Hybrid polymer solar cells based on ZnO

Oosterhout, S.D.

DOI:
10.6100/IR719558

Published: 01/01/2011

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Hybrid polymer solar cells based on ZnO

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
Technische Universiteit Eindhoven, op gezag van de
rector magnificus, prof.dr.ir. C.J. van Duijn, voor een
commissie aangewezen door het College voor
Promoties in het openbaar te verdedigen op dinsdag
6 december 2011 om 16.00 uur

door

Stefan Daniël Oosterhout

geboren te Sas van Gent
Dit proefschrift is goedgekeurd door de promotors:

prof.dr.ir. R.A.J. Janssen

Copromotor:
dr.ir. M.M. Wienk

Cover design: Thomas W.G. Dekker

Printed by: Wöhrmann Print Service, Zutphen

A catalogue record is available from the Eindhoven University of Technology Library


The research was supported by a TOP grant of the Chemical Sciences (CW) division of The Netherlands Organization for Scientific Research (NWO) and is part of the Joint Solar Programme (JSP). The JSP is cofinanced by the Foundation for Fundamental Research on Matter (FOM), Chemical Sciences of NWO, and the Foundation Shell Research.
## CONTENTS

1. **Introduction** ................................................................. 5  
   1.1 Solar energy ............................................................ 6  
   1.2 The bulk heterojunction concept and device performance ....... 7  
   1.3 Hybrid solar cells ..................................................... 11  
      1.3.1 Bilayer cells ....................................................... 11  
      1.3.2 Infiltration of polymers in porous inorganic materials .... 12  
      1.3.3 Inorganic nanoparticle-polymer blends ....................... 14  
      1.3.4 Precursor route to polymer-metal oxide blends ............. 15  
   1.4 Outline of the thesis ................................................ 17  
   References ........................................................................ 18  

2. **Zinc oxide precursors for hybrid polymer solar cells** ............ 23  
   2.1 Introduction .............................................................. 24  
   2.2 ZnO layers from different precursors ................................ 25  
   2.3 ZnO:P3HT blends using diethylzinc as precursor ................. 26  
   2.4 ZnO:P3HT blends using dibutylzinc as precursor ............... 31  
   2.5 ZnO:P3HT blends using ethylzinc isopropoxide as precursor ... 33  
   2.6 ZnO:P3HT blends using ethylzinc isopropoxide under inert conditions ... 35  
   2.7 Conclusions .............................................................. 37  
   2.8 Experimental ............................................................ 38  
   References ........................................................................ 40  

3. **The effect of 3D morphology on hybrid polymer solar cells** ...... 43  
   3.1 Introduction .............................................................. 44  
   3.2 Device characterization ............................................... 45  
   3.3 Photoinduced absorption ............................................. 47  
   3.4 Electron tomography and exciton diffusion calculations ....... 49  
   3.5 Conclusions .............................................................. 54  
   3.6 Experimental ............................................................ 54  
   References ........................................................................ 56  

4. **Controlling the morphology via side chain functionalization** .... 59  
   4.1 Introduction .............................................................. 60  
   4.2 Microscopic analysis ................................................... 61  
   4.3 Spectroscopic analysis ................................................. 63  
   4.4 Charge carrier generation ............................................ 65  
   4.5 Percolation pathways in ZnO ......................................... 66  
   4.6 Solar cell performance ................................................ 67
5. Hybrid polymer solar cells from zinc oxide and a small band gap polymer
   5.1 Introduction ................................................. 80
   5.2 Photoinduced charge transfer ................................ 81
   5.3 Processing conditions ....................................... 83
   5.4 ZnO contents and layer thickness .............................. 84
   5.5 Normal and inverted devices ................................ 88
   5.6 Annealing temperature ....................................... 89
   5.7 Comparison with PCBM:P3HS .................................. 92
   5.8 Comparing absorption and EQE ................................ 93
   5.9 Conclusions .................................................. 94
   5.10 Experimental .............................................. 95
   References ....................................................... 97

