport level of the semiconductor. An injection barrier can also arise from Fermi level pinning due to surface defects. It is quite rare for a contact between a metal and a semiconductor to be perfectly Ohmic, meaning that the injection barriers will have some finite value ($q\phi_{\text{inj}} > 0 \text{ eV}$).

3.4 Analytical description of charge-transport through single-carrier devices

In the following section the most commonly used analytical equations for SCLC analysis are introduced, derived and discussed. The limitations and the common pitfalls when using each equation are also discussed. All of the derivations start from the steady-state drift-diffusion current density equations (introduced in the section discussing drift-diffusion simulations),

$$J = qD \frac{dn(x)}{dx} + qn(x)\mu_n F(x) \quad (3.57)$$

$$J = -qD \frac{dp(x)}{dx} + qp(x)\mu_p F(x) \quad (3.58)$$

where J is the current density, q is the elementary charge, $D = \frac{k_B T}{q}$ is the Einstein-Smoluchowski diffusion coefficient, n is the electron density, p is the hole density, x is the spatial position inside the semiconductor, μ_n is the charge-carrier mobility for electrons, μ_p is the charge-carrier mobility for holes, and F is the electric field. The first term in the equations is the diffusion term (as seen by the diffusion coefficient, D) and the second term in the equations is the drift

term (as seen by the presence of the electric field, F). All derivations will be for the case where we only have electrons in the device (electron-only device), meaning that we will rely purely on eq. 3.57, but the derivations are completely analogous for the case of a hole-only device.

3.4.1 The Mott-Gurney law (ideal transport)

The most commonly used equation for analysing SCLC is the $J \propto V^2$ law introduced by Mott and Gurney which describes drift-only charge-transport through a trap-, doping- and energetic disorder free (intrinsic) semiconductor or insulator with Ohmic contacts to the injection and extraction metals. The Mott-Gurney (MG) law is, in the case of electron transport in an electron-only device, given by,

$$J = \frac{9}{8} \mu_n \varepsilon_r \varepsilon_0 \frac{V^2}{L^3} \quad (3.59)$$

where μ_e is the charge-carrier mobility of electrons, ε_r is the dielectric constant, ε_0 is the permittivity of free space, V is the applied voltage and L is the probed semiconductor layer thickness (the thickness of the semiconductor sandwiched by the two contact electrodes).

This equation offers some crucial insight into single-carrier charge transport across an intrinsic semiconductor, namely that we do not expect the drift current to increase linearly with the voltage (as we expect from charge transport across a metal or highly doped semiconductor, i.e., from Ohm's law). This result can seem rather surprising at first glance, but arises purely from the non-uniform distribution of the large concentration of space charge present in these types of devices.

Derivation

In order to solve eq. 3.57 we need to obtain a description of the electric field arising from the presence of space charge inside the single-carrier device. SCLC is usually assumed to be one-dimensional, so the Poisson equation is given by,

$$\frac{dF(x)}{dx} = -\frac{qn(x)}{\varepsilon_r \varepsilon_0} \quad (3.60)$$

where $n(x)$ is the electron space-charge density as a function of position, x , which is very large across the entire device due to the charge-carrier injection from the electrodes during the interface formation ($n(x)$ is largest at the interfaces, but will be much larger than n_i across the entire device). We will for the time-being assume that the diffusion part of the current can be

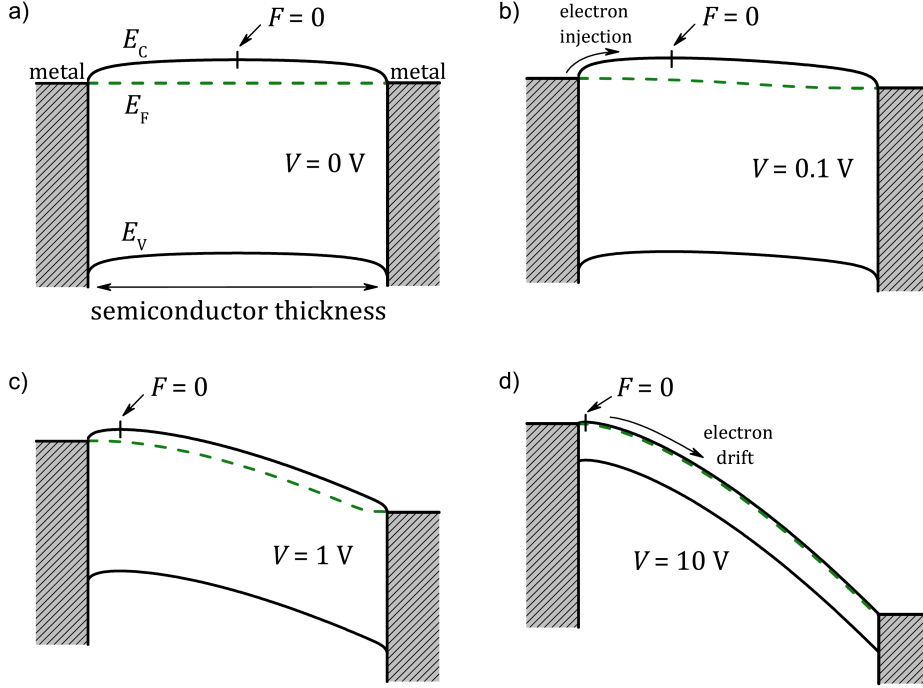


Figure 3.12: Schematic of energy level diagrams of a 100 nm 2 eV band gap electron-only device as a voltage is applied: a) 0 V applied voltage. b) 0.1 V applied voltage (close to equilibrium). c) 1 V applied voltage; the virtual electrode is close to the injection point, and the current begins to follow the MG law (eq. 3.59); d) 10 V applied voltage (shown in a different voltage scale); the virtual and physical electrode coincide, and the current approximately follows the MG law.

ignored (we will return to this justification later). The drift current density equation is then given by neglecting the diffusion term of eq. 3.57,

$$J = qn\mu_n F \quad (3.61)$$

and by combining eq. 3.60 with eq. 3.61 we get,

$$J dx = -\mu_n \epsilon_r \epsilon_0 F(x) dF(x). \quad (3.62)$$

In order to solve eq. 3.62 we need to assume boundary conditions for the integrals over the spatial position, x , and over the electric field, F . The boundary conditions for the spatial positions are easily chosen, as the space-charge density will extend across the entire device. In

the limit of drift currents only, which happens at some critical voltage, V_X (see fig. 3.12), we can assume that the electric field at the boundary, $x = 0$, vanishes, $F(0) = 0$. From this we can integrate the above equation,

$$J \int_0^x dx' = - \int_0^F \mu_n \varepsilon_r \varepsilon_0 F'(x) dF'(x). \quad (3.63)$$

Since the current across the device is in steady state, the current density, J , does not vary spatially. From eq. 3.63 we obtain an expression for the electric field distribution as a function of the spatial position,

$$F = -\sqrt{\frac{2Jx}{\mu_n \varepsilon_r \varepsilon_0}}. \quad (3.64)$$

In order to get an expression for the current density as a function of the voltage, we integrate eq. 3.64,

$$V = \int_0^L F dx = -\left(\frac{8J}{9\mu_n \varepsilon_r \varepsilon_0}\right)^{1/2} L^{3/2} \quad (3.65)$$

which upon rearrangement yields the MG law,

$$\boxed{J = \frac{9}{8} \mu_n \varepsilon_r \varepsilon_0 \frac{V^2}{L^3}}. \quad (3.66)$$

It is important to note here that the equation does not bear any mention of the effective density of states. This is because the equation was derived purely based on the spatial dependence of the electric field, given our choice of boundary conditions. Eq. 3.66 implies that the charge-carrier density inside an intrinsic semiconductor in a single carrier device will purely be governed by the thickness of the device. This is not obvious at this point in the discussion, but will become clear later in this chapter.

Slope curves

It is common to plot SCLC J - V curves on a double logarithmic (log-log) scale. Plotting it in this way yields useful information about the transport behaviour at low voltages which would otherwise be hidden (this will be discussed in more detail later in this chapter). When analysing

said J - V curves it is important to also examine the slope of the J - V curves on a log-log scale. This slope, m , is given by,

$$m(V) = \frac{d \log J}{d \log V}. \quad (3.67)$$

At this point it is not obvious why the slope itself is a function of the voltage. However, the slope will change as the transport transitions from one transport regime to another. From the definition of the slope, the current density will depend on the power of the voltage through,

$$J \propto V^{m(V)} \quad (3.68)$$

which means that m in the case of the MG law will be 2. Plotting J - V curves alongside m - V curves is powerful tool when analysing SCLC data.

Fitting

By examining eq. 3.66 we see that the only unknown in the equation should be the charge-carrier mobility. Therefore, fitting with the MG law to J - V curves obtained from SCLC measurements, one can then in principle extract the charge-carrier mobility given that the semiconductor/insulator is intrinsic and that enough voltage has been applied to assume that the current is dominated by drift. The potential ease of use of the MG law is one of the reasons for why SCLC is a very popular technique for investigating charge transport of organic semiconductors.

Figure 3.13 shows MG law fits (black dashed lines) to J - V curves obtained from drift-diffusion simulations of electron-only devices (green circles) with thicknesses varying from 100 nm to 10 μ m. The 2 eV band gap semiconductor in the simulated device is trap-, doping- and energetic disorder-free, i.e., intrinsic, using an input electron mobility of $1 \cdot 10^{-4}$ cm²/Vs, and a relative permittivity, ϵ_r , of 3 was used (the hole mobility was set equal to the electron mobility even though this value is irrelevant for the current density). The effective density of states of both electron and holes was set to 10^{19} cm⁻³. Figure 3.13a shows the MG law fits to the simulated J - V curves represented on a log-lin scale. Excellent fits are achieved between 5 and 10 V using the same values for the mobility, relative permittivity and thickness as was used for the simulations. However, the fits between 0 and 5 V are rather poor. Figure 3.13b shows the same curves on a double log scale. It is apparent that the current increases with a different voltage dependence at low voltage than at higher voltage. It is however interesting to note that the thickness scaling is the same from 0 to 10 V ($J \propto L^{-3}$). In figure 3.13c the slope of the

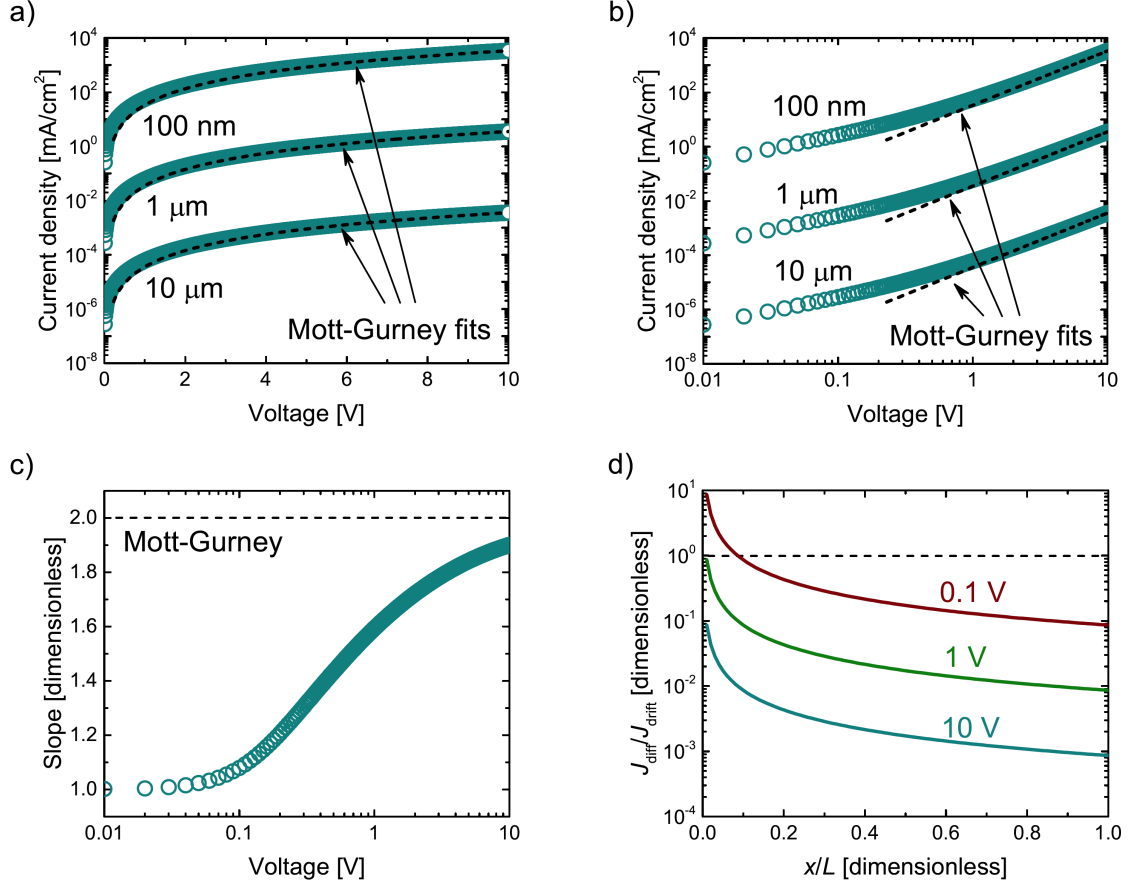


Figure 3.13: Fits with the MG law (dashed lines) to J - V curves from drift-diffusion simulations (green circles) of a trap-, doping and energetic disorder-free 2 eV band gap semiconductor, at various thicknesses with Ohmic contacts (zero injection barrier heights): a) on a log-lin scale and b) on a log-log scale. By using the same dielectric constant ($\epsilon_r = 3$) and electron mobility ($\mu_n = 10^{-4} \text{ cm}^2/\text{Vs}$) for both the simulations and the MG law, good fits are achieved. c) m - V curve of the 100 nm curve in a) and b). d) Ratio of diffusion current and drift current for a device of arbitrary thickness evaluated at 0.1, 1 and 10 V (the ratios were calculated at room temperature, $T = 300 \text{ K}$).

100 nm device shown in figure 3.13b is shown. It shows that the J - V curve goes from a linear regime at low voltage to a higher voltage regime. The reason for these trends will be discussed later in this chapter.

Charge-carrier density

Given the expression for the electric field as a function of the spatial position inside the semiconductor we can likewise calculate an expression for the charge-carrier density using Gauss' law ($n = -\{\varepsilon_r \varepsilon_0 / q\} dF/dx$) where F is given by eq. 3.64,

$$n = \frac{1}{q} \sqrt{\frac{J \varepsilon_r \varepsilon_0}{2 \mu_n x}}. \quad (3.69)$$

Note that this expression implies that the charge-carrier density tends to infinity at the boundary, $n \rightarrow \infty$ for $x \rightarrow 0$. This is of course an unphysical condition (as the charge-carrier density at the boundary will be fixed by the density of states) and we will later see that the choice of a more physical boundary condition will result in the Mott-Gurney being inaccurate even for a trap-, doping- and energetic disorder-free semiconductor. This will especially be the case for devices of thicknesses commonly used to probe charge-transport in organic semiconductors.

Diffusion contributions

During the derivation of the MG law we assumed that the contribution from diffusion of charge-carriers could be neglected. However, from the MG charge-carrier density, eq. 3.69, it is seen that the charge-carrier density changes spatially inside the device. This will give rise to a very small contribution to the diffusion current, even in the drift regime. The diffusion contribution across the semiconductor can approximately be calculated in the following way.

The diffusion current contribution in the MG regime is approximately given by,

$$J_{\text{diffusion}} \approx qD \frac{dn}{dx} = D \frac{d}{dx} \sqrt{\frac{J_{\text{drift}} \varepsilon_r \varepsilon_0}{2 \mu_n x}} = -\frac{D}{2x} \sqrt{\frac{J_{\text{drift}} \varepsilon_r \varepsilon_0}{2 \mu_n x}} = -D \frac{3}{8} \frac{\varepsilon_r \varepsilon_0 V}{(xL)^{3/2}}. \quad (3.70)$$

By division of eq. 3.70 by the MG law, by insertion of the diffusion coefficient, $D = \mu k_B T / q$, and by taking the absolute value, we obtain,

$$\left| \frac{J_{\text{diffusion}}}{J_{\text{drift}}} \right| = \frac{k_B T}{3q} \frac{1}{V} \left(\frac{x}{L} \right)^{-3/2}. \quad (3.71)$$

Figure 3.13d shows the calculation of the ratio of diffusion to drift current contributions as a function of the normalized spatial position inside the semiconductor, x/L . An arbitrary thickness of 100 nm was chosen, even though this value does not matter when using the dimensionless

parameters. At a low applied voltage (0.1 V) significant contributions to the diffusion current is observed near the injection interface. As the voltage is increased (1 V) the contributions become negligible, and becomes more negligible when a large voltage is applied (10 V). Given that we are in a voltage regime at or larger than 1 V, the assumption that diffusion currents across the device can be ignored is approximately valid.

We will later see that the onset for the validity of the MG law can analytically be calculated to be around 0.9 V at room temperature (300 K), which is in a voltage regime where diffusion currents can indeed be ignored.

3.4.2 Equations with traps (non-ideal transport)

The MG law was derived assuming that the semiconductor is trap free. For the case of organic semiconductors, where we normally either have some degree of energetic disorder, some degree of crystallinity, or chemical defects, we are bound to have some sort of charge-carrier trapping. This trapping will have an effect on the J - V curves in two distinct ways: i) the overall current will be reduced as the number of charge carriers available for conduction will be fewer; and ii) trapping will alter the shape of the J - V curves away from what is expected in the ideal case.

Charge carrier traps are usually modelled in three different ways, as already discussed in section 3.3.2, either as a discrete trap level in the band gap (in dimensions of cm^{-3}),

$$n_t = N_t \exp\left(\frac{E_F - E_t}{k_B T}\right) \quad (3.72)$$

a Gaussian distribution of states in the band gap (in dimensions of $\text{cm}^{-3}\text{eV}^{-1}$),

$$n_t = \frac{N_t}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{(E - E_t)^2}{2\sigma^2}\right\}. \quad (3.73)$$

or as an exponential tail of states extending from the band edge (in dimensions of $\text{cm}^{-3}\text{eV}^{-1}$),

$$n_t = \frac{N_t}{k_B T_c} \exp\left(-\frac{E}{k_B T_c}\right). \quad (3.74)$$

For simplicity, we will refer to the trap densities (in dimensions of cm^{-3}) in all three cases as N_t . They will however be addressed separately, so confusion should be minimal.

Discrete trap level (Rose's equation)

From a mathematical point of view, a discrete trap level is the easiest to consider, and the first addition of traps to the MG law using a discrete trap level was first done by Rose in 1955.

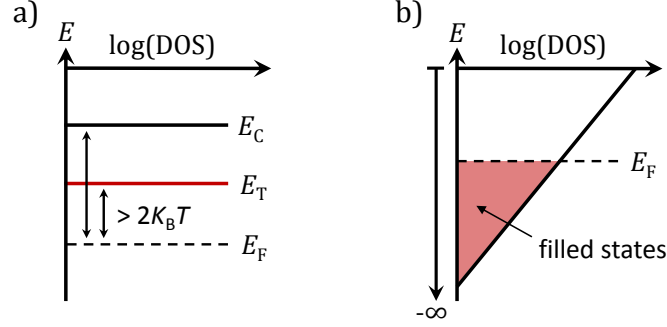


Figure 3.14: a) Schematic representation of the statistics used to derive Rose's equation (eq. 3.78), and b) the schematic representation of the statistics of the statistics used to derive the Mark-Helfrich equation (eq. 3.94).

Considering electron-only transport, as long as the Fermi level lies more than $2k_B T$ below the trap level we can describe both the population of free charge carriers, n_{free} and trapped charge carriers, n_t , using Boltzmann statistics assuming that both populations can be described by the same Fermi level (as seen in fig. 3.14a),

$$n_{\text{free}} = N_C \exp\left(\frac{E_F - E_C}{k_B T}\right) \quad (3.75)$$

$$n_t = N_t \exp\left(\frac{E_F - E_t}{k_B T}\right). \quad (3.76)$$

As long as the Fermi-level is below the trap level, there will be a fixed ratio, Θ , of free to trapped charge carriers given by (with E_C set to zero as the reference point),

$$\Theta = \frac{n_{\text{free}}}{n_t} = \frac{N_C}{N_t} \exp\left(\frac{E_t}{k_B T}\right). \quad (3.77)$$

It is then assumed that the MG law can be modified by this ratio of free to trapped charges, such that,

$$J = \frac{9}{8} \mu \varepsilon_r \varepsilon_0 \frac{V^2}{L^3} \frac{N_C}{N_t} \exp\left(\frac{E_t}{k_B T}\right) \quad (3.78)$$

which simply leads to a reduction of the current (but still $\propto V^2$) at low voltages (since E_t has a negative value compared to the reference point). As the voltage is applied and the Fermi level pushed upwards, the trap states are filled. For a 2 eV band gap semiconductor ($N_C = 10^{19} \text{ cm}^{-3}$) with a trap level positioned in the mid gap ($E_t = -1 \text{ eV}$) with a trap density of 10^{17} cm^{-3} , Θ will be $\approx 1.98 \cdot 10^{-15}$.

A natural extension of Rose's equation would be to consider a Gaussian distribution of traps rather than a discrete trap level. However, to the author's knowledge, it is not possible to calculate an analytical equation with a Gaussian trap distribution in the band gap. However, a Gaussian distribution can be included numerically in a drift-diffusion simulation.

Exponential tail states (the Mark-Helfrich equation)

The Mark-Helfrich (MH) equation was developed to try and explain the increase in the slope of the J - V curve on a log-log scale that had been observed experimentally. An exponential tail of states extending from the conduction band edge, n_t (in dimensions of $\text{cm}^{-1}\text{eV}^{-1}$) is described by,

$$n_t = \frac{N_t}{k_B T_c} \exp(-E/k_B T_c) \quad (3.79)$$

where N_t is the trap density (in dimensions of cm^{-1}) and T_c is the characteristic temperature of the tails (The conduction band edge is set to zero for reference). For simplicity, we define $k_B T_c$ as the characteristic energy of the tails, E_{ch} . The derivation assumes that the number density of trap sites somewhere in the device, x_0 , is greater than the space-charge density, $\rho(x_0)$, at that position. At $T = 0 \text{ K}$ we can then assume that all of the space charge is in the traps and the trap states will be filled up to the quasi-Fermi level (as seen in fig. 3.14b),

$$\rho(x_0) = q \int_{-\infty}^{E_F} \frac{N_t}{E_{\text{ch}}} \exp(-E(x_0)/E_{\text{ch}}) dE, \quad (3.80)$$

yielding,

$$\rho(x_0) = q N_t \exp(-E_F(x_0)/E_{\text{ch}}). \quad (3.81)$$

If we now increase the temperature above $T = 0 \text{ K}$, some charge carriers are allowed to escape the trap states, and these free charge carriers are given by Boltzmann statistics as,

$$\rho_{\text{free}}(x_0) = qN_C \exp(-E_F(x_0)/k_B T). \quad (3.82)$$

We can combine the above expressions for the total space-charge density, $\rho(x_0)$, and the free charge-carrier density, $\rho_{\text{free}}(x_0)$, to yield,

$$\rho_{\text{free}} = N_C q^{1-l} N_t^{-l} \rho^l, \quad (3.83)$$

where $l = E_{\text{ch}}/k_B T$. Similar for the derivation of the MG law, we now have to solve the drift-diffusion equation along with the Poisson equation (eqs. 3.57 and 3.60, respectively). Where the Poisson equation must be solved for all of the space-charge in the system, ρ , the current density will only depend on the free charge carrier density, ρ_{free} (here assuming a drift-dominated current density),

$$J = N_C q^{1-l} N_t^{-l} \rho^l \mu F(x) \quad (3.84)$$

$$\frac{dF(x)}{dx} = \frac{\rho(x)}{\varepsilon_r \varepsilon_0}. \quad (3.85)$$

Combining eqs. 3.84 and 3.85 we obtain,

$$J = N_C q^{1-l} N_t^{-l} \mu F(x) \left(\frac{dF(x)}{dx} \varepsilon_r \varepsilon_0 \right)^l. \quad (3.86)$$

We can rearrange the above equation to yield,

$$\frac{dF(x)}{dx} = \frac{N_t}{\varepsilon_r \varepsilon_0} q^{(l-1)/l} \left(\frac{J}{\mu N_C} \right)^{1/l} [F(x)]^{-1/l} \quad (3.87)$$

By combining all terms not depending on F into a single term, D , we obtain the expression,

$$[F(x)]^{1/l} dF = D dx. \quad (3.88)$$

Assuming the same boundary conditions as we assumed for the MG law, namely that the electric field is zero at $x = 0$, we write the integrals,

$$\int_0^F [F'(x)]^{1/l} dF' = \int_0^x D dx'. \quad (3.89)$$

The solutions to the integrals in eq. 3.89 are given as,

$$\frac{l}{l+1} F^{(1+l)/l} = Dx, \quad (3.90)$$

or rewritten in terms of the electric field,

$$F = \left(\frac{l+1}{l} D \right)^{l/(l+1)} x^{l/(l+1)}. \quad (3.91)$$

The spatial dependence of the electric field inside a single-carrier device with exponential tails, given by eq. 3.91, follows the same dependence as in the MG derivation, given by eq. 3.64, when $l = 1$, namely as $F \propto x^{1/2}$. To obtain an expression in terms of the voltage, we integrate the electric field across the entire thickness of the device,

$$V = \int_0^L F dx = \left(\frac{l+1}{l} D \right)^{l/(l+1)} \int_0^L x^{l/(l+1)} dx, \quad (3.92)$$

and we obtain,

$$V = \left(\frac{l+1}{l} D \right)^{l/(l+1)} \frac{l+1}{2l+1} L^{(2l+1)/(l+1)} \quad (3.93)$$

By insertion of D into eq. 3.93 and rearranging for the current density, J , we obtain the MH equation describing charge transport in a single-carrier device with an exponential tail of trap states,

$$\boxed{J = q^{1-l} \mu N_C \left(\frac{\varepsilon_r \varepsilon_0 l}{N_t (l+1)} \right)^l \left(\frac{2l+1}{l+1} \right)^{l+1} \frac{V^{l+1}}{L^{2l+1}}.} \quad (3.94)$$

J - V curves calculated from eq. 3.94 as a function of the characteristic energy are shown in figure 3.15a.

The Mark-Helfrich equation is interesting as it correctly predicts that both the slope of the J - V curve, m , increases

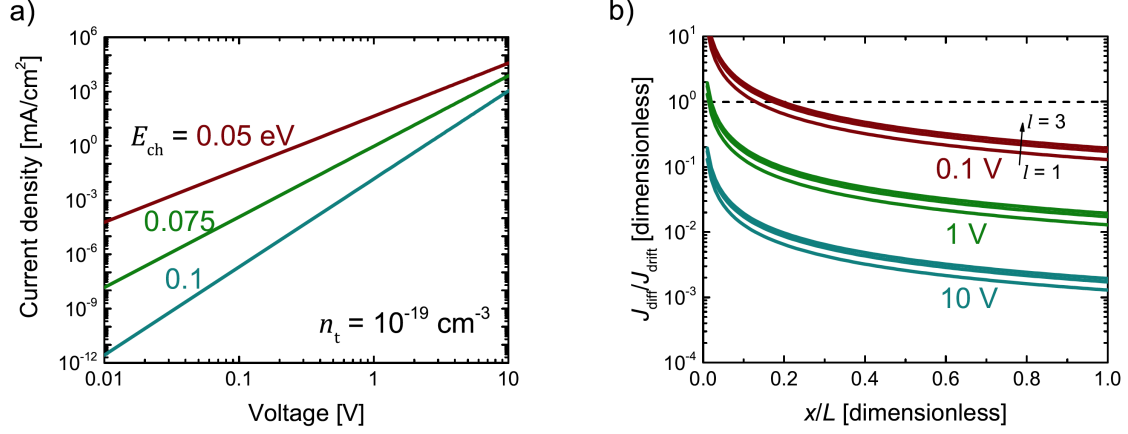


Figure 3.15: a) J - V curves obtained from the MH equation for varying values of the characteristic energy (0.05 eV, 0.075 eV and 0.1 eV). All other values were kept constant, $\mu = 10^4 \text{ cm}^2/\text{Vs}$, $N_C = 10^{-19} \text{ cm}^{-3}$, $\varepsilon_r = 3$, $N_t = n_t \cdot E_{\text{ch}}$ and $L = 100 \text{ nm}$. b) Ratio of diffusion current and drift current, eq. 3.96, for three devices of arbitrary thickness evaluated at 0.1, 1 and 10 V with varying degree of l (the ratios were calculated at room temperature, $T = 300 \text{ K}$).

$$m = l + 1 \quad (3.95)$$

and that the overall magnitude of the current density decreases with increase in characteristic energy, E_{ch} . However, there are some inherent problems with the MH equation, namely that it does not include diffusion currents which has been shown to be important to correctly describe the current[18]. Regardless of the inherent issues with the MH equation, it still offers great insight into the overall trend of the J - V curve when a tail of trap states is present in the band gap. For this reason, the equation should be considered merely in a qualitative manner.

Diffusion contributions

Similarly as during the derivation of the MG law, we can calculate the ratio of diffusion to drift currents in the case of exponential traps,

$$\left| \frac{J_{\text{diffusion}}}{J_{\text{drift}}} \right| = \frac{k_B T}{qV} \frac{l}{1+l} \left(\frac{x}{L} \right)^{-1}. \quad (3.96)$$

Figure 3.15b shows the calculation of the ratio of diffusion to drift current contributions of the MH equation as a function of the normalized spatial position inside the semiconductor,

x/L . Similarly as when evaluating the diffusion contributions from the MG law, an arbitrary thickness of 100 nm was chosen. At a low applied voltage (0.1 V) significant contributions to the diffusion current is observed near the injection interface. As the voltage is increased (1 V) the contributions become negligible, and becomes more negligible when a large voltage is applied (10 V). Given that we are in a voltage regime at or larger than 1 V, the assumption that diffusion currents can be ignored is more or less valid. As the depth of the exponential traps are increased, l increases, and from figure 3.15b it is seen that the diffusion contributions increase as well.

3.4.3 Diffusion currents at low applied voltages

In figure 3.13c it was observed that the current at low voltages does not follow the simple MG expression. This low voltage current will now be discussed. The equation governing the current density will not be derived explicitly (as the derivations are rather cumbersome), but the current density equation and the equation approximating the charge-carrier density will be compared to drift-diffusion simulations for validation.

The moving electrode (ME) equation

In a previous section we assumed drift dominated current at a significant applied voltage (so that $F(0) = 0$) from which we obtained the MG law. We will now derive an expression for the current density at a very small applied bias where the injected charge-carrier density will not deviate significantly from the equilibrium density. In that case, drift-dominated transport can not be assumed, and the full expression for the steady-state current density must, in fact, be considered.

At zero applied voltage the charge-carrier density inside a symmetric single-carrier device with Ohmic contacts can be approximated quite well by [137, 138],

$$n(x) = \frac{2\pi^2 \epsilon_r \epsilon_0 k_B T}{q^2 L^2} \frac{1}{\cos^2 \left[\pi \left(\frac{x}{L} - \frac{1}{2} \right) \right]}. \quad (3.97)$$

The charge-carrier density described by eq. 3.97 is due to the injection of charge carriers from the electrodes into the semiconductor during Fermi level equilibration. We therefore refer to the charge-carrier density described by eq. 3.97 as the equilibrium charge-carrier density.

Figure 3.16a shows drift-diffusion simulations of the charge-carrier density of a 50, 100 and 150 nm electron-only device. In the same graph, charge-carrier densities calculated from eq. 3.97 for the same thicknesses are shown. Both the numerical and analytical calculations were

performed assuming that $\varepsilon_r = 3$ and that the effective DOS of electrons is 10^{19} cm^{-3} . It is seen that eq. 3.97 describes the charge-carrier density very well (especially in the middle of the device).

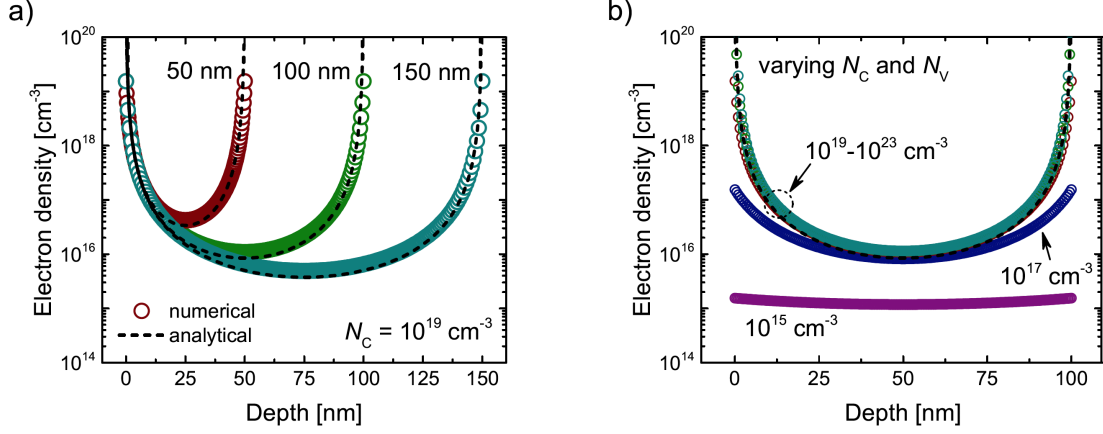


Figure 3.16: a) Numerical and analytical calculations of the electron density of a single-carrier device as a function of thickness. Both the analytical and numerical curves were calculated using the same values for the dielectric constant, $\varepsilon_r = 3$ at room temperature, $T = 300 \text{ K}$ (the numerical curves were calculated using an effective DOS of 10^{19} cm^{-3}). b) Numerical calculations for the electron density with varying values for the effective DOS (the analytical curve shown in a) is shown for reference).

Figure 3.16b shows the charge-carrier density for a 100 nm single-carrier device as a function of the choice of effective DOS (with the analytical result inserted as a dashed line). When a very low (and rather unphysical) value of 10^{15} cm^{-3} is used, eq. 3.97 no longer gives a good description. With a value of 10^{17} cm^{-3} , eq. 3.97 now describes the carrier density in the middle of the device fairly well, and with values for the effective DOS $> 10^{19} \text{ cm}^{-3}$, eq. 3.97 describes the carrier density well across most of the device.

It is important to consider the charge-carrier density across the entire thickness of the device, so we need to consider the average charge-carrier density. However, the arithmetic mean of eq. 4.7, $\langle n \rangle = L^{-1} \int_0^L n dx$, cannot be calculated, since the integral does not converge. n^{-1} can be integrated and, thus, the harmonic mean of the charge-carrier density can be written as,

$$\langle n \rangle = \frac{1}{\frac{1}{L} \int_0^L n^{-1} dx}. \quad (3.98)$$

This integral yields,

$$\langle n \rangle = \frac{4\pi^2 \epsilon_r \epsilon_0 k_B T}{q^2 L^2}. \quad (3.99)$$

The current density can now be calculated from $J = q\mu \langle n \rangle V L^{-1}$, yielding,

$$J = 4\pi^2 \frac{k_B T}{q} \mu_n \epsilon_r \epsilon_0 \frac{V}{L^3} \quad (3.100)$$

which is called the moving electrode (ME) equation describing current flow of the equilibrium charge carrier density[139, 140, 141]. Equation 3.100 describes space-charge-limited drift-diffusion conduction at a low applied voltage for a trap-, doping- and energetic disorder-free semiconductor or insulator in a symmetric single-carrier device (the diffusion contribution can be observed from the $k_B T/q$ term).

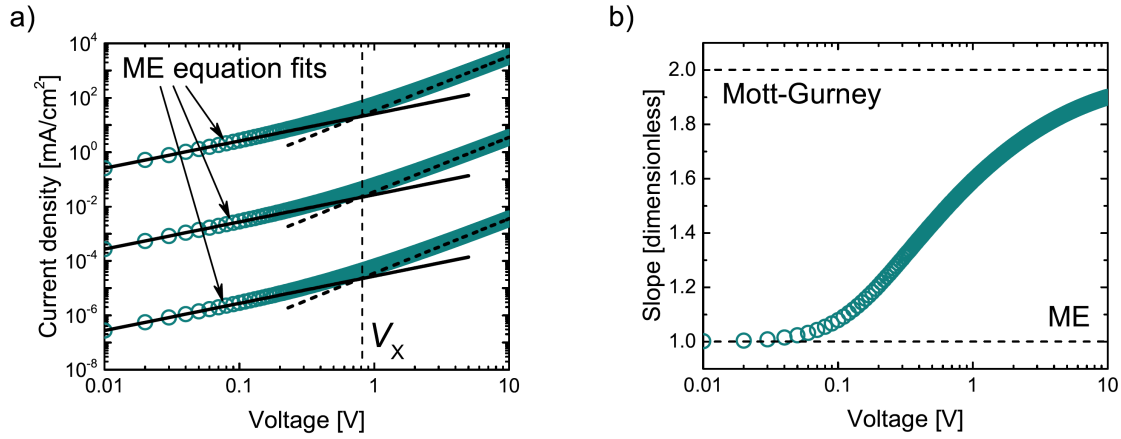


Figure 3.17: a) Fits with the ME equation (solid lines) and the MG law (dashed lines) to J - V curves generated from drift-diffusion simulations (green circles) of a trap-, doping and energetic disorder-free 2 eV band gap semiconductor, at various thicknesses, sandwiched between Ohmic contacts (zero injection barrier heights). The observed cross-over voltage for the simulated devices shown here, $V_X = 0.81$ V, is very close to the value obtained from eq. 3.103 at room temperature, $V_X(300 \text{ K}) \approx 0.9$ V, and does not change with increased thickness as was proposed by Mark and Lampert. b) m - V curves showing the MG law and ME equation fits.

Note that the ME equation (eq. 3.100), like the MG law (eq. 3.59) also follows a thickness scaling $\propto L^{-3}$. However, the current at low voltages increases linearly with the applied voltage ($J \propto V$) rather than by $J \propto V^2$, which was exactly what was observed in figure 3.13.

Figure 3.17a shows fits with the ME equation to the J - V curves shown in figure 3.13. Excellent fits are achieved using the same input values as was used for the drift-diffusion simulations. With a combination of the ME equation and the MG law we can now in principle describe both the low voltage regime and the MG regime.

It happens that the current density at low voltage (eq. 3.100) is dominated by the bottle-neck of charge-carriers, i.e., of the charge-carrier density in the middle of the device, $n_0 = n(L/2)$. In this case eq. 3.97 reduces to,

$$n_0 = n(L/2) = \frac{2\pi^2 \epsilon_r \epsilon_0 k_B T}{q^2 L^2} \quad (3.101)$$

which is a good approximation given that the effective DOS for electrons is within a range of realistic values ($> 10^{17} \text{ cm}^{-3}$). We can assume that at very small applied voltages the carrier density will not deviate significantly from eq. 3.101 (this will be shown in greater detail in a later chapter).

By comparison of eqs. 3.99 and 3.101, it is seen that,

$$\langle n \rangle = 2n_0. \quad (3.102)$$

This implies that the average charge-carrier density across the device is simply given by twice the charge-carrier density in the middle of the device, indicating that irrespective of the effective DOS, the charge-carrier density will be constant for a given dielectric constant, temperature and thickness.

Crossover voltage, V_X

Given the descriptions for the current densities at both low (the ME equation, eq. 3.100) and intermediate voltage (the MG law, eq. 3.59), we can calculate the crossover voltage between these regimes introduced in fig. 3.12. We do this by equating eqs. 3.59 and 3.100 yielding,

$$\boxed{V_X = \frac{32\pi^2}{9} \frac{k_B T}{q}} \quad (3.103)$$

The above transition voltage differs significantly from the transition voltage proposed by Lampert and Mark (for the crossover between Ohm's law and the MG law),

$$V_X = \frac{8}{9} \frac{\rho L^2}{\epsilon_r \epsilon_0} \quad (3.104)$$

which predicted that the onset to space-charge-limited conduction would depend on the thickness of the device and the dielectric constant. The Lampert and Mark transition voltage is only true if we are transitioning from an Ohmic conduction regime to a space-charge-limited current regime, which for an intrinsic semiconductor we will show will not happen, as the current even for low applied voltages is also space-charge-limited and described by eq. 3.100. For this reason, V_X will only depend on the temperature the device is being measured at (see fig. 3.17).

3.4.4 J - V description including a built-in voltage

The MG law was derived to account for the current density for a symmetric single-carrier device, i.e., a device without a built-in voltage (V_{bi}). However, due to a rather poor choice of available contact materials, contact asymmetry can sometimes not be avoided. For this reason it is important to either understand how to account for this built-in voltage or how to correct for it.

Figure 3.18a and b shows the difference in the energy level diagrams between a symmetric and asymmetric ($V_{bi} = 0.5V$) single-carrier device. Figure 3.18c and d shows the resulting J - V curves presented on different scales to show the difference in the current at both low and high voltage.

Modified Mott-Gurney law

It is by far the most common to correct for the built-in voltage rather than account for it. A common way to correct for the V_{bi} by shifting the voltage axis and hence assuming an effective voltage,

$$V_{\text{eff}} = V - V_{bi}. \quad (3.105)$$

The MG law can then be rewritten, assuming this effective voltage, to,

$$J = \frac{9}{8} \mu \varepsilon_r \varepsilon_0 \frac{(V - V_{bi})^2}{L^3}. \quad (3.106)$$

Simply correcting the MG law in this way is a fairly good approximation provided that the built-in voltage is known exactly. It should however be noted that other factors may influence the J - V curves in a similar manner (such as deep trap states[13]).

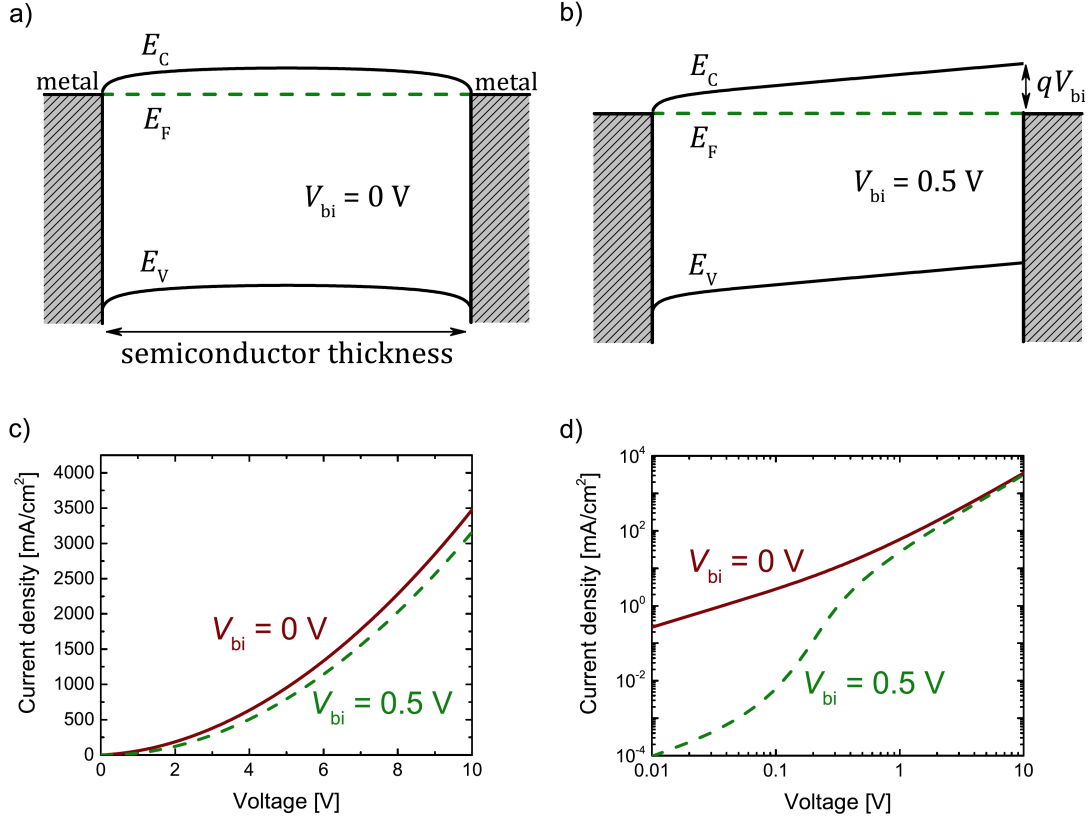


Figure 3.18: a) schematic of the energy levels of a 100 nm 2 eV band gap single-carrier device with $V_{bi} = 0$ V (symmetric). b) Schematic of the energy levels of an asymmetric single-carrier device with $V_{bi} = 0.5$ V. c) Forward bias J - V curves (injection from the left hand side) from the symmetric (red solid curve) and asymmetric device (green dashed curve) on a lin-lin scale. d) Forward bias J - V curves (injection from the left hand side) from the symmetric and asymmetric device on a log-log scale.

Figure 3.19 shows the effect of correcting the voltage axis by the V_{bi} . Figure 3.19a shows the conduction band edge and Fermi level of a symmetric device at $V = 0$ V and of an asymmetric device with $V_{bi} = 0.5$ V at $V = 0.5$ V, i.e., when the approximation has been used to bring the device back to flat band. Figure 3.19b shows the same conduction band edges and Fermi levels as in fig. 3.19a but when an additional 1 V is applied across the device. Comparing the two figures, it is clear that the energy levels resemble each other more closely in fig 3.19b. Figure 3.19c shows the J - V curves on a lin-lin scale. On this scale the curves can not be told apart. However, in fig. 3.19d, which shows the J - V on a log-log scale, it is seen that the magnitude of the current of the corrected J - V is overestimated at low voltages. At around 1 V applied voltage, the two J - V curves starts to overlap, which coincides with the observations from figs. 3.19a and b.

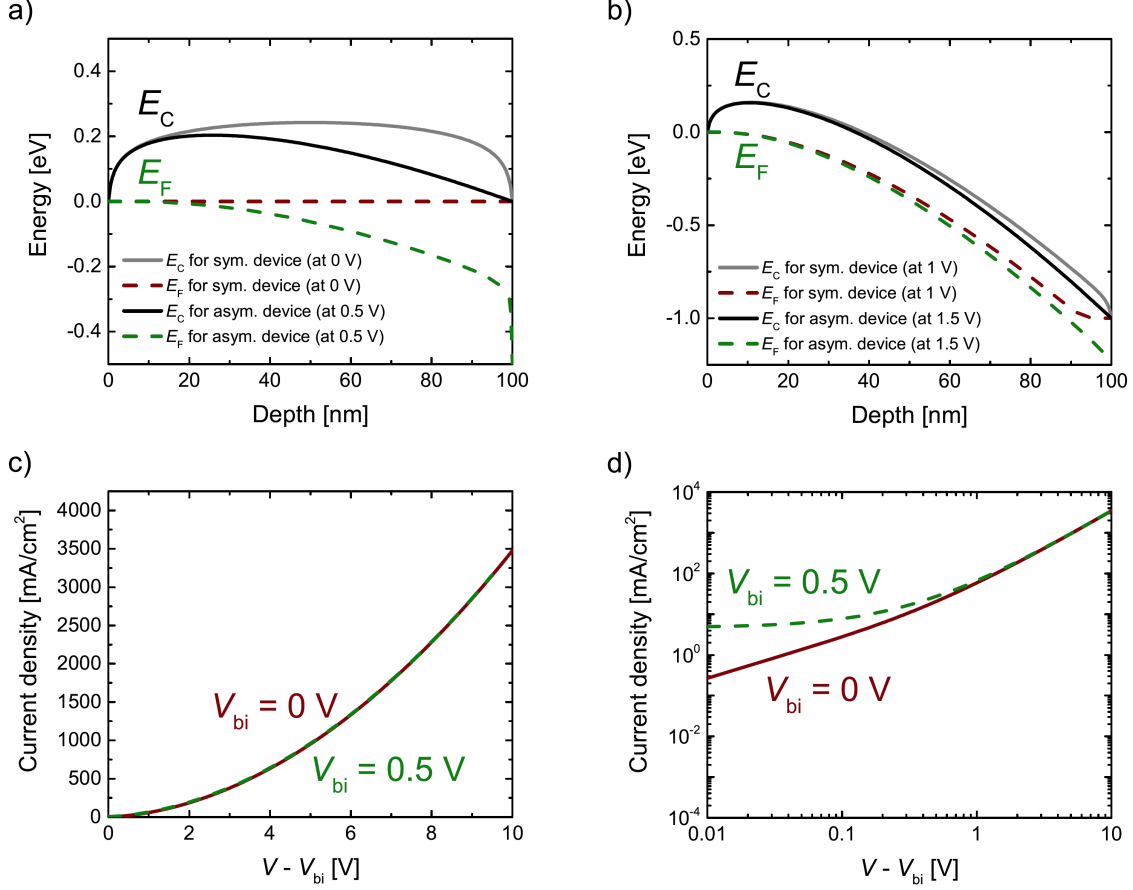


Figure 3.19: a) Conduction band edge and Fermi-level of a symmetric device at $V = 0$ V and an asymmetric device with a $V_{bi} = 0.5$ V at $V = 0.5$ V. b) Conduction band edge and Fermi-level of a symmetric device at $V = 1$ V and an asymmetric device with a $V_{bi} = 0.5$ V at $V = 1.5$ V. c) Forward bias J - V curves from the symmetric (red solid curve) and asymmetric device (green dashed curve) on a lin-lin scale with voltage axis correction ($V_{eff} = V - V_{bi}$). d) Forward bias J - V curves (injection from the left hand side) from the symmetric and asymmetric device on a log-log scale with voltage axis correction.

The V_{bi} equation

Even though the $V_{eff} = V - V_{bi}$ approximation can be rather good in the case where we can express the current density using the MG law at high voltages (which, of course, is only true in the case where the semiconductor is trap- and disorder-free, and where perfect Ohmic contacts are formed between the metal and the semiconductor at forward bias injection point), an accurate mathematical description of the low-voltage current which completely circumvents the voltage-axis correction approximation has been derived[89, 142], and has the additional advantage that

it also describes the current in the reverse bias direction.

By rewriting eq. 3.57 in the form of a first-order differential equation (in terms of the charge-carrier density and the valence band-edge) we obtain,

$$\left\{ \frac{dn(x)}{dx} + n(x) \left(\frac{1}{k_B T} \frac{dE_C(x)}{dx} \right) \right\} = \frac{J_n}{\mu_n k_B T} \quad (3.107)$$

using that $F = \frac{1}{q} \frac{dE_C}{dx}$ (when $[E_C] = \text{Joules}$). In order to solve the above differential equation, we multiply both sides of the equation by the integration factor $e^{\frac{1}{k_B T} \int \frac{dE_C(x)}{dx} dx}$,

$$\left\{ \frac{dn(x)}{dx} + n(x) \left(\frac{1}{k_B T} \frac{dE_C(x)}{dx} \right) \right\} e^{\frac{1}{k_B T} \int \frac{dE_C(x)}{dx} dx} = \left(\frac{J_n}{\mu_n k_B T} \right) e^{\frac{1}{k_B T} \int \frac{dE_C(x)}{dx} dx}. \quad (3.108)$$

The left hand side of the above equation can be rewritten using the reverse product rule to,

$$\frac{d}{dx} n(x) e^{\frac{1}{k_B T} \int \frac{dE_C(x)}{dx} dx} = \left(\frac{J_n}{\mu_n k_B T} \right) e^{\frac{1}{k_B T} \int \frac{dE_C(x)}{dx} dx}. \quad (3.109)$$

By integrating both the left hand side and the right hand side over the entire space-charge region (0 to L), and by using the corollary theorem of calculus, we obtain the following equation,

$$\mu_n k_B T n(x) e^{\frac{1}{k_B T} \int_0^L \frac{dE_C(x)}{dx} dx} \Big|_0^L = J_n \int_0^L e^{\frac{1}{k_B T} \int_0^L \frac{dE_C(x)}{dx} dx} dx. \quad (3.110)$$

Equation 3.110 can now be evaluated when the built-in voltage is either large or small.

Large V_{bi}

When a large V_{bi} is present across the semiconductor the conduction band edge will depend linearly on the spatial position inside the semiconductor (see fig 3.18b). The conduction band edge can therefore be described as,

$$E_C = q \left\{ V + \phi_{inj} \left(1 - \frac{x}{L} \right) + (\phi_{ext} - V) \frac{x}{L} \right\} \quad (3.111)$$

which yield the boundary conditions for the conduction band edge to be,

$$E_C(0) = q(V + \phi_{inj}) \quad (3.112)$$

$$E_C(L) = q\phi_{\text{ext}} \quad (3.113)$$

The boundary for the charge-carrier density is given by the injection barrier heights and the effective density of states (assuming Boltzmann statistics at the injection and extraction contacts),

$$n(0) = N_C \exp\left(-\frac{q\phi_{\text{inj}}}{k_B T}\right) \quad (3.114)$$

$$n(L) = N_C \exp\left(-\frac{q\phi_{\text{ext}}}{k_B T}\right) \quad (3.115)$$

The left hand side of eq. 3.110 can now be evaluated using the boundary conditions for the valence band edge and the charge-carrier density, whereas the right hand side of eq. 3.110 must be evaluated using the full expression for the conduction band edge (eq. 3.111). The integrals inside the exponentials can be evaluated simply by using the corollary, i.e., simply by from considering the boundary conditions. This evaluation leads to the following expression,

$$J_n = \frac{q\mu_n N_C (\phi_{\text{ext}} - \phi_{\text{inj}} - V) \left\{ \exp\left(\frac{qV}{k_B T}\right) - 1 \right\}}{L \exp\left(\frac{q\phi_{\text{inj}}}{k_B T}\right) \left\{ \exp\left(\frac{q\phi_{\text{ext}} - q\phi_{\text{inj}}}{k_B T}\right) - \exp\left(\frac{qV}{k_B T}\right) \right\}} \quad (3.116)$$

which is a general expression for the trap free drift-diffusion hole current density in a single-carrier device neglecting band bending at the interface (flat band picture) where $q\phi_{\text{ext}} - q\phi_{\text{inj}} = qV_{\text{bi}}$. Assuming an Ohmic injection contact, $q\phi_{\text{inj}} = 0$, the equation reduces to,

$$J_n = \frac{q\mu_n N_C (V_{\text{bi}} - V) \left\{ \exp\left(\frac{qV}{k_B T}\right) - 1 \right\}}{L \left\{ \exp\left(\frac{qV_{\text{bi}}}{k_B T}\right) - \exp\left(\frac{qV}{k_B T}\right) \right\}}. \quad (3.117)$$

Figure 3.20a shows simulated J - V curves along with fits with eq. 3.117 (the same input values were used for both the simulations and the analytical equation).

Equation 3.117 describes the current density for an asymmetric device very well given that the value for the built-in voltage is fairly high. Furthermore, in the reverse bias, the current obtained from eq. 3.117 will follow the same non-linear trend as expected from drift-diffusion simulations (see fig. 3.20c).

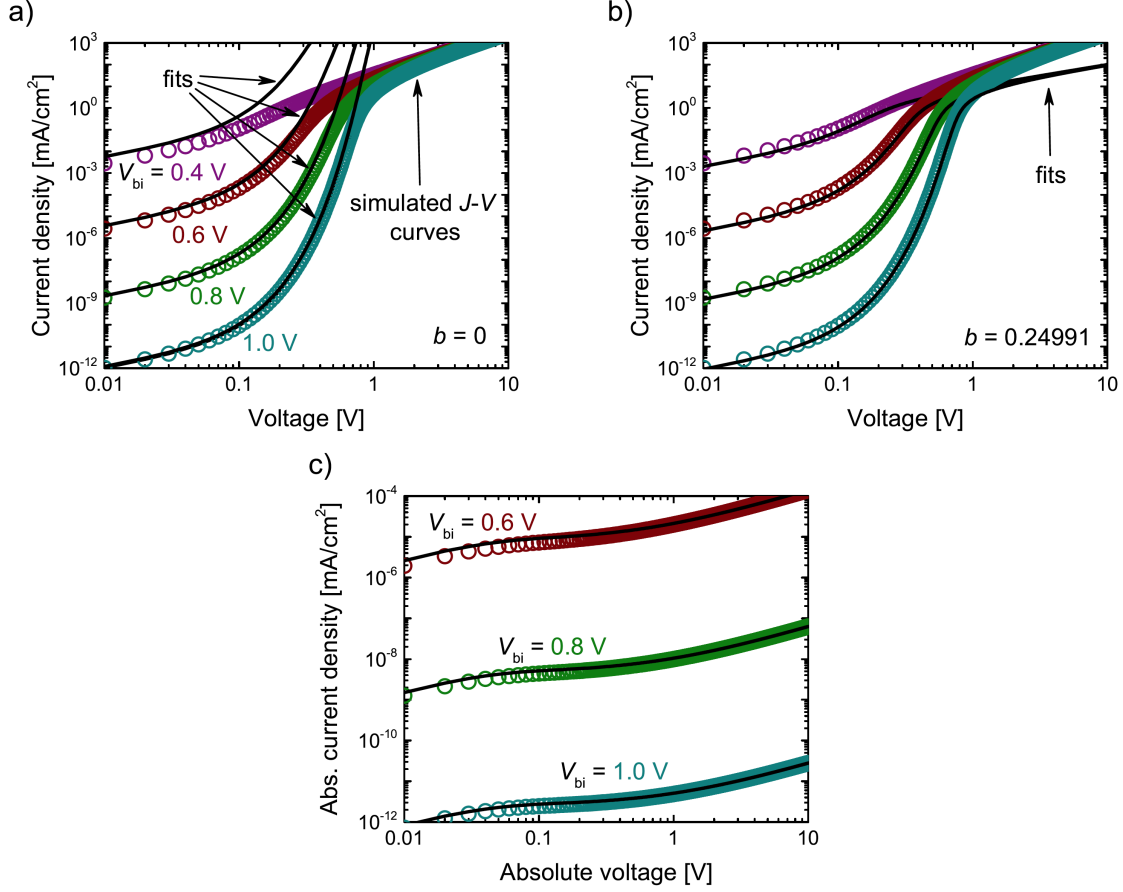


Figure 3.20: a) Simulated forward bias J - V curves of single-carrier devices with varying built-in voltage (coloured circles) and fits with eq. 3.117 (V_{bi} equation with $b = 0$). b) Same simulated curves but fits with eq. 3.123 with $b = 0.24991$. c) Simulated and calculated (from eq. 3.117) reverse bias currents.

Small V_{bi}

When the V_{bi} is low, the V_{bi} is slightly reduced due to band bending at the injecting interface. We denote this reduction in voltage as b . We can then modify the description of the transport level by b ,

$$E_C = q \left\{ V + (\phi_{inj} + b) \left(1 - \frac{x}{L} \right) + (\phi_{ext} - V) \frac{x}{L} \right\} \quad (3.118)$$

which yield the boundary conditions,

$$E_C(0) = q(V + \phi_{inj} + b) \quad (3.119)$$

$$E_C(L) = q\phi_{\text{ext}} \quad (3.120)$$

$$n(0) = N_C \exp\left(-\frac{q[\phi_{\text{inj}} + b]}{k_B T}\right) \quad (3.121)$$

$$n(L) = N_C \exp\left(-\frac{q\phi_{\text{ext}}}{k_B T}\right). \quad (3.122)$$

Solving eq. 3.110 given the above boundary conditions yield the following expression for the current density with a small V_{bi} ,

$$J_n = \frac{q\mu_n N_C (\phi_{\text{ext}} - \phi_{\text{inj}} - b - V) \left\{ \exp\left(\frac{qV}{k_B T}\right) - 1 \right\}}{L \exp\left(\frac{q\phi_{\text{inj}}}{k_B T}\right) \exp\left(\frac{qb}{k_B T}\right) \left\{ \exp\left(\frac{q\phi_{\text{ext}} - q\phi_{\text{inj}} - qb}{k_B T}\right) - \exp\left(\frac{qV}{k_B T}\right) \right\}} \quad (3.123)$$

When V_{bi} is larger than 0.8 V, b can usually be neglected, and eq. 3.123 reduces to eq. 3.116. However a good approximation for b when V_{bi} is smaller than 0.8 V is given by,

$$b = \frac{k_B T}{q} \left\{ \ln\left(\frac{q^2 N_C L^2}{2k_B T \varepsilon_r \varepsilon_0}\right) - 2 \right\}. \quad (3.124)$$

Figure 3.20b shows simulated J - V curves along with fits with eq. 3.123 with $b = 0.24991$.

In this study, all V_{bi} 's which arise from the contact asymmetry happens to be larger than 0.8 V, and for that reason we can restrain ourselves to using eq. 3.117 and 3.116. The derivation of 3.123 was simply given for completeness.

3.4.5 The saturation current equation

Ohmic contacts

In the saturation current limit, the semiconductor in the single-carrier device is filled with charge carriers to the upper limit of $n(x) = N_C = \text{uniform}$. We can calculate the internal electric field of the semiconductor at an arbitrary applied voltage, V , by using Gauss' law,

$$\int dF = - \int \frac{qN_C}{\varepsilon_r \varepsilon_0} dx. \quad (3.125)$$

By integration from the injection point to an arbitrary position inside the semiconductor, x , the above integral becomes,

$$\int_{-V/L}^F dF' = -\frac{qN_C}{\varepsilon_r \varepsilon_0} \int_0^x dx'. \quad (3.126)$$

By evaluation of the integral we obtain an expression for the electric field as a function of the spatial position,

$$F = -\frac{qN_C}{\varepsilon_r \varepsilon_0} x - \frac{V}{L}. \quad (3.127)$$

Note that the electric field here is different from that obtained for the Mott-Gurney law due to two distinct reason: (i) the fact that in the saturation limit the carrier density is constant across the semiconductor, whereas in the Mott-Gurney regime, the charge-carrier density varies spatially across the semiconductor; and (ii) the applied voltage in the saturation limit ensures that $F(0) \gg 0$ whereas for the Mott-Gurney law, $F(0) = 0$. The conduction band edge is obtained by using the relation, $F = \frac{1}{q} \frac{dE_C}{dx}$, obtaining,

$$\int dE_C = q \int F dx \quad (3.128)$$

and by integration from the injection interface to an arbitrary position inside the semiconductor,

$$E_C = -q \int_0^x \left(\frac{qN_C}{\varepsilon_r \varepsilon_0} x' + \frac{V}{L} \right) dx' \quad (3.129)$$

yielding,

$$E_C = -\frac{q^2 N_C}{2\varepsilon_r \varepsilon_0} x^2 - \frac{qV}{L} x. \quad (3.130)$$

As long as a very large voltage is applied, the second term of right hand side of eq. 3.130 dominates and the conduction band edge decreases linearly across the device.

The V_{bi} equation (eq. 3.117) derived in the previous section, assumed that the energy level in which the transport takes place (the conduction band edge in the case of electron transport and the valence band edge in the case of hole transport) depends on the spatial position in linear fashion. This was due to an asymmetry in the contact work functions.

For a symmetric device, in the saturation limit, where so many charge carriers have been injected into the semiconductor that they are spread out uniformly across the entire semiconduc-

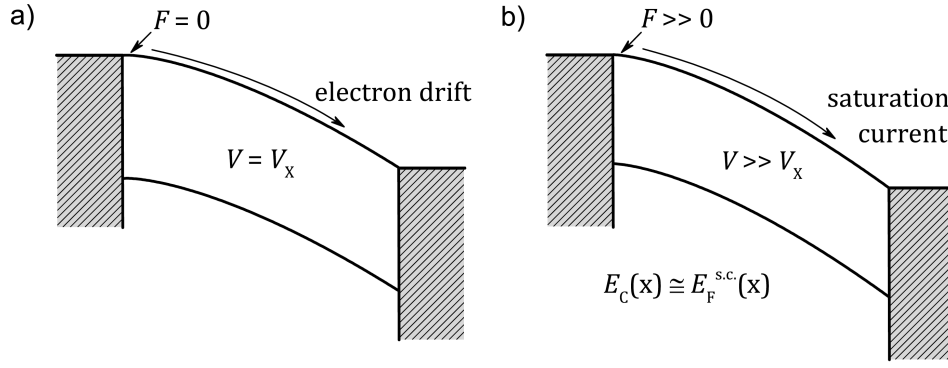


Figure 3.21: Schematic of energy level diagrams of an electron-only device during an applied voltage: a) under moderate applied voltage ($V = V_X$), the virtual and physical electrode coincide, and the current approximately follows eq. 3.100. b) in the saturation limit ($V \gg V_X$), the electric field at the injecting interface is much larger than 0 and the transport level depends on the spatial position in an approximately linear way (the linear dependence increases with increased applied voltage). In the saturation limit, the current follows either eq. 3.131 or 3.132 depending on the contacts.

tor, the transport level will also depend linearly on the spatial position inside the semiconductor. For that reason, we can set the V_{bi} to zero in eq. 3.117 and we yield the saturation current equation,

$$J = q\mu_n N_C \frac{V}{L} \quad (3.131)$$

which is the current density equation in the saturation limit, which also happens to be equal to Ohm's law. This is not surprising since the semiconductor is highly degenerate in this limit, similar to the situation where a large density of dopants are present.

With injection barriers

If non-ideal contacts to the semiconductor are used such that there is an injection barrier for injection and extraction (here assumed that the device is symmetric), the equation can be rewritten to,

$$J = q\mu_n N_C \frac{V}{L} \exp\left(-\frac{q\phi_{inj/ext}}{k_B T}\right) \quad (3.132)$$

which is eq. 3.116 when $q\phi_{ext} = q\phi_{inj} \neq 0$. I will later show that the onset to the saturation

current, which will happen at low voltages either when the semiconductor layer is thin or when there is a small injection barrier height, will influence the analysis of an intrinsic semiconductor in a symmetric single-carrier device if the Mott-Gurney law is used.

Limit of perfect blocking contacts

In the limit where the contacts are perfectly blocking, the injection barriers are equal to half the band gap, $\phi_{\text{inj/ext}} = E_g/2$. Since there will be no injection of charge-carriers from the electrode to equilibrate the Fermi level, because the Fermi level is already perfectly matched with the electrode Fermi levels, the conduction and valence band edges will be spatially constant at equilibrium (see fig. 3.22a). When a voltage is applied across such a device, injection from the contacts is limited due to the large injection barrier, and the charge-carrier density will for that reason not change, i.e., the charge-carrier density remains approximately constant (see fig. 3.22b). We can describe the current using eq. 3.132, which in the limit of perfect blocking contacts becomes,

$$J = q\mu_n N_C \frac{V}{L} \exp\left(-\frac{qE_g}{2k_B T}\right). \quad (3.133)$$

The intrinsic carrier density, n_i , which is governed by the magnitude of the band gap and the effective density of states, is given by $N_C \exp\left(-\frac{qE_g}{2k_B T}\right)$ (given that the effective density of states of electrons and holes are equal, $N_{\text{eff}} = \sqrt{N_C N_V} = \sqrt{N_C N_C} = N_C$). In terms of the intrinsic charge-carrier density, eq. 3.133 reduces to,

$$J = q\mu n_i \frac{V}{L} \quad (3.134)$$

which is Ohm's law describing intrinsic charge-carrier conduction in a semiconductor with flat bands. This is the lower bound of the current passing through a semiconductor or insulator.

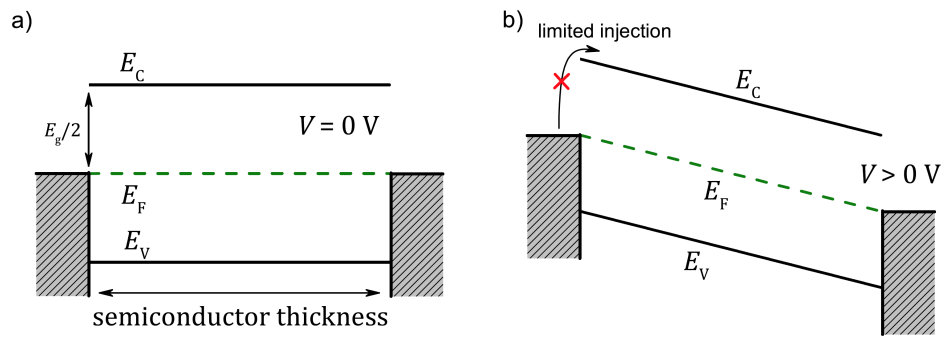


Figure 3.22: a) A semiconductor sandwiched between two perfectly blocking contacts (at zero applied voltage). b) The same device with a bias applied across the device (further injection of charge-carriers is limited).

Part II

RESULTS CHAPTERS

Chapter 4

Interpretation of SCLC in the Low Voltage Regime

4.1 Abstract

In this chapter, we discuss the validity of a SCLC approach which has recently been commonly used in the solution-processable solar cell community. The approach consists of determining the total charge-carrier density of the semiconducting layer in a single-carrier device by combining Ohm's law, fitted in the low voltage regime, and the Mott-Gurney (MG) law, fitted in a regime where $J \propto V^2$ [8, 67]. In principle, if the two laws are used in combination, the only unknown between the two equations will be the charge-carrier density. We show that this approach is seldom valid, due to the fact that whenever Ohm's law is applicable, which is in the high doping limit, the MG law is usually not, and *vice versa*. We show that when an undoped semiconductor is measured in a single-carrier device, even though a linear J - V relationship is observed at voltages up to at least 0.1 V, the charge-carrier density across the entire thickness of the semiconductor is not correctly estimated using Ohm's law, as this only correctly gives the charge-carrier density in the middle of the device. In fact, since most of the charge carriers inside a single-carrier device reside at the device boundaries, the charge-carrier density will be wrongly estimated by up to several orders of magnitude using this approach.

If the doping concentration is increased to very large values, the total charge-carrier density is distributed uniformly across the device in which case using Ohm's law becomes a sensible way of measuring the product of mobility, μ , and doping density, N_{doping} , in the sample. However, in the high-doping limit, the current will be fully governed by the doping density, and is no longer limited by the space-charge at the interfaces, and it will no longer be possible to determine the charge-carrier mobility using the MG law. This leaves the value for the mobility as an unknown

in the mobility-doping density product in Ohm’s law. So even though Ohm’s law can estimate the total charge-carrier density in the device to high precision, the MG law cannot be used to estimate the mobility, again rendering the approach of using the two laws in combination useless. We discuss the error involved in using the approach and finish the chapter discussing whether a small window exists where the method is accurate.

The work presented in this chapter was done by the author under the supervision of Prof. Jenny Nelson and in collaboration with Prof. Thomas Kirchartz. A published version called ”On the Correct Interpretation of the Low Voltage Regime in Intrinsic Single-Carrier Devices” was published in Journal of Physics: Condensed Matter in March 2017[143].

4.2 Introduction

4.2.1 Background and motivation

Since Mott and Gurney first introduced the concept of space-charge-limited currents through semiconductors[11], a large number of studies have used SCLC measurements to determine not only the charge-carrier mobility of organic semiconductors[14, 23, 128, 144] but have also used the method to estimate the reduction of the free charge-carrier density in the semiconductor due to the presence of traps[12, 14, 15, 23, 144]. Whilst a number of questions still exists regarding estimating mobilities and trap states in organic semiconductors from SCLC, such as how to correctly model the transport properties of organic semiconductors and whether the MG law offers any insight into the transport properties of such semiconductors, it is still one of the most commonly used charge-transport methods.

Recently, a method based on SCLC measurements was introduced to the solution-processable solar cell community. The method was proposed to be used to estimate the free charge-carrier density in intrinsic, i.e., trap free, semiconductors using a simple approach[8, 67]. This approach uses a combination of Ohm’s law, fitted in the linear low voltage regime, together with the MG law, fitted in the Mott-Gurney regime. However, the approach is based on a number of assumptions which might not be entirely justified, such as the linear J - V regime observed at low voltages being due to Ohmic conduction, and the method could potentially lead to both wrongly estimated mobilities and charge-carrier densities.

4.2.2 Review of commonly used analytical equations

As was already mentioned in chapter 3 (section 3.4.1), the most commonly used method for analysing SCLC J - V curves is to use analytical models, and the most commonly used analytical

model is the MG law, which describes the drift current through an undoped and trap free semiconductor in a single-carrier device with Ohmic contacts[11]. For electron-only transport, the MG law is given by,

$$J = \frac{9}{8} \mu_n \varepsilon_r \varepsilon_0 \frac{V^2}{L^3} \quad (4.1)$$

where μ_n is the electron mobility, ε_r is the dielectric constant, ε_0 is the vacuum permittivity, V is the applied voltage, and L is the thickness of the semiconducting layer. The MG law has been extensively used to probe charge-transport through organic semiconductor due to the assumption that most organic semiconductors are intrinsic.

As mentioned above, a common assumption which has been cited on numerous occasions in both experimental, theoretical and review papers, that the low voltage regime in J - V curves obtained from intrinsic semiconductors, is only governed by Ohmic conduction by the intrinsic charge carrier population, n_i [1, 17, 145, 146, 147]. In that case, the current density, in the low voltage regime, is simply given by Ohm's law,

$$J = q \mu n_i \frac{V}{L}. \quad (4.2)$$

where q is the elementary charge, and μ , in this case, will be due to a combination of both electrons and holes ($\mu = \mu_n + \mu_p$). Note that the intrinsic charge-carrier density, n_i , will be spatially uniform across the entire thickness of semiconductor given that the material is likewise uniform.

It is easy to understand why such an assumption might be made as the J - V relationship is, indeed, observed to usually be linear at low voltages. However, there's a number of reasons for why the J - V relationship can be linear at low voltage, namely either due to doping, i.e., a large spatially uniform charge carrier across the entire semiconductor, a large degree of background current due to shunt pathways through the probed semiconductor, or due to the equilibrium charge-carrier density due to injection of charge carriers from the contacts into the semiconductor. We will show that where a linear J - V relationship due to doping can be considered to be Ohmic, the linear J - V due to the equilibrium charge-carrier density, which will be the dominant charge-carrier density in undoped semiconductor, will not be Ohmic.

In the limit where the semiconductor in the single-carrier device is highly doped, i.e., a very large density of dopants are distributed uniformly across the semiconductor, it can be assumed that the current density follows Ohm's law,

$$J = q\mu N_{\text{doping}} \frac{V}{L} \quad (4.3)$$

where N_{doping} can either be due to donor or acceptor like defects. Note the similarity between the assumptions made about eq. 4.2 and eq. 4.3, namely that the charge-carrier density is uniformly distributed across the semiconductor.

It was shown in chapter 3 that the current in the low voltage regime, for a thin single-carrier device made from an intrinsic semiconductor, is primarily governed by the equilibrium charge-carrier density in the middle of the device, which is many orders of magnitude larger than the intrinsic charge-carrier density. The current density, within this picture, can be described the moving electrode (ME) equation[137, 140, 141],

$$J = 4\pi^2 \frac{k_B T}{q} \mu_n \epsilon_r \epsilon_0 \frac{V}{L^3}. \quad (4.4)$$

where $k_B T$ is the thermal energy. It is worth noting that both Ohm's law (eqs. 4.2 and 4.3) and the ME equation (eq. 4.4) describes a current which is linearly proportional to the applied voltage. However, where Ohm's law (describing true Ohmic conduction), describes the current of uniformly distributed charge carriers (either n_i or N_{doping}), the ME equation can be considered to describe the current due to the equilibrium charge carriers in the middle of the device only.

4.2.3 Research question

We here show that since Ohm's law and the MG law do not hold under the same conditions, the method of using a combination of the two laws to determine the charge-carrier density across the thickness of an intrinsic semiconductor is inaccurate. We show that this is because the linear J - V regime is not due to intrinsic charge carriers, and in the limit where the doping density is large enough that using Ohm's law becomes a good method to estimate the doping density in the semiconductor, the MG law is no longer valid as the current flowing through the semiconductor is no longer space-charge limited.

4.3 Methods

The validity of the approach is discussed using the numerical drift-diffusion solver, *ASA*, introduced in chapter 3. We calculate the J - V curves (from 0.01 to 10 V) and the charge-carrier

Table 4.1: Table of fixed and variable values used in the drift-diffusion simulations to model the electron-only devices with and without doping.

Quantity	Symbol	Value	Units
Band gap	E_g	2	eV
Effective electron density of states	N_C	10^{19}	cm^{-3}
Effective hole density of states	N_V	10^{19}	cm^{-3}
Donor density	N_D	variable	cm^{-3}
Dielectric constant	ϵ_r	3	-
Active layer thickness	L	variable	nm
Electron band-like mobility	μ_n	10^{-4}	cm^2/Vs
Hole band-like mobility	μ_h	10^{-4}	cm^2/Vs
Injection barrier height at $x = 0$ (single-carrier)	$q\phi_{\text{inj}}$	0	eV
Injection barrier height at $x = L$ (single-carrier)	$q\phi_{\text{ext}}$	0	eV
Surface recombination velocity	S	10^5	m/s
Series resistance	R_S	0	Ωm^2
Shunt/parallel resistance	R_P	∞	Ωm^2
Temperature	T	300	K

density profiles, when the device is either undoped or when the device has a profound doping concentration, N_D whilst fitting with both Ohm's law and the MG law to simultaneously extract a value for the charge-carrier density and the charge-carrier mobility. We then test whether using both Ohm's law and the MG law is a sensible way of measuring the product of mobility and doping density in the sample, both in the low and high doping limit.

For simplicity, we will only discuss electron-only devices as hole-only devices would function in a completely analogous manner. All devices were calculated using similar device and materials values, besides the value for the semiconductor thickness and the doping density, as shown in table 4.1. The electron mobility was rather arbitrarily set to $10^{-4} \text{ cm}^2/\text{Vs}$ in the simulations (the choice of this value only affects the magnitude of the current density but not the slope of the J - V curves). Ohmic contacts were assumed, $q\phi_{\text{inj}} = q\phi_{\text{ext}} = 0 \text{ eV}$, and it was assumed that the devices were either intrinsic (undoped, $N_D = 0$ and trap free, $N_t = 0$) or doped but trap free (with $N_D > 0$). Since the electron-only devices in this chapter only contain a single carrier type, recombination can be neglected.

4.4 Results

This results section is divided into five subsections. We first discuss the possibility of the low voltage regime being due to intrinsic charge carriers only. Values from previously derived analytical expressions for the charge-carrier density, in both the middle of the device and across the entire thickness device, are compared to numerically calculated values. We then perform the same analysis to a device with a doped semiconductor. We subsequently compare results from using Ohm's law and the MG law over a large range of thicknesses and doping densities and we investigate whether a parameter space exists where the methods can be used in combination without too much error. Finally, we relate our finding to the findings in the literature.

4.4.1 Ohm's law applied to an intrinsic single-carrier device

We first discuss the depth of the space-charge regions formed at the metal/semiconductor interfaces. We then discuss the relative magnitudes of the intrinsic and equilibrium charge-carrier densities and discuss their influence to the current observed at low voltage.

Depth of the space-charge regions in a single-carrier device and the relative contribution of the intrinsic charge-carrier density to the total charge-carrier density

The interface physics between a metal and an undoped (Ohmic and near-Ohmic contacts) or doped (Schottky contacts) semiconductor was discussed in detail in chapter 3. However, we will here shortly discuss the formation of a space-charge layer near the vicinity of a metal/semiconductor interface forming an Ohmic contact during interface formation, as it is paramount for this part of the thesis.

When a semiconductor comes into contact with a metal, charge carriers are injected from the metal into the semiconductor in order to equilibrate the Fermi level across the interface. During this Fermi level equilibration between a metal contact and a semiconductor, which form an Ohmic contact (prior to the application of a bias voltage), the injected charge carriers from the metal to the semiconductor will greatly increase the charge-carrier density in the vicinity of the interface to a value many orders of magnitude higher than the intrinsic charge-carrier population. We denote this increase in the charge-carrier density as a space-charge layer and we simply denote this quantity by n for electrons (and p for holes, even though this density can usually be neglected in symmetric single-carrier devices). These injected charge carriers, n , along with the intrinsic charge carrier density, n_i , are available for conduction of electricity, and the depth of the space-charge layer will be roughly equal to the Debye screening length, L_D ,

$$L_D = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{q^2 n_\gamma}} \quad (4.5)$$

where n_γ is the concentration of the carrier type that is in the majority at the contact, and $k_B T$ is the thermal energy (the subscript, γ , is merely to help distinguish between the different charge-carrier densities).

For a single-carrier device i.e., two metal/semiconductor interfaces, the charge-carrier density across the entire device will then greatly exceed the intrinsic charge-carrier density if the thickness of the semiconductor layer is less than twice the Debye length ($L < 2L_D$). This is sometimes referred to as *overlapping contacts* (a schematic of this phenomenon is shown in fig. 4.1a). Additionally, since the majority of the injected charge carriers reside near the interfaces, the charge-carrier density will be highly non-uniform (fig. 4.1b).

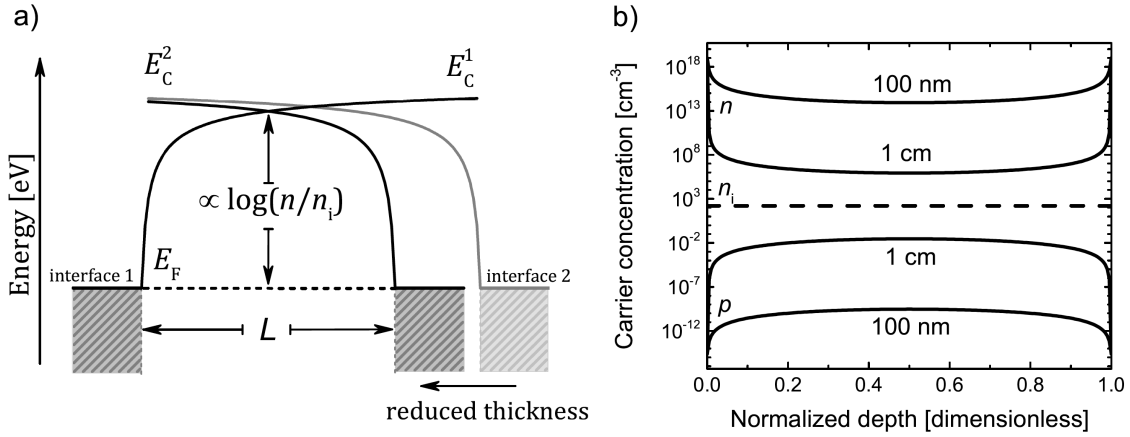


Figure 4.1: a) Energy level diagram of a single-carrier device made from an undoped semiconductor at thermal equilibrium. b) Carrier density profiles of a 100 nm and a 1 cm single-carrier device (black lines). The intrinsic charge carrier density is shown for comparison as a dashed line. The hole density in a thin electron-only device can be neglected since the electron density is so high ($np = n_i^2 = \text{constant}$).

From fig. 4.1b it is seen that the intrinsic charge carrier density, n_i , will be uniformly distributed across the thickness of the semiconductor, but will be many orders of magnitude less than the equilibrium charge carrier density, n , which is highly non-uniform (with most of the charge carriers residing near the metal/semiconductor interfaces) even if the semiconductor is very thick ($L \gg 100$ nm).

In the case where a metal forms an Ohmic contact with an intrinsic organic semiconductor,

the charge carrier density in eq. 4.5 will be equal to the intrinsic carrier density, $n_\gamma = n_i$, which is governed by the magnitude of the band gap and the effective density of states of electrons and holes only,

$$n_i = \sqrt{N_C N_V} \exp\left(-\frac{E_g}{2k_B T}\right). \quad (4.6)$$

So for an intrinsic 2 eV band gap semiconductor with $\epsilon_r = 3$ and an effective density of states for both electrons and holes of 10^{19} cm^{-3} (at $T = 300 \text{ K}$), sandwiched between two metals, L_D will be several centimetres. Typical active layer thicknesses for organic optoelectronic devices are on the order of hundreds of nm, therefore, the space-charge regions will be much thicker than the thickness of the active layer in a normal device, and we will have highly *overlapping contacts*. For that reason, the equilibrium charge-carrier density, n , will almost always be greater than the intrinsic charge-carrier density, n_i , in an organic intrinsic single-carrier device, especially at the metal/semiconductor interfaces (as shown in fig. 4.1b). The uniformly distributed intrinsic charge carrier density can therefore be neglected compared to the equilibrium charge-carrier density when considering electrical conduction, and the linear J - V relationship at low voltages can for that reason not be due to the intrinsic charge carriers as this density is completely masked by the much larger equilibrium charge-carrier density.

On a side note, for the screening length to decrease below 50 nm, which is necessary to achieve *separation of contacts* in a 100 nm thick device, the carrier concentration must be larger than $2 \cdot 10^{15} \text{ cm}^{-3}$. To achieve the carrier density to separate the contacts for a 100 nm device, those charge-carriers would have to be added via doping, or E_g would have to be decreased to less than 0.44 eV, which is close the value of very low inorganic band gap semiconductors (bulk germanium has a band gap of approximately 0.67 eV and bulk lead sulphide a band gap of approximately 0.37 eV) and is much less than the band gap for any organic semiconductor used for opto-electronic devices, which are usually larger than 1.7 eV.

Another indication that the current at low voltage is not due to intrinsic charge carriers, is due to the fact that the current scales with L^{-3} rather than L^{-1} . Figure 4.2a shows simulated J - V curves for ideal electron-only devices. Figure 4.2b shows that the current density scales with L^{-3} over the entire voltage range for the simulated thicknesses. Had the current at low voltage been due to the intrinsic charge carriers only, or any mechanism giving rise to true Ohmic conduction for that matter, the current would have scaled inversely with thickness in accordance with eq 4.2.