6. Zinc oxide nanorods as template for hybrid polymer solar cells
   6.1 Introduction .................................................. 100
   6.2 Nanorod growth ............................................ 101
   6.3 Polymer infiltration into a ZnO nanorod carpet ............... 101
   6.4 Infiltration of a ZnO:P3HT blend into a ZnO nanorod carpet 105
   6.5 Photovoltaic performance of inverted devices .................. 108
   6.6 Photovoltaic performance of devices utilizing a ZnO nanorod carpet 110
   6.7 Conclusions .................................................. 113
   6.8 Experimental .............................................. 113
   References ....................................................... 115

Summary ........................................................ 119

Samenvatting ...................................................... 123

Curriculum Vitae .................................................. 127

Publications ....................................................... 129

Dankwoord ........................................................ 131
1. INTRODUCTION

Abstract

This chapter introduces the concept of hybrid organic-inorganic solar cells. Following a general introduction to solar energy, the main strategies used in making organic and hybrid organic-inorganic solar cells will be discussed. Subsequently, an outline of the thesis is given.
1.1 Solar energy

With the increasing demand for energy, and the limited availability of fossil fuels, there is a need for a renewable, sustainable energy source. One source that always will be available is the energy of the sun. The energy of the sun may be captured in roughly three ways: as heat, electricity, or chemical energy. Heat may be used directly or used to power for example an electricity generator. Sunlight may be used to drive chemical reactions, where energy is stored in chemical bonds. Finally, sunlight can be converted directly into electricity. Since electricity is possibly the most valuable and versatile form of energy, it deserves a lot of attention.

Photovoltaic devices convert sunlight into electricity. In such solar cells, photons from the sun excite electrons in a semiconductor material and thereby create positive and negative charges that move to opposite electrons and generate a voltage difference. Several types of photovoltaic devices exist nowadays. The most common commercial photovoltaic solar energy conversion systems are based on silicon, an inorganic semiconductor. Other well-known photovoltaic semiconductor materials include gallium arsenide (GaAs), copper indium gallium selenide (CIGS), cadmium telluride (CdTe), dye sensitized wide band gap semiconductors, and organic polymers. An overview of the different cell types and their maximum confirmed power conversion efficiency at this moment is summarized in table 1.1.

<table>
<thead>
<tr>
<th>Technology</th>
<th>power conversion efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon (crystalline)</td>
<td>25.0</td>
</tr>
<tr>
<td>Silicon (thin film)</td>
<td>16.7</td>
</tr>
<tr>
<td>GaAs</td>
<td>27.6</td>
</tr>
<tr>
<td>CIGS</td>
<td>19.6</td>
</tr>
<tr>
<td>CdTe</td>
<td>16.7</td>
</tr>
<tr>
<td>Dye sensitized</td>
<td>10.4</td>
</tr>
<tr>
<td>Organic polymer</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Three major factors determine whether a solar energy technology will be commercially interesting or not: the final device should be efficient, durable, and cheap. The solar energy conversion systems that are most widely used today are based on silicon technology. Silicon solar cells date back to 1954, have a large history, and are well-studied. Silicon solar cells are efficient and have very good lifetime, lasting for at least two decades before replacement/recycling is needed. One drawback is the high costs that are associated with manufacturing high purity solar grade silicon in combination with the thick, several 100 micrometers, crystalline silicon layers needed to absorb all light.
To make cheaper solar cells, use of materials that are easier to make and to process is one of the options. One technique would be printing of solar cells, similar to the way newspapers are printed. For this choice, organic solar cells are a good option because organic materials are usually solution processable. When incorporated in a roll-to-roll printing process, large scale production of solar cells can be achieved, reducing the production costs. When the price is reduced significantly, a slightly lower efficiency or lifetime of the devices is acceptable. This is the strength and opportunity for polymer solar cells.