With the observation that the intrinsic charge-carrier density will be completely masked

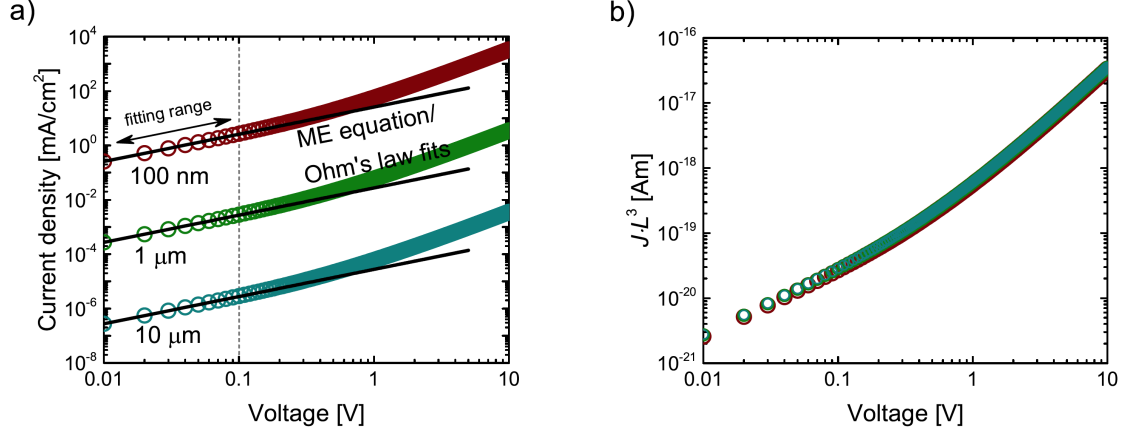


Figure 4.2: a) Numerically calculated J - V curves of ideal (undoped and trap free semiconductor) electron-only devices with Ohmic contacts. Fits with either the ME equation or Ohm's law are shown as solid lines. b) Same curves as in a) but with the y-axis scaled with L^{-3} .

in a single-carrier device, and the fact that the current scales with L^{-3} , it is safe to conclude that the current at low voltages is not due to the intrinsic charge-carrier density and cannot be described with $J = q\mu n_i V/L$ (eq. 4.2).

Comparison of analytical and numerical expressions for the equilibrium charge-carrier density

A more reasonable assumption is that the low voltage regime is not governed by Ohmic conduction of the intrinsic charge-carrier density only, but rather by Ohmic conduction by a combination of the equilibrium charge-carrier density, n , arising due to injection of charge-carriers from the contact during Fermi level equilibration, and the intrinsic charge-carrier density, n_i (which would then be negligible, relative to the equilibrium concentration since $n(x) \gg n_i$). Whereas the current at low voltage is in fact due to the equilibrium concentration, the charge-carrier density is not uniform (see fig. 4.1b), and the current is for that reason, not truly Ohmic.

As previously discussed in chapter 3, the charge-carrier density as a function of the spatial position inside the semiconductor in the electron-only device, $n(x)$, can to a good approximation be described analytically[138], by,

$$n(x) = \frac{2\pi^2 \epsilon_r \epsilon_0 k_B T}{q^2 L^2} \frac{1}{\cos^2 \left[\pi \left(\frac{x}{L} - \frac{1}{2} \right) \right]}. \quad (4.7)$$

Equation 4.7 was used to derive the ME equation, which fits very well to the current at low

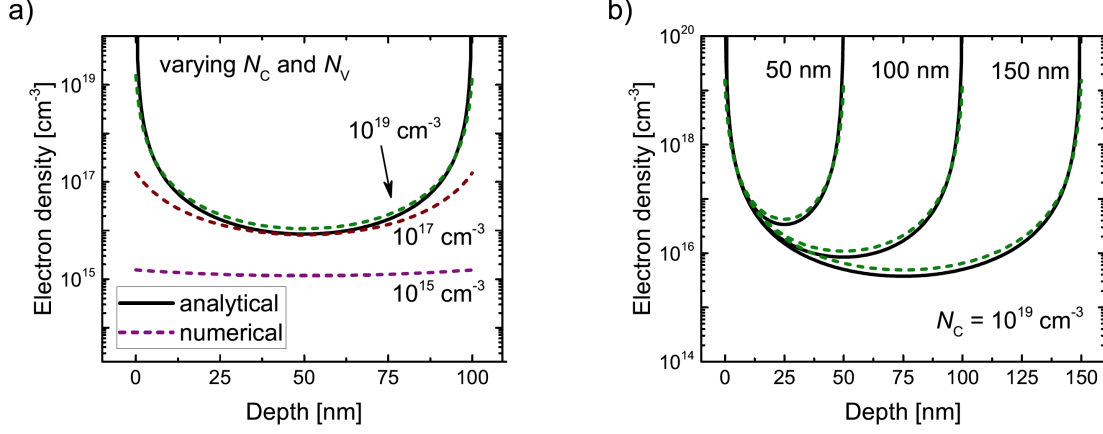


Figure 4.3: a) Comparison of eq. 4.7 to numerically calculated electron density curves as a function of device depth (using different values for the effective density of states). b) Similar comparison, but with increased semiconductor thickness (with a fixed effective density of states).

voltage, as shown in fig. 4.2a. Figure 4.3a shows a comparison between eq. 4.7 and the numerically calculated charge-carrier density inside a 100 nm device. We repeated the numerical calculations for different values of the effective density of states, which has a large impact on the magnitude of the carrier density at the device boundaries, $n(0) = n(L) = N_C \exp(-q\phi_{\text{inj}}/k_B T)$. It is seen that eq. 4.7 is a good approximation when the effective density of states is of the order which is normally seen in semiconductors ($> 10^{17} \text{ cm}^{-3}$). As seen in fig. 4.3b, eq. 4.7 gives a good spatial description of the charge-carrier density even when the thickness is varied. However, importantly, eq. 4.7 predicts that the charge-carrier density blows up to infinity at the device boundaries, which is, of course, non-physical as the charge-carrier density at the boundaries is ultimately determined by the effective density of states and the injection barrier heights.

We firstly discuss how well the charge-carrier density in the middle of the device can be estimated using eq. 4.7 and we then discuss how well the charge-carrier density across the entire device can be estimated using the same equation. The charge-carrier density in the middle of the device, $n_0 = n(L/2)$, is, within the approximation of eq. 4.7, given by,

$$n_0 = \frac{2\pi^2 \epsilon_r \epsilon_0 k_B T}{q^2 L^2}. \quad (4.8)$$

A comparison between eq. 4.8 and the charge-carrier density in the middle of numerically calculated single-carrier devices is shown in fig 4.4a. Excellent agreement is observed, especially for

thicknesses above 100 nm (increasing the effective density of states in the numerical calculation will increase the charge-carrier density for the low thickness devices, increasing the overlap), meaning that eq. 4.7 (and hence eq. 4.8) describes the charge-carrier density in the middle of a single-carrier device very well.

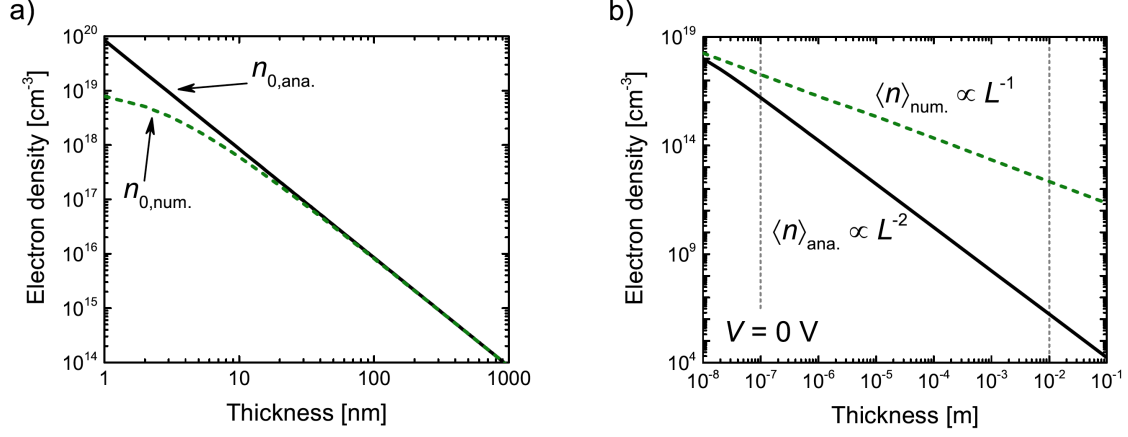


Figure 4.4: a) Numerical calculation of the electron density in the middle of the device as a function of thickness (green dashed line) compared to the analytical expression, eq. 4.8 (black solid line). b) Comparison of the spatial average of the numerical and analytical electron density over a large range of thicknesses. The two thicknesses shown in fig. 4.1b are shown as grey dashed lines. The effective density of states was set to 10^{19} cm^{-3}

Since Ohmic conduction (as defined above) is not only due to the charge carriers in the middle of the device but rather due to all the charge carriers inside the semiconductor, it is important to consider the entire thickness of the device and not just the middle of the device, and we therefore need to consider the average charge-carrier density.

The arithmetic mean of eq. 4.7, $\langle n \rangle = L^{-1} \int_0^L n dx$, cannot be calculated, since the integral does not converge. However n^{-1} can be integrated and, thus, the harmonic mean of the charge-carrier density can be written as,

$$\langle n \rangle_{ana.} = \frac{1}{\frac{1}{L} \int_0^L n^{-1} dx}. \quad (4.9)$$

This integral yields,

$$\langle n \rangle_{ana.} = \frac{4\pi^2 \epsilon_r \epsilon_0 k_B T}{q^2 L^2} \quad (4.10)$$

which is equal to twice the value of the charge-carrier density in the middle of the device, $2n_0$. This implies that the harmonic average charge-carrier density across the device is simply given by twice the charge-carrier density in the middle of the device, indicating that irrespective of the effective density of states, the charge-carrier density will be constant for a given dielectric constant, temperature and thickness.

Furthermore, by writing $J = q\mu_n \langle n \rangle_{\text{ana.}} V/L$ or $J = 2q\mu_n n_0 V/L$, we can obtain the ME equation,

$$J = 4\pi^2 \frac{k_B T}{q} \mu_n \epsilon_r \epsilon_0 \frac{V}{L^3}. \quad (4.11)$$

This implies that if the ME equation is fitted to the J - V curve (as seen in fig. 4.2), and it is assumed that the low voltage regime follows Ohm's law, the apparent charge carrier density will be given by eq. 4.10.

However, for a symmetric single-carrier device with Ohmic contacts, the actual charge-carrier density is mainly governed by the charge-carrier density at the device boundaries (see fig. 4.3), which in turn is governed by the effective density of states,

$$n(0) = n(L) = N_C. \quad (4.12)$$

This means that the device boundaries will have a large influence on average charge-carrier density. In fig. 4.4b the harmonic average value of the charge-carrier density of numerically calculated single-carrier devices, $\langle n \rangle_{\text{num.}}$, is compared to the analytical charge carrier density, $\langle n \rangle_{\text{ana.}}$ (meaning that we compare the harmonic average in both cases, where one expression is derived analytically and the other expression is calculated numerically). It is seen that $\langle n \rangle_{\text{num.}}$ decreases with increased thickness closely following a $\propto L^{-1}$ relation whereas $\langle n \rangle_{\text{ana.}}$ decreases like $\propto L^{-2}$ (eq. 4.10). As the thickness increases, the actual charge-carrier density in the device will be much higher than what is estimated using eq 4.10. For a 100 nm device, the difference between the apparent density and the actual density is about an order of magnitude and for a μm thick device the charge-carrier density will be underestimated by about two orders of magnitude.

We have shown that the actual charge carrier density inside the entire length of a single-carrier device cannot be accurately described by eq. 4.10. Since estimating the charge carrier density using eq. 4.10 corresponds to using Ohm's law, we can conclude that the current in the linear low voltage regime is not due to Ohmic conduction. It was however seen that eq. 4.8

very well describes the charge-carrier density in the middle of the device. From this it is clear that using Ohm's law to determine the total (or average) charge-carrier density of an intrinsic organic single-carrier device is not meaningful, since only the charge carriers in the middle of the device contribute to the current. The ME equation will only yield the charge-carrier density in the middle of the device whilst the total charge-carrier density is mostly governed by the charge-carrier density at the device boundaries.

4.4.2 Ohm's law applied to a doped device

In this section, we discuss the extent to which the semiconductor will have to be doped in order for Ohm's law to correctly describe the charge-carrier density across the entire thickness of the semiconductor. The J - V curves and charge-carrier density profiles are calculated as a function of device thickness and doping concentrations (similar to the intrinsic case).

Increase in charge-carrier density uniformity with increased doping density

From the discussion in the previous section it is clear that the reason for why Ohm's law does not yield the correct value for the spatial average charge-carrier density across the device, is due to the fact that the charge-carrier density is highly non-uniform, with the majority of the equilibrium charge carriers residing near the contacts, whilst the current is mainly due to charge carriers in the middle of the device (the ME equation, eq. 4.4).

With a large amount of charge carriers present at the boundaries in a 100 nm single-carrier device at thermodynamic equilibrium (see fig. 4.1b and fig. 4.3), it is expected that a very large concentration of dopants (at least of the order of the equilibrium charge carrier density, $N_{\text{doping}} > n_0$) must be introduced in order for the equilibrium injected charge-carrier density to become negligible in comparison to the doping charge-carrier density and for the total charge-carrier density to be uniform across the device. Figure 4.5 shows calculated energy levels and charge-carrier densities of four 100 nm, 2 eV band gap, electron-only single-carrier devices with Ohmic contacts. Like before, the effective density of states is set to 10^{19} m^{-3} . However, this time, the density of additional free charge carriers from donor type dopants, N_D is allowed to vary from 0 to 10^{18} cm^{-3} .

Figure 4.5a-d shows the energy levels and 4.5e-h shows the charge-carrier density as a function of device depth of the calculated devices when the doping concentration is increased beyond n_0 . It is seen from figs. 4.5a-b and e-f, that an approximate 10^{16} cm^{-3} donor concentration must be added to the semiconductor in order to increase the charge-carrier density substantially above that seen for an intrinsic semiconductor at thermodynamic equilibrium (the charge-carrier

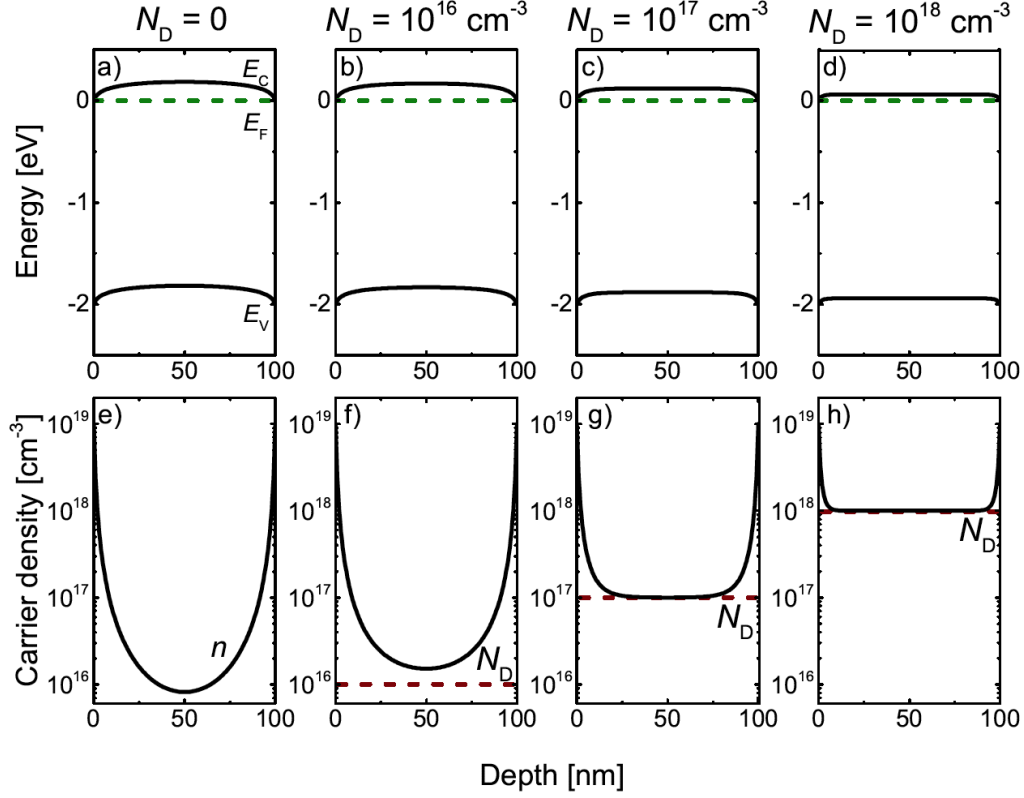


Figure 4.5: Energy level diagrams of an electron-only single-carrier device (at zero applied bias) made with an intrinsic semiconductor a) and electron-only devices with increasing concentrations of ionized donors, N_D b)-d). Charge-carrier density diagrams e)-h) of the devices shown in a)-d).

density of the intrinsic device seen in fig. 4.5e is indistinguishable from a device with a doping density of 10^{15} cm^{-3}). From this it is possible to predict that the J - V behaviour, from above mentioned device, will remain as though coming from an intrinsic material until the semiconductor has a doping concentration of approximately 10^{16} cm^{-3} , i.e., the device will behave as if the semiconductor is intrinsic as long as $N_D < n_0$.

A doping concentration of 10^{16} cm^{-3} corresponds to the Debye screening length (eq. 4.5) decreasing to around 20 nm which is slightly more than the value needed to separate the two space-charge regions ($1.7 \cdot 10^{15} \text{ cm}^{-3}$ for $L_D = 50 \text{ nm}$). However, even in the case of 10^{16} cm^{-3} added charge carriers from donors, the charge-carrier density present at thermodynamic equilibrium, is still not negligible, especially not at the interfaces (fig. 4.5f). As the concentration of donors reaches 10^{17} cm^{-3} the space-charge regions are well separated (fig. 4.5c) and the equilibrium charge-carrier density is now negligible in the middle of the device and the total charge-carrier density in the middle of the device is equal to the doping density (fig. 4.5g). At

10^{18} cm^{-3} added donors, the Debye length is around 2 nm and therefore much smaller than the device thickness (fig. 4.5d), meaning that the total charge-carrier density is nearly uniform, and equal to the doping concentration over 90% of the total device thickness (fig. 4.5h). From these calculations we can predict that the current density can be well described by the ME equation up to doping levels as high as 10^{16} cm^{-3} ($N_D < n_0$) but will tend towards Ohmic conduction at higher doping levels ($N_D > n_0$).

Current density at low voltage in a doped device

In the case where a large amount of doping is added to the semiconductor to increase the charge-carrier density beyond the equilibrium charge-carrier density, we assume that the total current density at low voltage can be expressed by Ohm's law (merely as a sum of eqs. 4.3 and 4.4),

$$J = q\mu_n \left(\frac{4\pi^2 k_B T \varepsilon_r \varepsilon_0}{q^2 L^2} + N_D \right) \frac{V}{L} \quad (4.13)$$

and the apparent charge-carrier density, can be written analytically as,

$$\langle n \rangle_{\text{ana.}} = \frac{4\pi^2 k_B T \varepsilon_r \varepsilon_0}{q^2 L^2} + N_D. \quad (4.14)$$

Equation 4.14 can be considered as being the charge-carrier density one would obtain if one were to fit with Ohm's law (eq. 4.13) using μ_n as an input value either already known or obtained from the MG law. One would then either obtain a underestimation of the charge-carrier density if the doping density is too low, or a good approximation for the charge-carrier density if the doping density is high.

The simulated J - V curves of the single carrier devices presented in fig. 4.5 are presented in fig. 4.6a. The current density of the single-carrier device with the intrinsic semiconductor (black line) is seen to vary from a linear regime at low voltages ($J \propto V$) to a higher order regime at higher voltages ($J \propto V^m$ where $m > 1$) which is what is expected from eqs. 4.4 (the ME equation) and 4.1 (the MG law), respectively (fig. 4.6b). As the donor concentration is increased, the overall current is seen to increase, and the linear J - V regime is seen to extend over the entire voltage range at very high doping concentrations, as was expected from the discussion of fig. 4.5. As was mentioned earlier, the MG law can only be fitted where $J \propto V^2$, but it is seen that the slope of the J - V curves on a log-log scale decreases away from 2 when the doping concentration is increased. For this reason it is not possible to obtain a fit to the

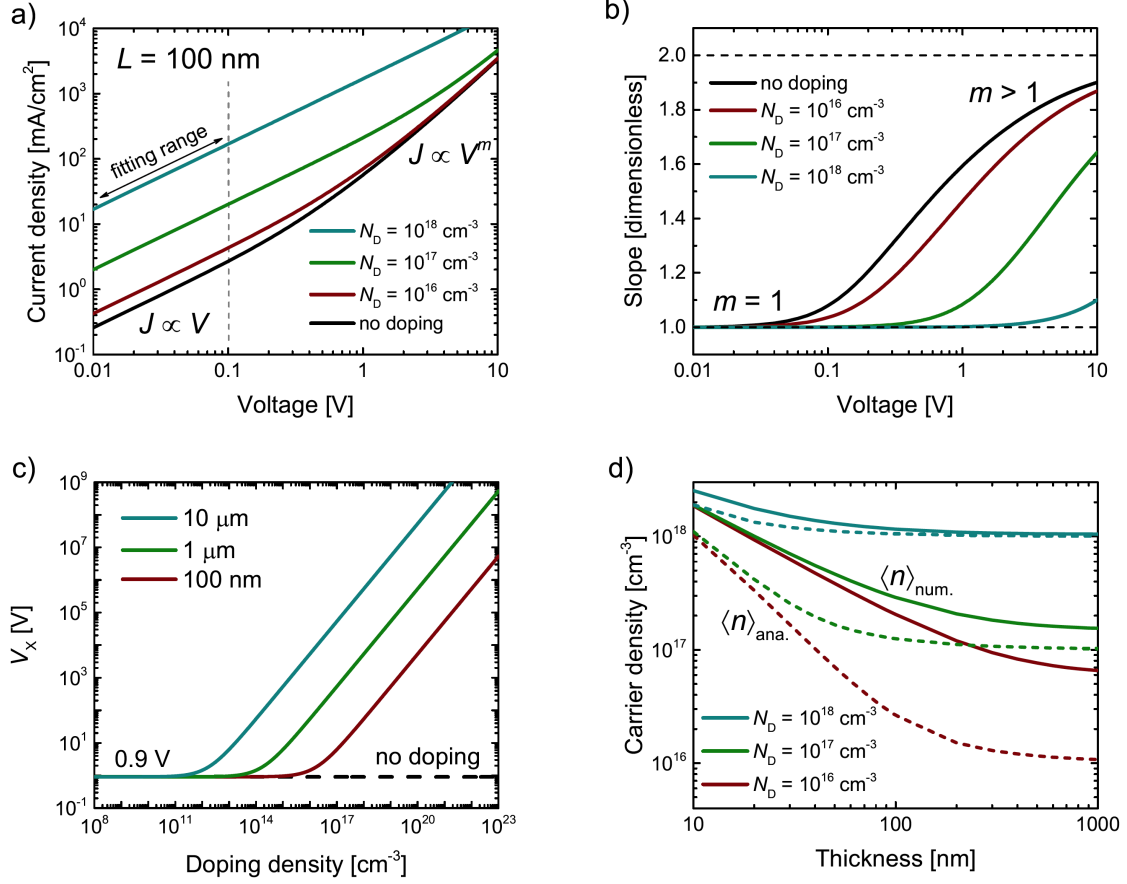


Figure 4.6: a) Numerically calculated current density-voltage curves of 100 nm single-carrier devices with different doping concentration. b) Slope-voltage (m - V) profiles of the J - V profiles. c) Transition voltage, V_X (eq. 4.15), at 300 K, as a function of added doping density, N_D , for three thicknesses (100 nm, 1 μm and 10 μm). $V_X \approx 0.9$ V for an undoped device is shown as a dashed line for reference. d) Comparison of the actual charge-carrier densities of the doped devices determined from the numerical calculations (solid lines) and the charge-carrier density determined from eq. 4.14.

J - V curves for the doped devices using the MG law, i.e., the current through the single-carrier device is no longer space-charge limited due to the very large doping density.

In the presence of doping, we can derive an expression for the cross-over voltage from the low voltage regime to the MG regime by equating eqs. 4.1 (the MG law) and 4.13, to,

$$V_X = \frac{32\pi^2}{9} \frac{k_B T}{q} + \frac{8}{9} \frac{q N_D L^2}{\epsilon_r \epsilon_0} \quad (4.15)$$

where the first term is the cross-over voltage from the low voltage regime to the MG regime, and the second term is the shift in the cross-over voltage due to the presence of doping. Since the left hand side of eq. 4.15 only scales with temperature, the cross-over voltage from linear a current to the square-law behaviour will happen at a specific voltage for all thicknesses at room temperature if the semiconductor is intrinsic (for the parameters used, this cross-over voltage is ≈ 0.9 V). However, a highly doped device will show a linear behaviour up to higher voltages. For example, V_X will increase by 0.6 V (to around 1.5 V) if the doping density is around 10^{16} cm^{-3} for the 100 nm device. This is exactly what was observed in figs. 4.6a and b.

V_X as a function of doping density for a devices with different thicknesses is shown in fig. 4.6c. Figure 4.6c can in principle be used as a tool to estimate the doping density based on the transition voltage. If the linear regime J - V regime is observed at voltages above 0.9 V (as was seen in fig. 4.6b), and the thickness scaling of the Ohmic region is seen to follow L^{-1} rather than L^{-3} , then this is an indication that the device is highly doped ($> 10^{16}$ cm^{-3} for a 100 nm device).

Figure 4.6d shows the comparison between the charge-carrier density from eq. 4.14 and the numerically calculated average charge-carrier density as the semiconductor is increasingly doped from 10^{16} cm^{-3} to 10^{18} cm^{-3} . Even at a doping concentration as high as 10^{16} cm^{-3} , the charge-carrier density obtained using eq. 4.15 underestimates the true value by an order of magnitude for devices with thicknesses above 100 nm. As the doping concentration is increased to 10^{17} cm^{-3} the charge-carrier density can be estimated to within less than a factor of 2, when measuring thick devices, and when the semiconductor is highly doped (10^{18} cm^{-3}), the charge-carrier density can be estimated by eq. 4.15 with a reasonable certainty. This means that the semiconductor must be heavily doped, for Ohm's law to be valid with a reasonable accuracy, for devices, with thicknesses, interesting for opto-electronics.

4.4.3 Comparing Ohm's law and Mott-Gurney law using similar parameters

Up until this point, our efforts have been put into investigating whether Ohm's law can be used to estimate the average charge-carrier density of the semiconductor (undoped and doped) given that the mobility is known in advance. However, it is apparent from figs. 4.6a and b that fitting with the MG law becomes increasingly difficult (or rather impossible) with increased doping density as the $J \propto V^2$ behaviour is no longer observed. We can however use a trick of simply evaluating (or force fitting with) the MG law at the point of maximum slope and extract a value for the mobility. This mobility will of course not be correct and further reflect the issues with the method we are testing.

Despite being impossible to fit with the MG law when a large doping density is present, we now test using Ohm's law and the MG law, simultaneously, on electron-only devices over a large range of thicknesses and doping concentrations. Figure 4.7a shows the ratio of the charge-carrier density from Ohm's law (eq. 4.13) and the actual charge-carrier density. The figure shows that in order for Ohm's law to be valid at reasonably low doping concentrations (10^{12} cm^{-3}) the device thickness will have to be on the order of centimetres (purple region). Likewise, in order to use Ohm's law to measure the charge-carrier density in a thin device, the doping concentration must be very high (as was also seen in fig 4.6). As the doping concentration and the thickness are simultaneously increased, the charge-carrier density can be determined from Ohm's law, in all of the purple region of fig. 4.7a, with an error of less than 20%.

Figure 4.7b shows the ratio of the charge-carrier mobility, obtained by force fitting with the MG law to the simulated J - V curves from devices similar to those in fig 4.6a, to the input charge-carrier mobility ($10^{-4} \text{ cm}^2/\text{Vs}$). As mentioned above, by a forced fit we mean that the equation is evaluated in the voltage region of maximum slope, $V = V(m_{\text{max}})$ even though the magnitude of the slope is less than two, i.e., V^m with $m_{\text{max}} < 2$ as seen in fig. 4.6b. We see, from fig. 4.7b, that since a fit with an equation under conditions where it should not hold, is being attempted, the mobility is quickly overestimated by many orders of magnitude when the thickness and/or the doping concentration is increased. It is however seen that the mobility can be obtained using the MG law, with an error of less than 20%, for a thin device even when a large amount of doping is present, as was predicted from fig. 4.5.

If the mobility of a $1 \text{ }\mu\text{m}$ thick device with a doping density of 10^{17} cm^{-3} were measured with a forced fit with the MG law, the mobility would be overestimated by more than an order of magnitude which, in return, would lead to an underestimation of the charge-carrier density by an order of magnitude. A similar situation would arise for a 1 cm thick device where the mobility would be overestimated, by many orders of magnitude, at all calculated doping

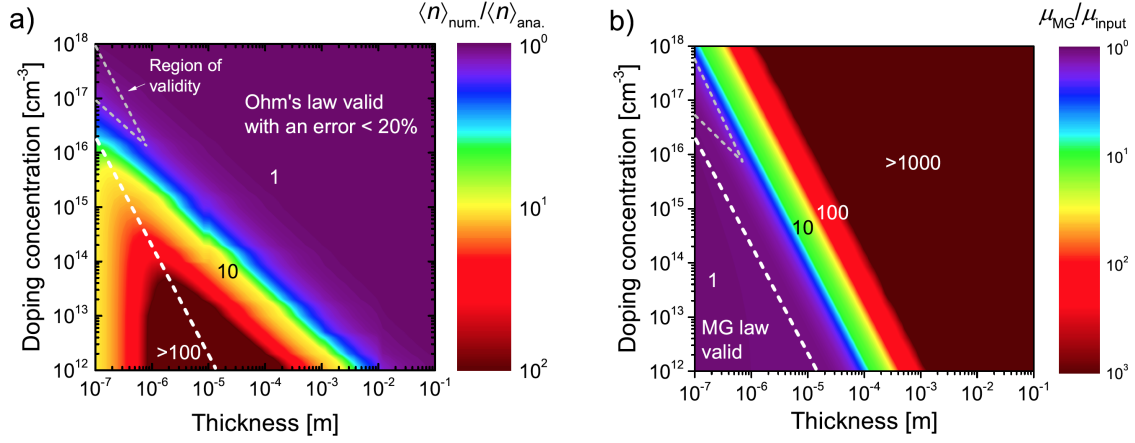


Figure 4.7: a) Ratio of the actual charge carrier density, $\langle n \rangle_{\text{num.}}$, from numerical calculations to the apparent carrier density from Ohm's law, eq. 4.14, when the doping concentration is increased for devices in a thickness range of 100 nm to 10 cm (Ohm's law is valid in the purple region with an error of less than 20%). The device will behave as though it is intrinsic when the values for the doping concentration, and thickness, are on the left of the dotted line. b) Ratio of the charge carrier mobility obtained from the MG law, μ_{MG} , to the input mobility for the numerical calculations (the MG law is valid in the purple region with an error of less than 20%). The area indicated by the grey dashed lines is where the conductivity can be determined by evaluating the MG law at high voltages and Ohm's law at low voltages, simultaneously.

densities. If a 100 nm or a 1 μm thick device with a low doping concentration of 10^{13} cm^{-3} had been measured, the mobility could be determined from the MG law, but the charge-carrier density would be underestimated by several orders of magnitude.

By comparing fig. 4.7a with 4.7b, it is clear that the two equations are rarely valid under the same conditions (very little overlap between the two purple regions). However, there is a small area where both equations can be applied with a negligible error (area indicated by grey dashed lines). We speculate that it happens only around the point where the space-charge regions no longer overlap, but before the equilibrium charge carrier density becomes negligible compared to the doping density. The situation is however very different when the equations are evaluated simultaneously outside of this region.

4.4.4 Condition for validity

We now discuss whether there are conditions when Ohm's law and the MG law can be applied to the same J - V curve.

It is possible to express a condition for when Ohm's law and the MG law should hold together, namely when the first and second term of eq. 4.15 are equal,

$$\frac{32\pi^2}{9} \frac{k_B T}{q} = \frac{8}{9} \frac{q N_D L^2}{\epsilon_r \epsilon_0}. \quad (4.16)$$

This condition can be expressed as,

$$N_D L^2 = \frac{4\pi^2 k_B T \epsilon_r \epsilon_0}{q^2} \quad (4.17)$$

or in terms of the doping density, semiconductor thickness and relative permittivity only,

$$N_D L^2 \approx \epsilon_r \cdot 5.6 \cdot 10^7 \text{ m}^{-1}. \quad (4.18)$$

When the left hand side of eq. 4.18 is larger than the right hand side, Ohm's law should be approximately valid (i.e., the semiconductor will be sufficiently doped) and when the left hand side is smaller than the right hand side the MG law should be approximately valid (i.e., the device will behave as if the semiconductor is intrinsic). When the left hand side equals the right hand side of the equation, the two equations should, in principle, be able to be used in conjunction.

Using the condition given by eq. 4.18, the upper limit for the doping concentration of a semiconductor in a single-carrier device, that allows it to follow space-charge-limited behaviour, can be seen from fig 4.7a. This upper limit is shown by the inserted white dashed line, where on the left hand side, the ratio, $\langle n \rangle_{\text{num.}} / \langle n \rangle_{\text{ana.}}$, increases linearly, as the thickness of the device approaches twice the Debye length ($L \rightarrow 2L_D$). On the right hand side of the dashed line, the charge-carrier density from Ohm's law approaches that of the actual charge-carrier density, as the thickness of the semiconductor is now exceeding twice the Debye length ($L > 2L_D$). This is causing $\langle n \rangle_{\text{num.}} / \langle n \rangle_{\text{ana.}}$ to tend towards unity where Ohm's law is valid. It is seen that eq. 4.17 does not give us a condition for where Ohm's law can be used, but rather an upper limit for how much you can dope the semiconductor whilst the transport through it remains space-charge limited.

While eq. 4.18 does not describe when Ohm's law is valid, very well, it is seen that the condition very well describes a limit for where the MG law can safely be used (see fig. 4.7b). The validity condition (eq. 4.18) can then be used as a tool to help determine whether the measured single-carrier device is in a parameter regime where the MG law can be used to describe the charge transport, but does not tell you where Ohm's law and the MG law can be used in combination. Since the window of applicability of using the method is very narrow (the grey dashed regions shown in figs. 4.7a and b), the likelihood of correct analysis is very small. For that reason, this work suggests that this method should not be used.

4.4.5 This study in relation to the literature

Most noteworthy, Shi *et al* used the method of combining Ohm's law and the MG law to estimate the charge-carrier density of intrinsic lead halide perovskites in mm thick single-carrier devices[8]. A study which has been cited numerous times in the literature (and the method has for that reason been copied on numerous occasions). It is quite apparent that it is not possible to use the two models in combination for such thicknesses regardless of the doping densities used in this study, as the two purple regions do not overlap (where Ohm's law could yield a meaningful value for the charge-carrier density with reasonably high doping levels, the MG law would yield a mobility which is overestimated by many orders of magnitude).

4.5 Conclusion

In this chapter we set out to investigate whether Ohm's law and the MG law could be used under the same conditions to extract a meaningful value for the charge-carrier density of the semiconductor. We used drift-diffusion simulations to investigate undoped and doped semiconductors

in symmetric single-carrier devices.

We found that as long as the space-charge regions overlap, the charge-carrier density in a single-carrier device is mainly governed by the equilibrium charge-carrier density and not by the intrinsic charge-carrier density nor the doping density. Under these circumstances, given by the herein derived validity condition, the mobility can be determined by the MG law to a reasonably good approximation.

We found that in order for a calculated 100 nm single-carrier device to be affected by doping, and for the use of Ohm's law to yield a meaningful result for the charge-carrier density when fitted to the low voltage regime, a doping density higher than 10^{16} cm^{-3} , i.e., significantly larger than the equilibrium charge-carrier density, must be added to the semiconductor. When the doping density is lower than the equilibrium charge-carrier density, Ohm's law does not correctly yield the charge-carrier density across the entire thickness of the semiconductor. As the doping density is increased, using Ohm's law becomes a reasonable approach for determining the charge-carrier density-mobility product. However, in the high doping limit where Ohm's law is valid, the MG can no longer be correctly fitted and, and even if the law is force fitted, will yield a mobility which overestimates the true value by many orders of magnitude. If this mobility is used in Ohm's law, this will yield a charge-carrier density which is underestimated by many orders of magnitude, rendering the method of using the two laws in combination useless in the most common cases.

Surprisingly, a small window of application is found, namely when the device is very thin and when the doping concentration is very high. However, since this window of applicability is so small, we discourage using the MG law in conjunction with Ohm's law as it is unphysical in most cases, and the chance for correct analysis is minimal. A more reliable approach is to use drift-diffusion solvers (as used in this study) to fit the obtained J - V curves as this method can correctly include the effect of space-charge.

Chapter 5

Exploring the Limitations of the Mott-Gurney Law

5.1 Abstract

Using drift-diffusion simulations, we investigate the voltage dependence of the drift current in single carrier devices. It is shown that for both low and high voltages, the current increases linearly with the applied voltage. Whereas the linear J - V behaviour at low voltages is mainly due to the equilibrium charge-carrier density in the middle of the device (as was discussed extensively in the previous chapter), the linear J - V behaviour at high voltage is caused by charge-carrier density saturation due to a high degree of injection due to the large applied voltage (also called emission limited transport). As a consequence, the current density at both low and high voltage does not follow the Mott-Gurney (MG) law, and we show that for trap-free devices, only in the intermediate voltage range, can the space-charge-limited drift current be observed to approach the MG description of charge transport.

We show that, depending on the thickness of the semiconductor layer and the size of the injection barriers at the metal/semiconductor interfaces, the two linear J - V regimes (the low and high voltage regimes, respectively) can dominate the whole voltage range, and the intermediate MG regime can shrink or disappear entirely. In this case, which will especially occur for thicknesses and injection barrier heights typical for single-carrier devices used to probe organic semiconductors, a meaningful analysis using the MG law will become unachievable, because a square-law fit can no longer be achieved, resulting in the mobility being substantially underestimated.

The work presented in this chapter was performed under the supervision of Prof. Jenny Nelson and Dr. Saif Haque and in collaboration with Dr. Davide Moia and Prof. Thomas

Kirchartz. A published version called "Exploring the Validity and Limitations of the Mott-Gurney Law for Charge-Carrier Mobility Determination of Semiconducting Thin-Films" was published in Journal of Physics: Condensed Matter in February 2018[148]

5.2 Introduction

5.2.1 Background and motivation

A vast amount of effort has been put into adapting the simple MG law[11] to account for non-ideal features, such as traps and energetic disorder[12, 14, 16]. However, to the authors knowledge, no-one used numerical simulations of device response to address whether the MG law is suitable for analysis of theoretically ideal (undoped, energetic disorder and trap-free) materials in a symmetric single-carrier device with a semiconductor thickness and injection properties of those normally used to study charge-transport of organic semiconductors (i.e., semiconductor thicknesses ranging from 50 to 300 nm and injection barrier heights as high as 0.3 eV).

During the derivation of the MG law (which was shown in detail in chapter 3), the charge-carrier density, as a function of distance, x from the injecting contact, was shown to be,

$$n(x) = \frac{1}{q} \sqrt{\frac{J \epsilon_r \epsilon_0}{2 \mu_n x}}. \quad (5.1)$$

where J is the current expressed from the MG law, q is the elementary charge, ϵ_r is the dielectric constant, ϵ_0 is the vacuum permittivity and μ_n is the electron mobility. By taking the limit $x \rightarrow 0$ in eq. 5.1, n tends to infinity at the injecting contact. This limit is however unphysical and results from the boundary conditions used for the analytical derivation of the MG law, as the charge-carrier density at the boundaries will be determined by the density of states and the injection barrier heights, $n(0) = N_C \exp(-q\phi_{\text{inj}}/k_B T)$.

Furthermore, eq. 5.1 follows the same spatial dependence, independent of device thickness or applied voltage (e.g., comparing the charge-carrier density of a 100 nm device with a 2 V applied voltage to a 200 nm device at 1 V applied voltage will show the same decrease in charge-carrier density with x , even though the magnitude of the charge-carrier density will be different). This is also unphysical condition arising from the boundary conditions. Because the MG law predicts a charge-carrier density that follows eq. 5.1, the MG law is unable to account for the accumulation, and eventual saturation (large uniform density across the length of the semiconducting layer) of charge carriers inside the single-carrier device when either a large bias

voltage is applied or when the semiconductor is very thin (as the spatial dependence and the value of the charge-carrier density at $x = 0$ will be unchanged).

5.2.2 Research question

Due to the fact that the MG does not account for saturation currents, we here address the fundamental question of whether the MG law is applicable to the case of an ideal material. Our analysis rests particularly on the physical validity of the above mentioned boundary conditions assumed in the MG law derivation and on the importance of charge-carrier saturation in devices, with typical injection barrier heights and with semiconductors of typical thicknesses, that are used for charge-transport measurements of organic semiconductors. We also briefly discuss the situation where traps are present and how that influences the results.

Through drift-diffusion simulations, we studied the current density-voltage and charge-carrier density profiles of ideal and non-ideal single-carrier devices of intrinsic semiconductors and semiconductors where transport is limited by traps. We ask whether the charge-carrier accumulation can, and must, be accounted for numerically when the semiconductor film is thin, appreciable voltages are applied and/or when appreciable injection barriers are present. We evaluate the accuracy of the MG law for simulated single-carrier devices when saturation currents dominate and investigate whether the mobility obtained from the MG law in this limit is meaningful.

5.3 Review of analytical equations

We first review the analytical equations describing space-charge-limited transport in ideal (undoped and trap free) semiconductors, namely the MG law and the ME equation, and then discuss the Mark-Helfrich equation which describes space-charge-limited transport in a semiconductor with exponential tails.

5.3.1 Analytical descriptions for SCLC without traps

A schematic of an equilibrated symmetric single-carrier device with Ohmic contacts is shown in fig. 5.1a (a similar schematic was shown in the previous chapter). We define Ohmic contacts as contacts where there are negligible injection barrier heights at the metal/semiconductor interfaces, $q\phi_{\text{inj/ext}} = 0$ eV. However, it is here important to mention that an additional barrier for electron flow exists besides the injection barriers, namely the internal diffusion barrier, $q\phi_{\text{diff}}$, which is defined as the difference between the conduction band edge energy and Fermi level at

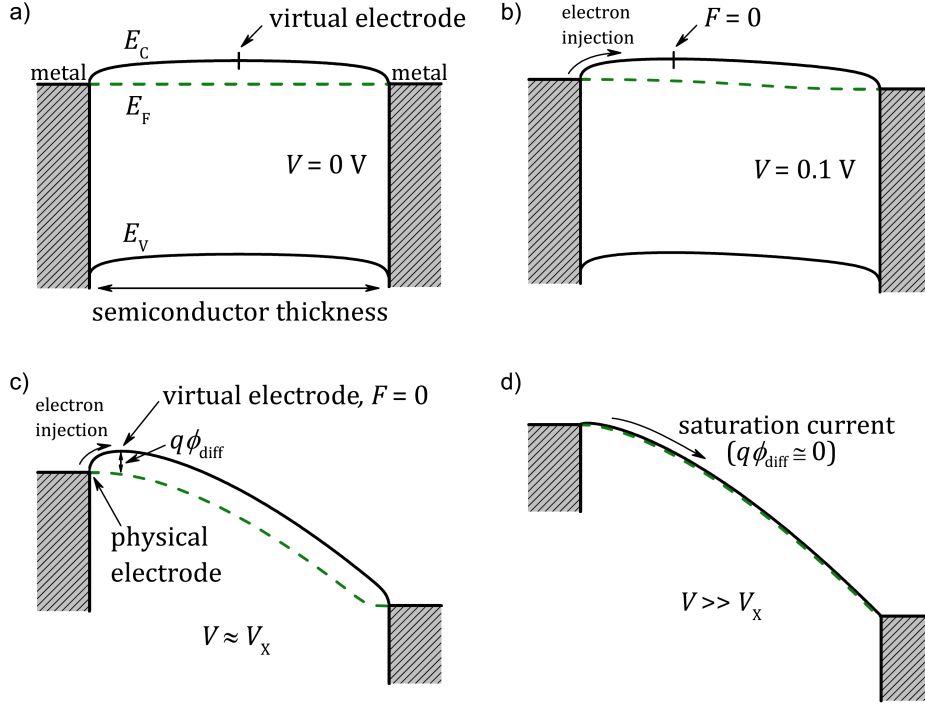


Figure 5.1: a) Schematic (based on numerical simulations) of energy level diagrams of an electron-only at equilibrium showing the position of the virtual electrode. b) Energy levels when a small voltage is applied across the device. c) Energy levels under a moderate applied voltage, $V \approx V_X$, where V_X is the voltage onset to drift dominated currents. The virtual electrode is shown to move towards the physical electrode. d) Energy levels when a large voltage is applied ($V \gg V_X$).

the virtual electrode (which is the point where the electric field is zero). Even though charge carriers have entered the device through the injection barrier, which for an Ohmic contact would be zero, the charge-carriers must cross the diffusion barrier for current to flow through the device. This results in a total barrier height hindering charge-transport which can be treated as a sum of the internal diffusion barrier height and the injection barrier height, $q\phi_{\text{tot}} = q\phi_{\text{diff}} + q\phi_{\text{inj}}$. As will be seen below, as the voltage is applied across the device, $q\phi_{\text{diff}}$ will reduce in height while $q\phi_{\text{inj}}$ will remain constant.