For efficient polymer solar cells, the morphology of the active layer is very important. This will be described in the next section in more detail. Shortly, the active layer is a bulk heterojunction of an electron donating and an electron accepting material. These materials are mixed to a certain degree of intimacy, which is essential for making and transporting charges and thus for the device performance. Obtaining the morphology with the optimal degree of mixing and interconnectivity is a major challenge in present polymer solar cell research. Moreover, when a carefully designed morphology is achieved, it should remain intact over the lifespan of the device. Unfortunately, in most polymer solar cells, the morphology is unstable with respect to heat and time. Due to migration of molecules within the active layer over time the morphology changes, usually leading to a decrease in photovoltaic performance.

To create a stable morphology, hybrid polymer solar cells are an option. Hybrid means that an organic polymer (usually the electron donor) is combined with an inorganic (electron accepting) material. The morphology of the inorganic material will remain intact over the lifespan of the device, while the polymer is not able to change its morphology due to the presence of the inorganic material.

The aim of this thesis is exploring the fabrication of hybrid organic polymer - inorganic metal oxide solar cells focusing on designing their morphology and achieving an optimum, possibly high power conversion efficiency.

1.2 The bulk heterojunction concept and device performance

In an organic or hybrid organic-inorganic solar cell, electron donating and electron accepting materials are present. In a typical organic polymer solar cell, a conjugated polymer, like poly(3-hexylthiophene) (P3HT), is used as electron donor and combined with the electron accepting [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). After absorption of a photon, e.g. in the donor material (see figure 1.1a), an electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), leading to a bound electron-hole pair in the donor material, referred to as an exciton. The exciton has a short lifetime (in the order of 400 ps) before it will decay to its
ground state. Therefore the exciton is able to diffuse only over a small distance. When the exciton reaches the interface with the electron acceptor, and the electron affinity of the acceptor is high enough (i.e. the HOMO and LUMO of the acceptor are sufficiently lower than the HOMO and LUMO of the donor), the electron will be transferred to the LUMO of the acceptor as indicated in the figure. At this point, the electron and hole are still bound to each other across the interface of the two materials, and this state is referred to as the charge transfer state. Due to the macroscopic electric field created by the different work functions of the two electrodes, the charges can be separated and drift to their respective electrodes, such that a voltage difference across the solar cell is created.

The exciton diffusion length for P3HT has been reported to be in the range of 2.6 to 12 nm. Consequently, only excitons created in the electron donor that are within this range to the interface with the acceptor have a chance of creating charges and contribute to the photocurrent. In a flat bilayer device, this would lead to a maximum donor layer thickness of $\sim 12$ nm, as any more donor material would not be able to contribute to the photocurrent, because it is too far away from the interface from the acceptor.

To overcome this limitation, the bulk heterojunction concept is introduced (figure 1.1b). In a bulk heterojunction, the donor and acceptor material are blended in an intimately mixed layer, where the donor material is always in close contact with the acceptor. In this way, an exciton will always be generated close to a donor/acceptor interface, leading to charge separation.

Next, the charges need to find their way to their respective electrodes. Consequently, both the donor and acceptor material should have continuous percolating pathways for holes and electrons to find their way to the corresponding electrode.

![Device operation](image1.png)

**Fig. 1.1:** Device operation scheme and illustration of a bulk heterojunction, sunlight entering from top.
For characterizing a bulk heterojunction solar cell, a current density - voltage ($J-V$) curve is measured. In such a measurement, the current through the device is measured for a range of positive and negative voltages applied to the electrodes. In the dark, this measurement yields almost no current at negative voltage (reverse bias) and a positive current above a certain positive threshold voltage (forward bias), meaning that the device acts as a diode. An example of a $J-V$ curve in the dark is shown in figure 1.2a.

Upon illumination, electrons and holes will be created in the active layer at the donor-acceptor interface. After separation of these charges, the positive charge carriers are in the HOMO of the electron donor and the negative charge carriers are in the LUMO of the acceptor and give rise to a potential difference across the two electrodes that are in contact with the active layer. This potential is referred to as the open circuit voltage ($V_{oc}$). When the electrodes are brought into electrical contact, without any load, electrons are free to move from the negative electrode to the positive electrode. Because the illumination continues, a quasi equilibrium will establish in which the current density is proportional to the illumination intensity. The current density measured when the two electrodes are short-circuited is referred to as the short circuit current ($J_{sc}$).

In both conditions, $V_{oc}$ and $J_{sc}$, the power output of the cell is zero, because the power is equal to the product of voltage and current. The maximum power output can be found if the voltage is multiplied with the current at a certain potential. In order to find this maximum power point (MPP), a $J-V$ curve under illumination is measured (figure 1.2c). Figure 1.2d shows the power output as function of voltage.

The fill factor ($FF$) is defined as in equation 1.1:

$$FF = \frac{MPP}{V_{oc} \cdot J_{sc}}$$  \hspace{1cm} (1.1)

Graphically the $FF$ is the ratio of the small rectangle (a) in figure 1.2c and the large rectangle (b). In the ideal case, the $FF$ should approach 1.

Although a diode has a much higher current in forward bias that in reverse the reverse current is not zero. This reverse current is also referred to as leakage current, and may be characterized best in a semilogarithmic plot of the $J-V$ curve in the dark (figure 1.2b). The leakage current is visible in reverse bias and in positive bias up to a particular voltage, depending on the diode characteristics. In the figure this is indicated between points A and B. At a bias corresponding to flat-band conditions, injection from the negative contact into the LUMO of the acceptor material and from the positive contact into the HOMO of the donor material starts and current starts to flow, this is the exponential region between B and C in the figure.
Fig. 1.2: Characteristics of a typical polymer solar cell under different conditions.

At some point, saturation of the exponential region is observed, identified by a change in slope at high bias. This is due to the internal resistance in the device, shown at voltage C and higher.
1.3 Hybrid solar cells

In hybrid solar cells, an organic material is combined with an inorganic material to yield a solar cell. Usually, because electron transport is poor in most organic materials, an inorganic acceptor is used. The organic material is then the electron donor and hole transporter. There are several strategies and device configurations to obtain a hybrid heterojunction. These are described in the following subsections.

1.3.1 Bilayer cells

A hybrid heterojunction is in its simplest form a flat junction between an organic and inorganic material. The first photovoltaic hybrid junction was published by Ozaki et. al. who used a ZnS-polyacetylene heterojunction and demonstrated a photovoltaic effect. The first silicon-organic heterojunction was reported by Sailor et. al., who used poly-(CH$_3$)$_3$Si-cyclooctatetracene on a crystalline silicon surface with a conversion efficiency of 1% and higher. A more recent example of a P3HT-silicon flat heterojunction has been reported by Matsumo et. al., who reported a power conversion efficiency of 2.46%.

Horowitz and Garnier used a junction between doped poly(3-methylthiophene) (P3MT) and n-GaAs. This device has shown a power conversion efficiency of 3.5%. The function of the P3MT is not exactly clear, it may act as p-type semiconductor or as an insulator or passivation layer between the n-GaAs and the metal top contact.

The idea of using a doped polymer:inorganic heterojunction is quite popular as it can enhance performances of the non-hybrid devices, where the organic layer is omitted. A high efficiency for a flat hybrid system was shown by Bereznev et. al., who used a layer of polypyrrole or poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on top of CuInS$_2$ leading to a photovoltaic performance of 4.14%.

In all these bilayer devices, the inorganic semiconductor is the photoactive material; any light absorbed by the organic materials does not contribute significantly to the photocurrent. Transparent metal-oxide semiconductors, however, give the opportunity to the organics to produce the photocurrent, the advantage being that the polymer can be designed in such a way that the absorption and energy level offset can be tuned to match the desired properties of the heterojunction.

Electron transfer between the organic material poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and the metal oxide TiO$_2$ was first shown by Savinije et. al. In such a solar cell, the thickness of the active part of the light absorbing organic material must be in the range of the exciton diffusion length because the excitons need to reach the electron acceptor (in this case TiO$_2$) to create charges. Any light absorption further away from the interface than the exciton diffusion length will not lead to...
higher currents, because the excitons will not be able to reach the interface with the acceptor material. An efficiency of 0.15% was achieved, which was later improved to 0.3% by Slooff et. al. with poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) and to 0.4% by applying poly(2,5-dimethoxy-1,4-phenylene-1,2-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-1,2-ethylene) (M3EH-PPV) onto TiO$_2$ by Breeze et. al.