The moving electrode equation

As was explained in detail in chapters 3 and 4, when a small voltage is applied across a symmetric single-carrier device with Ohmic contacts (as shown in fig. 5.1b), a linear current-voltage dependence is observed at low voltages up until around 0.9 V at room temperature (300 K).

This linear current-voltage relationship can be described accurately by the moving electrode (ME) equation[137, 140],

$$J = 4\pi^2 \frac{k_B T}{q} \mu_n \varepsilon_r \varepsilon_0 \frac{V}{L^3} \quad (5.2)$$

where $k_B T$ is the thermal energy, V is the applied voltage and L is the thickness of the semiconductor layer. As discussed extensively in the previous chapter (chapter 4), even though the ME eq. has a similar form to Ohm's law (linear J - V relation), the ME eq. does not describe a true Ohmic current, as only the charge-carrier density in the middle of the device govern the ME current, and not the total charge-carrier density.

Given that T , ε_r and L of the sample are known, the ME eq. can, in principle, be fitted to the low voltage regime and the mobility can be extracted. It is important to note that the ME eq. only correctly gives the current density at low voltages when the semiconductor is trap free, undoped as long as the current is not limited by poor injection from the metal contacts.

The Mott-Gurney law

When a large enough voltage is applied across a single-carrier device, so that $F(x=0) \rightarrow 0$, $q\phi_{\text{diff}}$ is approximately zero, and the current across the device will mainly be governed by drift (as shown in fig. 5.1c). Making the approximation that the field is zero at the injecting contact, along with other assumptions listed below, the analytical equation describing space-charge-limited transport, called the MG law, is given by[11],

$$J = \frac{9}{8} \mu_n \varepsilon_r \varepsilon_0 \frac{V^2}{L^3}. \quad (5.3)$$

As discussed in chapter 4, we denote the transition voltage from the ME eq. to the MG law as V_X , which is around 0.9 at room temperature (if the device is undoped). The charge-carrier mobility of the electrons (or the holes, depending on the choice of contacts) can in principle be obtained by fitting of the MG law to the J - V curve obtained from the SCLC measurement in the region where $J \propto V^2$, i.e., in the MG voltage regime, much like the ME equation can, in principle, be used to extract the mobility at low voltages.

As mentioned above (and as discussed in chapter 3), the MG law is only applicable given that a number of assumptions are true:

- (i) The intrinsic carrier concentration is negligible when current is flowing, meaning that the current is mainly governed by the equilibrium charge carrier density.

- (ii) Both the contacts for injection and extraction are Ohmic, meaning that $q\phi_{\text{inj/ext}} \approx 0$ eV and charge carriers are always available to enter and leave the device (the semiconductor is in contact with metals that act as electron reservoirs).
- (iii) The material is defect free (undoped and trap free), and free from energetic disorder.
- (iv) The current density is governed by drift only, which implies the previously mentioned condition of vanishing electric field at the injecting interface.

Where some of these assumptions can be justified, some are never or rarely true, even for an ideal device. Assumption i) can be justified as follows (and has already been discussed extensively in chapter 4): Upon contact between a metal and a semiconductor, charge carriers flow to equilibrate the Fermi level throughout the semiconductor. In a symmetric single carrier device, where the semiconducting material is sandwiched between two metal contacts with equal or similar work functions (which form Ohmic contacts), injected charge carriers, from the metal into the semiconductor, will form a region of space-charge extending throughout the entire semiconducting layer. The density of intrinsic carriers, n_i , can then be neglected entirely as the density of injected charge carriers greatly exceeds this quantity. This is especially true near the metal/semiconductor interfaces, where the charge-carrier density will be the highest. Also, since injection of further charge carriers, when applying a bias voltage across the device, is of the same type as those already present in the device, the current through the device is space-charge-limited and does not depend on intrinsic charge carriers (even at a low applied voltage). We refer the reader back to chapter 4 for further clarification.

The other assumptions, ii), iii) and iv), are however generally not true in practice: Regarding assumption ii), we define our contact potentials as the difference between E_F^{metal} and the respective band-edge energy (here the conduction band edge for an electron-only device),

$$q\phi_{\text{inj/ext}}(x=0) = E_C(x=0) - E_F^{\text{metal}}(x=0). \quad (5.4)$$

Perfect Ohmic contacts are then defined as $q\phi_{\text{inj/ext}} = 0$ eV. Realising Ohmic contacts to a semiconductor is, however, not always easily achieved, as surface states can pin the Fermi level in the sub-gap region, and low work function materials such as Ba (2.7 eV), Ca (2.9 eV) and Al (4.1 eV) are highly reactive with the ambient atmosphere, causing them to oxidize (which will change their work functions, leading to a poorer match between E_F^{metal} and E_C). For this reason, one cannot always assume to have perfect Ohmic contacts, and cannot always assume to

have a negligible built-in voltage, even though one would expect this from the literature values for the metal work functions and from the energetics of the semiconductor.

Assumption iii) is also usually not true since most semiconducting materials are semi-crystalline or amorphous which means they are usually not defect or energetic disorder free. Defects and energetic disorder can act as trap sites, and defects can also give rise to unintentional doping. This will either decrease (traps) or increase (doping) the overall magnitude of the current whilst drastically changing the shape of the J - V curve. The presence of trap states in a semiconductor usually gives rise to non-negligible diffusion current terms[12, 13].

As a consequence of iv), the electric field will increase within the device as,

$$F(x) = -\sqrt{\frac{2Jx}{\mu_n \epsilon_r \epsilon_0}} \quad (5.5)$$

where x is the position from the injecting interface. The charge-carrier density can then be derived using Gauss' law to eq. 5.1. It is important to note, again, that the analytical expression of the charge-carrier density in the MG regime (eq. 5.1) tends to infinity at the injecting contact. As previously mentioned, this is a non-physical situation resulting from the boundary conditions imposed on the electric field at the device boundary ($F = 0$ at $x = 0$). Having a finite charge-carrier density at the device boundaries rather than allowing the charge-carrier density to extend to infinity, as is the case in a real device, will have an influence on the current density, as will be shown below.

The saturation (emission limited) current equation

At high voltages (beyond the MG regime), numerical calculations show that a large density of charge carriers are injected into a single-carrier device to an extent where the charge-carrier density across the device is uniform (fig. 5.1d). This is called the saturation limit, and is also referred to as the injection limit. In this limit, the internal diffusion barrier height, $q\phi_{\text{diff}}$, will be exactly equal to zero. Assuming boundary conditions set through eq. 5.4 at the device edges, a constant charge-carrier concentration at the metal/semiconductor interfaces is achieved when the injection barriers and the effective density of states in the semiconductor (N_C) are specified,

$$n_{\text{interface}} = N_C \exp\left(-\frac{q\phi_{\text{inj/ext}}}{k_B T}\right). \quad (5.6)$$

From this definition of the contacts, the upper limit for the charge-carrier density at the boundaries will be $n_{\text{interface}} = N_C$ given that the injection barriers are vanishing. It should here be

noted that the software used for the numerical calculations, *ASA*, assumes Boltzmann statistics as the boundaries (see eq. 5.6). In the case where $q\phi_{\text{inj/ext}} < 0.1$ eV, using Boltzmann statistics is no longer entirely justified and the boundaries should formally be described by Fermi-Dirac statistics. However, since the error is small as long as $q\phi_{\text{inj/ext}} \approx 0$ eV (the error would become large as $q\phi_{\text{inj/ext}} < 0$ eV), and since we are going to consider $q\phi_{\text{inj/ext}} > 0.1$ eV as well, we will initially refer to the situation where $q\phi_{\text{inj/ext}} = 0$ eV and ignore the issues with using Boltzmann statistics.

At high voltages, a single-carrier device will be almost completely uniformly filled with charge carriers across the entire thickness of the semiconductor. For this reason, the current at these high voltages will be due to charge-carrier saturation. The charge-carrier density inside the device, n , is given from the relative position of the Fermi level of the semiconductor, $E_F^{\text{s.c.}}$, and the conduction band edge, E_C , through,

$$n = N_C \exp\left(-\frac{E_C - E_F^{\text{s.c.}}}{k_B T}\right). \quad (5.7)$$

Neglecting injection barriers for the moment (noting that this violates Boltzmann statistics), when a large voltage is applied, and a large number of charge carriers are injected into the device from the electrodes ($E_C - E_F^{\text{s.c.}} \rightarrow 0$), the carrier concentration will tend towards uniformity across the entire thickness of the device ($n \rightarrow n_{\text{interface}} = N_C$). In this case, the electric field, F , inside the semiconductor is negligible, and the electric field across the semiconductor decreases linearly and arises solely from the applied voltage, $F_{\text{voltage}} = V/L$, i.e., arising from the charge carriers accumulating on the contacts. With the inclusion of injection barriers (now no longer violating Boltzmann statistics as long as $q\phi_{\text{inj/ext}} > 0.1$ eV), the limit for saturation is now given by $E_C - E_F^{\text{s.c.}} \rightarrow q\phi_{\text{inj/ext}}$ and the saturation current density is, in the high voltage limit, then given by the saturation current (SC) equation[131],

$$J = q\mu_n N_C \frac{V}{L} \exp\left(-\frac{q\phi_{\text{inj/ext}}}{k_B T}\right). \quad (5.8)$$

With the SC equation (eq. 5.8) describing the high voltage regime, we now have three equations governing the entire voltage range when we include the ME equation (eq. 5.2) describing the low voltage regime, and the MG law (eq. 5.3) describing the intermediate MG regime.

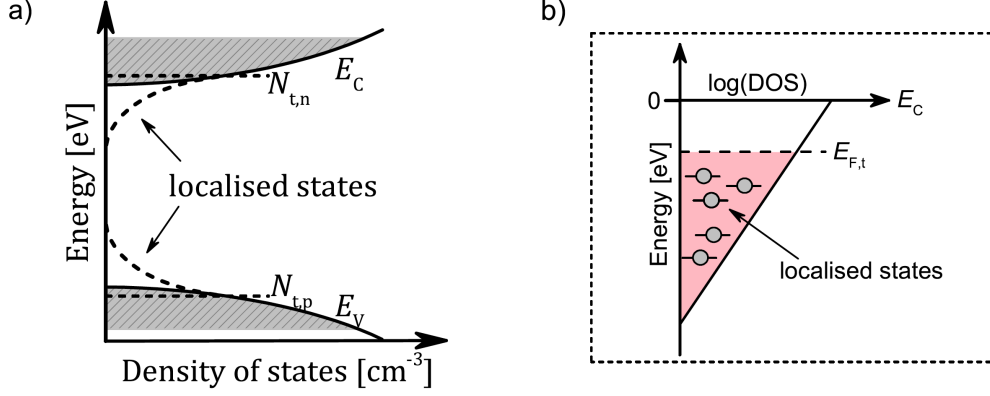


Figure 5.2: a) Energy level diagram for a semiconductor with traps in the form of exponential tails. The localised states are seen to extend from the conduction and valence band edges. b) Conduction band tail, showing charge-carriers as localised states below the trap quasi-Fermi level, $E_{F,t}$. Charge carriers are assumed to be able to contribute to conduction when re-emitted from traps into the transport level.

5.3.2 Analytical description for SCLC in the presence of traps

One of the commonly used analytical equations which describes SCLC charge transport in a semiconductor with traps, assumed in the form of localised charge carriers in exponential tails, (see figs. 5.2a and b),

$$h = n_t \exp\left(\frac{E}{E_{ch}}\right) \quad (5.9)$$

where $n_t = N_t/E_{ch}$ is the trap density per unit energy right below the conduction band edge (E_C), and E is the energy measured below the conduction band edge (note that the conduction band edge is set to zero, $E_C = 0$ eV, and the energy increases upwards, as shown in fig 5.2b); is the Mark-Helfrich (MH) equation[12, 14],

$$J = q^{1-l} \mu_n N_C \left(\frac{\epsilon_r \epsilon_0 l}{N_t(l+1)} \right)^l \left(\frac{2l+1}{l+1} \right)^{l+1} \frac{V^{l+1}}{L^{2l+1}} \quad (5.10)$$

described in chapter 3. Similar to the MG law, the MH equation is a drift-only transport equation which assumes a vanishing electric field at the injecting contact. The MH equation predicts that exponential tail states in the band gap give rise to a stronger power-law dependence of voltage on current than expected from the MG law in the intermediate voltage regime.

However, it was recently shown that this equation is not accurate since it fails to account for diffusion currents, which can make a significant contribution to the total current, especially when traps are present[18]. The MH equation is however still a useful qualitative tool even though the equation is not quantitatively correct.

5.4 Simulation results

5.4.1 Methods and objectives

From the analytical descriptions describing trap free space-charge-limited transport, namely the ME equation (eq. 5.2), the MG law (eq. 5.3) and the SC equation (eq. 5.8), we expect that the current density will follow $J \propto V$ at low voltages, will then transition into following $J \propto V^2$ at intermediate voltages, and will then follow $J \propto V$ again at very high voltages, when the semiconductor is close to saturation.

The analytical equations governing the low, intermediate and high voltage regimes (eqs. 5.2, 5.3 and 5.8, respectively) are in this section compared to numerical drift-diffusion simulations of intrinsic semiconductors in either ideal (Ohmic) or non-ideal (non-Ohmic) single-carrier devices. Devices with a degree of traps in the form of exponential tails are also considered. We seek to establish whether two linear regimes can influence the intermediate MG regime as injection barriers, and the semiconductor thickness, are varied.

All fixed, and varied, materials and device constants are listed in table 5.1. These values were chosen to represent typical organic semiconductor conditions. Because the results depend strongly on thickness of the semiconductor, a 50 nm, 100 nm and 500 nm case will be presented. We will show results with a variation of the injection barrier heights from 0 eV to 0.3 eV. We will also show results with the inclusion of traps in the form of exponential tails. The simulations themselves must contain a distribution of both electron and hole traps, $E_{\text{ch},n}$ and $E_{\text{ch},p}$ (as the software will otherwise try to divide by 0 as seen in eq. 5.9), however, since we are only considering electrons, the hole density is set to zero in the simulations and hole traps can be ignored. For that reason, we will denote $n_{t,n}$ and $E_{\text{ch},n}$ as n_t and E_{ch} , respectively.

In general, as substantial injection barriers, $q\phi$ are included at the metal/semiconductor interfaces, it is expected that the slope of the J - V curve on a log-log scale,

$$m = \frac{d \log J}{d \log V} \quad (5.11)$$

will decrease towards $m = 1$, across the entire voltage range, as the barrier heights are in-

Table 5.1: Table of fixed and variable values used in the drift-diffusion simulations to model the electron-only devices with and without traps (tails).

Quantity	Symbol	Value	Units
Band gap	E_g	2	eV
Effective electron density of states	N_C	10^{19}	cm^{-3}
Effective hole density of states	N_V	10^{19}	cm^{-3}
Dielectric constant	ϵ_r	3	-
Active layer thickness	L	variable	nm
Electron band-like mobility	μ_n	variable	cm^2/Vs
Hole band-like mobility	μ_h	10^{-4}	cm^2/Vs
Injection barrier height at $x = 0$ (single-carrier)	$q\phi_{\text{inj}}$	0	eV
Injection barrier height at $x = L$ (single-carrier)	$q\phi_{\text{ext}}$	0	eV
Density of tail states (electrons)	$n_{t,n}$	variable	$\text{cm}^{-3}\text{eV}^{-1}$
Density of tail states (holes)	$n_{t,p}$	0	$\text{cm}^{-3}\text{eV}^{-1}$
Characteristic tail energy (electrons)	$E_{\text{ch},n}$	variable	eV
Characteristic tail energy (holes)	$E_{\text{ch},p}$	0.05	eV
Neutral electron capture rate coefficient	c_n^0	10^{-10}	$\text{cm}^{-3}\text{s}^{-1}$
Positive electron capture rate coefficient	c_n^+	10^{-12}	$\text{cm}^{-3}\text{s}^{-1}$
Neutral hole capture rate coefficient	c_p^0	10^{-10}	$\text{cm}^{-3}\text{s}^{-1}$
Negative hole capture rate coefficient	c_p^-	10^{-12}	$\text{cm}^{-3}\text{s}^{-1}$
Surface recombination velocity	S	10^5	m/s
Series resistance	R_S	0	Ωm^2
Shunt/parallel resistance	R_P	∞	Ωm^2
Temperature	T	300	K

creased. However, Since the presence to traps tends to increase the power law dependence (see the MH equation), i.e., increase m , we will show that with a combination of traps and injection limitation, $m = 2$ can be achieved. This does, of course, not mean that a fit with the MG law is physically valid. However, lack of information about interface properties of the probed semiconductor and the contacts, along with lack of information about traps in the semiconductor, could lead to a naïve interpretation with the MG law in this case. We show that the obtained mobility, in this case, can be underestimated by orders of magnitude.

5.4.2 Numerically calculated J - V curves: Ohmic contacts

Figure 5.3a shows calculated J - V profiles of symmetric and trap-free 50, 100 and 500 nm electron-only devices with Ohmic contacts ($q\phi_{\text{inj}} = 0$ eV). Fits with the MG law (eq. 5.3) and the ME equation (eq. 5.2) to the 500 nm device are shown as solid lines (when fitted to the 500 nm device, the ME equation and the MG law both yielded the same mobility as the one used for the simulations). Figure 5.3b shows J - V profiles of electron-only devices with Ohmic contacts and traps in the form of exponential tail states extending from the transport levels, i.e., from the conduction and valence band edges ($E_{\text{ch}} = 0.05$ eV and $n_{\text{t}} = 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$). In figure 5.3c we show the slopes (eq. 5.11) of the J - V curves in fig. 5.3a and b as a function of voltage. For the trap-free single-carrier devices, the onset for the increase in the slope away from a linear dependence ($m = 1$) at low voltages occur at the same voltage, V_{X} , for all three thicknesses. We also show, that for a 50 nm device, the slope does not reach, and retain, a value of $m = 2$ but rather $m = 1.9$, which decreases towards unity at higher voltages. As the thickness of the semiconductor is increased to 100 nm, the maximum slope increases ($m = 1.95$), but also tends back towards unity at higher voltages. For the devices containing traps, the slope is seen increase to above $m = 2$ for all three thicknesses, but does not reach the same value for the maximum slope value. The MH equation predicts that $m = E_{\text{ch}}/k_{\text{B}}T$, which would reach a value of $m = 2.92$ for all three thicknesses. However, the values for the slope maxima are $m = 2.56$ and $m = 2.70$ for the 50 and 100 nm device respectively and is approaching what is expected from the MH equation for the 500 nm device ($m = 2.86$). Figure 5.3d shows the maximum slope values for a series of single-carrier devices as a function of increased thicknesses and dielectric constants. The deviation of the slope maximum from $m = 2$ is seen to be more profound as the dielectric constant is increased towards values typical for inorganic and hybrid semiconductors.

It is quite apparent that the slope maximum deviates dramatically from $m = 2$, rendering the MG law useless for fitting, when the thickness of the device is decreased. We will in the

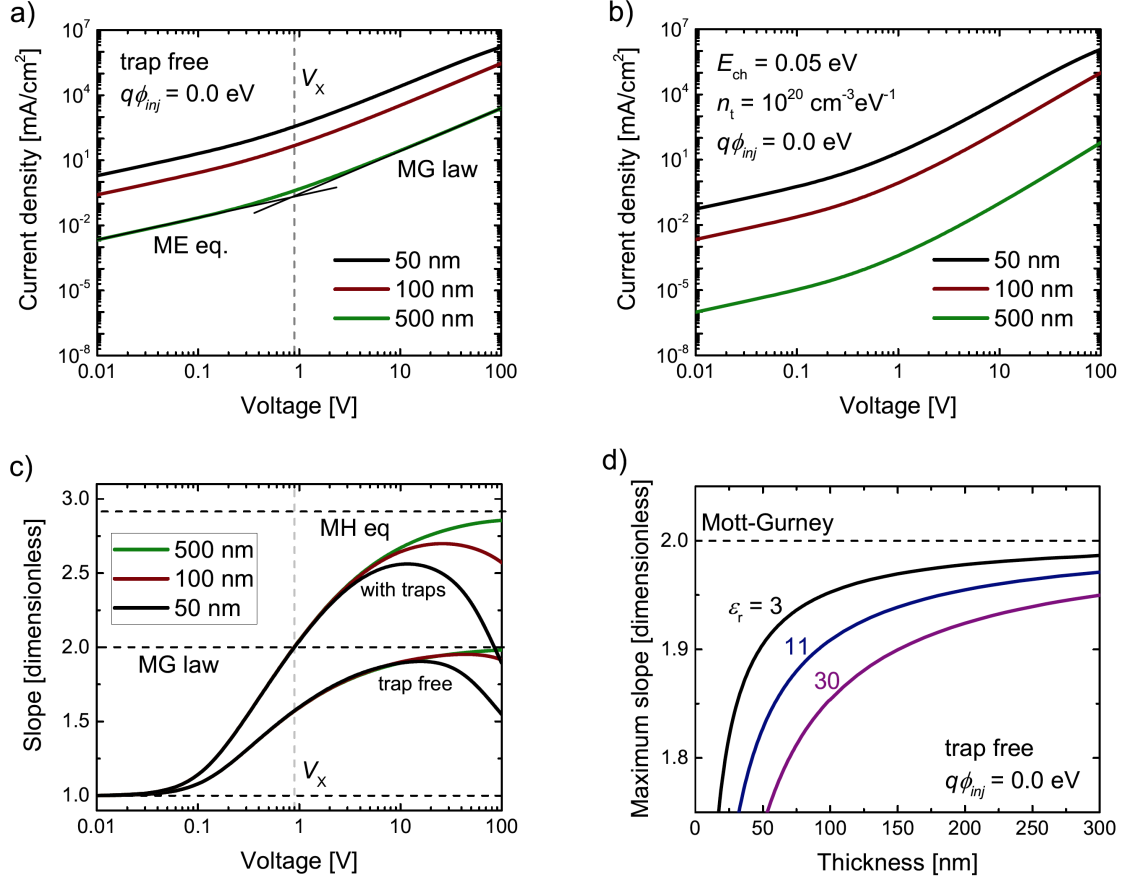


Figure 5.3: a) Numerically calculated current density-voltage profiles for 50, 100 and 500 nm electron-only devices with Ohmic contacts. Fits with the ME equation (eq. 5.2) and the MG law (eq. 5.3) are shown as solid lines. b) Current density-voltage profiles for 50, 100 and 500 nm electron-only devices with Ohmic contacts and traps ($E_{\text{ch}} = 0.05$ eV and $n_t = 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$). c) Slope-voltage profiles showing the voltage of the onset to drift dominated currents, V_X (the expected slopes for the ME equation, the MG law and the MH equation (eq. 5.10) are shown as dashed lines). d) Maximum slope for devices with increasing thickness showing the deviation of the slope from the value of 2 (dashed line) for the cases of a dielectric constant similar to organic ($\epsilon_r = 3$), inorganic ($\epsilon_r = 11$) and lead-halide perovskites ($\epsilon_r = 30$).

next section consider cases when non-ideal contacts are used.

5.4.3 Numerically calculated J - V curves: Non-Ohmic contacts

The numerical results shown in fig. 5.3 are for ideal devices, where perfect injection is achieved through Ohmic contacts. However, a more realistic case is when the injection contacts are

non-Ohmic, i.e., the injection barriers at the device boundaries are finite, $q\phi_{\text{inj}} > 0$ eV. It has previously been reported that devices with 0.2 eV barrier heights still show nearly Ohmic carrier injection[111]. We however show here, that the effect of injection barriers heights is highly dependent on the thickness of the probed semiconductor, and a thin device ($L = 50$ nm) will be influenced to a higher degree than a thick device ($L = 500$ nm).

In figs. 5.4a, b and c we show numerically calculated J - V curves for 50, 100 and 500 nm devices with finite injection barriers (0, 0.1 and 0.2 eV). Even with a small injection barrier height of 0.1 eV present in the 50 nm device (fig. 5.4a), we observe a significant decrease in the current density at all voltages. Where the slope at low voltages is mostly unaffected ($m = 1$), the slope in the high voltage regime is lower compared to the simulated device without injection limitation. We see a much more significant reduction of the current when a 0.2 eV injection barrier is included in the simulation. In this case the current increases linearly with the voltage at all simulated voltages, which is what would be expected from either the ME eq. or the SC eq. but not from the MG law. For the 100 nm device, increasing the injection barrier up to 0.1 only has a small influence on the overall magnitude and shape of the J - V curve (fig. 5.4b) compared to that of a 50 nm device. However, when a 0.2 eV injection barrier is introduced, the current is also greatly reduced and the slope is linear as was seen for the 50 nm with 0.2 eV injection barriers. For the 500 nm device (fig. 5.4c), increasing the injection barriers up to 0.1 eV only has a small effect on the overall magnitude and shape of the J - V curve. We observe only a small overall reduction of the current and slope with an injection barrier of 0.2 eV.

Figure 5.4d, e and f show the electron densities inside the single-carrier devices, before an applied voltage is applied. The electron density for the 50 nm device (fig. 5.4d) is seen to decrease across the entire thickness of the semiconductor as injection barriers are increased (as is expected by considering eqs. 5.6 and 5.7). Furthermore, as the injection barriers are increased to 0.2 eV, the electron density is almost uniform across the device. The uniformity of the electron density coincides with when the current density is linear. Figures 5.4e and f similarly show that the linear current observed at low voltages coincide with the electron density becoming uniform across the device (in fig. 5.4c, the current never reaches a linear trend since the electron density is not close to being uniform).

In fig. 5.5a we show the slope of a 100 nm device as the injection and extraction barriers are simultaneously increased (0, 0.026, 0.052, 0.1 and 0.2 eV). The maximum slope value decreases with injection barrier heights whilst the slope maximum position shifts to lower voltages. We observe a transition to a linear regime at high voltages. In fig. 5.5b we show that the transition to the linear regime scales with V/L^2 , and in fig. 5.5c we show that the transition scales with

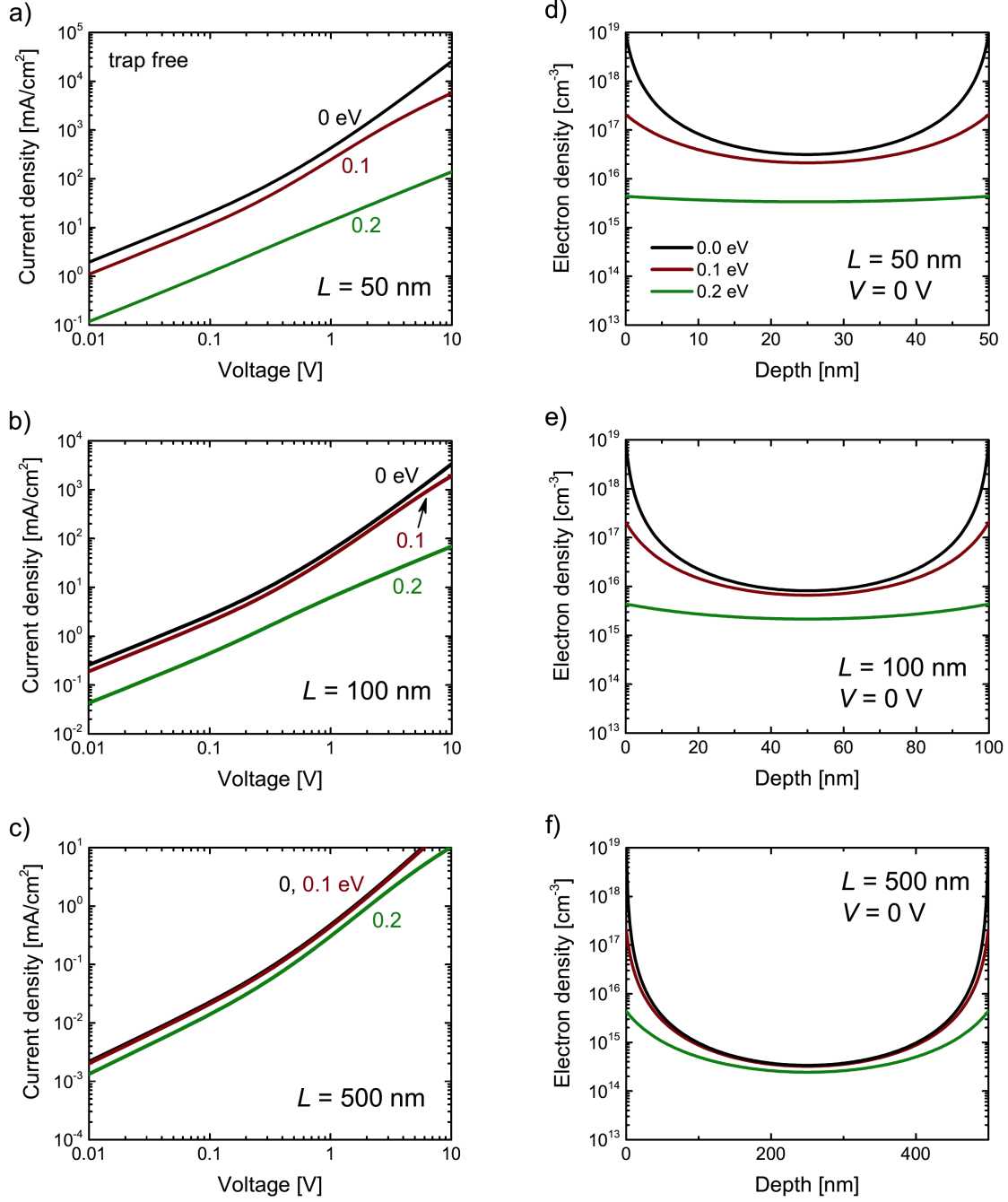


Figure 5.4: Numerically calculated J - V curves of single-carrier devices with varying degree of injection limitation (0, 0.1 and 0.2 eV): a) 50 nm, b) 100 nm and c) 500 nm. d), e) and f) shows the corresponding electron densities as a function of the position from the injecting contact at zero applied voltage with varying degree of injection limitation.

an exponential term containing the injection barrier height ($\exp\{q\phi_{\text{inj}}/k_{\text{B}}T\}$).

In fig. 5.3c we show that the maximum slope increases beyond $m = 2$ when a significant density of traps are present. However, in fig. 5.5d we show that with a combination of traps

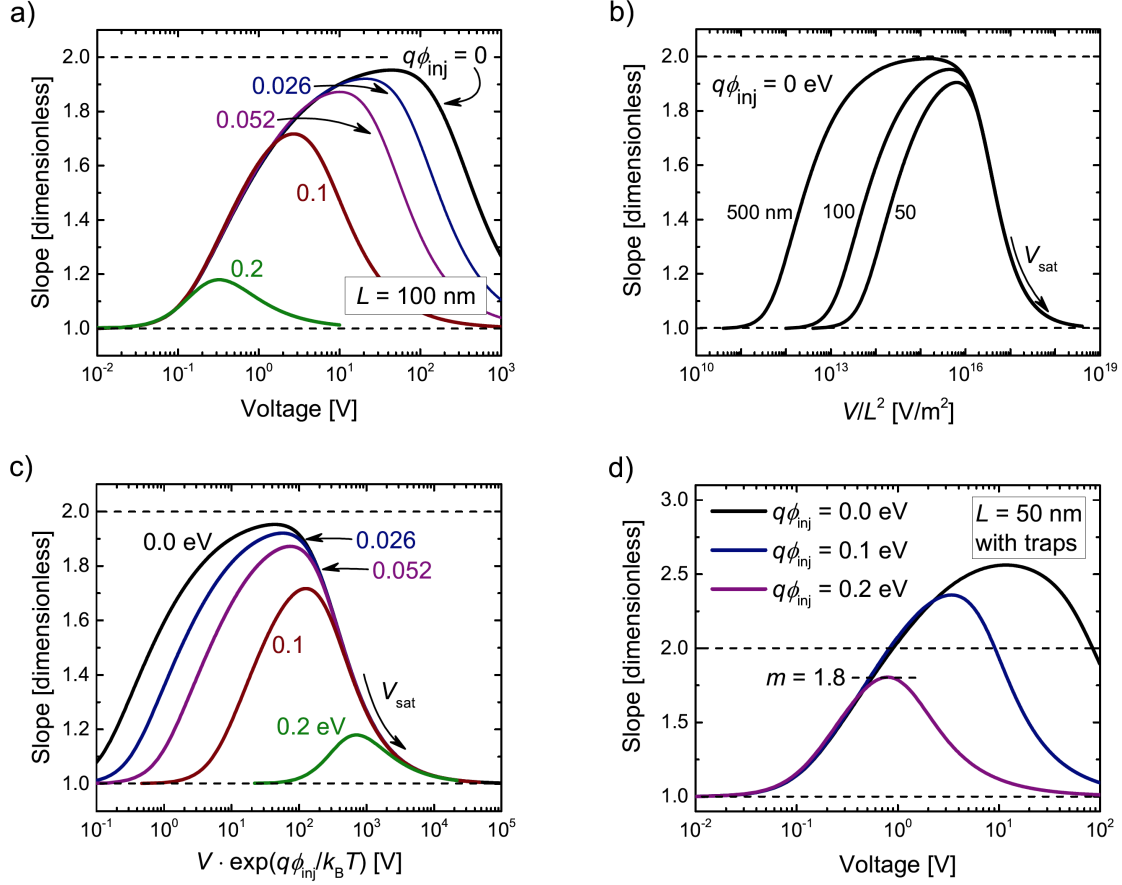


Figure 5.5: a) Slope-voltage curves of a 100 nm device with increasing injection barriers (0, 0.026, 0.052, 0.1 and 0.2 eV). b) Slope as a function of V/L^2 for electron-only devices with thicknesses of 50, 100 and 500 nm. The voltage axis was corrected in order to show scaling for the transition to the saturation current. c) Slopes of a 100 nm device with increasing injection barriers when the voltage axis is corrected for by the exponential term governing injection limitation. The voltage onset for Ohmic currents, V_{sat} , is seen to scale accordingly. d) Slope-voltage curves of a 50 nm device with injection limitation and exponential band tails ($E_{\text{ch}} = 0.05$ eV, $n_t = 10^{20}$ cm⁻³eV⁻¹).

and injection limitation a slope maximum with $m < 2$ can be achieved. From this it is clear that with a certain combination of traps and injection limitation $m = 2$ could also be achieved leading to an incorrect analysis if the MG law is used.

From what we have shown above, it is clear that the thickness of the semiconductor in the device will determine the overall effect of the injection barrier heights, and that injection barriers will only influence the SCLC data in a very minor way when the semiconductor thickness is

larger than 500 nm. Furthermore, we show that the transition to the linear saturation regime, V_{sat} , scales both with an $\exp(q\phi_{\text{inj}}/k_{\text{B}}T)$ term and with an $1/L^2$ term. We will explore this transition voltage to the linear regime, further, later in this chapter.

5.4.4 Fitting with the MG law and the ME eq.

Despite sometimes being impossible to fit the MG law even in the ideal case (fig. 5.1a, c and d), and even less so for devices with realistic contacts (fig. 5.3a), the MG law (eq. 5.3) might still yield reasonable results if the mobility is calculated using values for the voltage and current density around the region of maximum slope (a similar fitting approach was used in the previous chapter). This means, that we evaluate the MG law at $V = V(m_{\text{max}})$, which will cause this "fit" with the MG law to intersect the J - V curve (since the MG has $m = 2$ and $m_{\text{max}} < 2$ for some of the numerically calculated ideal devices investigated here). In order to assess the error introduced when using the ME equation (eq. 5.2) and the MG law (eq. 5.3) to obtain the charge carrier mobility, the equations were fitted in this way to simulated J - V curves from devices with Ohmic and non-Ohmic contacts.

In fig. 5.6a we show the obtained charge-carrier mobility when fitting with the MG law (eq. 5.3) relative to the electron mobility used as an input ($\mu_{\text{input}} = 10^{-4} \text{ cm}^2/\text{Vs}$). In fig. 5.6b we show the equivalent graph for fitting with the ME equation (eq. 5.2). We fitted the ME equation between 0 and 0.1 V, as this range is seen to be linear in the case of both Ohmic and non-Ohmic injection (figs 5.5a). However, this fit is not always physically correct, as non-Ohmic contacts reduce the overall current and the ME equation cannot account for this.

For Ohmic contacts we show that both eq. 5.3 and eq. 5.2 yield good results even at very small thicknesses ($< 50 \text{ nm}$). That the MG law yields good results is rather surprising since the slope maximum in this case was 1.9 and not 2 (fig. 5.3c). The estimated mobility when using the ME equation is, surprisingly, less correct as compared to using the MG law. We show that when small injection barriers are added ($q\phi_{\text{inj}} = 0.1 \text{ eV}$), even though the slope maximum will not reach 2, the mobility can still be estimated within a reasonable accuracy using the MG law, provided that the device is not too thin ($L > 50 \text{ nm}$). When we increase the injection contacts to a realistic value of 0.2 eV, the MG law gives a mobility which significantly deviates for small thicknesses, whereas the mobility from the ME equation deviates at all thicknesses investigated here. With 0.3 eV barrier heights, mobilities obtained from both equations deviate dramatically.

From the above we show that in order to use the MG law or the ME equation to estimate mobilities for intrinsic semiconductors, it is important to minimize injection barriers and to

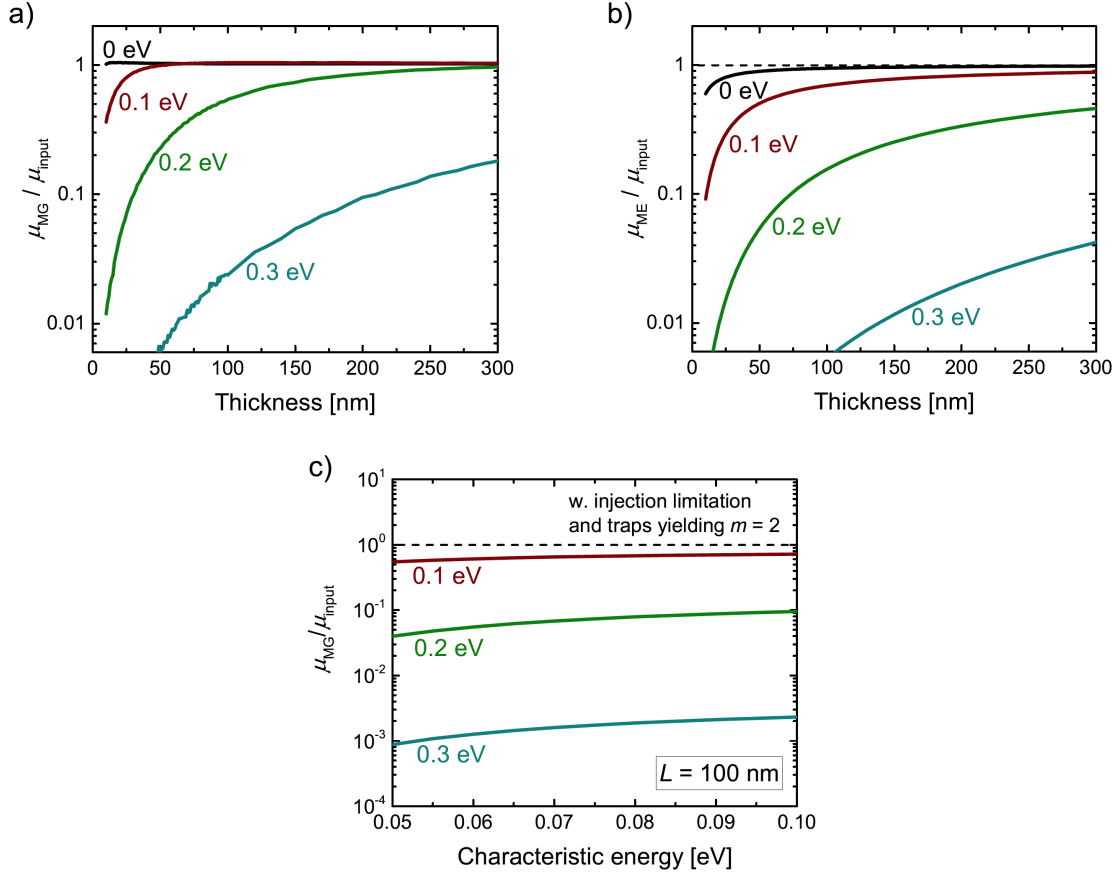


Figure 5.6: Extracted mobility values using analytical equations when the injection barriers are increased (0.1, 0.2 and 0.3 eV); a) extraction of mobility when fitting with the MG law at the slope maximum, and b) extraction of the mobility when fitting with the ME eq.. The values are normalized with respect to the input value for the mobility. c) Fitting results with the MG law when $m = 2$ due to a combination of tail states and injection barriers.

measure devices with thicknesses larger than 50 nm, as the estimated mobilities will be highly underestimated in both cases if these precautions are not taken.

Figure 5.6c shows the ratio of the obtained mobility using the MG law to the input mobility when traps and injection limitation was included to a 100 nm device to force $m = 2$. To do this, the injection barrier heights were fixed (to either 0.1, 0.2 or 0.3 eV) and as the characteristic tail energy, E_{ch} , was varied from 0.05 to 0.10 eV, the trap density, N_t was allowed to vary until $m = 2$ at some point along the J - V curve. The required trap characteristics for a 100 nm device with varying degree of injection limitation, and examples of slope-voltage curves of some of these simulated devices, are shown in fig 5.7a and b. From fig. 5.6c it is quite apparent that the mobility can be greatly underestimated even though the equation was fitted to a J - V curve

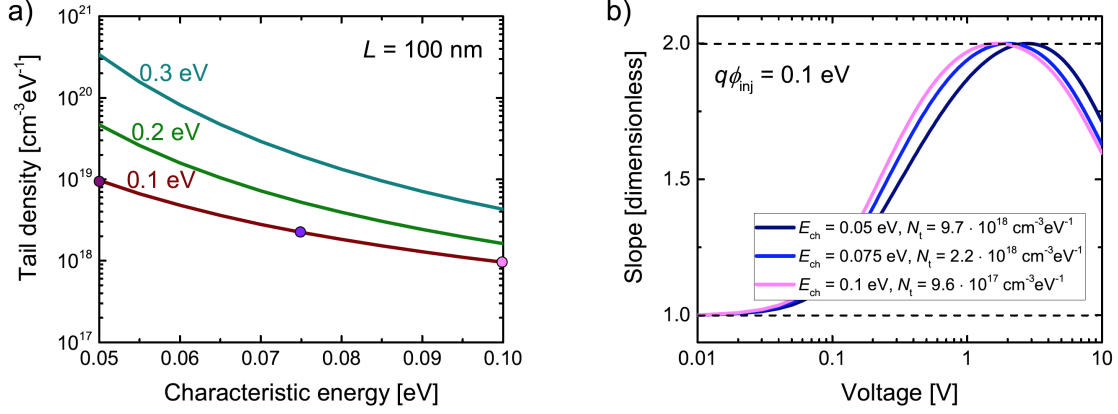


Figure 5.7: a) Required tail density values at specific characteristic energies to reach $m = 2$ for a 100 nm device with varying degree of injection limitation. b) Examples of m - V curves where $m = 2$ was obtained using a combination of varying density and energy of exponential tails and injection limitation (0.1 eV barrier heights).

that appeared to be obtained from an ideal device.

5.5 Analytical results

In order to give an analytical explanation to the drop in the maximum slope from $m = 2$ to much lower values at intermediate voltages, we here discuss the cross-over voltages, denoting the transition between transport regimes, in this section.

5.5.1 Transition from the low voltage regime to the MG regime

The temperature dependent cross-over voltage between the low voltage (ME) regime and the MG regime, observed in figure 5.1a, was previously derived by equating the ME equation (eq. 5.2) with the MG law (eq. 5.3), to be[138],

$$V_X = \frac{32\pi^2}{9} \frac{k_B T}{q}. \quad (5.12)$$

This equation replaced the onset equation, $V_X = (8/9) \{(nqL^2)/(\epsilon_r \epsilon_0)\}$, derived by Mark and Lampert (which states that the onset is thickness dependent) which was derived for symmetric single-carrier devices of intrinsic semiconductors with Ohmic contacts[17]. At room temperature, eq. 5.12 approximately gives 0.9 V (see fig. 5.3a).

5.5.2 Transition from the MG regime to the saturation regime

We here derive the crossover voltage from the MG regime to the saturation regime by equating the MG law (eq. 5.3) with the SC eq. (eq. 5.8), which includes a term accounting for the reduction of the charge-carrier density at the boundaries due to poor injection,

$$V_{\text{sat}} = \frac{8}{9} \frac{qL^2}{\varepsilon_r \varepsilon_0} N_C \exp\left(-\frac{q\phi_{\text{inj}}}{k_B T}\right) \quad (5.13)$$

From eq. 5.13 we show that the onset to saturation currents follow an L^2 thickness scaling, which we also showed numerically (fig. 5.5b). Contrary to the onset from the low voltage current regime to the MG regime (eq. 5.12), an effect of injection barriers on the shift of the cross-over voltage to saturation currents can be seen from eq. 5.13, which predicts that the voltage onset will scale with the exponential term containing the injection barrier height. We also showed this effect numerically in fig. 5.5c.

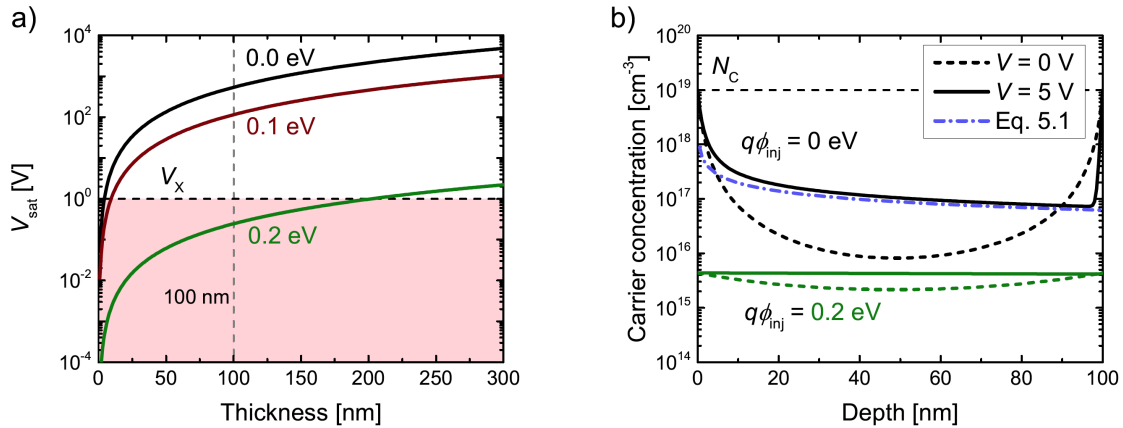


Figure 5.8: a) V_{sat} as a function of device thickness with varying injection barrier heights (0, 0.1 and 0.2 eV). The onset to the MG regime, V_X , is shown as a black dashed line. $V_{\text{sat}}(0.0 \text{ eV}, 100 \text{ nm}) = 53.6 \text{ V}$, whereas $V_{\text{sat}}(0.2 \text{ eV}, 100 \text{ nm}) = 0.2446 \text{ V}$, i.e., much lower than $V_X = 0.9 \text{ V}$. The red region shows the situation where the two linear regimes overlap and the MG law cannot express the intermediate voltage regime. b) Electron concentration at 0 V (dashed lines) and 5 V (solid lines) in a 100 nm device with and without injection barriers, as shown by black colours and green colours (the value for the effective density of states is shown for reference). The carrier density as calculated from eq. 5.1 is shown as a dot-dashed blue line.

In fig. 5.8a we show calculations of eq. 5.13 as a function of device thickness with either

perfect Ohmic contacts ($q\phi_{\text{inj}} = 0.0$ eV) or with non-Ohmic contacts with small injection barriers ($q\phi_{\text{inj}} = 0.1$ and 0.2 eV). The thickness independent transition voltage to the MG regime, V_X , is shown as a reference as a black dashed line. It is seen that, under certain conditions, the onset to the saturation current is occurring before the current has transitioned into the MG regime. To supplement this, fig. 5.8b shows that when 5 V is applied across a 100 nm device with Ohmic contacts, the electron density in the device approximately follows the electron density derived from assuming drift-only transport (eq. 5.1), i.e., the current approximately follows the MG law. On the contrary, when 5 V is applied to an injection limited device (0.2 injection barriers), the electron density is completely uniform across the depth of the device, i.e., the current regime has transitioned into saturation without transitioning through the MG regime.

Equation 5.13 is a useful tool to determine the bias voltage range in which analysis with the MG is meaningful. Furthermore, eq. 5.13 can be used to investigate which effect the device and material parameters, such as the choice of contacts and semiconductor thickness, will have on the onset to Ohmic saturation currents (fig. 5.8a). While V_{sat} is larger than 100 V for a 100 nm device with Ohmic contacts, the inclusion of realistic injection barriers will shift V_{sat} to lower than 1 V (fig. 5.8a).

The deviation of the MG law observed at intermediate voltages can now be well explained in the context of the discussed cross-over voltages, V_X and V_{sat} (eqs. 5.12 and 5.13, respectively).

5.6 Discussion

We observe that for practically relevant thicknesses (around 100 nm) there is a slight deviation from the behaviour predicted by the MG law ($m < 2$) when no injection barriers are present (figs. 5.3c and d). This deviation is sensitive to the semiconductor thickness as shown by the calculated behaviour of a 50 nm thick film which shows a larger deviation from the MG law than an 100 and 500 nm film (figs. 5.3c and d). However, the deviation from the MG law becomes strikingly relevant as soon as one considers practically relevant injection barriers (0.1, 0.2, and 0.3 eV) even for a 100 nm device (see figs. 5.5a and 5.6a).

When a large voltage is applied across a thin device (50 nm) with Ohmic contacts, it is seen that the current is dominated by saturation of the charge-carrier density (fig. 5.3b). Even though the transition to complete saturation happens at a very high voltage, the maximum value of the slope is reduced to around $m = 1.9$. The reduction in the slope value makes a fit with the MG law impossible. Even though the reduction in the slope maximum away from $m = 2$ for a 50 nm device with Ohmic contacts is more apparent than for a 100 nm, some deviation is still seen for the 100 nm device (fig 5.3c).

With injection barriers introduced at the interfaces, a dramatic reduction of the maximum slope value is observed (fig. 5.5a). Interestingly, the cross-over voltage from the linear regime at low voltage, V_X , is seen to be neither affected by the thickness of the device nor the injection barrier heights (fig 5.3c and 5.5a). This observation from the numerical calculations agrees with eq. 5.12.

From figs. 5.5b and c it is seen that the onset to the saturation regime, V_{sat} , changes both with thickness and injection barrier heights. This agrees with our derived transition voltage, eq. 5.13. Figure 5.8a shows comparisons of calculations of V_{sat} , with varying injection barrier heights, to V_X . When $V_{\text{sat}} \leq V_X$, a lowering of the slope away from $m = 2$ at all voltages is observed. This is because the current has transitioned into the saturation regime before becoming a space-charge-limited drift current, i.e., the two linear regimes overlap and the MG regime has disappeared (see fig. 5.8b). In fig. 5.8a it is also seen that the value for V_{sat} is close to V_X for the 10 nm device with Ohmic contacts, whereas the 100 nm device has a much higher onset voltage to saturation currents. This explains why the slope of a thin device has a low maximum value, whilst a thicker device has a maximum value approaching $m = 2$.

The effect of the slope maximum lowering was seen to be even more profound when realistic (non-Ohmic) contacts are used (see fig. 5.5a). The lowering of the slope is assigned to the carrier density being almost uniform even before a voltage is applied (see fig. 5.8b). When electrons are injected into the almost saturated device, the charge-carrier density will then quickly tend towards uniformity, and the current will follow the SC equation at a much lower voltage ($V_{\text{sat}} < 1$ V for a 100 nm device when $q\phi_{\text{inj}} = 0.2$ eV). So even for ideal semiconductors, this transition to saturation currents, which happens at very low voltages for devices with a realistic semiconductor thickness and realistic injection barriers, makes fitting with the MG law meaningless since the current density is never proportional to V^2 . This also means that if $m = 2$ or $m > 2$ is observed for thin devices, then an extrinsic mechanism such as traps or energetic disorder must be present, and in such cases the MG law is again not applicable since this model was developed for intrinsic semiconductors (see fig. 5.5d). Furthermore, if $m = 2$ is in fact observed for reasonably thin devices, a combination of traps and injection limitation could be present in the device, rendering analysis with the MG law meaningless (see fig. 5.6c).

In order to estimate the size of the error in mobility, extracted when non-ideal features are present, we used the MG law to fit to SCLC J - V curves when small injection barriers (0.1 eV) was present. We showed that the obtained mobility will not deviate dramatically given that the thickness of the probed semiconductor is larger than 50 nm (fig. 5.6a). However, for slightly larger injection barriers (0.2 eV) an underestimation of the mobility of almost an order

of magnitude can be expected for a 50 nm device. Measuring a thicker device (100 nm) will yield a more accurate value for the mobility, but will still be underestimated. Figures 5.6 and 5.8 in combination can be used as a helpful tool to predict when, and by how much, the charge-carrier mobility will be wrongly estimated when either using the MG law or the ME equation.

That the MG law and the ME equations do not yield accurate values for the charge-carrier mobility when traps are present in the semiconductor, is not surprising. However, that the equations yield poor results when used to characterise intrinsic (undoped and trap free) semiconductors is both surprising and intriguing. The MG law is very commonly used to estimate the mobility of organic thin films in devices, with thicknesses and barrier heights of sizes examined in this chapter, but we have here shown that the MG law is not accurate, even for ideal semiconductors, due to the potential overlap between the two linear J - V regimes. This is a fundamental problem with the analysis of SCLC measurements, and people wishing to probe charge-transport using the MG law should be cautious. As an alternative to using the examined analytical equations for SCLC analysis, the authors propose to use drift-diffusion simulation software (like *ASA*) which can include both the effect seen at low voltage and include the effect of saturation at high voltage. Using such a tool, one can correctly model the current density of a symmetric single-carrier device over the entire voltage range, and an accurate value for the mobility can be extracted.

5.7 Conclusion

By comparing the results from the analytical equations with numerical calculations we have shown that a strong deviation from the MG law towards an Ohmic saturation current is seen when simulating single-carrier devices of intrinsic semiconductors with realistic (non-Ohmic) injection contacts. We show this to be due to an increased accumulation and eventual saturation of charge carriers inside the device when a voltage is applied. We show that the onset for these Ohmic currents to follow a square scaling law with thickness and an exponential scaling law with injection barrier heights, meaning that this phenomenon is even more profound, and occurring at even lower voltages, when the device thickness of the material is decreased and/or when the injection barrier heights are increased towards realistic values. The thinner the device and larger the injection barriers, the more difficult it becomes to fit the MG law to the current density-voltage curves, and the larger the deviation of the obtained mobility values compared to the real mobility values becomes. We quantify the deviation of the charge carrier mobility when determined using the MG law, or the ME equation, and we show that the mobility can be underestimated by several orders of magnitude compared to when obtained using numerical

fitting. Furthermore, we show that a combination of injection limitation and traps (which usually give rise to an increase in the slope) can give a slope of 2. We show that using the MG law in this situation, rather naïvely, will lead to an underestimation of the mobility by up to many orders of magnitude. In order to use the discussed analytical expressions for analysis of SCLC data from intrinsic single-carrier devices, it is important to minimize injection barriers and to measure devices with thicknesses larger than 50 nm (the MG law becomes increasingly accurate with increased semiconductor thickness, given that the semiconductor is trap-free). However, the authors propose to use drift-diffusion solvers rather than the examined analytical equations for the analysis of SCLC J - V curves. The analysis presented in this chapter can be used to help design the correct device architecture for charge-carrier mobility measurements while helping to estimate the error involved in the extracted values when measuring intrinsic semiconductors.

Chapter 6

Experimental Study of Charge Transport in Spiro-OMeTAD

6.1 Abstract

In this chapter we perform an experimental charge transport study on the already highly studied hole transport molecule, Spiro-OMeTAD. We show that by allowing the band-like mobility, trap characteristics, injection barrier heights and the shunt resistance to vary in a multiple-trapping drift-diffusion device model, a numerical fit can be obtained to the entire J - V curve from experimental space-charge-limited current measurements on both symmetric and asymmetric single-carrier devices. This approach yields a band-like mobility that is more than an order of magnitude higher than the effective mobility obtained using analytical approximations, such as the Mott-Gurney (MG) law and the moving electrode (ME) equation.

We show that where the analytical approximations require a temperature-dependent effective mobility to achieve fits, the numerical model can yield a temperature-, electric field- and charge-carrier density-independent mobility.

Finally, we present a novel analytical model describing trap limited current flow through a semiconductor, in a symmetric single-carrier device. We compare the band mobility and trap characteristics obtained from fits with this analytical model to the results from the numerical model, showing excellent agreement. This work shows the importance of accounting for traps and injection barriers, explicitly, when analysing current density-voltage curves from space-charge-limited current measurements.

The work presented in this chapter was performed under the supervision of Prof. Jenny Nelson and Dr. Saif Haque and in collaboration with Dr. Xingyuan Shi and Prof. Thomas Kirchartz. The author performed the majority of the work, Nelson and Haque supervised

the project, Shi assisted with the experiments, and Kirchartz and Nelson assisted with the analysis and the simulations. A published version called "Charge Transport in Spiro-OMeTAD Investigated through Space-Charge-Limited Current Measurements" was published in Physical Review Applied in April 2018[149].

6.2 Introduction

6.2.1 Background and motivation

As we have discussed in chapter 3 and shown in chapters 4 and 5, extracting charge-carrier mobilities for organic semiconductors from SCLC measurements is complicated, in practice, by non-ideal factors such as trapping in defects, injection barriers and built-in voltages. Whereas analytical equations have been derived to describe charge-transport when either traps[12, 14, 15] or a built-in voltage resulting from contact asymmetry is present[89, 142], no analytical model exists that describes the common practical situation where both a large built-in voltage and traps are present. As a result, less suitable models such as the MG law are often used to analyse the experimental data, despite evidence for both trapping and built-in voltages. Whilst more sophisticated drift-diffusion simulations can be used to analyse the experimental data more accurately, only a small number of publications adopt that approach[20, 21, 22, 23].

6.2.2 Research question and methods

In the previous chapter (chapter 5), we already touched on the issues with using analytical models when analysing SCLC measurements used to probe thin semiconductors in devices with realistic injection barrier heights. Here we further discuss the importance of using models which are more sophisticated than the MG law and/or the ME equation, since organic semiconductors are usually affected by energetic disorder and traps along with injection issues.

We here investigate whether by allowing the charge-carrier band mobility, trap characteristics and injection barrier heights to vary in the drift-diffusion device model (*ASA*), is a better model for analysing SCLC J - V curves. Because of temperature sensitive parameters such as injection barrier heights and traps, we perform temperature dependent SCLC measurements. Furthermore, since the equilibrium charge-carrier density is highly affected by the thickness of the semiconductor, hence determining the effect of traps on the J - V curves, we perform SCLC measurements with different semiconductor thicknesses. For completion, we do this for both symmetric (no built-in voltage) and asymmetric (including a built-in voltage) hole-only devices. All varied and fixed values of quantities used during the simulations are listed in table 6.1.

Table 6.1: Table of fixed and variable values used in the drift-diffusion simulations to model the electron-only and hole-only devices with and without traps and injection limitation and/or asymmetry.

Quantity	Symbol	Value	Units
Band gap	E_g	2	eV
Effective electron density of states	N_C	10^{19} or 10^{20}	cm^{-3}
Effective hole density of states	N_V	10^{19} or 10^{20}	cm^{-3}
Dielectric constant	ϵ_r	3	-
Active layer thickness	L	variable	nm
Electron band-like mobility	μ_n	10^{-4}	cm^2/Vs
Hole band-like mobility	μ_h	variable	cm^2/Vs
Injection barrier height at $x = 0$ (single-carrier)	$q\phi_{\text{inj}}$	variable	eV
Injection barrier height at $x = L$ (single-carrier)	$q\phi_{\text{ext}}$	variable	eV
Density of tail states (electrons)	$n_{t,n}$	variable	$\text{cm}^{-3}\text{eV}^{-1}$
Density of tail states (holes)	$n_{t,p}$	variable	$\text{cm}^{-3}\text{eV}^{-1}$
Characteristic tail energy (electrons)	$E_{\text{ch},n}$	variable	eV
Characteristic tail energy (holes)	$E_{\text{ch},p}$	variable	eV
Neutral electron capture rate coefficient	c_n^0	10^{-10}	$\text{cm}^{-3}\text{s}^{-1}$
Positive electron capture rate coefficient	c_n^+	10^{-12}	$\text{cm}^{-3}\text{s}^{-1}$
Neutral hole capture rate coefficient	c_p^0	10^{-10}	$\text{cm}^{-3}\text{s}^{-1}$
Negative hole capture rate coefficient	c_p^-	10^{-12}	$\text{cm}^{-3}\text{s}^{-1}$
Surface recombination velocity	S	10^5	m/s
Series resistance	R_S	0	Ωm^2
Shunt/parallel resistance	R_P	variable	Ωm^2
Temperature	T	variable	K

During the fitting procedure we fix the injection barrier heights to a specific value and allow the mobility and trap characteristics to vary to obtain fits across the thickness and temperature series. Besides fitting with the numerical model, we also fit with the MG law and the ME equation to the temperature series and compare the obtained mobilities from the analytical models to the obtained mobilities from the numerical model.

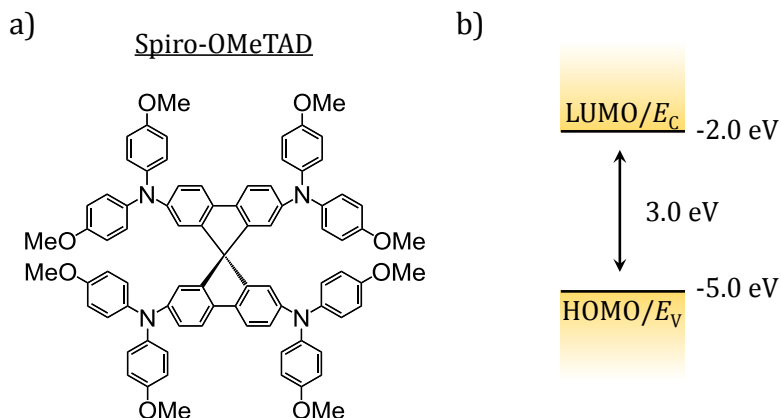


Figure 6.1: a) Molecular structure of investigated molecule, Spiro-OMeTAD, and b) molecular energy levels: Lowest unoccupied molecular orbital, LUMO, with energy of -2.0 eV, highest occupied molecular orbital, HOMO, with energy of -5.0 eV, resulting in a band gap of 3.0 eV. The HOMO and LUMO levels can be considered as the valence and conduction band edge energies, E_V and E_C .

For the work shown in this chapter we selected the small molecule, Spiro-OMeTAD (fig. 6.1a), which is commonly used as a hole selective interlayer for dye-sensitized solar cells and lead halide perovskite cells. Spiro-OMeTAD was chosen based on the expectation that its amorphous microstructure is largely insensitive to the layer thickness allowing for a thickness series to be performed. Approximate values (taken from the literature) for the HOMO and LUMO levels, and the magnitude of the band gap are shown in fig. 6.1b[111, 150, 151, 152]. Furthermore, Spiro-OMeTAD is expected to be more or less intrinsic in its pristine state, showing non-dispersive transport in time of flight measurements[111], whereas it's usually used in solar cell devices in a doped state[153].

This investigation will help aim towards using a drift-diffusion simulation approach to improve the accuracy of the determined mobility relative to traditional approaches of using analytical equations.

6.3 Review of analytical equations

As has already been shown in chapter 3, different analytical equations have been derived to analyse SCLC data. We here review the analytical equations used for this thesis chapter.

6.3.1 Analytical model describing SCLC in the low voltage regime

The first model, presented here, apply to the low voltage regime where in practice a linear J - V relationship is often observed. It has previously been shown that linear currents observed in SCLC J - V curves are due to one of, or a combination of, the following effects: flow of equilibrium charge-carriers at low voltages in symmetric single-carrier devices [137, 140, 141, 143], a large increase of the charge-carrier density away from the equilibrium value due to doping[143, 154], or bulk saturation of charge carriers inside the device either at high bias or with large injection barriers[131].

As discussed in detail in chapters 3 and 4, in the absence of traps, doping and a V_{bi} , the current density at low voltages is given by the ME equation[137, 140, 141, 143],

$$J = 4\pi^2 \frac{k_B T}{q} \mu_n \varepsilon_r \varepsilon_0 \frac{V}{L^3} \quad (6.1)$$

where $k_B T$ is the thermal energy, q is the elementary charge, μ_n is the electron band mobility, ε_r is the dielectric constant, ε_0 is the vacuum permittivity, V is the applied voltage and L is the semiconductor thickness.

6.3.2 Analytical model describing SCLC in the intermediate voltage regime

As has been discussed in detail in chapters 3 and 5, the most commonly used method for fitting data obtained from single-carrier devices is to use the MG law[11],

$$J = \frac{9}{8} \mu_n \varepsilon_r \varepsilon_0 \frac{V^2}{L^3}. \quad (6.2)$$

In chapter 5 we established that the MG law is only approximately valid for organic semiconductors when the semiconductor thickness exceeds 50 nm and injection barrier heights are small or vanishing. The MG law describes the drift current in an idealised single-carrier device, made from a trap-free and undoped semiconductor in the intermediate voltage regime. However, organic semiconducting materials are rarely trap free, rendering the simple MG theory unsuitable for describing charge transport for most realistic cases. It is however still common to assume

an effective mobility, μ_{eff} in the case where the MG law is used even though the semiconductor contains traps. This effective mobility is sometimes defined as [13, 18],

$$\mu_{\text{eff}} = \mu_{\text{band}} \frac{\langle \rho_{\text{free}} \rangle}{\langle \rho_{\text{total}} \rangle} \quad (6.3)$$

where $\langle \rho_{\text{free}} \rangle = L^{-1} \int_0^L \rho_{\text{free}}(x) dx$ is the spatial average of the free charge-carrier density in the semiconductor and $\langle \rho_{\text{total}} \rangle = L^{-1} \int_0^L \{ \rho_{\text{free}}(x) + \rho_{\text{trapped}}(x) \} dx$ is the spatial average of the total charge-carrier density in the semiconductor.

6.3.3 Analytical model describing SCLC in the the intermediate voltage regime with traps

As already discussed in chapters 3 and 5, one of the few analytical equations which describes SCLC in a semiconductor with traps assumed in the form of exponential tails, is the Mark-Helfrich (MH) equation [12], which is given by,

$$J = q^{1-l} \mu_n N_C \left(\frac{\varepsilon_r \varepsilon_0 l}{N_t (l+1)} \right)^l \left(\frac{2l+1}{l+1} \right)^{l+1} \frac{V^{l+1}}{L^{2l+1}} \quad (6.4)$$

where N_C is the effective electron density of states, N_t is the trap density per unit volume, and $l = E_{\text{ch}}/k_B T$, where E_{ch} is the characteristic energy of the tail states.

It was however recently shown that the MH equation is not accurate since it fails to account for diffusion currents, which can make a significant contribution to the total current when traps are present [18].

6.3.4 Contact asymmetry (V_{bi})

Besides assuming the semiconductor to be trap free, the ME equation and the MG law assume that there is a negligible energy barrier for both injection and extraction ($q\phi_{\text{inj/ext}}$) from the metal contacts into the semiconductor. This criterion can however rarely be met in real experimental cases, and a finite injection barrier can have a significant influence on the probed charge-transport behaviour (especially if the thickness of the semiconductor is less than 50 nm). With $q\phi_{\text{inj/ext}} = 0$ eV being assumed, the MG law therefore also implicitly requires that there exists no built-in voltage, V_{bi} , across the device arising from a difference in the work functions (WFs), and hence the injection barrier heights, $V_{\text{bi}} = q\phi_{\text{ext}} - q\phi_{\text{inj}}$, a feature which is often difficult to achieve from a practical device fabrication perspective. This will become clear in the experimental section where the device architecture and the expected energetics are discussed.

The limited choice of contact materials available to match very deep (> 6 eV below vacuum level), or very shallow (< 2 eV below vacuum level), transport levels, will usually result in metal/semiconductor interfaces with significant injection barriers.

The most commonly used approach for dealing with built-in voltages is to correct the voltage axis. To do this an effective applied voltage, $V_{\text{eff}} = V - V_{\text{bi}}$, is defined where the V_{bi} is either used as a fitting parameter in the MG law (or other analytical equations of variant types, such as the MH equation or the Murgatroyd equation[16]), or is chosen from the literature values of the contact work functions[7, 10]. As discussed in chapter 3, this somewhat indirect approach is however rather risky, since the band diagram at $V = 0$ V for a symmetric device and $V = V_{\text{bi}}$ for an asymmetric device are not necessarily similar. At a significant applied bias such that the built-in voltage is overcome, and if, hypothetically, the value of V_{bi} is exactly known, then using this effective voltage approach is a good approximation. The V_{bi} is however rarely known precisely in advance, and is sometimes estimated by shifting the voltage axis to a regime where $J \propto V^2$ over a range of the measured voltages which, as we have discussed in chapter 3, can lead to a misinterpretation of the charge-carrier mobility values, especially when traps are present.

As mentioned in chapter 3, an analytical drift-diffusion expression for the current density across a single-carrier device with a built-in voltage (up to $V = V_{\text{bi}}$) has previously been derived to[89],

$$J = \frac{q\mu_n N_C (V_{\text{bi}} - V) \left\{ \exp\left(\frac{qV}{k_B T}\right) - 1 \right\}}{L \left\{ \exp\left(\frac{qV_{\text{bi}}}{k_B T}\right) - \exp\left(\frac{qV}{k_B T}\right) \right\}}. \quad (6.5)$$

From eqs. 6.4 and 6.5 above, it is clear that even though analytical models exist to describe both a built-in voltage and traps separately, no analytical model exists to describe the common practical situation where both traps and a large built-in voltage is present as a result of the chosen contacts and the probed semiconductor.

6.3.5 Pinholes and current pathways

The linear J - V relationship of an intrinsic semiconductor at low voltages is described by the ME equation (given that the device is not short circuited). However, linear currents can however also arise at low voltages in single-carrier devices through shunts due to low resistance pathways through the semiconducting film. This linear current density, in the case where shunt currents dominate, is given by Ohm's law as,

$$J = (\rho_P)^{-1} \frac{V}{L} \quad (6.6)$$

where ρ_P is the shunt resistivity, or parallel resistivity (in units of Ωcm^2). As we will show, shunt currents are especially relevant for asymmetric devices with a large V_{bi} since the current density at voltages ($V < V_{bi}$) is very low. Note that the larger the V_{bi} the higher the chance that shunt currents will dominate the J - V curve in the low voltage regime.

6.4 New analytical results and comparison with simulations

As was discussed above, the most commonly used analytical equation describing space-charge-limited transport through a semiconductor with traps is the MH equation. However, Fischer *et al* have shown that this equation is imprecise since it neglects diffusion[18].

We now derive an analytical expression describing charge-transport in the low voltage regime when the semiconductor has an exponential distribution of traps extending from the band edge. We then compare the trap characteristics and mobility obtained from this analytical equation to the MH equation, when fitted to data of simulated devices, and we show that our equation is more accurate at extracting both the mobility and traps. We then use this equation to analyse experimental J - V curves in a later section and compare the results using our analytical equation to the results from our numerical drift-diffusion solver.

6.4.1 Derivation of the new analytical equation for trap-limited transport

As we have already discussed in chapters 3 and 4, ref [138] has shown that the equilibrium charge-carrier density in a symmetric, intrinsic and trap-free single-carrier device, $n(x)$, can be described, to a very good approximation, by,

$$n(x) = \frac{2\pi^2 \varepsilon_r \varepsilon_0 k_B T}{q^2 L^2} \left[\cos^2 \left\{ \pi \left(\frac{x}{L} - \frac{1}{2} \right) \right\} \right]^{-1} \quad (6.7)$$

where x is the spatial position from the injecting contact, and all the other symbols have their usual meaning. As we discussed in chapter 4 (and as we will also show here), eq. 6.7 precisely describes the charge-carrier density in area around the middle of a symmetric single-carrier device, $x = L/2$, but produces un-physical singularities at the device boundaries, $x = 0$ and $x = L$ where the charge-carrier density described by eq. 6.7 blows up to infinity, whereas the real charge-carrier density will have some finite value (as seen in fig. 6.2a). By taking $x = L/2$, the equilibrium charge-carrier density in the middle of the device, n_0 , is given by,

$$n_0 = \frac{2\pi^2 \varepsilon_r \varepsilon_0 k_B T}{q^2 L^2}. \quad (6.8)$$

A comparison of eq. 6.8 with numerically calculated values of the electron density in the middle of a device is shown in fig. 6.2b (solid lines).

The arithmetic mean of eq. 6.7, $\langle n \rangle = L^{-1} \int_0^L n dx$, cannot be calculated, since the integral does not converge. However n^{-1} can be integrated and, thus, the harmonic mean of the charge-carrier density can be written as,

$$\langle n \rangle_{\text{ana.}} = \frac{1}{\frac{1}{L} \int_0^L n^{-1} dx}. \quad (6.9)$$

This integral yields,

$$\langle n \rangle_{\text{ana.}} = \frac{4\pi^2 \varepsilon_r \varepsilon_0 k_B T}{q^2 L^2} \quad (6.10)$$

which is, of course, just $2n_0$. Upon insertion of this charge-carrier density into the drift current equation, $J = q\mu_n \langle n \rangle_{\text{ana.}} VL^{-1}$, we obtain the ME equation. As previously discussed, the ME equation is a very good approximation of the current density in an intrinsic single-carrier device at low voltages. Since eq. 6.8 is a very good approximation of the charge-carrier density in the middle of device at low applied voltages, due to the overall shape and magnitude of the charge-carrier density profile not changing significantly between 0 and 0.1 V (fig 6.2a), the ME equation is a very good description of the current density in that voltage range.

It is important to note that the harmonic mean of the charge-carrier density, $\langle n \rangle_{\text{ana.}}$, does not give the same value of the arithmetic mean of the charge-carrier density of a device calculated using a numerical approach, $\langle n \rangle_{\text{num.}}$, since the device boundaries are not correctly described in the analytical approximation. For this reason, the ME equation cannot be directly used to determine the charge-carrier density of the entire device, but only in the middle of the devices, which we have already discussed in chapter 4[143]. Figure 6.2b shows that $\langle n \rangle_{\text{num.}} > \langle n \rangle_{\text{ana.}}$, in general, for an intrinsic and trap-free device.

We now proceed to derive an expression for the J - V response of a single-carrier device in the low voltage regime in the presence of exponential tails. The following derivation follows from the assumptions of trapped and free charge-carrier density statistics, in exponential tails, given by ref. [12]. For simplicity, the derivation is given for the case of electron transport since it is

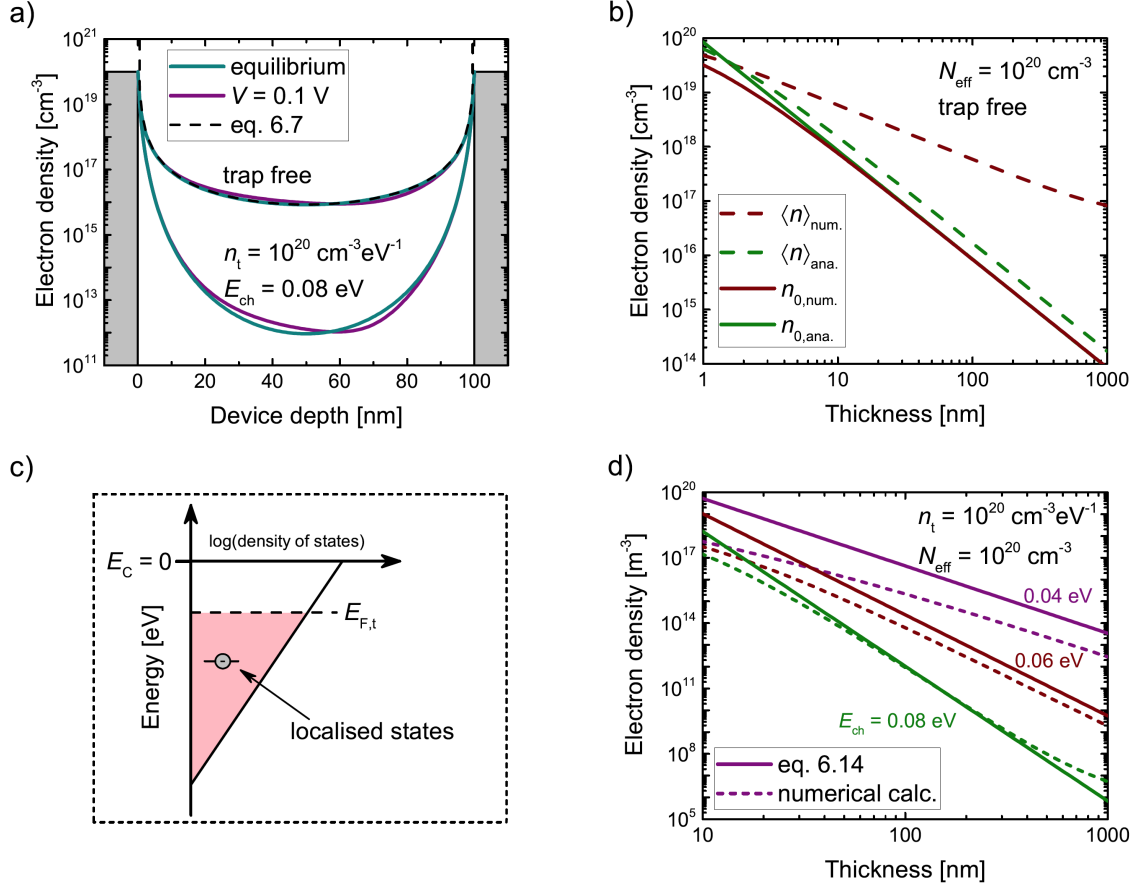


Figure 6.2: a) Electron density as a function of spatial position of a trap free device and a device with localized states in the form of exponential tail trap states in comparison with the eq. 6.7. b) Average electron densities, $\langle n \rangle$, of the numerical calculation (red dashed line) and the analytical approximation, eq. 11 (green dashed line), and electron density in the middle of the device, n_0 , from the numerical calculation (solid red line) and from eq. 9 (solid green line). c) Schematic of the description of the localised states in the band gap. In this case $T = 0 \text{ K}$ is assumed for the representation of the occupied density of states. d) Electron density in the middle of the device calculated using eq. 6.14 (solid lines) and from numerical calculations (dashed lines) when an exponential distribution of trap states are included. The characteristic energy of the distribution is varied between 0.04, 0.06 and 0.08 eV.

conceptually more intuitive to think of electrons (the derivation in the case of hole transport is completely analogous).

The density, h , of localized states in the band gap (electron traps) per unit volume and energy interval, far away from the device contacts, i.e., in the middle of the device ($x = L/2$),

is described by,

$$h = n_t \exp\left(\frac{E}{E_{\text{ch}}}\right) \quad (6.11)$$

where $n_t = N_t/E_{\text{ch}}$ is the trap density per unit energy right below the conduction band edge (E_C), and E is the energy of the trap measured below the conduction band edge (note that, the conduction band edge is set to zero, $E_C = 0$ eV, and the energy increases upwards, as shown in fig 6.2c). Given that N_t is much larger than the total amount of charge carriers in the middle of the device at absolute zero, $n_0(T = 0 \text{ K})$, it is safe to assume that all of these charge carriers will be trapped and will fill the exponential tail states up to a quasi-Fermi level, $E_{\text{F,t}}$. Within this assumption we can write,

$$n_0 = \int_{-\infty}^{E_{\text{F,t}}} \frac{N_t}{E_{\text{ch}}} \exp\left(\frac{E}{E_{\text{ch}}}\right) dE = N_t \exp\left(\frac{E_{\text{F,t}}}{E_{\text{ch}}}\right) \quad (6.12)$$

As the temperature is increased ($T > 0 \text{ K}$), some charge-carriers will escape the traps and will be free to conduct. Given that the Fermi level governing free charge carriers is more than a few $k_{\text{B}}T$ away from the conduction band edge, we can describe the free charge-carrier density using Boltzmann statistics (again implying $E_C = 0$ eV),

$$n_{\text{free}} = N_C \exp\left(\frac{E_{\text{F}}}{k_{\text{B}}T}\right) \quad (6.13)$$

where N_C is the effective density of electron states at the conduction band. Assuming that $E_{\text{F}} = E_{\text{F,t}}$ which is a fair assumption given that $E_{\text{ch}} > k_{\text{B}}T$, we can combine the above two expressions and express the free charge-carrier density in terms of the total charge-carrier density as,

$$n_{\text{free}} = N_C N_t^{-l} n_0^l \quad (6.14)$$

where $l = E_{\text{ch}}/k_{\text{B}}T$. Figure 6.2d shows a comparison of eq. 6.14 with numerical calculations of the charge-carrier density as the characteristic energy is varied from 0.04 eV to 0.08 eV (with a fixed N_C and n_t). Since the current is only governed by the free charge-carrier density, we can now describe the drift current as,

$$J = q\mu_{\text{n}}n_{\text{free}}\frac{V}{L} = q\mu_{\text{n}}N_C \left(N_t^{-l}n_0^l\right)\frac{V}{L}. \quad (6.15)$$

Since we are only concerned about the trap density far away from the contacts, we can describe the total charge-carrier density by $2n_0$, where n_0 is given by eq. 6.8. We then obtain,

$$J = q^{1-2l} \mu_n N_C \left(\frac{4\pi^2 \varepsilon_r \varepsilon_0 k_B T}{N_t} \right)^l \frac{V}{L^{2l+1}}. \quad (6.16)$$

which describes the current density at low applied voltages when some charge carriers are trapped in exponential tails. Note that we do not need to introduce the concept of an effective mobility (at least not from the perspective of traps, whereas injection limitation will still give rise to a characteristic energy that the new equation cannot account for) since the reduction of free charge-carriers are included implicitly through $N_C N_t^{-l} n_0^l$. Equation 6.16 reduces to the ME equation in the trap free limit. The accuracy of eq. 6.16 is compared to the accuracy of the MH equation in the following section.

6.4.2 Accuracy of eq. 6.16 compared to the MH equation

In order to evaluate how well eq. 6.16 determines the trap characteristics compared to the MH equation, both equations were fitted to J - V curves generated from drift-diffusion simulations of symmetric single-carrier devices containing traps in the form of exponential tails. We examine how the fitting values of E_{ch} and N_t compared to the input values of the same parameters,

$$\gamma = \frac{E_{ch}^{out}}{E_{ch}^{in}} \quad \text{and} \quad \delta = \frac{N_t^{out}}{N_t^{in}}. \quad (6.17)$$

Figure 6.3 shows γ and δ as a function of E_{ch} when either the trap density, the semiconductor thickness or the temperature is varied. The following values were kept fixed during the fitting procedures with both the numerical simulations and the equations: $N_C = 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$, $E_g = 2 \text{ eV}$ and $\mu_n = 10^{-4} \text{ cm}^2/\text{Vs}$.

Figure 6.3a, b and c show the ratio of characteristic energy obtained from fitting eq. 6.16 and the MH equation compared to the input characteristic energy as this energy is varied. A very small deviation from unity is seen in all examples when eq. 6.16 is used, indicating that the low voltage J - V regime (0 to 0.1 V) can be very well reproduced. Moreover, the ratios are seen to converge for large values of the characteristic energy. Figure 6.3c, e and f show the ratio of the trap density obtained from fitting to the input trap density using eq. 6.16. In all cases the trap density is estimated within an order of magnitude. Where excellent agreement is found with eq. 6.16, the results using the MH equation are seen to deviate.