The combination of TiO$_2$ with P3HT showed a power conversion efficiency 0.19%, but could be improved to 0.69% (under monochromatic light conditions) by applying a layer of poly (N-dodecyl-2,5-bis(2'-thienyl)pyrrole-2,1,3-benzothiadiazole) (PTPTB) in between the TiO$_2$ and P3HT layer. The improvement was realized by energy transfer to the thin (4 nm) PTPTB layer, and subsequent charge transfer to the TiO$_2$ layer.

ZnO has been used for bilayer solar cells, the highest reported efficiency being 0.09%, but hybrid bilayer solar cells based on ZnO are merely used as model systems.

In order to enhance exciton separation at larger layer thicknesses, a bulk heterojunction may be used as discussed in section 1.2. There are various ways to create a mixed organic:inorganic bulk heterojunction layer, like infiltrating an organic material into a porous or structured inorganic semiconductor, blending inorganic nanoparticles with an organic material and subsequent layer deposition, or making use of a precursor which converts into a semiconductor during deposition. The different ways to accomplish these bulk heterojunctions are discussed in the following sections.

### 1.3.2 Infiltration of polymers in porous inorganic materials

The idea of using a porous electrode was originally used in dye sensitized solar cells, where there is a monolayer of light absorbing molecules on a mesoporous inorganic acceptor layer, and a liquid electrolyte to transport the holes. A porous inorganic material such as TiO$_2$ has a large surface area, which would enhance the charge generation not only in a dye sensitized solar cell but also in a hybrid solar cell. The p-type polymer is then used both to absorb light and to transport the holes. The main challenge in this concept is to fill the pores efficiently.

The concept of infiltrating a polymer in nanoporous TiO$_2$ was first demonstrated by Van Hal et. al. It was shown that poly(p-phenylene vinylene) (PPV) and polythiophene derivatives in the excited state are able to donate an electron to the TiO$_2$, meaning that charge separation takes place in this system. One of the first publications on filling a nanoporous inorganic semiconductor with a conjugated polymer yielding a hybrid solar cell was by Carter et. al., who reached a power conversion efficiency of 0.18% using MEH-PPV and TiO$_2$. 
Several groups are working on filling pores.\textsuperscript{26,27} The best devices are made when a surface modifier is used, not only to enhance charge transport at the donor-acceptor interface, but also to enhance the absorption spectrum to improve the device performance up to 2.6\%.\textsuperscript{28}

Filling a randomly created nanoporous morphology is not the only way; also more controlled morphologies of inorganic n-type semiconductors may be synthesized and filled with a p-type organic material. The advantage of this method would be that the morphology can be tuned in such a way that filling is relatively easy compared to a randomly porous structure. Usually, nanorods oriented perpendicular to the surface are appealing for this method, because charges then have the ability to migrate via a straight path to the electrode, as well as that filling will be relatively easy (figure 1.3).

Different semiconductors may be used to fill with an organic material. For example CdTe may be used, the advantage of this material being that it also absorbs light due to its band gap energy of 1.45 eV. The material combination of ordered CdTe nanorods with poly(3-octylthiophene) has first been shown by Kang et. al., reaching a power conversion efficiency of 1.06\%.\textsuperscript{29} CdS nanorods may also be used, leading to an efficiency of 0.60\%.\textsuperscript{30}

More environmentally friendly materials like ZnO and TiO\textsubscript{2} are also being investigated by various groups. Ravirajan and Peiró reached a power conversion efficiency of 0.20\% upon incorporating P3HT in an oriented ZnO nanorod carpet, created by growing the ZnO nanorods onto a seed layer of ZnO.\textsuperscript{31,32} Olson et. al.\textsuperscript{33} reached a power conversion efficiency of 0.53\% when P3HT was incorporated into a ZnO nanorod carpet deposited in a similar fashion using a different growth solution. The highest efficiency to date for hybrid cells based on ZnO nanorods has been achieved by Baeten et. al.,\textsuperscript{34} the efficiency being 0.76\%.