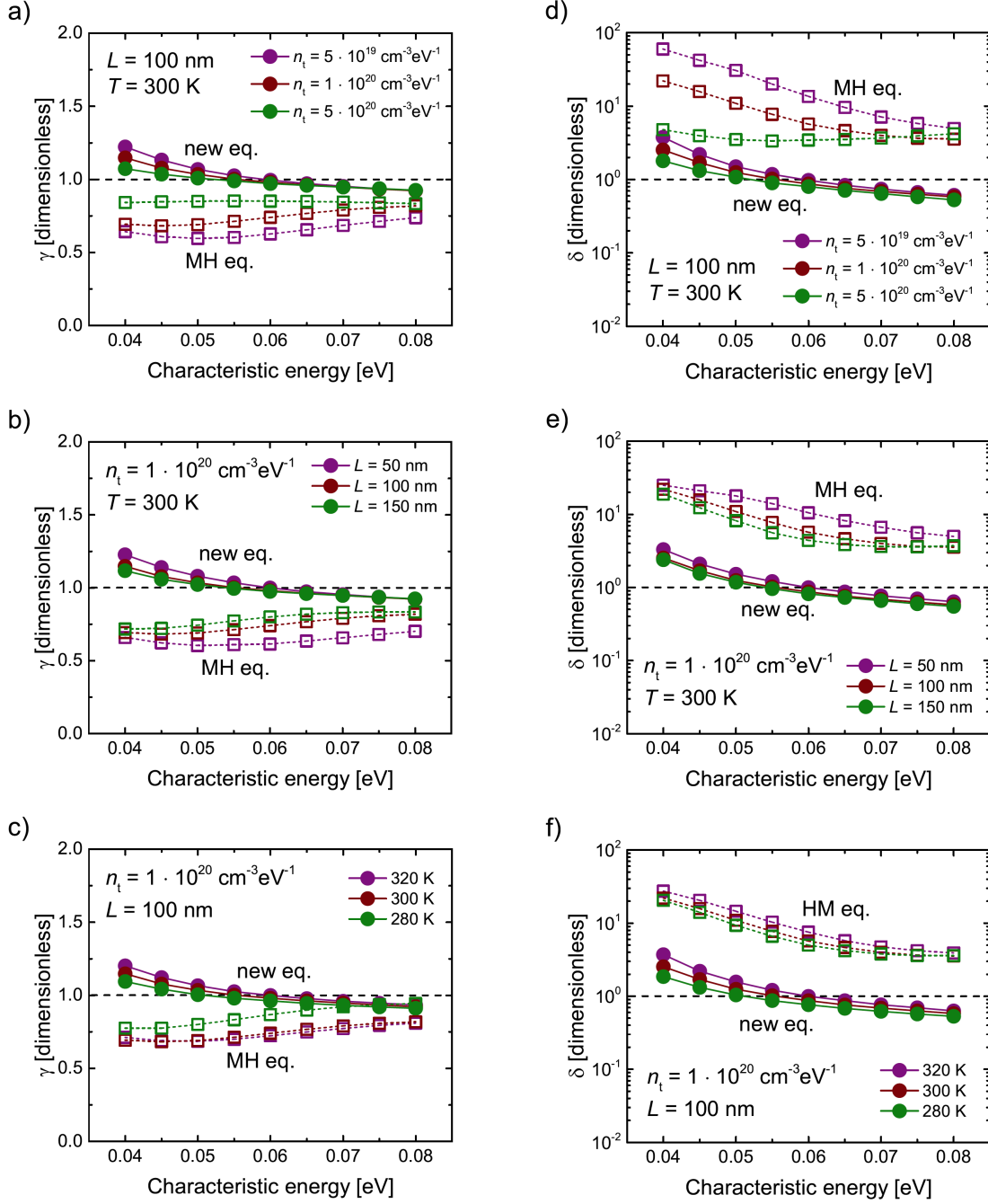


Figure 6.3: Accuracy of eq. 6.16 compared to the MH equation between the input values for the trap characteristics to the output values obtained from fitting either the MH eq. or eq. 6.16 to the simulated J - V curves, γ and δ , when the band mobility is kept fixed. a+d) fixed temperature and thickness and varied trap density, b+e) fixed trap density and temperature and varied thickness, c+f) fixed trap density and thickness and varied temperature.

6.5 Experimental results and discussion

We here test the various models introduced, both analytical and numerical, against experimental SCLC data using the amorphous hole transport semiconductor, Spiro-OMeTAD.

The device fabrication, SCLC measurements, and analysis using analytical equations and the numerical drift-diffusion solver, of the single-carrier devices used for the study (here hole-only Spiro-OMeTAD devices) is explained in detail in this section.

6.5.1 Device fabrication

Both symmetric and asymmetric hole-only devices of Spiro-OMeTAD were fabricated in order to test the theoretical models over a wide voltage range of J - V data for both device types. The devices are made using a $2.54\text{ cm} \times 2.54\text{ cm}$ glass substrates with six 0.045 cm^2 device areas to be measured. This is the same device substrates used for our solar cell research.

Most photovoltaic devices studied on lab scale are fabricated on transparent conductive oxides, such as indium tin oxide (ITO), which are deposited on either glass or on flexible plastics such as polyethylene terephthalate (PET). Even though this part of the thesis is not directly concerned about solar cells, it is still convenient to use the same contacts for SCLC as one would for solar cell devices. This ensures that the active material is deposited onto a surface with same roughness and wetting which will give the same film properties as in the solar cells. For this reason we fabricated our single-carrier devices using a thin layer of ITO. The work function of ITO has been cited to be between 4.5 and 5.0 eV depending on how it's treated, with the value leaning towards a lower value of 4.5 eV when untreated[155, 156, 157]. When ordering ITO covered glass slides, they are usually covered in a protective plastic layer. To ensure that the ITO is free of contaminants during the device fabrication, the substrates are ultrasonicated in acetone and IPA for 15 minutes, respectively. They are then dried on a hot plate for 10 minutes to evaporate excess solvents.

A common hole-selective material for organic optoelectronic devices is the conductive and semi-transparent polymer blend, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). Literature values for the WF of this conductive polymer blend range between 4.8 and 5.4 eV below the vacuum level, making it a promising contact for most donor materials[155, 158, 159, 160], with a majority of papers leading towards a value around 5.2 eV. Furthermore, we and other people in the literature have used PEDOT:PSS as a hole selective contact for a number of solar cell architectures[161, 57, 162, 63, 163, 164] and in a variety of light-emitting diode devices[165, 166, 167, 168]. For our hole-only devices we spun cast PEDOT:PSS from a water solution onto the cleaned glass slides containing a pre-defined ITO strip at 3500 rpm for 30 s (figs. 6.4a and b). The substrate containing the PEDOT:PSS thin film was heated/annealed on a hot plate at 120°C for 10 minutes to evaporate any excess water in the film. The resulting PEDOT:PSS thickness after the heating is around 30 nm (fig. 6.4c).

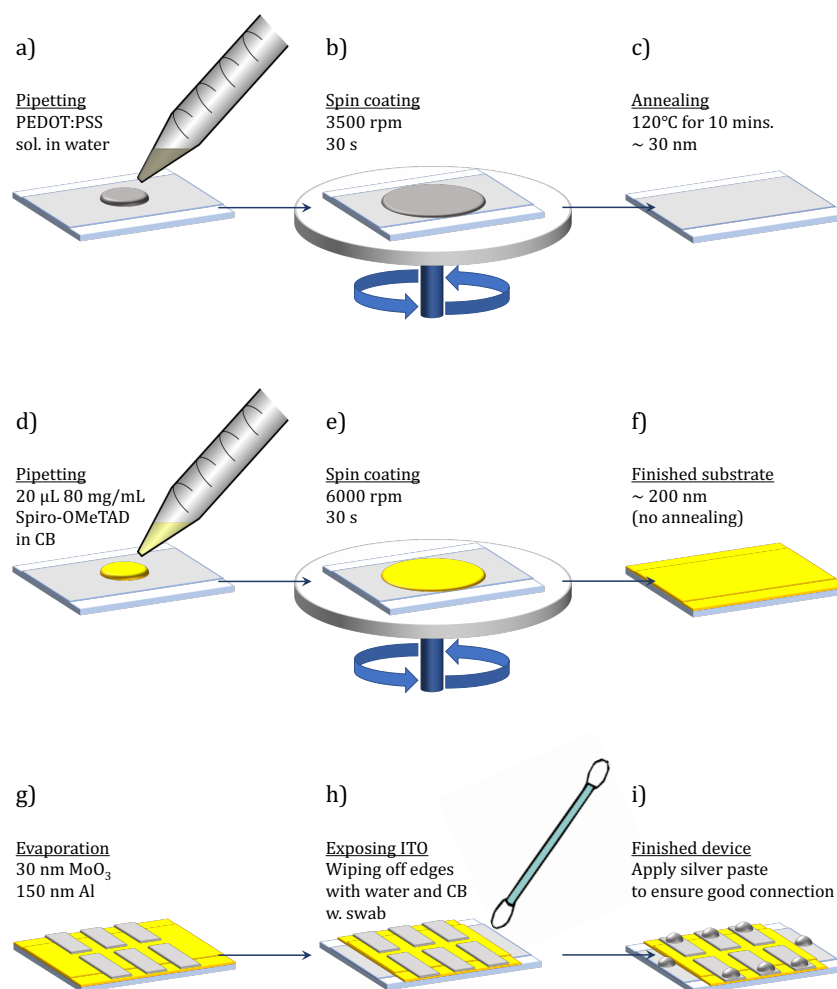


Figure 6.4: a) The PEDOT:PSS solution is applied to the glass slide containing a pre-defined layer of ITO (around 80 nm). b) The substrate is spun at 3500 rpm for 30 s. c) The substrate containing PEDOT:PSS is annealed at 120°C for 10 minutes to evaporate the remaining water out of the films. The resulting PEDOT:PSS film is transparent to the eye and is around 30 nm thick. d) The Spiro-OMeTAD solution is applied to the substrate. e) The substrate is spun at 6000 rpm for 30 s. The finished Spiro-OMeTAD film is a semi-transparent yellow colour with a thickness of around 200 nm. g) Back contacts of 30 nm MoO₃ and 150 nm Al are evaporated onto the substrate through a shadow mask. h) The ITO strip is exposed using a cotton swab and solvents. i) Conductive silver paste is applied to both the ITO strip and the back contacts to ensure good connection to the substrate holder.

Thin films of Spiro-OMeTAD of varying thicknesses were spin cast from chlorobenzene (CB) onto the ITO/PEDOT:PSS substrates under atmospheric conditions (figs. 6.4d and e). Given

a 80 mg/mL solution spun cast at 6000 rpm for 30 s, a Spiro-OMeTAD film thickness of around 200 nm is achieved (fig. 6.4f). The thickness of the Spiro-OMeTAD layer can be varied using either a different solution or by spinning the 80 mg/mL solution at different speeds. Since the Spiro-OMeTAD films are amorphous when processed from solution (only a very few groups have managed to make Spiro-OMeTAD single crystals, such as the work by Dong *et al.* using an anti-solvent approach[169]) the film microstructure is not affected by the solution concentration or the spin speed. However, a substantial spin speed is preferred to achieve a homogeneous thickness across the entire sample to ensure device reproducibility. The HOMO and LUMO levels of Spiro-OMeTAD are usually cited to be around -5 and -2 eV, with a band gap of around 3 eV[111, 150, 151, 152]. As already mentioned in the introduction, Spiro-OMeTAD is expected to be more or less intrinsic in its non-doped state, showing non-dispersive transport in time of flight measurements[111].

For the asymmetric devices, a back contact consisting of a thick layer of aluminium (150 nm) was evaporated under high vacuum (of $\approx 10^{-6}$ mbar). Aluminium has a cited work function between 4.0 and 4.4 eV below the vacuum level[170, 171, 172]. For the symmetric devices, a 30 nm layer of molybdenum oxide (MoO_3) followed by a thick layer of aluminium (150 nm) was evaporated (fig. 6.4g). MoO_3 has literature values for the WF ranging between 6 and 6.9 eV[173, 174, 175]. An alternative metal to aluminium could have been used, like silver or gold. It is expected that the ITO/PEDOT:PSS and the MoO_3/Al contacts will form a symmetric device with Spiro-OMeTAD while ITO/PEDOT:PSS and Al will form an asymmetric device with Spiro-OMeTAD. The energy level profiles of the finished devices, symmetric and asymmetric, are depicted in fig. 6.5a and b.

Based on the values for the contact WFs shown in fig. 6.5a, one could expect that the V_{bi} of the device is between 1 to 2 V, rendering the device asymmetric (as the difference between the literature work function values of PEDOT:PSS and MoO_3 could easily exceed 1 eV). However, Fermi level pinning between a metal contact and an organic compound whose HOMO level is shallower than the contact WF, will shift this contact WF to match the HOMO level (upon thermodynamic equilibration), rendering both effective WFs to be equal to the HOMO level and the built-in voltage therefore to be zero (fig. 6.5a). This means that the device will be symmetric and the current density, probing either in the forward or reverse bias, will be of similar magnitude and follow the same slope. Assuming Fermi level pinning between PEDOT:PSS and Spiro-OMeTAD, the built-in voltage would be estimated to be ≈ 0.9 V for the asymmetric device, given by the difference in the HOMO level of Spiro-OMeTAD and the work function of aluminium (fig. 6.5b). However, interface states (potentially bearing considerable dipole

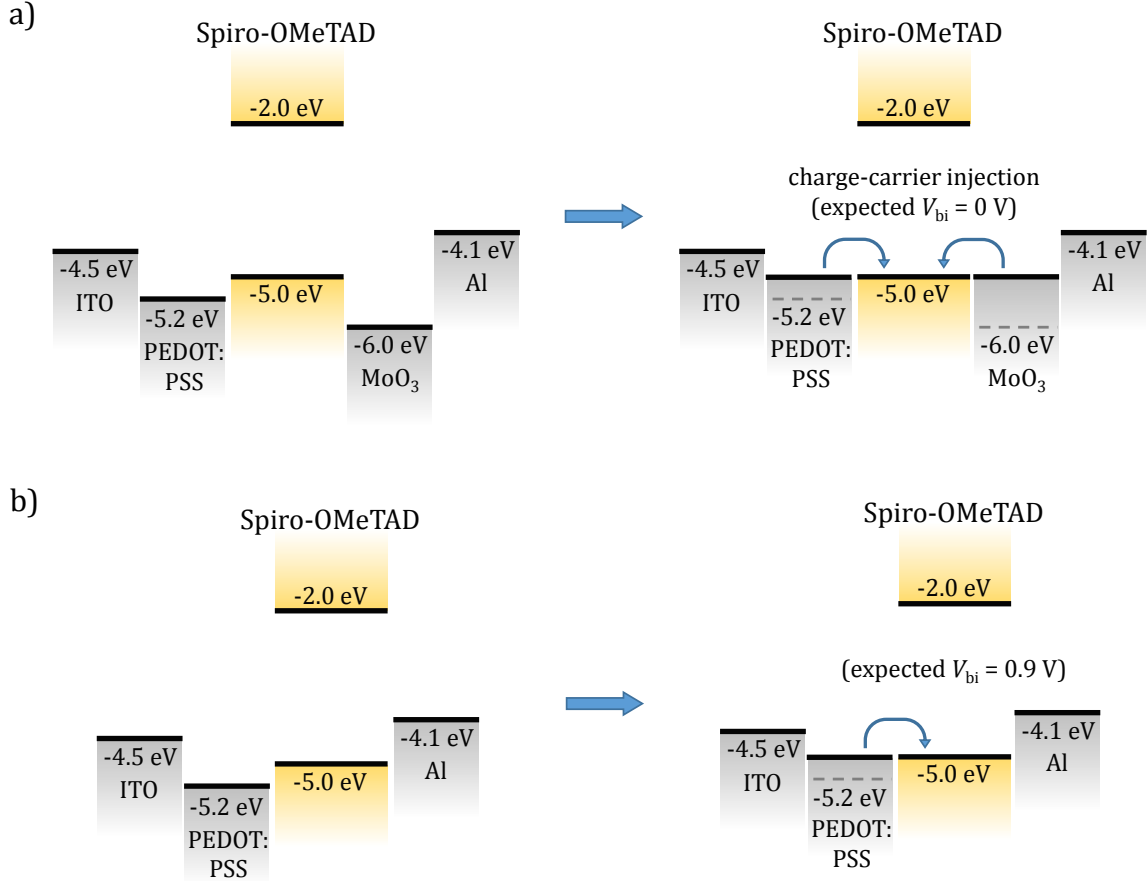


Figure 6.5: Energetics of finished devices. a) Symmetric device where Fermi-level pinning between both of the contact materials (PEDOT:PSS and MoO₃) to the Spiro-OMeTAD film ensure that the V_{bi} is zero. b) Asymmetric device, where Fermi level pinning between one contact material and the Spiro-OMeTAD gives rise to an expected V_{bi} of 0.9 V.

moments) between the contacts and the organic material, and the highly reactive nature of aluminium under ambient atmospheric conditions, might give rise to deviations from these estimated V_{bi} values (as will be shown from the results of the analysis below).

On a side note, some semiconducting polymers and small molecules have their HOMO levels lying much deeper than 5.1 eV below the vacuum level, meaning that PEDOT:PSS will not form a perfectly injecting contact with such materials. Sandwiching a deep HOMO (more than 6 eV below the vacuum level) material between PEDOT:PSS and MoO₃, for example, would allow for Ohmic injection from MoO₃ into the HOMO level, whereas the PEDOT:PSS would form an injection-limited contact, while at the same time resulting in the formation of a V_{bi} across the device due to the difference in the contact WFs. This means that even though we expect that PEDOT:PSS and MoO₃ will form a symmetric device with Spiro-OMeTAD,

that is not a guarantee that it will form a symmetric device with other materials. Because of this, and due to the lack of contact materials in general, it is common to measure SCLC on asymmetric single-carrier devices, since such devices are more straight forward to fabricate than symmetric single-carrier devices. However this V_{bi} will greatly affect the J - V curves at low and intermediate bias voltages until the internal voltage is overcome[89, 142].

6.5.2 Experimental J - V curves and analytical fits

With the symmetric and asymmetric devices complete, we performed two types of steady-state J - V experiments: room temperature and temperature-dependent measurements using a cryostat. We recorded the currents of the samples using a Keithley SMU 236 in a nitrogen atmosphere for the room temperature measurements and in helium for the cryostat-based temperature-dependent measurements. We measured the samples in a temperature range from 200 to 300 K.

Figure 6.6a shows the experimental J - V curves of a symmetric 200 nm hole-only device and an asymmetric 230 nm device (note that the current density shown is an absolute current density as the reverse bias current, probing from 0 to -5 V will yield a negative value for the current density which can not be plotted on a log-log scale). A fit with the MG law gave a value for the effective charge-carrier mobility of $\mu_{MG} = 1.09 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$ for the asymmetric Spiro-OMeTAD (the symmetric device data gave a similar value). In contrast to the non-rectifying behaviour observed for the current density between the forward and reverse bias in the symmetric device, a significant rectifying behaviour is present for the asymmetric device. Since a large asymmetry between the forward and reverse bias current is observed, a significant V_{bi} must be present and the current in the low voltage regime must be given by eq. 6.5 and/or eq. 6.6.

As previously mentioned, the local slope of the J - V curve on a log-log scale is given by,

$$m = \frac{d \log J}{d \log V} \quad (6.18)$$

such that,

$$J \propto V^{m(V)}. \quad (6.19)$$

It is seen from the slopes in fig. 6.6b that the forward bias current for the asymmetric device goes from a linear dependence at low voltages ($m = 1$) up until around 1 V, to a large peak

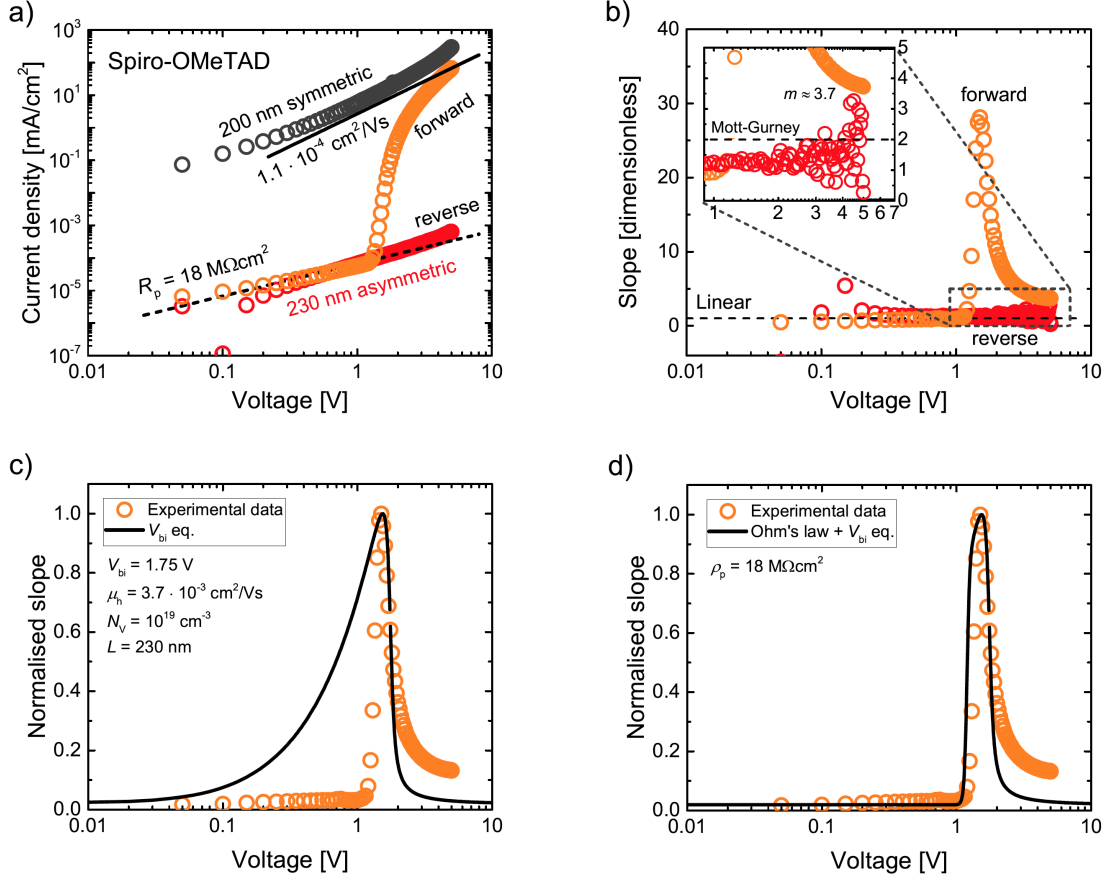


Figure 6.6: a) Forward and reverse bias J - V curves obtained from SCLC measurements of symmetric (grey circles) and asymmetric Spiro-OMeTAD hole-only devices (orange and red circles) of 200 and 230 nm respectively. Since the forward and reverse bias curves overlap for the symmetric device, only the forward bias curve is shown. A forced fit with the MG law to the asymmetric data is shown as a solid line. b) m - V plots of the J - V data against voltage. c) Fit with the V_{bi} equation (eq. 6.5) to the asymmetric device m - V data, obtaining a built-in voltage of 1.75 V. d) Fit to the asymmetric data using a sum of the V_{bi} equation and Ohm's law due to a low shunt resistance (eqs. 6.5 and 6.6).

at around 1.5 V ($m \approx 30$), and eventually approaches values which are larger than what would be expected from trap-free behaviour ($m = 2$) at high voltages, namely $m \approx 3.7$ at 5 V. Also, the reverse bias current is seen to be linear with voltage over the entire voltage range for the asymmetric device, which is not expected if the reverse current density is purely arising from an injection barrier (as was shown in chapter 3). Figure 6.6c shows a fit with the V_{bi} equation (eq. 6.5) to the m - V data, yielding a built-in voltage of 1.75 V (assuming that the barrier height for

injection was negligible, $q\phi_{\text{inj}} = 0$ eV, giving $q\phi_{\text{inj}} = 1.75$ eV). This value for the V_{bi} is much larger than the one expected from the literature values for the contact work functions, $V_{\text{bi}} = 0.9$ V (see fig. 6.5). The reason for this is not clear.

From the large observed slope at high voltages, it is expected that a proper charge-transport analysis cannot be achieved using the simple MG theory, as a large slope value is an indication of traps[12]. In order to elucidate this, we measured SCLC in symmetric devices as a function of temperature (since trap-influenced charge-transport is highly temperature dependent).

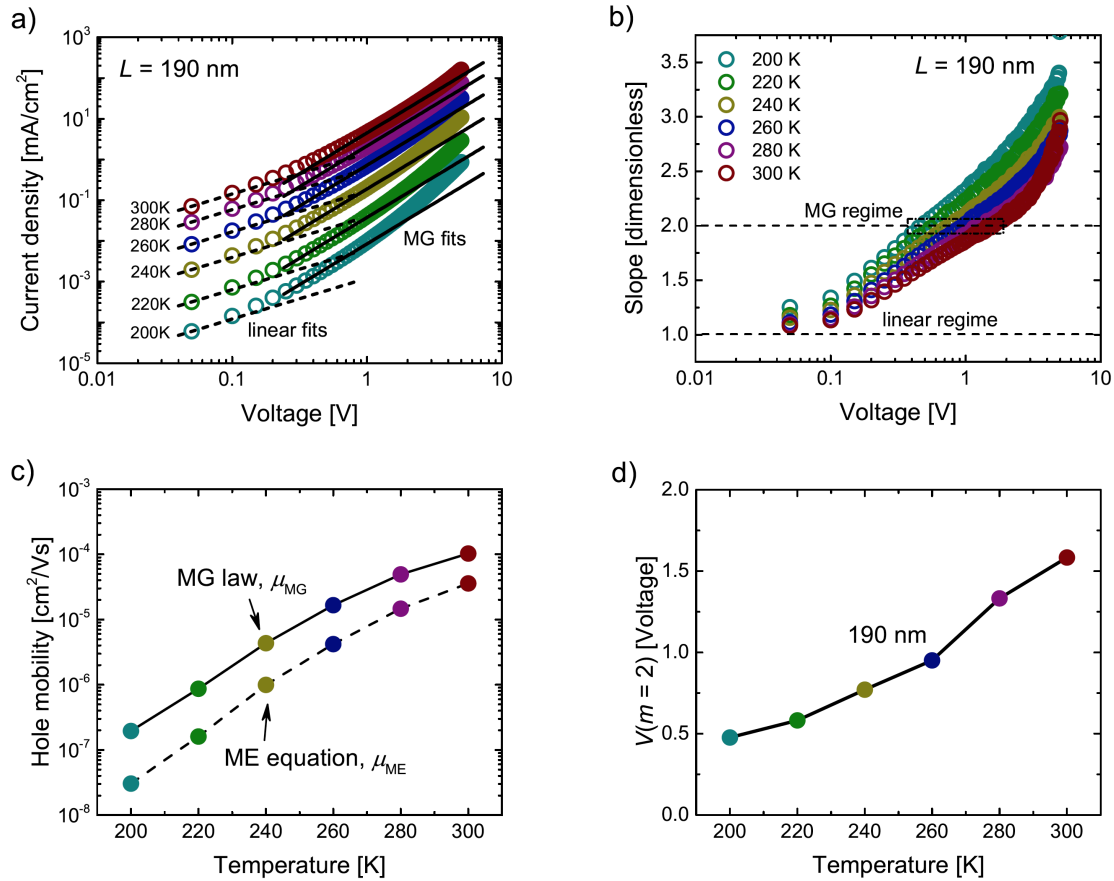


Figure 6.7: a) J - V curves of symmetric Spiro-OMeTAD devices at temperatures varying from 200K to 300K in steps of 20 K, showing fits with the MG law (solid lines) and the ME equation (dashed lines). b) m - V curves. c) Obtained hole mobilities from the MG law and the ME equation. d) The voltage at which the MG law was used for fitting.

Figure 6.7a shows the temperature series from a 190 nm symmetric hole-only device, at temperatures varying from 200 K to 300 K, along with linear fits with the ME equation (dashed lines) and fits with the MG law (solid lines). m - V curves of the J - V curves are shown in fig. 6.7b. The linear regime and the MG regime are shown as dashed lines (the linear equations

were fitted in the low voltage regime, and the MG law was fitted at the point where $m = 2$). It is seen that a linear J - V behaviour is observed at low voltages, but that the current follows some higher order of the voltage at high voltages, which is evidence of traps. Figure 6.7c shows the hole mobilities obtained using the MG law and the ME equation. A strong temperature dependence is observed in both cases. The voltage at which the MG law was fitted is shown in fig. 6.7d.

6.5.3 Qualitative simulation results

In order to understand the effect of a V_{bi} and shallow traps on J - V curves, both separately and in combination (as would be the case of the asymmetric device), we performed qualitative drift-diffusion simulations of 100 nm single-carrier devices, with or without traps and injection limitation. Figure 6.8 shows the results of the simulations where the charge-carrier band mobility was arbitrarily chosen to be $10^{-4} \text{ cm}^2/\text{Vs}$. The choice of the value of the mobility in this context is not important as the mobility only affects the magnitude of the current density and does not affect the transition between voltage regimes.

Figure 6.8a compares the forward bias current density of a trap-free symmetric single-carrier devices with a trap-free asymmetric single-carrier device with a V_{bi} of 0.5 V. The V_{bi} introduces a diffusion barrier for the charge-carriers to overcome in forward bias before drift currents can dominate the J - V curve, whereas the reverse bias current will be injection limited with a barrier height equal to the magnitude of the qV_{bi} . In forward bias, the energetic barrier manifests itself by an overall lowering of the current density at low voltages with an exponential increase of the current density with voltage (see eq. 6.5). The corresponding m - V curves for fig. 6.8a are seen in fig. 6.8d, where the slope is seen to have a large peak until reaching the slope value of the device without a built-in voltage ($m \approx 2$).

Figure 6.8b shows the comparison between a trap-free and symmetric single-carrier device and a symmetric single-carrier device with some density of tail states ($E_{ch} = 0.050 \text{ eV}$ and $n_t = 5 \cdot 10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$). The traps are seen to lower the current across the entire voltage range due to the lowering of the number of free charge-carriers present for conduction. Figure 6.8e shows the corresponding m - V curves to fig. 6.8b, where the slope at high voltages is seen to approach a value substantially higher than $m = 2$.

Figure 6.8c shows the comparison between a trap-free and symmetric device with a device with both traps and a V_{bi} . We see that the V_{bi} , in this case, dominates at low voltages whereas the traps dominate at higher voltages. That the V_{bi} dominates at low voltages is of course completely dependent on the choice of the values chosen for the simulation. However, given

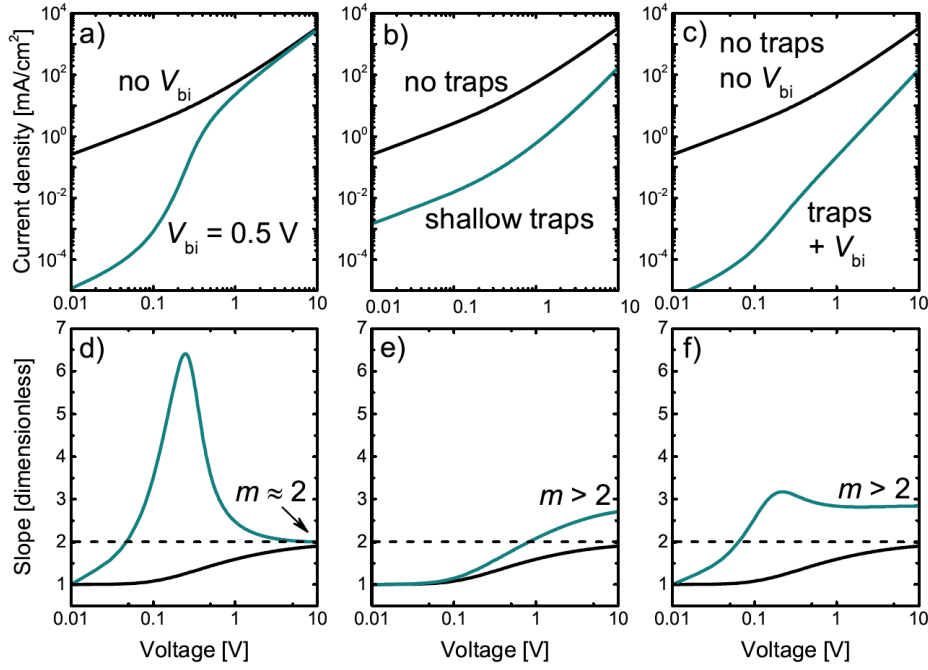


Figure 6.8: Drift-diffusion simulations of J - V curves of single-carrier devices with a) built-in potential of 0.5 V, b) traps in the form of exponential tails ($E_{\text{ch}} = 0.050$ eV and $n_t = 5 \cdot 10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$), and c) a combination of a built-in potential and traps. d-f) show the corresponding slope plots of a-c). The dashed line represents the slope value of the MG law.

that the V_{bi} is relatively high and the trap density and characteristic energy is relatively low, one can assume that the V_{bi} will be the dominant factor. The corresponding m - V curves to fig. 6.8c is shown in fig. 6.8f, where the peak due to the V_{bi} is slightly lowered due to the presence of traps. Most importantly, the slope at high voltages still takes a value which is larger than what is expected from the MG law. So from considering the m - V curves alone we can already determine that the transport in the device is governed by traps in the form of exponential tails and that there is a substantial V_{bi} .

Comparing figs. 6.6a and b with figs. 6.8c and f, it is seen that the drift-diffusion model, including traps and a V_{bi} , can reproduce the same qualitative trend as seen in the experimental curves at intermediate and high voltages, but fails to reproduce the linear regime observed at low voltages. The current in the low voltage regime can, however, be modelled as a combination of diffusion currents due to a large V_{bi} and a shunt current.

Figure 6.9 shows the effect on simulated J - V curves and the corresponding m - V curves, of a trap-free asymmetric single-carrier device with a V_{bi} of 0.5 V present as the shunt resistance

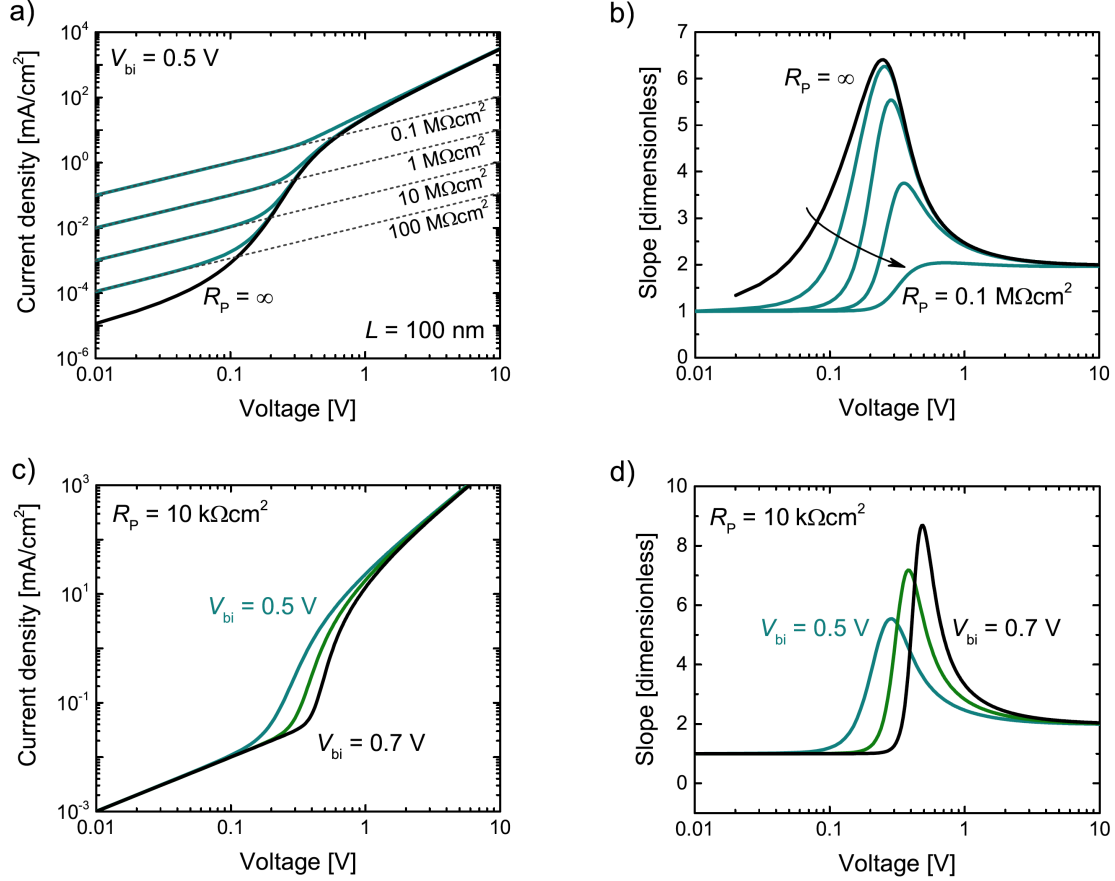


Figure 6.9: Drift-diffusion simulations: a) J - V curves of an asymmetric single-carrier device ($V_{bi} = 0.5$ V) with decreasing shunt resistance, i.e., increasing shunt current (from $R_p = \infty$ to $R_p = 0.1$ MΩcm²), and b) corresponding m - V curves. c) Simulated J - V curves with a fixed shunt resistance ($R_p = 10$ kΩcm²) with a varying V_{bi} from 0.5 V to 0.7 V, and d) corresponding m - V curves.

is lowered (the situation $R_p = \infty$ is when no shunt current is present). By comparing fig. 6.8a with fig. 6.9a it is seen that where the increase of the current of the asymmetric device without a shunt current is seen to increase exponentially on a log-log scale, the addition of a shunt current is acting to linearise the current density at low voltages. Consequently, if the shunt resistance is so low that it completely masks the space-charge limited current, the device is considered completely short-circuited, and the current across the device will be due to shunt pathways only. The linearisation of the current can also be seen from fig. 6.9b where the slope is seen to remain linear up to higher voltages. Additionally, the sharpness of the peak caused by the V_{bi} is seen to increase, and then decrease, while the magnitude of the peak is seen to decrease as the shunt resistance is decreased (the peak ultimately disappears when the current

is completely linear with voltage). From this, a very sharp peak can then be attributed to a combination of a large V_{bi} and the presence of a significant shunt current.

Given that the linear current regime is observed to voltage up to around 1 V in the experimental J - V curves (see fig. 6.6b), the linear currents at very low voltages can be described, in both forward and reverse bias, using Ohm's law (see the dashed line in fig. 6.6a) and a value for the shunt resistivity of $\rho_P = 18 \text{ M}\Omega\text{cm}^2$ can be extracted for the asymmetric device. Using this value for the shunt resistance, a fit with the sum of the V_{bi} equation (eq. 6.5) and Ohm's law (eq. 6.6) gave the fit seen in fig. 6.6d. Also, given that a deviation of the power-law dependence of the J - V curves away from $m = 2$ at high voltages is observed (fig. 6.6b), it is evident that the charge transport is governed by traps.

6.5.4 Numerical fitting results

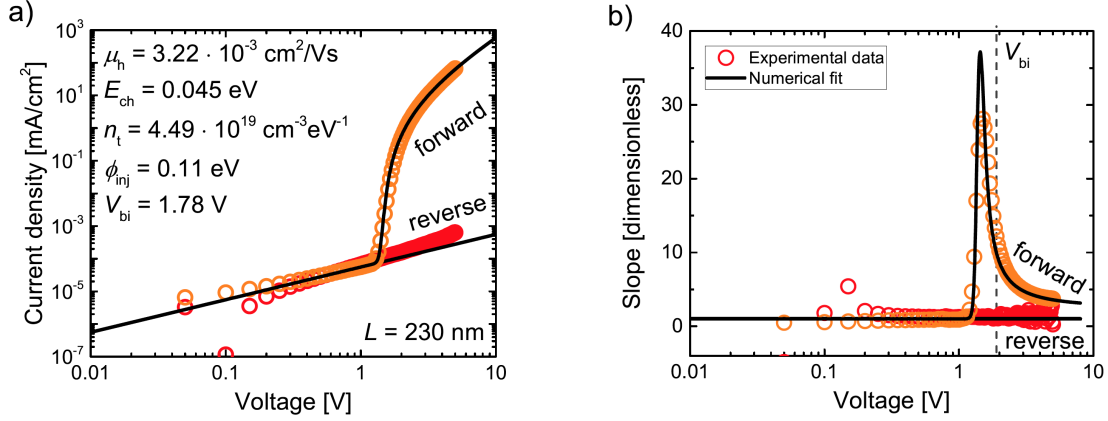


Figure 6.10: a) Numerical fits to the asymmetric SCLC J - V data allowing for traps, injection limitation and shunt currents. b) The fits to the J - V curves shown for the m - V curve.

We here show fits to the SCLC data using the numerical drift-diffusion solver, rather than analytical equations, allowing for both injection limitation and exponential tails. We fitted the shunt resistance to the (linear) reverse bias current (0 to -5 V). Subsequently, we allowed for the hole band-like mobility, μ_h , characteristic tail energy, E_{ch} , tail state density, n_t , and injection and extraction barrier heights, $q\phi_{inj}$ and $q\phi_{ext}$, to vary during the fitting process to the forward bias current (0 to 5 V).

Excellent fits to both the forward and reverse bias asymmetric J - V data are shown in fig. 6.10a and fits to the m - V data are shown in fig. 6.10b ($\rho_P = 18 \text{ M}\Omega\text{cm}^2$, obtained from fitting to the reverse bias current, and the device thickness were used as an input values). Since the J - V

curve has quite distinct landmarks, such as the low voltage regime extending to high voltages, and the very sharp transition to non-linear J - V behaviour, a confident fit could be obtained. The band-like hole mobility was found to be $\mu_h = 3.22 \cdot 10^{-3} \text{ cm}^2/\text{Vs}$, the tail characteristic energy was found to be $E_{\text{ch}} = 0.045 \text{ eV}$, the tail density was found to be $n_t = 4.49 \cdot 10^{19} \text{ cm}^{-3}\text{eV}^{-1}$, and the injection barriers were found to be $q\phi_{\text{inj}} = 0.11 \text{ eV}$ and $q\phi_{\text{ext}} = 1.89 \text{ eV}$, respectively, leading to a $V_{\text{bi}} = 1.78 \text{ V}$. The V_{bi} was found to give a similar value to the V_{bi} obtained from using eq. 6.5. The value for the V_{bi} is however much higher than expected from the literature values of the contact work functions. This difference is likely due to oxidation of the aluminium contact forming a thin aluminium-oxide layer at the contact/semiconductor interface[172]. If the MH equation was used to estimate the trap characteristics from our device data, it would give a much higher estimate of E_{ch} ($J \propto V^{l+1}$ with $l = E_{\text{ch}}/k_{\text{B}}T$) of 0.070 eV .