TiO\textsubscript{2} is similar to ZnO in band gap and work function. Besides that, TiO\textsubscript{2} is already used extensively and successfully in dye sensitized solar cells,\textsuperscript{22} and is therefore an
interesting material for use in hybrid solar cells as well. Wei et. al. have shown a power conversion efficiency of 0.39%, using TiO$_2$ nanorods grown onto a TiO$_2$ compact layer via a precursor solution at high temperature and incorporating MEH-PPV as polymer.$^{35}$

A combination of a dye sensitized cell and a hybrid solar cell, was demonstrated by Mor et. al.$^{36}$ Here, TiO$_2$ nanotubes are grown onto a TiO$_2$ compact layer, and functionalized with an organic dye that absorbs infrared light. P3HT is used both as light absorber and hole transporting material, similarly as in the hybrid solar cells described above. The advantage of the dye is complementary absorption with the P3HT, and functionalization of the TiO$_2$ surface which enhances polymer infiltration. The efficiency reached with this device configuration is as high as 3.2%.

1.3.3 Inorganic nanoparticle-polymer blends

Blending inorganic nanoparticles with organic materials is a widely studied method for creating hybrid bulk heterojunctions for solar cell applications. There are many types of particles that may be used to blend with organic materials, such as CdSe/CdTe,$^{37-40}$ PbS/PbSe/PbTe,$^{41-45}$ CuInS$_2$/CuInSe$_2$,$^{46-49}$ InP$^{50}$ or metal oxides such as TiO$_2$ or ZnO nanoparticles.$^{24,51-59}$

Advantages of CuInS$_2$ and CuInSe$_2$ are high absorption coefficients, which make this type of semiconducting nanoparticles interesting for blending with a hole-conducting or semiconducting polymer. A blend of CuInS$_2$ has first been shown by Arici et. al.$^{46}$ who mixed the particles with PEDOT:PSS on an interface with PCBM to reach an external quantum efficiency up to 2%.$^{47}$ Blends of CuInSe$_2$ with P3HT have shown efficiencies of 0.19%.$^{48,49}$

Other nanoparticles that are used more often are CdSe and CdTe nanoparticles. Initially quantum efficiencies of up to 12% were achieved by blending CdSe particles with MEH-PPV.$^{37,38}$ Controlling the surfactants for the particles was critical. Capping molecules like trioctylphosphine oxide (TOPO) are mostly used for stabilization of the particles, but act as insulator in a solar cell bulk heterojunction because as they are in between the semiconducting particles and hinder electron transport. Exchanging TOPO for pyridine, the electron transport between the particles is enhanced. An enhanced power conversion efficiency of 2.8% was obtained by Sun et. al., by using a different particle geometry.$^{39}$ To date, the highest efficiency has been reported by Dayal et. al.$^{40}$ which is 3.2% for a poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] blend with CdSe.

Lead-derived semiconductors like PbS, PbSe, and PbTe may also be used in hybrid solar cells. The advantage of these materials is the low band gap of the semiconductor, which may be increased by changing the nanoparticle size, due to the quantum confine-
1.3. Hybrid solar cells

This tunability combined with a strong absorption, makes it a promising candidate for use in hybrid photovoltaics.

Blending PbS nanoparticles with MEH-PPV, however, did not lead to very efficient devices (maximum EQE of $\sim 0.0008\%$), probably because electron transfer from MEH-PPV to PbS is not efficient, which is possibly due to the capping layer of the nanoparticles (octylamine) that inhibits charge transfer between the two materials. Moreover, the ability to transfer excitation energy from the polymer to the nanocrystal is more likely than electron transfer. The highest reported efficiency for a lead chalcogenide hybrid solar cell to date is 0.14% for a PbSe:P3HT blend.

TiO$_2$ and ZnO are promising materials for application in hybrid polymer solar cells, due to their abundance and non-toxicity. Early experiments with TiO$_2$ nanoparticles and PPV have shown low efficiencies, demonstrating the difficulties in blending TiO$_2$ nanoparticles with polymers. Poor mixing of the two materials limits the device performance.