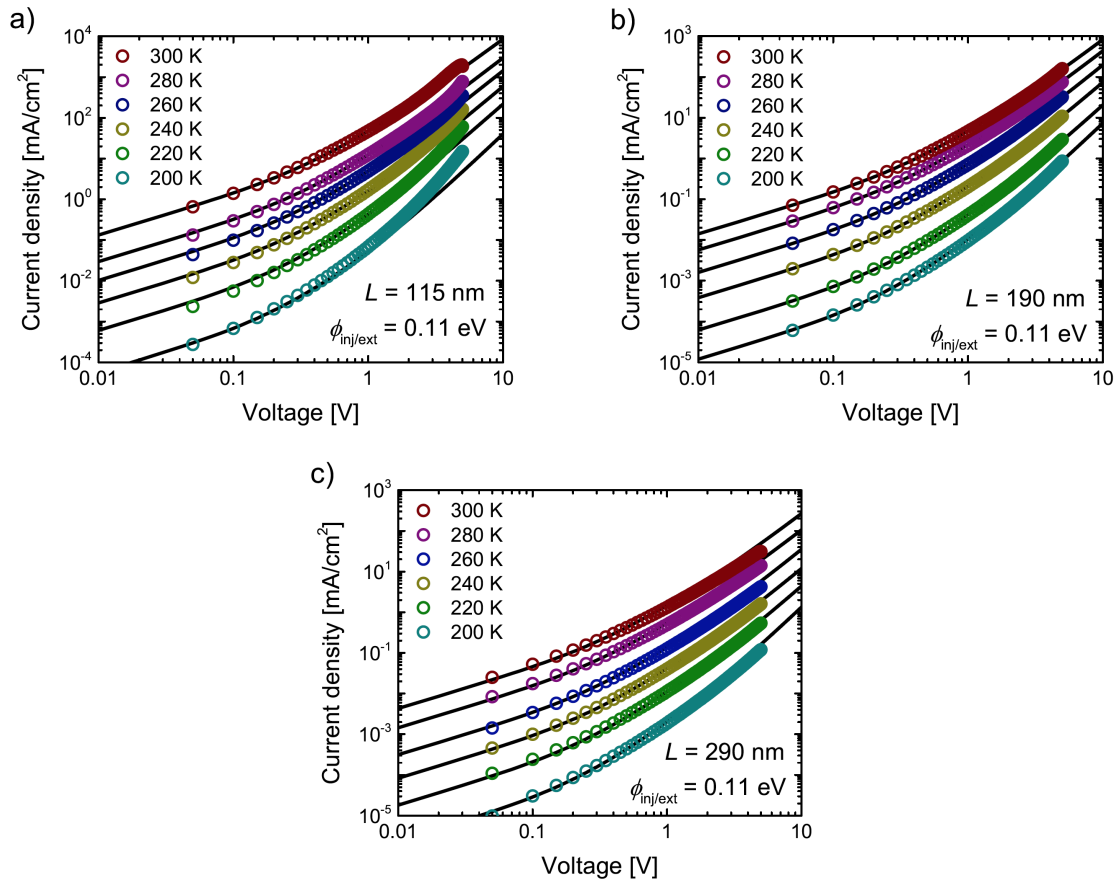


Figure 6.11: Experimental SCLC J - V curves, from symmetric hole-only devices, as a function of temperature (200 K to 300 K in steps of 20 K) along with fits with the drift-diffusion solver (solid lines): a) 115 nm, b) 190 nm, and, c) 290 nm. The fit results are shown in fig. 6.12.

Besides the data from the 190 nm symmetric hole-only device shown in fig. 6.7a, a 115 and

a 290 nm device was measured, and fitted, as a function of temperature. Figure 6.11a, b and c show the fits to the temperature series of the 115, 190 and 290 nm devices, with the inclusion of exponential tails and injection barriers as those used for the fits to the asymmetric data.

A convergence in the obtained mobility, trap characteristics and injection properties was found across all thicknesses and all temperatures. All obtained values are summarised in fig. 6.12a-i. Both the mobility and trap characteristics were found to be similar to the values obtained from the asymmetric device. The barrier heights for both injection and extraction were found to be 0.11 eV.

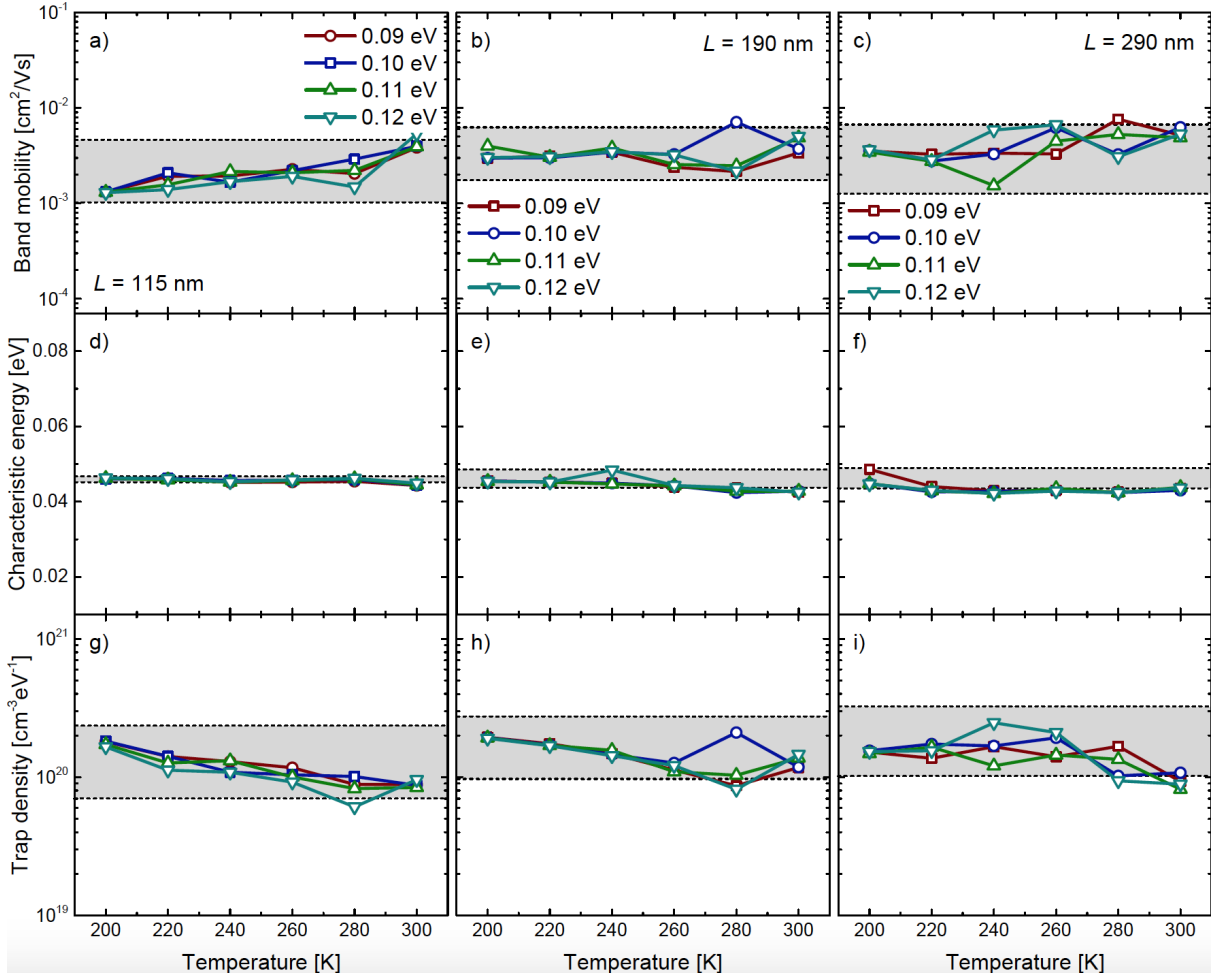


Figure 6.12: Fitting results to the SCLC temperature series of a 115 nm, 190 nm, and a 290 nm device: a-c) The band-like hole mobility, μ_h ; d-f) the characteristic tail energy, E_{ch} ; g-i) the tail density, n_t . All fit values are shown as a function of device temperature and injection barrier heights (symbols).

Figure 6.12a, d and g show the fitting results to the temperature series of a 115 nm device. The inclusion of injection barriers were needed in order to fit to the whole temperature series

without significant variation of both the band mobility, characteristic energy and the trap density. Minimal variation was obtained when an injection barrier between 0.09 eV and 0.12 eV was included. The best fits were obtained using injection barrier heights for both injection and extraction of 0.11 eV. Figure 6.12a shows the band hole-mobility for the 115 nm device as a function of temperature at different injection barrier heights. A slight increase of the mobility with temperature is observed. Figure 6.12d shows the obtained characteristic energy. Figure 6.12g shows the obtained trap density. Where the hole-mobility was seen to increase with temperature slightly, the trap density was seen to decrease with temperature (but with a factor of three or less). Figure 6.12b, e and h show the fitting results to the temperature series of a 190 nm device. Similar to the 115 nm case, the inclusion of injection barriers were needed in order to fit to the whole temperature series without significant variation of both the band-like mobility, characteristic energy and the trap density. Contrary to the 115 nm case, the 190 nm case does not show a significant increase of the mobility with temperature (see fig. Figure 6.12b). A slight decrease in the trap density was however observed with increased temperature as with the 115 nm case (but this time around a factor of two, as seen in fig. 6.12h). Figure 6.12c, f and i show similar results for the fits to a 290 nm device as was shown for a 115 nm and a 190 nm device. Similar to the 115 nm device, the mobility is seen to increase with temperature while the trap density is decreasing with temperature.

Figure 6.13a compares the hole mobility values obtained from fits with the numerical model to mobilities obtained by fitting with the MG law or the ME equation which does not consider traps to the same devices. Whereas a temperature-dependent mobility was obtained using analytical fits with the MG law and the ME equation, a temperature independent band-like mobility was obtained using numerical fits, when including traps and injection limitation. From the numerical model, the obtained charge-carrier mobility at room temperature (300 K) was found to be more than an order of magnitude higher than the effective mobility, and more than four orders of magnitude higher at 200 K. While the mobility returned by the numerical model is a band mobility, the mobility returned by the analytical equations represents the band mobility weighted by the effects of trapping and poor charge injection. The temperature dependence of the charge transport then originates from injection limitation along with de-trapping being a thermally activated process that becomes more difficult at lower temperatures, and not from a temperature dependent band mobility.

Figure 6.13b compares the temperature-independent band mobility with the mobility obtained from our derived analytical expression (eq. 6.16) and the effective mobility extracted from fitting with the MG law, modified by the ratio of the arithmetic mean of the total to free

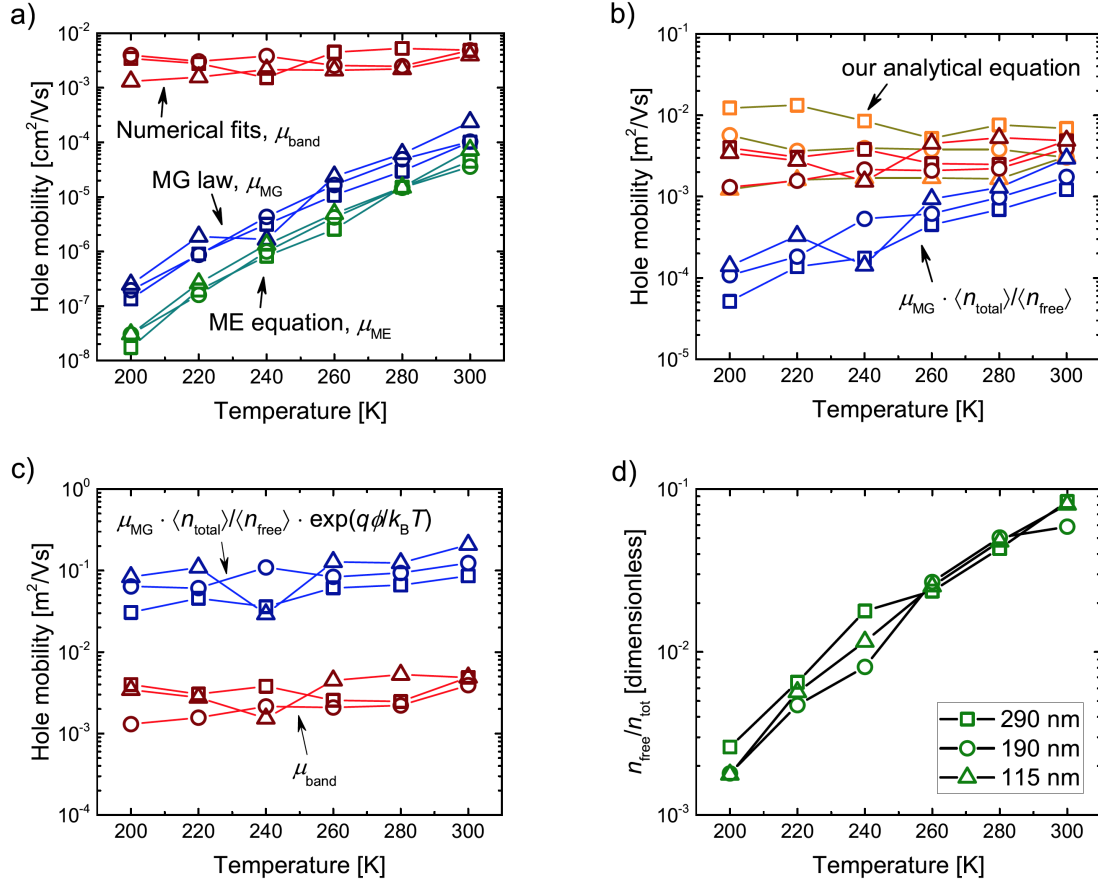


Figure 6.13: a) Hole mobilities from numerical fits and analytical fits to the symmetric SCLC temperature series. The set of various symbols refers to values inferred from devices with different semiconducting layer thicknesses: 290 (squares), 190 (circles) and 115 nm (triangles), respectively. b) Comparison of the band mobility with the effective mobility from the MG law modified by the ratio of total to free charge carriers and the mobility obtained from our derived analytical expression, eq. 6.16. c) Comparison of the band mobility with the MG mobility modified for both traps and injection limitation at the metal/semiconductor interfaces. d) the ratio of free to total charge carrier in the device. Calculated from simulations.

charge carriers obtained from the drift-diffusion simulations,

$$\mu_{\text{eff}} = \mu_{\text{MG}} \frac{\langle n_{\text{total}} \rangle}{\langle n_{\text{free}} \rangle}. \quad (6.20)$$

The calculations of the free to total charge carrier ratios, $\langle n_{\text{free}} \rangle / \langle n_{\text{total}} \rangle$, are shown in fig. 6.13d. Note that the modification of the MG mobility was only possible by simulating the densities of

free and trapped holes in the device. Thus, this modification would not be available if a purely analytical approach was used. The ratio, $\langle n_{\text{total}} \rangle / \langle n_{\text{free}} \rangle$, was evaluated at the same applied voltage as the MG law (the voltage at which $m = 2$). Good agreement is found between the mobility obtained from our analytical equation (eq. 6.16) and the mobility obtained from the numerical fits when the average value for the characteristic energy and trap density from the simulations, averaged over all thicknesses and temperatures, was used in the analytical equation ($n_t = 1.31 \cdot 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$ and $E_{\text{ch}} = 0.044 \text{ eV}$, respectively). Similar to fitting with the MH equation, in order to use eq. 6.16 for determining the mobility and trap characteristics, without any prior knowledge of either the mobility or trap characteristics, a thickness and temperature series should be analysed to reach a convergence of the obtained values (as was done here). Contrary to the excellent agreement between the values obtained using eq. 6.16 and the values obtained from the numerical calculations, the overall magnitude of the effective mobility from the modified MG law is seen to only approach the band mobility at 300 K.

Figure 6.13c compares the band mobility with the effective mobility now corrected for both trapping and a term describing injection limitation,

$$\mu_{\text{eff}} = \mu_{\text{MG}} \frac{\langle n_{\text{total}} \rangle}{\langle n_{\text{free}} \rangle} e^{\frac{q\phi_{\text{inj}}}{k_B T}}. \quad (6.21)$$

Interestingly, the temperature independence of this effective charge-carrier mobility is now comparable to that of the band mobility, however with the overall magnitude being an order of magnitude too high, showing that a simple *ad hoc* inclusion of injection limitation is not reasonable.

6.6 Conclusion

We investigated whether by allowing the charge-carrier band mobility, trap characteristics and injection barrier heights, is a better model for analysing SCLC J - V curves. We performed temperature and thickness dependent SCLC measurements on Spiro-OMeTAD in single-carrier devices and used a numerical drift-diffusion solver for the analysis of the J - V curves. We showed that a numerical fit could be obtained to the entire J - V curve measured from both a symmetric and asymmetric single-carrier devices made from Spiro-OMeTAD. We determined the charge-carrier mobilities and trap densities for both the symmetric and the asymmetric devices to agree within a factor of less than two. Moreover, the hole band mobility obtained from numerical fitting was more than an order of magnitude higher ($4.56 \cdot 10^{-3} \text{ cm}^2/\text{Vs}$) than when determined using the MG law ($2.30 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$) at room temperature (300 K) and

more than four orders of magnitude higher at 200 K. We further showed that, where simple analytical equations require a temperature-dependent mobility to achieve fits, either using a more physically correct analytical model accounting for traps, as the novel analytical model we presented in this paper, or using a numerical model, will give rise to a more physically correct temperature-independent band mobility whilst simultaneously yielding information about trap characteristics. Our analysis and results highlight the importance of: showing, and using a numerical model to fit to, the entire J - V curve while accounting for traps, the built-in potential and injection limitation; or to use a more sophisticated analytical model which can correctly account for traps, such as eq. 6.16.

Chapter 7

The Impact of Fullerene Oxidation on the Stability of Organic Solar Cells

7.1 Abstract

In this chapter, we evaluate the impact of the degree of photo-oxidised phenyl-C61-butyric acid methyl ester (PCBM), oPCBM, on the performance in terms of the cells power conversion efficiency (which is determined from its J_{SC} , V_{OC} and fill factor, as seen in fig. 7.1) and stability of polymer:fullerene solar cells using the benchmark polymer, PCDTBT (see fig. 7.2).

We found that a minor fraction of oPCBM in the PCDTBT:PCBM films, induced by illumination of the PCBM solution for a few minutes in air, can result in drastic degradation of device performance. We systematically investigated the effect on the charge-transport mechanisms by introducing minor fractions of oPCBM to an otherwise un-degraded PCDTBT:PCBM solution (0.2 to 3.6 wt%), and we used this to explain the losses in device efficiency. We identified the effects of photo-oxidation of PCBM on its chemical structure, and connect this to specific changes in its electronic structure, which significantly alter the electron transport behaviour. We explain the effect of photo-oxidation on solar cell device J - V characteristics, electron mobility and density of states with the same model of photo-induced defects acting as trap states. For completion, the study extends to include other benchmark polymers such as P3HT, PTB7 and PCE10 (see fig. 7.2), showing similar results.

The highly photo-active nature of fullerenes, and the strong correlation of the degree of oPCBM to the decrease in device performance suggest that photo-oxidation must be taken into account during the processing of fullerene-based electronic devices, and that the fullerenes

themselves must ultimately be replaced if organic solar cells are to be commercialised.

The work presented in this chapter was performed under the supervision of Dr. Zhe Li, Prof. Jenny Nelson, Dr. Wing Tsoi, and Prof. James R. Durrant. The work shown in this chapter was conducted by Dr. Harrison Lee, Ms. Beth Rice and the author. The author fabricated a large volume of the single-carrier devices, analysed all the SCLC data and ran all the drift-diffusion simulations of both the single-carrier devices and the solar cells. A version of this study called "The Role of Fullerenes in the Environmental Stability of Polymer:Fullerene Solar Cells" was published in *Energy & Environmental Science* in January 2018[176].

7.2 Introduction

7.2.1 Background and motivation

A number of challenges exist that must be overcome to achieve the commercialisation of organic solar cells. Of particular importance is the environmental stability of such cells (as a solar cell is exposed to a number of extreme weather conditions such as wind, rain and heat). Organic solar cells can potentially be cheaply produced through roll-to-roll processes, but stability is important to ensure long lifetimes of the modules. Whilst organic solar cells have shown encouraging improvements in performance with efficiencies increasing from 3% to over 12% in the last decade[177], commercialisation has been limited by their relatively short operating lifetimes. Reports have shown that exposure to ambient atmospheric conditions typically results in fast decrease in device performance, especially when the cells are exposed to light[178, 179]. A strategy to address this challenge is to use device encapsulation. Encapsulation creates a physical barrier for the diffusion of oxygen into the device, thereby hindering the oxygen induced degradation reaction[180]. However, encapsulation significantly increases the fabrication cost and hence reduces the commercialisation prospects. For this reason, it is important to understand the degradation processes of the components used in the solar cells.

As explained in chapter 1, organic solar cells typically comprise of a donor polymer (being the main absorber) and a fullerene derivative acceptor (see fig. 7.1). So far, most studies have been focused on the environmental stability of the polymer part of the cell[180, 181, 182, 183]. However, fullerene derivatives have been known to be sensitive to photo-induced reactions since the early 1990s[184, 185]. The fullerene derivative, PCBM (see fig. 7.2), can form covalent intermolecular C-C bonds under UV or visible illumination in inert atmosphere. This can lead to the formation of dimers or higher oligomers, which has been correlated with loss in OPV device performance[186, 187]. Furthermore, PCBM, and other fullerene derivatives, have been shown to

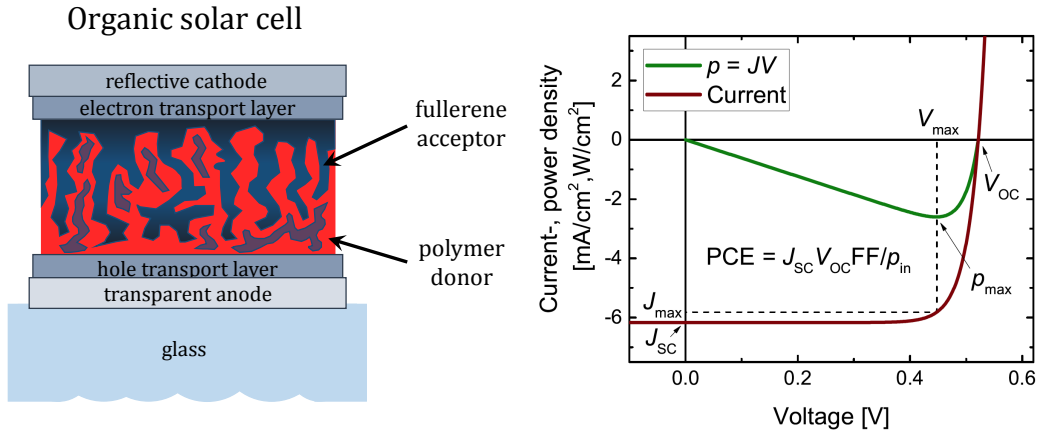


Figure 7.1: Left: Schematic of an organic solar cell, showing the intermixed donor and acceptor phases. Right: Ideal solar J - V curve, showing the V_{OC} , the J_{SC} , the maximum power point, and the squareness of the curve also called the fill factor.

undergo photo-oxidation when in the presence of oxygen, with the two most commonly observed products being epoxide and carbonyl groups forming on the fullerene cage[188]. While the photo-oxidation of fullerene derivatives has previously been investigated, and a small number of studies has shown a detrimental effect of device performance[189, 190], little has been reported on its exact mechanism involved and its direct effect on charge-transport and device performance, with a few groups suggesting that formation of trap states is the main culprit[191, 192].

7.2.2 Research question

We set out to evaluate the impact of the degree of oxidised PCBM (oPCBM) on the performance in terms of the cells power conversion efficiency and stability of PCDTBT:PCBM solar cells. We will systematically investigate the effect of introducing minor fractions of oPCBM to an otherwise un-degraded PCDTBT:PCBM solution (0.2 to 3.6 wt%) using matrix-assisted laser desorption/ionization mass spectrometry and space-charge-limited current measurements. We aim to identify the effects of photo-oxidation of PCBM on its chemical structure using quantum chemical calculations, and connect this to specific changes in its electronic structure, which significantly alter the electron transport behaviour. We then investigate whether solar cell device response can be modelled using the information gained from the mass spectrometry and charge-transport measurements.

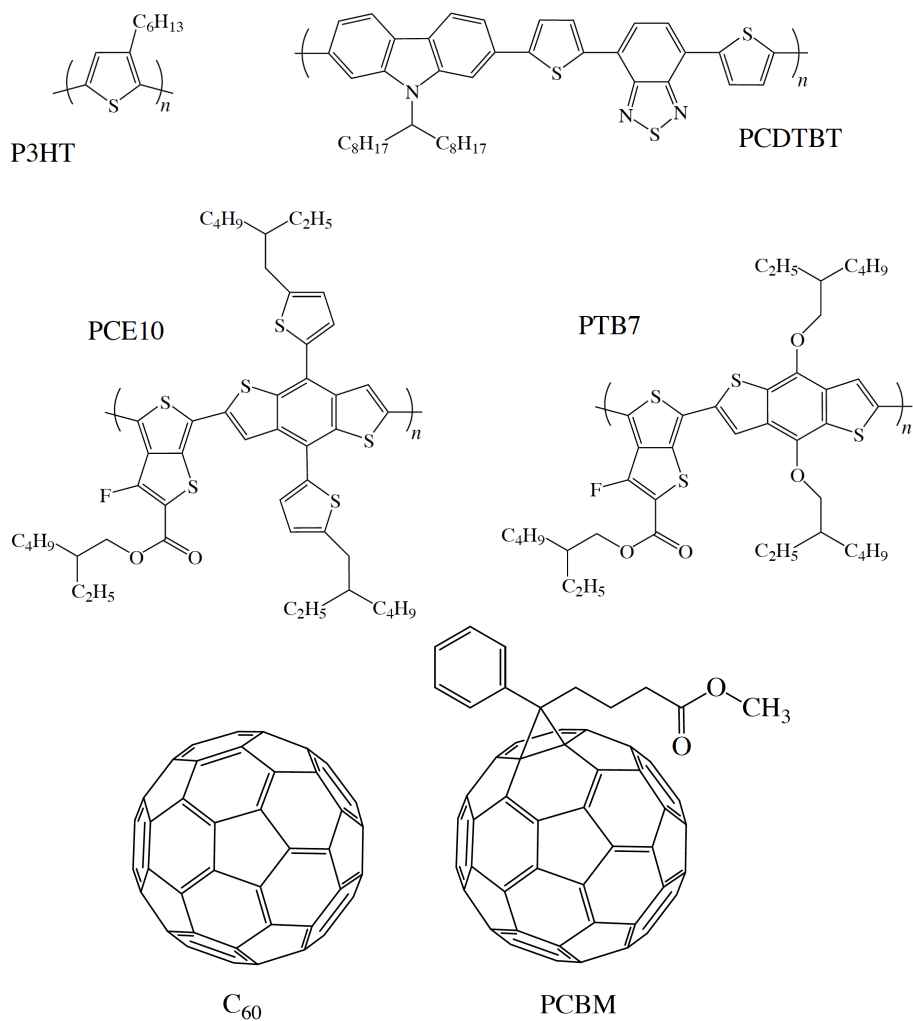


Figure 7.2: The studied materials: The highly studied polymers, P3HT and PCDTBT, the most commonly used acceptor material, PCBM (and its unfunctionalised mother, C₆₀), and the high efficiency benchmark polymers, PTB7 and PCE10.

7.2.3 Authors contributing to this chapter

We here briefly state who performed the measurements presented in this thesis. The solar cells were fabricated and measured by Dr. Harrison Lee, who also performed the mass spectrometry measurements. Beth Rice performed the quantum mechanical calculations. The author fabricated and measured the single-carrier devices together with Dr. Harrison Lee. The author analysed the single-carrier device data and simulated solar cell device response based on the information yielded from the single-carrier devices.

7.3 PCBM degradation results

We here systematically study the degradation route of PCBM and the resulting chemical products using matrix-assisted laser desorption/ionization mass spectrometry. We then calculate the electronic structures of the proposed chemical species and show that a fraction of oPCBM can lead to electron traps, due to their lower energetic states.

7.3.1 Solution and film degradation

We degraded the PCBM molecules in a controlled manner, with two routes being used for the degradation of the PCBM. The two approaches should yield slightly different degradation uniformities throughout the films, and are as follows:

- (i) Degradation of the PCBM solution prior to film formation and device fabrication, by exposing the PCBM solution to AM1.5G solar simulated light and ambient air. This degradation approach ensures an approximate uniform distribution of defects throughout the solution and hence the film.
- (ii) Film formation using a non-degraded solution, and subsequent degradation of the blend films using AM1.5G solar simulated light and ambient air. This approach should give an approximate exponential decrease of defects from the top of the device which was exposed to light and air (since the absorption should approximately follow the Beer-Lambert law).

We degraded PCDTBT:PCBM blend films fabricated on PEDOT:PSS coated ITO glass substrates under AM1.5G solar simulated light in dry air (with a relative humidity of $\approx 30\%$) for different periods of time. PCBM molecules in solution were degraded under AM1.5G solar simulated light for 72 hours in dry air or nitrogen.

7.3.2 MALDI-ToF

We carried out mass spectrometry (MS) on the un-degraded and degraded PCBM samples to investigate the chemical composition of the products of PCBM photodegradation.

MS is a technique used to help understand the chemical structure of a molecule, by ionizing the chemical species and sorting the resulting ions based on their masses. During a typical mass spectrometry procedure, a sample, which may be a solid, a solution/liquid, or a gas, is ionized. This ionization may cause some of the molecules in the sample to break up into charged fragments. The fragments are then accelerated through an electric or magnetic field, thereby separating them according to their mass-to-charge ratio. The charged fragments are ultimately

detected by a mechanism capable of detecting charged particles, such as an electron multiplier. The resulting mass spectrum can then ideally be identified by correlating the detected masses to known masses through a characteristic fragmentation reference pattern.

Matrix-assisted laser desorption/ionization (MALDI) is a particular type of mass spectrometry ionization technique which uses a laser sensitive matrix, containing the molecules to be investigated. This is used in order to create ions from large molecules with minimal fragmentation[193, 194]. MALDI is usually applied to large organic molecules, such as polymers, dendrimers and other macromolecules, which tend to fragment into much smaller pieces when using conventional ionization methods (MALDI minimises fragmentation, making analysis less combersome). The methodology of the MALDI measurement is usually a three-step proces[195]:

- (i) The sample to be investigated is mixed with a suitable matrix material and applied to a metal plate.
- (ii) A pulsed laser is set to irradiate the sample, triggering ablation (removal of material from the surface if an object by vaporization) of the sample and matrix material.
- (iii) The measured molecules are finally ionized by being either protonated or deprotonated in the hot plume of ablated gases. The molecules are then accelerated into a mass spectrometer and analysed.

The time-of-flight (ToF) mass spectrometer is widely used with MALDI. The ToF measurement procedure is ideally suited to the MALDI ionization process since it allows for the use of a pulsed laser, firing individual pulses, rather than using a continuous laser source (allowing for very high laser powers which is ideal for ablation). Furthermore, the ToF spectrometer is usually equipped with an electric field mirror that reflects ions, doubling the ion flight path, and thereby increasing the resolution.

In MALDI-ToF, ions are accelerated by an electric field of known strength, F . This acceleration results in a given ion having the same kinetic energy as any other ion that has the same charge ($2QF = mv^2$), where Q is the total charge of the measured species, and v is the velocity, with v then depending on the mass-to-charge ratio, m/Q (heavier ions with the same charge as a light ion will reach a lower velocity, and ions with more charge will have a higher velocity compared to an ion with equal weight but with less charge). The time that it subsequently takes for the ions to reach the detector (at a known distance from the sample) is then measured and plotted. The time of flight will then depend on v , and therefore is a measure of its m/Q ratio. When presenting data, it is common to use the dimensionless m/z , where z is the number

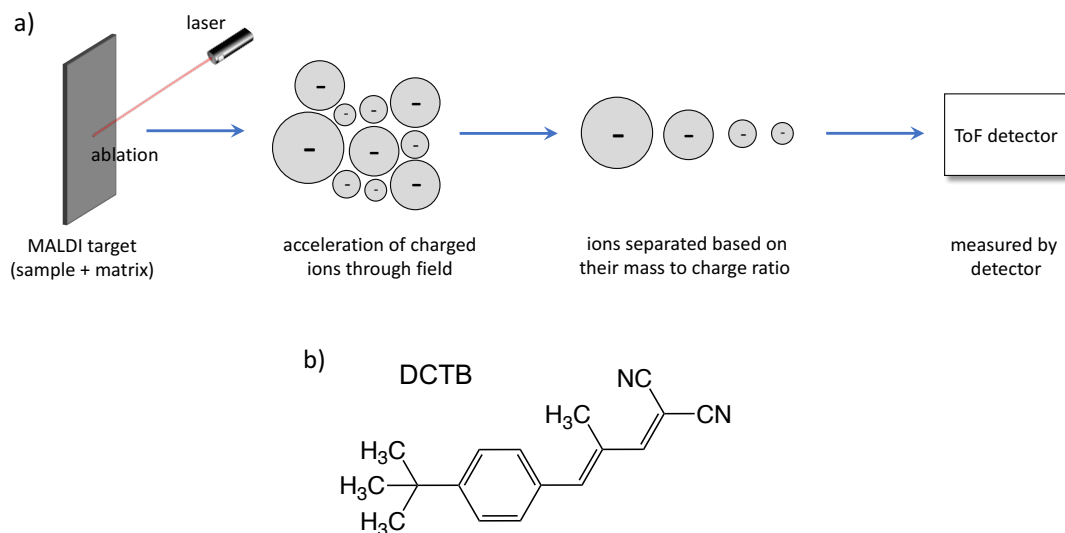


Figure 7.3: a) Schematic of the MALDI-ToF experiment: A powerful laser is used to ablate the sample together with the matrix; the formed charged ions are then accelerated through a field towards the detector; the ions get separated due to their relative mass and magnitude of charge; the ions hit the detector and the spectrum is plotted as a function of mass-to-charge ratio, m/Z . b) The matrix material mixed with PCBM to make the MALDI-ToF samples, DCTB.

of elementary charges q on the ion ($z = Q/q$). This quantity is informally called the mass-to-charge ratio, even though it more accurately represents the ratio of the mass number of the molecule or fragment and its charge, Z . From the ratio m/z , and known experimental parameters, MALDI-ToF can help identify the ions being measured. The MALDI-ToF experiment is shown schematically in fig. 7.3a.

We used the following procedure for the MALDI-ToF measurements (performed by Dr. Harrison Lee): Un-degraded and degraded PCBM was dissolved in chlorobenzene, in separate solutions, at an approximate concentration of 1 mg/mL (the blend samples, PCDTBT:PCBM, for the measurements were prepared by re-dissolving the blend films after degradation). The matrix material used for the MALDI measurements, trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was dissolved in chlorobenzene at a concentration of 20 mg/mL (see fig. 7.3b). The sample and matrix solutions were blended such that the matrix compound was ≈ 250 -1000 fold in molar excess, with 1 μ L of sample solution to 49 μ L of matrix solution. For each blend mixture, approximately 0.5 μ L of solution was applied onto the MALDI target and left to dry in air. The MALDI-ToF spectra were acquired using negative-reflectron

mode (a mass reflectron is a type of ToF mass spectrometer) using an ultrafleXtreme mass spectrometer (Bruker Daltonics, Bremen, Germany), equipped with a Smartbeam-II Nd:YAG laser (with a laser wavelength of $\lambda = 355$ nm which is suitable for ablation of PCDTBT). Data was acquired using flexControl software v3.4, while post-acquisition processing of the data was performed by flexAnalysis software v3.4 (by Dr. Harrison Lee at Swansea University). PCBM and oPCBM were observed as negatively charged ion species. The mass spectra are shown in figs. 7.4a-d, with fig. 7.4a being the mass spectrum for the un-degraded PCDTBT:PCBM blend, figs. 7.4b and c being the spectra of re-dissolved films of degraded PCBM, and fig. 7.4d being the spectrum of a solution degraded PCBM film.

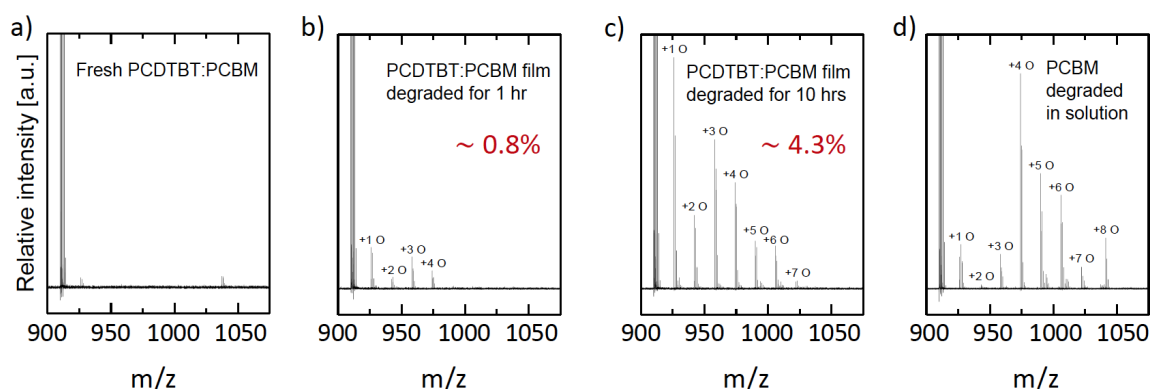


Figure 7.4: Negative ion mode MALDI-TOF measurements of a) fresh un-degraded PCBM; b) PCDTBT:PCBM blend thin film degraded for 1 hour under AM1.5G in air; c) PCDTBT:PCBM blend thin film sample degraded for 10 hours under AM1.5G in air; and d) neat PCBM degraded in solution.

By comparing fig. 7.4a with 7.4b it is seen that oPCBM species (with up to 4 oxygen atoms) were formed upon degradation of the blend sample when exposed to light and air for 60 minutes. By increasing the illumination duration to 10 hours, the degree of oxidation is further increased (up to 7 oxygen atoms) as is seen in fig. 7.4c. Analysis of the C_{12} -isotopic peaks gives a total of 0.8% oPCBM in the PCDTBT:PCBM blend film after 60 minutes of degradation, which is further increased to 4.3% after 10 hours of degradation.

From the MALDI-ToF analysis it is evident that PCBM species containing extra oxygen are present in the degraded samples. It is however not possible to directly determine which chemical species are present. This is however in agreement with previous studies proposing epoxide and carbonyl defects[188].

7.3.3 Degradation mechanism and energy level calculations

With clear evidence of oPCBM in the PCDTBT:PCBM thin films observed from MALDI-ToF, we here seek to confirm and/or establish the microscopic mechanism for the reduction in device performance upon degradation. For this, we studied the nature of the chemical defects formed upon photo-oxidation. It will be shown later, that the insight provided by this part of the study is consistent with the results obtained from SCLC measurements, and allows us to qualitatively reproduce, through simulations, the observed behaviour of experimental solar cells.

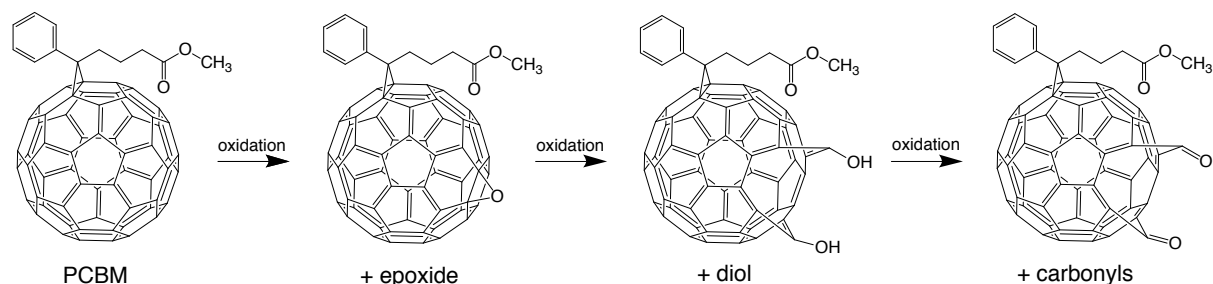


Figure 7.5: The degradation process proposed by Xiao *et al*[188]. From left to right shows increasing degree of oxidation: neat PCBM; PCBM with an epoxide defect positioned randomly on the fullerene cage; PCBM with an intermediate diol (two alcohol) defect causing the cage to split open; PCBM with two carbonyl defects. The position of the defect was chosen arbitrarily in the schematic.

The effect of photo-oxidation of the PCBM on their HOMO and LUMO levels was explored using electronic structure calculations of oxidation products, namely PCBM containing epoxide, diol and carbonyl defects (with intermediate diol defects needed to form carbonyls), following the reported oxidation mechanism proposed by Xiao *et al*[188]. This oxidation mechanism proposes that epoxides form on the PCBM cage, which turns into an intermediate diol defect and eventually forms carbonyls upon further oxidation (see fig. 7.5).

We carried out quantum chemical calculations on the defect structure in order to evaluate their effect on electronic processes and to help model the effect of degradation on electronic properties (the calculations were performed by Beth Rice). For each type of defect, we identified all isomers with defects across two six-membered rings, and then calculated the HOMO and LUMO energies as well as the total energy of the species using the delta-SCF method, DFT and TD-DFT (see fig. 7.5). Several oxidised species with multiple defects (like two epoxides, or an epoxide and a carbonyl) were included in the study, for completeness. All the calculations were performed using B3LYP level of theory with the 6-31g* basis set. The TD-DFT calculations

yielded the excitation energies, where the first excited state is taken to be added to the Kohn-Sham HOMO energy to obtain the LUMO energy. For each used method, the differences in HOMO and LUMO energies, relative to those of un-degraded PCBM, were similar.

The different isomers (of degraded PCBM containing epoxides, diols and carbonyls) are included in proportion to their thermodynamic probability of occurrence, which is calculated using a Boltzmann average of the total energy for the neutral species. For each defect type, the average HOMO and LUMO energies were then calculated. The oxidised PCBM species with the lowest total energy tend to have defects close to the phenyl butyric acid methyl ester side-chain.

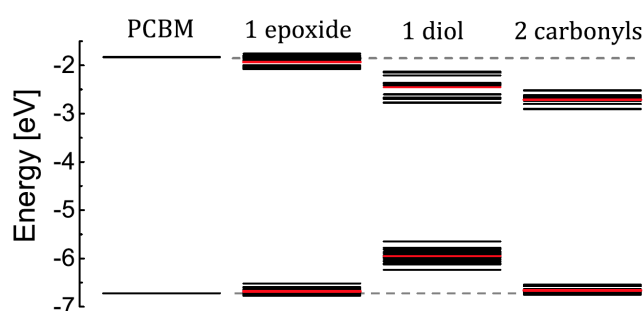


Figure 7.6: From left to right: HOMO and LUMO energies (calculated using a delta-SCF method) for un-degraded PCBM, PCBM with one epoxide defect, PCBM with one diol defect and PCBM with two carbonyls defects. The different energies correspond to different possible positions of the defects on the fullerene cage. Boltzmann averages, based on total energy calculations, are given by the red lines. The chemical structures were shown in fig. 7.5.

The LUMO levels for the oPCBM are deeper in energy (relative to the vacuum level) than for un-degraded PCBM for almost all defect types (especially in the case of carbonyl defects). The effect of degradation on the energy level of the HOMO, however, is negligible for the epoxide and carbonyl species, but not for the diol defect species. Due to the relative change of the LUMO levels (deeper), it is expected that the oxidised species introduce electron trap states, which in return will affect electron transport. On the contrary, since the HOMO levels remained relatively unchanged (it is expected that the diol defects quickly further oxidise to carbonyls), the effect on the hole transport is expected to remain relatively unchanged, and can therefore be approximately ignored (also, the hole transport is expected to occur through the polymer phase in a uniform polymer:fullerene blend and not through the fullerene so it is unlikely to influence the electrical response of the solar cell device).

From the above calculations, it is expected that the distribution of electron trap states to extend relatively deep (several tenths of an eV) into the band gap. The shape of the total density of trap states (the sum and broadening of all calculated species) is, however, difficult to predict precisely, since the number of different defect types is not known (they were here simply calculated as the thermodynamic average). The epoxide and carbonyl species would most likely give rise to a broadening around the un-degraded PCBM LUMO energy along with some deeper trap states. Additionally, the overall density of defect states is expected to increase with prolonged degradation of the PCBM, again making it difficult to predict the relative DOS, and hence the superposition, of the un-degraded and degraded PCBM.

7.4 Experimental results

With the expectation, from the MALDI-ToF measurements (performed by Dr. Harrison Lee) and the first principle calculations (performed by Beth Rice), that degradation of PCBM primarily gives rise to electron traps, thereby hindering electron transport, solar cell and electron-only devices were studied. Solar cells were studied to directly observe the effect of PCBM degradation on the solar cell performance and single-carrier devices were studied to observe the effect of PCBM degradation on the charge-transport characteristics and whether this effect could explain the effect on solar cell device performance.

7.4.1 Single-carrier and solar cell device fabrication

The two types of devices were fabricated in two different locations using two different recipes: the solar cells were fabricated at Swansea University by Dr. Harrison Lee, whereas the single-carrier devices were fabricated both at Swansea University by Dr. Harrison Lee and at Imperial College London by the author. Even though the devices were fabricated by two different people, there was only a slight difference in the fabrication procedures. The results are assumed to be fully comparable.

Solar cells

ITO glass substrates were cleaned using ultrasonication in acetone, and subsequently in IPA, for 10 minutes, respectively, and the substrates were subsequently treated with oxygen plasma. The hole selective contact polymer blend, PEDOT:PSS was spin cast onto plasma treated ITO substrates at 4000 rpm for 40 s, followed by thermal annealing at 150°C for 10 minutes. Both the polymer donor, PCDTBT, and the fullerene acceptor, PCBM, were co-dissolved in CB with a total concentration of 18 mg/ml for over 12 hours in a 1:2 wt% polymer:fullerene blend ratio.

The blend solution was spin cast onto the ITO/PEDOT:PSS coated substrates in air, resulting in an active layer thickness of ≈ 70 nm. Subsequently, a 30 nm thick Ca layer and a 100 nm thick Al layer were thermally evaporated onto the blend layer under vacuum. The devices were encapsulated by glass slides, using an epoxy glue, in a nitrogen filled glovebox prior to testing. The solar cells had the following device architecture: glass/ITO/PEDOT:PSS/blend/Ca/Al/glass. The device areas were slightly different from the areas of the devices shown in chapter 6, and define an active area of 0.15 cm^2 . We measured the J - V curves using a Keithley 2400 SourceMeter under AM1.5G illumination and a Newport 92193A-1000 solar simulator with a light intensity of 90 mW/cm^2 .

Single-carrier devices

Similar to the devices presented in chapter 6, ITO covered glass substrates were cleaned using ultrasonication in acetone, and subsequently in IPA, for 10 minutes, respectively. Electron selective titanium dioxide (TiO_2) films were deposited onto the ITO by spin casting of a precursor solution containing 70 μL titanium isopropoxide, 55 μL ethanolamine and 1 mL 2-methoxyethanol. The substrates were sintered in an oven for 1 hour at 500°C . The resulting TiO_2 films were approximately 20 nm thick. TiO_2 is widely used as an electron transport layer in dye-cells[196, 197, 198], has been used as an electron selective contact to PCBM in inverted organic solar cell structures[199, 200, 201], and has even been used as the electron accepting phase in organic/inorganic hybrid solar cells [202]. The energy levels for TiO_2 vary in the literature[203, 204].

Un-degraded and degraded PCBM solutions were spun onto the substrates with a target film thickness of around 80 nm for all solutions. This was done in order to ensure the J - V curves are qualitatively comparable to each other, and directly comparable to the fabricated solar cells. Subsequently, a 30 nm thick calcium (Ca) layer and a 150 nm thick aluminium (Al) layer were thermally evaporated onto the films under high vacuum, which act as electron selective contact (Ca has a work function of around 2.9 eV). The resulting electron-only device had the following device architecture: glass/ITO/ TiO_2 /PCBM:oPCBM/Ca/Al. The device areas were of similar size to the devices studied in chapter 6 ($\approx 0.045 \text{ cm}^2$). We measured the current through the devices using a Keithley 236 Source Measure Unit. The devices were both stored and measured in the dark under inert atmosphere (N_2). Representative J - V curves are shown in fig. 7.9.

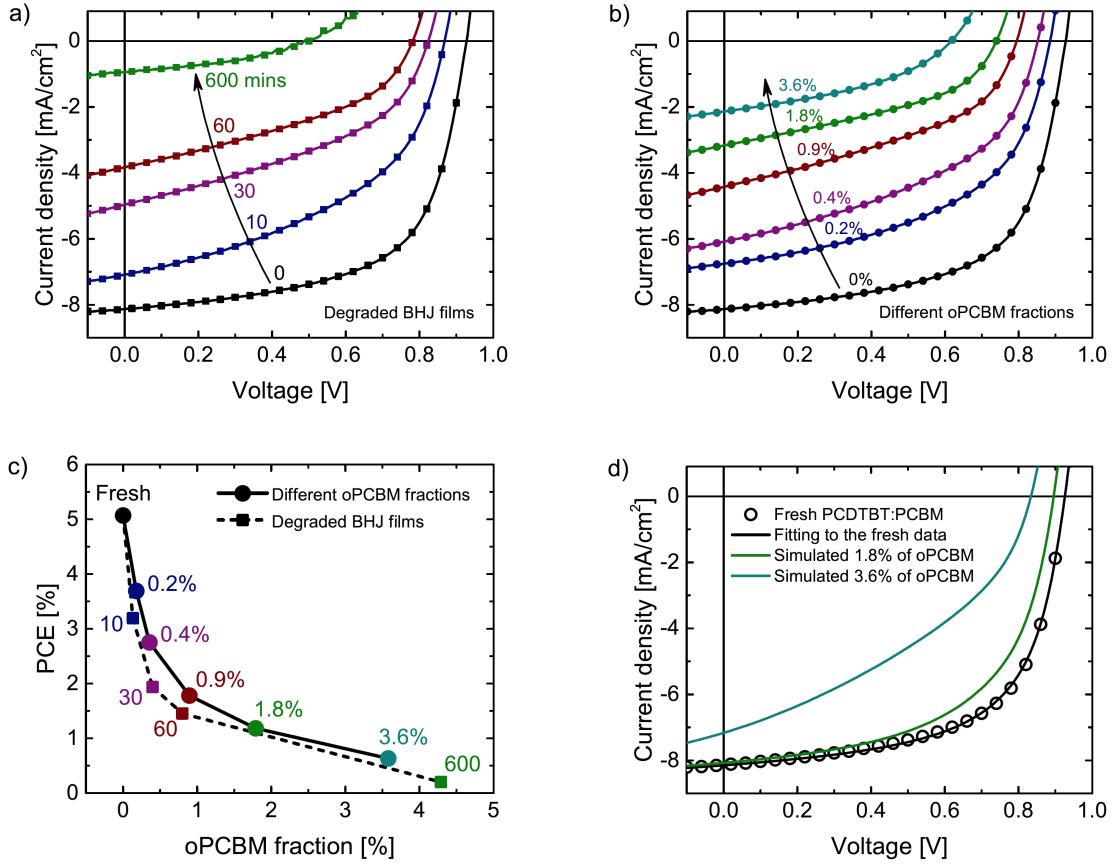


Figure 7.7: Experimental and simulated solar cell J - V characteristic: a) PCDTBT:PCBM devices with different degradation times under solar simulated light (in air), before top electrode deposition; b) PCDTBT:PCBM blends with different fractions of oPCBM added prior to film processing; c) comparison of PCE loss as a function of oPCBM fraction for the two sets of devices; and d) experimental (open circles) and simulated J - V characteristics for fresh PCDTBT:PCBM (black) and devices with increasing fraction of oPCBM, reconstructed from the mobilities, trap energies and trap densities obtained from the SCLC analysis (see table 7.3).

7.4.2 Solar cell characteristics

We investigated the decrease in performance of solar cells due to degradation. Figure 7.7a shows J - V characteristics of typical PCDTBT:PCBM solar cell devices having undergone different durations of degradation after film formation (but prior to contact evaporation). With 10 minutes of degradation, a loss in the PCE of more than 40% was observed. This is seen to be due to a simultaneous decrease in J_{SC} , V_{OC} and fill factor. After 60 minutes of degradation, a loss in PCE of more than 70% is observed, relative to the un-degraded devices. Devices exposed

to air in the dark did not show any sign of degradation, which is a clear indication that the degradation mechanism is driven by the combination of light and air.

Figure 7.7b shows the solar cell characteristics of devices with a fraction of oPCBM mixed with un-degraded PCBM in blends with pristine PCDTBT, and shows a similar trend in the J - V characteristics as observed in fig. 7.7a. As described above, the second round of devices were prepared in such a way as to isolate the impact of PCBM degradation. A comparison of the resulting PCE for the devices shown in figs. 7.7a and b is shown in fig. 7.7c. From the MALDI-ToF data it was estimated that a PCBM solution degraded for 72 hours contained 3.6% of oPCBM (which was used to directly compare the samples which were degraded after film formation with the devices containing pre-degraded PCBM). For that reason, fig. 7.7c shows that the main reason for device performance loss, is due to degradation of the PCBM molecule, and not due to degradation of the polymer. The solar cell characteristics are summarised in table 7.1.

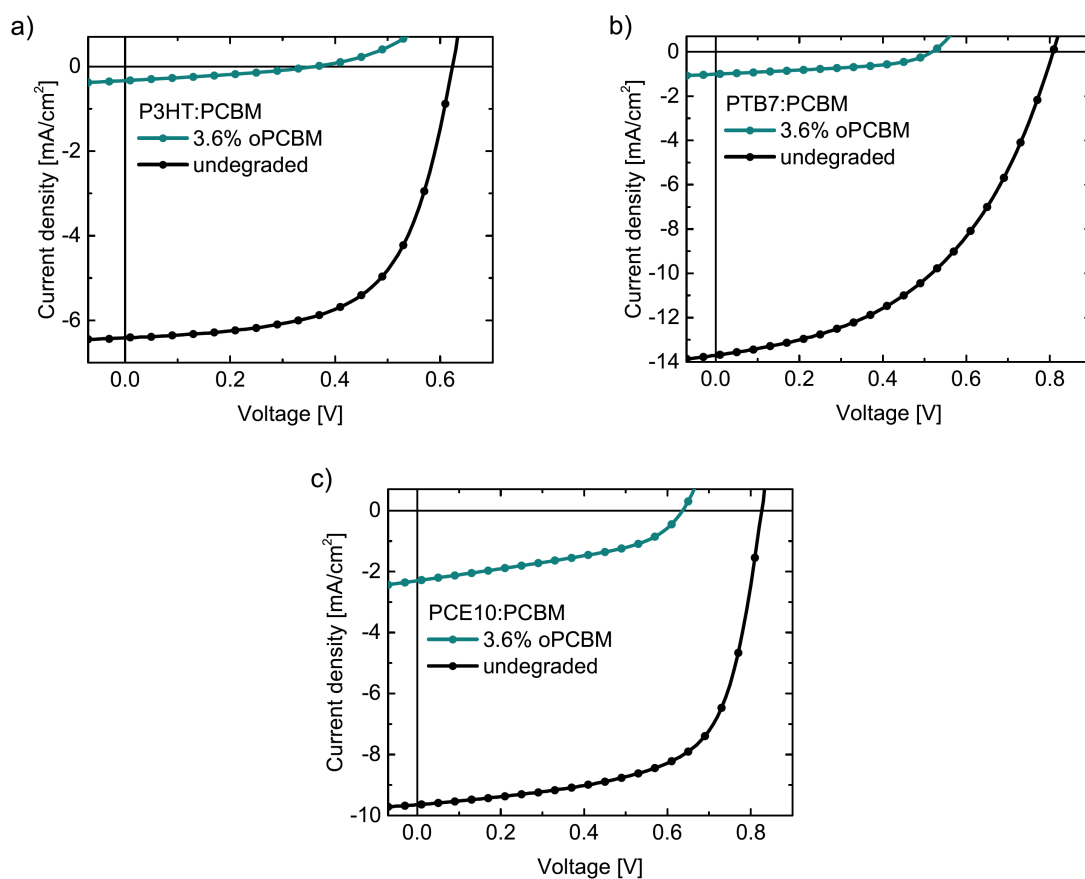


Figure 7.8: J - V characteristic of devices using other OPV benchmark polymers as the donor: a) P3HT, b) PTB7, and c) PCE10 in blends with fresh PCBM and degraded PCBM (w. 3.6% of oPCBM).

Table 7.1: Summary of J - V characteristics with and without device degradation.

Degradation of PCDTBT:PCBM films				
Degradation time [min.]	J_{SC} [mA/cm ²]	V_{OC} [V]	fill factor [%]	PCE [%]
0	8.13	0.928	61.5	5.01
10	7.09	0.868	46.5	3.19
30	4.96	0.823	42.4	1.93
60	3.83	0.782	40.5	1.35
600	0.95	0.488	39.5	0.20

Degradation of PCBM solutions				
oPCBM content [%]	J_{SC} [mA/cm ²]	V_{OC} [V]	fill factor [%]	PCE [%]
0	8.13	0.928	61.5	5.01
0.2	6.76	0.885	51.4	3.69
0.4	6.08	0.852	45.7	2.85
0.9	4.42	0.795	42.2	1.78
1.8	3.17	0.740	42.0	1.18
3.6	2.14	0.617	39.8	0.63

Exposure of PCDTBT:PCBM films to oxygen in the dark				
Exposure time [min.]	J_{SC} [mA/cm ²]	V_{OC} [V]	fill factor [%]	PCE [%]
0	8.13	0.928	61.5	5.01
60 (different sample)	7.73	0.932	64.5	5.18

To investigate the generality of this effect, we further extended our studies to blends with other benchmark OPV polymers, namely P3HT and PTB7 and PCE10, which exhibited qualitatively similar effects (see fig. 7.8). From figs. 7.7 and 7.8 it is apparent that the presence of oPCBM in the blend films has a drastic impact on the performance of polymer:fullerene solar cells. This extended part of the work was performed by Dr. Harrison Lee.

7.4.3 Experimental SCLC and fitting results

We here investigate whether the reduction in solar cell performance can be explained by the change in charge-transport when oxidised species are added to the PCBM. We first measured SCLC on the electron-only devices discussed above, made from PCBM solutions with different fractions of oPCBM (0%, 0.18%, 0.72%, 1.80% and 3.60%). We then fit the simulated curves to the experimental data and extract values for the trap characteristics. Subsequently we simulate solar cell J - V responses using the values obtained from the SCLC and compare that to the experimental solar cell J - V curves.

SCLC measurements

The effects on the J - V curves arising from a variation in the device thickness were minimised by comparing devices with approximately the same thicknesses of between 70 and 110 nm. The devices were measured both in forward bias (0 to 5 V) and in reverse bias (0 to -5 V) in steps of 0.05 V. No appreciative difference between the forward and reverse bias currents was observed, which is an indication of a negligible V_{bi} . Representative J - V curves of the PCBM electron-only devices, containing a fraction of oPCBM (shown by their %), are shown in figs. 7.9a to e.

Fits to the SCLC J - V curves using the drift-diffusion solver

From the J - V curves shown in figs. 7.9a to e it is not immediately obvious that the charge-transport becomes worse with increased degradation (as seen from the comparable magnitude of the current density at high voltages). However, the overall shape of the J - V curves changes due to the increased degree of trapping. The simulated J - V curves using the drift-diffusion model were fitted to all the experimental J - V curves allowing for a narrow Gaussian distribution of trap states per unit volume, N_T , centred around an energy level, E_T below the conduction band transport level (see fig. 7.10). This was chosen in preference to an exponential tail of states, or a more complex DOS with multiple features, which we also tested, because it provided the best fit to the data with the fewest fitting parameters. N_T , E_T , the electron band-like mobility, μ_n , and the injection barrier heights at $x = 0$ ($q\phi_{inj}$) and at $x = L$ ($q\phi_{ext}$) were allowed to vary

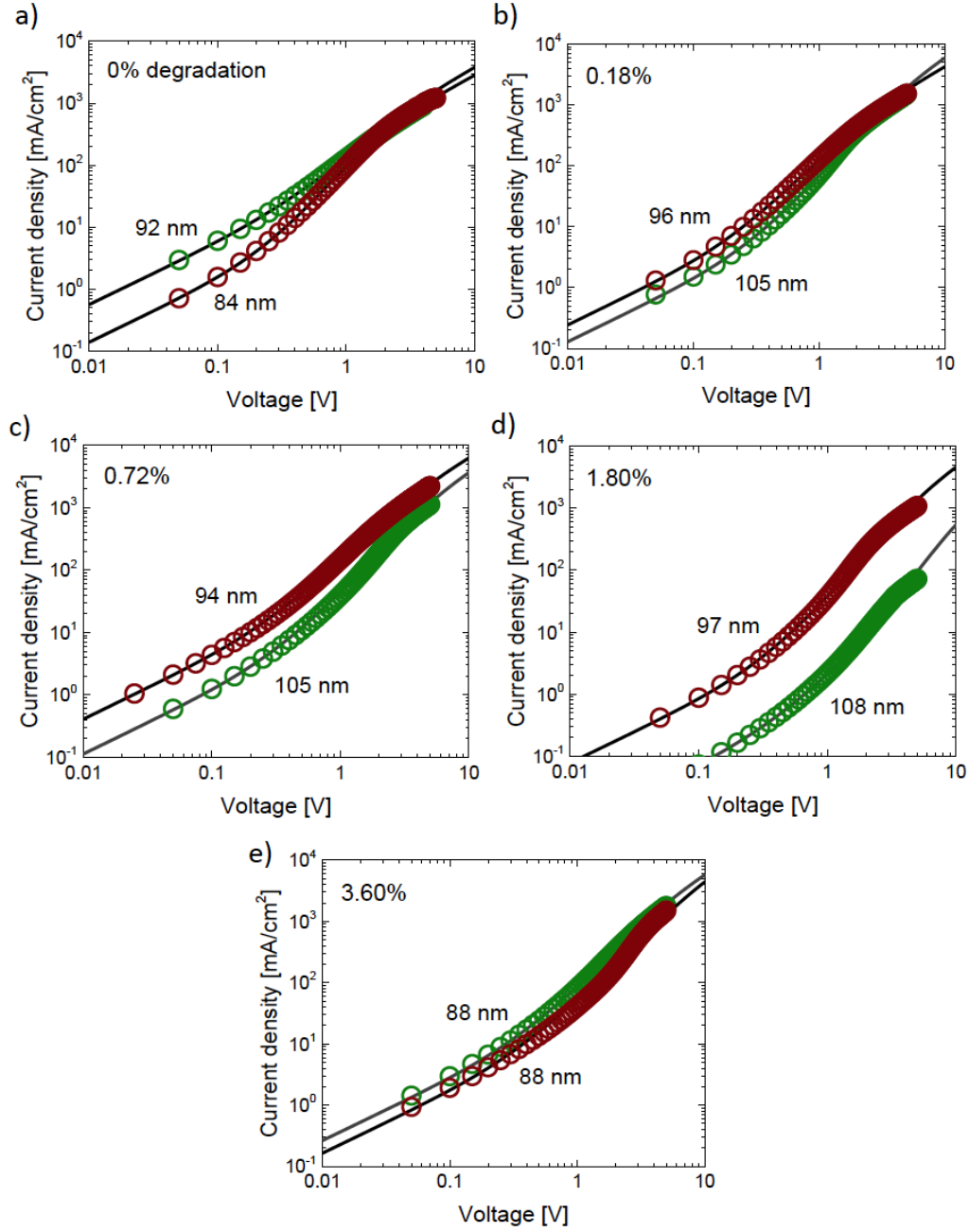


Figure 7.9: a-e) SCLC J - V data for PCBM electron-only devices with increasing concentrations of oPCBM in the PCBM phase. Experimental curves are presented with open circles and the obtained fits using the drift-diffusion model are shown with solid lines. Fitting parameters are presented in table 7.2 and discussed in the text.

during the fitting procedure. The width of the Gaussian was set to 0.1 eV. As mentioned above, since there was no difference between the forward and reverse bias currents, the V_{bi} is negligible and hence $q\phi_{inj} = q\phi_{ext}$. Similar to the case of the hole-only devices in chapter 6, since only a

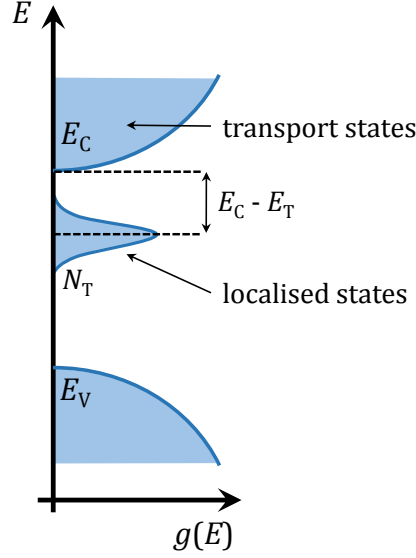


Figure 7.10: Schematic of the DOS used to fit to the data. A Gaussian distribution of, N_T electron trap states were included in the model at E_T .

single carrier type is present in the devices used for the SCLC measurements, recombination is negligible in symmetric single-carrier devices. The fits to the experimental data are shown as solid black lines in fig. 7.9, the results of the fitting are shown in fig. 7.11, and the input values for the drift-diffusion simulations are shown in table 7.2.

Figures 7.11a, b, c and d show the obtained values of μ_n , N_t , and E_t , and the injection barrier heights, respectively, for different fractions of oPCBM using a large set of nominally identical devices. Figure 7.11a shows that the band-like mobility decreases by approximately one order of magnitude when the fraction of oPCBM is increased from 0.18% to 3.6%. Figure 7.11b shows that N_t increases by around an order of magnitude in the same range that the mobility decreases. Figure 7.11c shows that the trap level due to the presence of oPCBM and the transport level of un-degraded PCBM (located at the reference point, 0 eV) approach each other with increased degree of degradation, although the sample-to-sample variation in the extracted trap depth becomes rather large. From fig. 7.11d it is seen that the injection barrier heights are determined to be around 0.15 eV and are more or less insensitive to degradation. The SCLC results are consistent with the formation of both shallow and deep states below the LUMO of the PCBM, as expected from the quantum chemical calculations discussed in the previous section. The shallow states would serve both to push down the effective transport level and to reduce the band-like mobility due to a reduction in the transport level DOS, as shown, illustratively, in fig. 7.12.

Table 7.2: Table of fixed and variable values used in the drift-diffusion simulations to model both the single-carrier devices and the solar cells.

Quantity	Symbol	Value	Units
Band gap	E_g	variable	eV
Effective electron density of states	N_C	10^{19}	cm^{-3}
Effective hole density of states	N_V	10^{19}	cm^{-3}
Dielectric constant	ϵ_r	3	-
Active layer thickness	L	70	nm
Electron band-like mobility	μ_n	variable	cm^2/Vs
Hole band-like mobility	μ_h	$3 \cdot 10^{-3}$	cm^2/Vs
Injection barrier height at $x = 0$ (single-carrier)	$q\phi_0$	variable	eV
Injection barrier height at $x = L$ (single-carrier)	$q\phi_L$	variable	eV
Injection barrier height for electrons (solar cell)	$q\phi_n$	variable	eV
Injection barrier height for holes (solar cell)	$q\phi_h$	0.2	eV
Gaussian trap density	N_T	variable	cm^{-3}
Gaussian trap level	E_T	variable	eV
Gaussian standard deviation	σ_T	0.1	eV
Surface recombination velocity	S	10^5	m/s
Neutral electron capture rate coefficient	C_n^0	10^{-10}	cm^3s^{-1}
Positive electron capture rate coefficient	C_n^+	10^{-10}	cm^3s^{-1}
Neutral hole capture rate coefficient	C_p^0	10^{-10}	cm^3s^{-1}
Negative hole capture rate coefficient	C_p^-	10^{-10}	cm^3s^{-1}
Solar generation rate	G	$7.7 \cdot 10^{21}$	cm^3s^{-1}
Direct band-to-band recombination rate	R_{direct}	$2.2 \cdot 10^{-20}$	cm^3s^{-1}
Series resistance	R_S	$3.1 \cdot 10^{-4}$	Ωm^2
Shunt/parallel resistance	R_P	0.29	Ωm^2

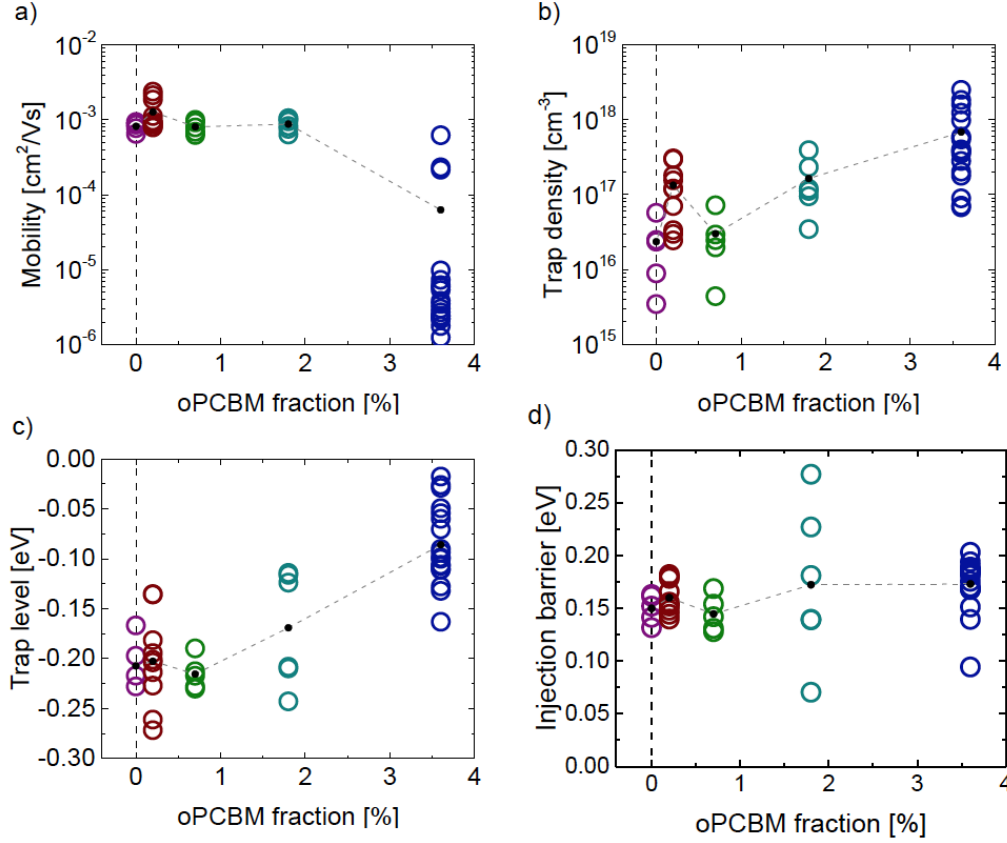


Figure 7.11: SCLC fitting results as a function of oPCBM fraction of total concentration. a) Band-like electron mobility, b) total deep trap density, c) trap level relative to the LUMO level (conduction band edge), and d) the injection barrier heights at the injection and extraction contacts (symmetric devices).

Simulation of solar cell response using the values obtained from the SCLC measurements

Using the fitting results from the SCLC analysis (seen in table 7.3), we were able to qualitatively reproduce the trend of the solar cell J - V characteristics when allowing for an increasing fraction of oPCBM using the drift-diffusion model (see fig. 7.7d). We used the obtained values for μ_n , the injection barrier heights, and the DOS of the pristine, 1.8% degraded and 3.6% degraded films to represent the cases of fresh, partly and fully degraded blend films (we allowed for the electronic band gap to decrease as the transport level and the trap level approaches each other, as seen in fig. 7.12). Since we were here simulating solar cells rather than single-carrier devices, we included band-to-band ($R_{\text{direct}} = 2.2 \cdot 10^{-20} \text{ cm}^3\text{s}^{-1}$) and band-to-trap recombination, governed by the electron and hole densities along the capture and emission rate coefficients for electrons

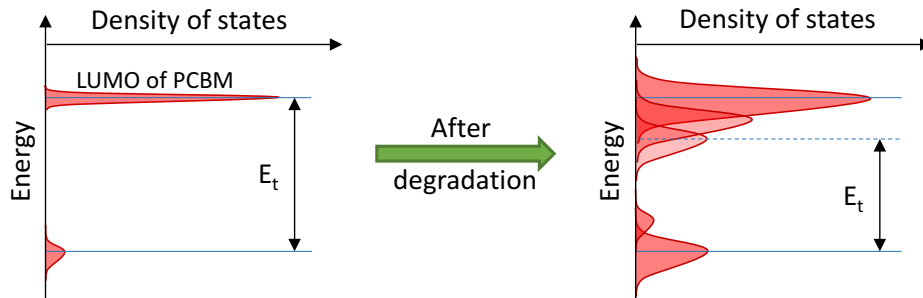


Figure 7.12: Illustrative DOS model before (left) and after the inclusion of degraded species (right). It is shown that the transport energy level (dashed line) decreases in energy with the introduction of defect species, effectively reducing the energy difference between the transport level and the trap level, and reducing the effective transport level DOS (see fig. 7.11).

and holes (which were all set to the same value, $10^{-10} \text{ cm}^3\text{s}^{-1}$). Series and shunt resistances were required for a fit to the un-degraded solar J - V curve with values of $R_S = 3.1 \cdot 10^{-4} \Omega\text{m}^2$ and $R_P = 0.29 \Omega\text{m}^2$, respectively. By simply adding traps and recombination in the drift-diffusion model, whilst varying the DOS, energy level and mobility according to the values obtained from the SCLC fits, we could reproduce the trend in J - V curves observed in the real devices (see fig. 7.7). This agreement verifies the link between the presence of electron traps and the observed loss in device performance.

7.5 Conclusion

In this chapter we have shown that proposed products of the photo-oxidation of PCBM, namely epoxide and carbonyl defects on the fullerene cage, will act as electron traps in PCBM:oPCBM thin films, and we established a quantitative relationship between the presence of such electron traps and the change in performance of PCDTBT:PCBM solar cell devices.

We showed that SCLC electron transport measurements giving values for the charge-carrier mobility and the density of states in degraded PCBM were consistent with the presence of a distribution of electron trap states extending to approximately 0.2 eV below the conduction band edge. We showed that this measured distribution of trap states matched with the proposed defect species.

By using a drift-diffusion model to account for the effect of the determined electron traps, we were able to explain the loss in solar cell open-circuit voltage, short-circuit current and fill factor, upon introduction of oPCBM. More generally, we show that, when the degradation mechanism and/or the degradation products are known, it is possible, in principle, to predict

Table 7.3: Summary of average values obtained from fitting to the SCLC J - V curves. These values were subsequently used for the solar cell J - V simulations.

Values for the 0% oPCBM solar cell device				
Quantity		Symbol	Value	Units
Band gap		E_g	1.398	eV
Injection barrier height for electrons (solar cells)		ϕ_n	0.2	eV
Electron band-like mobility		μ_n	$8.2 \cdot 10^{-4}$	cm^2/Vs
Gaussian trap density		N_T	$2.4 \cdot 10^{16}$	cm^{-3}
Gaussian trap level		E_T	-0.207	eV
Values for the 1.8% oPCBM solar cell device				
Quantity		Symbol	Value	Units
Band gap		E_g	1.363	eV
Injection barrier height for electrons (solar cells)		ϕ_n	0.165	eV
Electron band-like mobility		μ_n	$8.8 \cdot 10^{-4}$	cm^2/Vs
Gaussian trap density		N_T	$1.6 \cdot 10^{17}$	cm^{-3}
Gaussian trap level		E_T	-0.172	eV
Values for the 3.6% oPCBM solar cell device				
Quantity		Symbol	Value	Units
Band gap		E_g	1.277	eV
Injection barrier height for electrons (solar cells)		ϕ_n	0.0785	eV
Electron band-like mobility		μ_n	$6.3 \cdot 10^{-5}$	cm^2/Vs
Gaussian trap density		N_T	$6.8 \cdot 10^{17}$	cm^{-3}
Gaussian trap level		E_T	-0.086	eV

the effect on device operation.

It was found that even exposure to low light conditions, typical of those found in laboratory environments, is sufficient to drive the photo-oxidation of PCBM in the investigated blend films. This observation suggests that unintentional exposure of the thin films to light and oxygen, especially during sample preparation, device fabrication and characterisation, is just as problematic as illumination of the device during solar cell operation. The results of this chapter suggest that PCBM, the most commonly used acceptor used for organic solar cells, is a less than ideal candidate for the commercialisation of stable organic solar cells due to their intrinsic susceptibility to oxidation. These findings highlight the importance of developing alternative electron non-fullerene accepting and/or transporting materials with improved photochemical stability, or to develop a cheap device encapsulation method.

Chapter 8

Concluding remarks

The focus of this thesis was two-fold: i) Understanding the limits to the current methodology employed for space-charge-limited current measurements and the limitations to the simple analytical models currently being employed for studying charge transport through single-carrier devices. ii) To show how the charge-transport characteristics obtained from space-charge-limited current measurements can be used to qualitatively describe the trend of solar cells. To do this, we conducted both experimental studies on model materials along with numerical analysis using a drift-diffusion model. In this chapter we outline the conclusions drawn from the chapters in the thesis and suggest some future work building on the work presented here.

8.1 Thesis summary

In the first result chapter, we discussed whether the Mott-Gurney law and Ohm's law could be used in combination to determine the charge-carrier density of an intrinsic semiconductor in a single-carrier device. We found that if the doping density is low, the space-charge regions, arising from the contact/semiconductor interfaces, overlap, and the charge-carrier density in the probed semiconductor in the single-carrier device is governed by space charge only and neither by the intrinsic charge-carrier density nor the doping density. Under these circumstances the mobility can to a good approximation be determined by the Mott-Gurney law. Hence, when the doping density is low, Ohm's law does not correctly yield the charge-carrier density and the method of using the two equations in combination is not valid. However, as the doping density is increased to very large values, using Ohm's law becomes a reasonable approach for determining the charge-carrier density-mobility product. But, under these conditions, the semiconductor is no longer governed by space-charge and the Mott-Gurney law cannot be correctly fitted and will yield a mobility which overestimates the true value by many orders of magnitude. As a

consequence, when this "Mott-Gurney mobility" is used in Ohm's law the analysis will yield a charge-carrier density which is underestimated by many orders of magnitude, rendering the method of using the two laws in combination useless in the most common cases (both in the low and high doping limits). To our surprise, we found a small window where the two equations could be used in combination, namely when the device is simultaneously very thin and the doping concentration is very high. However, since this window of applicability is so small, we discourage using the Mott-Gurney law in conjunction with Ohm's law as it is unphysical in most cases, and the chance for correct analysis is minimal.

In the second result chapter, we show that a strong deviation from the Mott-Gurney law towards an Ohmic saturation current is seen when simulating thin single-carrier devices of intrinsic semiconductors with realistic (non-Ohmic) injection contacts. This is shown to be due to an increased accumulation and eventual saturation of charge carriers inside the device when a voltage is applied. The thinner the device and larger the injection barriers, the more difficult it becomes to fit the Mott-Gurney law to the current density-voltage curves, and the larger the deviation of the obtained mobility values compared to the real mobility values becomes.

In the third result chapter, we show that by allowing the charge-carrier mobility, trap characteristics, injection barrier heights and the shunt resistance to vary, a numerical fit could be obtained to the entire J-V curve measured from both a symmetric and asymmetric single-carrier device made from an organic semiconductor, here the common hole transport material, Spiro-OMeTAD. We showed that, where simple analytical equations require a temperature-dependent mobility to achieve fits, either using a more physically correct analytical model accounting for traps, as the novel analytical model we presented in this chapter, or using a numerical model, will give rise to a more physically correct temperature-independent band mobility whilst simultaneously yielding information about trap characteristics. These results highlight the importance of showing, and using a numerical model to fit to, the entire J-V curve while accounting for traps, the built-in potential and injection limitation, or to use a more sophisticated analytical model which can correctly account for traps.

In the fourth result chapter it was shown that common products of the photo-oxidation of the most commonly used acceptor used for organic solar cells, PCBM, namely epoxide and carbonyl defects on the fullerene cage, act as electron traps. It was found that even exposure to low light conditions, typical of those found in laboratory environments, is sufficient to drive the photo-oxidation of PCBM. By using a drift-diffusion model to account for the effect of the determined electron traps, the loss in solar cell device performance was explained. A quantitative relationship between the presence of electron traps to the change in device performance

of PCDTBT:PCBM solar cell devices was hence established. This observation suggests that unintentional exposure of the thin films to light and oxygen, especially during sample preparation, device fabrication and characterisation, is just as problematic as illumination of the device during solar cell operation. The results of this chapter suggest that PCBM is a less than ideal candidate for the commercialisation of stable organic solar cells due to their intrinsic susceptibility to oxidation. For this reason, these findings highlight the importance of developing alternative electron non-fullerene accepting and/or transporting materials with improved photochemical stability, or to develop a cheap and efficient device encapsulation method.

8.2 Future work

We here propose a number of both theoretical and experimental studies which could act as a continuation from the work in this thesis.

Even though theoretical models for space-charge-limited current measurements have been extensively studied, the commonly used analytical models currently being employed have their limitations. For once, none of these models can account for poor injection due to energy barriers at the interface. We have shown that injection barriers become increasingly important to account for when considering single-carrier devices with thin semiconducting layers. It would be immensely powerful if the simple analytical equations, such as the Mott-Gurney law and the moving electrode equation, could be modified to account for poor injection. It would be even more powerful if an analytical expression already accounting for traps could be further modified to account for both injection and traps. In order to achieve this, we suggest that an expression for the charge-carrier density across the semiconducting layer, accounting for the trend towards charge-carrier density uniformity due to the injection barriers, must be derived, both in the low voltage regime and in the Mott-Gurney regime. These expressions can then be used to derive analytical equations for the moving electrode transport regime and the Mott-Gurney transport regime when the current is limited by both traps and injection limitation. With such equations, most of the issues faced today when applying analytical equations to analyse J - V curves obtained from SCLC measurements could be circumvented.

Interfaces, whether they are metals, oxide semiconductors or doped organic semiconductors, are usually included into drift-diffusion simulations simply through specification of the injection barriers in the boundary conditions and through a resistance added in series with the semiconducting layer to account for the limiting conductivity of the contacts. However, it is possible to directly model both interlayers and metal contacts by simulating the contact layers either as metals or as doped or un-doped semiconductors. When doing so, the conductivity of

the contacts and the injection barriers can be directly accounted for. The conductivity of the contact will ultimately determine the position of the Fermi level which will determine injection barriers due to the relative position between the Fermi level and conduction band edge. We here propose that directly including contacts and interlayers in the drift-diffusion simulations is important when the contacts are not heavily doped, when the contact layers are thick and when there is a large difference in dielectric constants (giving rise to large screening effects) between the probed semiconductor and the contact materials. It would be very interesting to examine how the inclusion of interlayers, and subsequent negligence of these during the fitting, will affect the overall outcome of the analysis. This work would highlight the need for either using highly doped and very thin interlayer materials with dielectric constants close to the probed semiconductor, or carefully accounting for a lack thereof.

Not directly related to the work in this thesis, we think that there is much work to be done towards agreeing on how to conduct SCLC measurements and subsequently how to analyse the obtained data. Recently there was somewhat of a revolution in the photovoltaic community with the scientific journals now requiring careful specifics on how the solar cells were measured, and whether they were preconditioned. Even though different models are still being applied for the analysis of solar J - V curves, this approach is definitely steering things in the right direction. Different groups not only plot SCLC J - V curves differently (linear scales, semi-log scales and double-log scales) they also usually do not show their entire J - V curve, but rather tend to only show the part of the curve which is compelling towards the story they are trying to sell. Furthermore, they tend to apply which ever model is easiest to fit their data or whichever will yield the highest value for the mobility. For this reason, different groups tend to publish very different numbers even for the same materials. So how could we revolutionise SCLC measurements? It is difficult to state which approach is better without much scrutiny, but we implore the people who wish to publish SCLC to adopt certain unified approaches, such as showing their entire curve, plotting their graphs on a double-log scale (which has historically been the main approach of choice), and to discuss any deviations of the curves away from what would be expected in theory (traps, injection limitation, etc.). Furthermore, if V_{bi} corrections on the voltage axis are used, the curve should be shown before and after this correction, and either measured or estimated values for this V_{bi} should be clearly stated. This will help the rest of the community to better understand their results, which assumptions were used to fit the curve (or parts of the curve), and could potentially be a means of achieving a unification of the methodology used.

List of publications

List of published publications directly related to the thesis:

1. J. A. Röhr, T. Kirchartz, and J. Nelson. On the Correct Interpretation of the Low Voltage Regime in Intrinsic Single-Carrier Devices. *Journal of Physics: Condensed Matter*, 29(20):205901(9), 2017
2. J. A. Röhr, D. Moia, S. A. Haque, T. Kirchartz, and J. Nelson. Exploring the Validity and Limitations of the Mott-Gurney Law for Charge-Carrier Mobility Determination of Semiconducting Thin-Films. *Journal of Physics Condensed Matter*, 30(10):105901(13), 2018
3. J. A. Röhr, X. Shi, S. A. Haque, T. Kirchartz, and J. Nelson. Charge Transport in Spiro-OMeTAD Investigated through Space-Charge-Limited Current Measurements. *Physical Review Applied*, 9(4):044017, 2018
4. H. K. H. Lee, A. M. Telford, J. A. Röhr, M. F. Wyatt, B. Rice, J. Wu, A. de Castro Maciel, S. M. Tuladhar, E. Speller, J. McGettrick, S. Pont, T. Watson, J. R. Durrant, W. C. Tsoi, J. Nelson, and Z. Li. The Role of Fullerenes in Environmental Stability of Polymer:Fullerene Solar Cells. *Energy & Environmental Science*, 11:417–428, 2018

List of published papers, and papers currently in submission/review, that are not related to the work in the thesis:

1. C. J. M. Emmott, J. A. Röhr, T. Kirchartz, A. Urbina, N. J. Ekins-daukes, and J. Nelson. Organic Photovoltaic Greenhouses: a Unique Application for Semi-Transparent PV? *Energy & Environmental Science*, 8:1317–1328, 2015
2. S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C.-H. Tan, E. Collado-Fregoso, A.-C. Knall, J. R. Durrant, J. Nelson, and I. McCulloch. A Rhodanine Flanked

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3. D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Röhr, S. Holliday, A. Wadsworth, S. Lockett, M. Neophytou, C. J. M. Emmott, J. Nelson, C. J. Brabec, A. Amassian, A. Salleo, T. Kirchartz, J. R. Durrant, and I. McCulloch. Reducing the Efficiency–Stability–Cost Gap of Organic Photovoltaics with Highly Efficient and Stable Small Molecule Acceptor Ternary Solar Cells. *Nature materials*, 16(March):363–370, 2017
4. Z. Fei, F. D. Eisner, X. Jiao, M. Azzouzi, J. A. Röhr, Y. Han, M. Shahid, A. S. R. Chesman, C. D. Easton, C. R. McNeill, T. D. Anthopoulos, J. Nelson, and M. Heeney. An Alkylated Indacenodithieno[3,2-b]thiophene-Based Nonfullerene Acceptor with High Crystallinity Exhibiting Single Junction Solar Cell Efficiencies Greater than 13% with Low Voltage Losses. *Advanced Materials*, 30(8):1705209(7), 2018
5. I. Sanchez-Molina, J. A. Röhr, A. M. Telford, L. Martinez, J. Nelson, J. McNaughten, P. O’Brien, B. Saunders, and S. A. Haque. On the Role of Electron and Hole Transfer in Polymer:Lead Sulphide Quantum Dot Solar Cells: a Spectroscopic Study. *in submission*

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(DOI: <https://doi.org/10.1103/PhysRevApplied.9.044017>)

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(DOI: <https://doi.org/10.1039/C7EE02983G>)

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