A performance (0.42%) using TiO$_2$ nanoparticles and P3HT for hybrid solar cells was reported by Kwong et. al., an efficiency of 1.14% has been reported by Chang et. al., by blending TiO$_2$ nanorods with P3HT.

An disadvantage of TiO$_2$ is that it needs a high annealing temperature to ensure electrical interparticle contact. These high annealing temperatures are incompatible with most polymers. ZnO already forms a crystalline structure at room temperature. A high efficiency of 1.6% has been reported for a blend of ZnO particles with MDMO-PPV by Beek et. al., and an efficiency of 0.9% for a blend of ZnO nanoparticles with P3HT. In these blends the ZnO particles are not intentionally capped with surfactants but may carry acetate or methanol at the surface.

1.3.4 Precursor route to polymer-metal oxide blends

An alternative to infiltration or blending of inorganic nanoparticles with polymers to achieve a bulk heterojunction structure of an organic and inorganic material, is the so-called precursor method. In this method, a precursor for the inorganic material is mixed with the organic material in solution, and this precursor converts into the desired inorganic semiconductor upon deposition. This approach was first demonstrated by Van Hal et. al., who used titanium(IV) isopropoxide (Ti(i-PrO)$_4$) as precursor for TiO$_2$ and blended this with MDMO-PPV to fabricate a bulk heterojunction solar cell. The precursor was converted to TiO$_2$ by first exposing it to moisture for hydrolysis during the sol-gel process, and subsequent high vacuum treatment for the condensation reaction into TiO$_2$. X-ray photoelectron spectroscopy has shown that at least 65% of the precursor was converted into TiO$_2$ in the bulk heterojunction. Atomic force microscopy measurements have shown that TiO$_2$ particles had a size in the nanometer range. Although the conversion into TiO$_2$
was not complete, evidence for charge separation of the MDMO-PPV to TiO$_2$ was given by photoluminescence and photoinduced absorption measurements \[60\] Solar cells were made, giving rise to an optimized efficiency of 0.20%. Slooff et al. reproduced the results reaching an efficiency up to 0.22\% \[61\] and reached a power conversion efficiency up to 0.17\% for a similarly produced poly(3-octylthiophene):TiO$_2$ blend.

The main disadvantage of these hybrid bulk heterojunctions is the forming of TiO$_2$ that needs a high temperature to form a crystalline material, which is incompatible with the use of most polymers. \[62\] ZnO, on the other hand, already forms a crystalline material at lower temperatures. \[63\] Available precursors for ZnO are for example zinc acetate, or the more reactive diethylzinc. Zinc acetate needs a very high temperature to convert to ZnO, but the diethylzinc converts to Zn(OH)$_2$ at room temperature upon exposure to moisture, which can be subsequently condensed into ZnO at a temperature as low as 110 °C. \[64\]

The precursor method for making polymer:ZnO hybrid solar cells was first introduced by Beek et al. who used diethylzinc as ZnO precursor. \[64\] In this method, diethylzinc reacts by exposure to moisture during the deposition step, mainly yielding Zn(OH)$_2$ as reaction product. In contrast to the hydrolyzed TiO$_2$ precursor, Zn(OH)$_2$ can be converted into crystalline ZnO at a moderate temperature of 100 °C, verified by absorption measurements, \[64\] which is a compatible temperature for commonly used polymers like MDMO-PPV and P3HT.

Application of these hybrid bulk heterojunctions in solar cells, using MDMO-PPV as polymer, resulted into 1.1\% efficient devices, a significant improvement compared to the precursor-based MDMO-PPV:TiO$_2$ solar cells. The reported efficiency was lower compared to the nanoparticle-based MDMO-PPV solar cells which provided 1.6\%. \[59,64\] At least in part this is due to reaction of the ZnO precursor with the polymer backbone that was observed as a blue shift of the absorption spectrum of MDMO-PPV in the films with ZnO. \[58,64\] Moet et al. \[65\] have further analyzed the origin of the blue shift of the MDMO-PPV absorption after the sol-gel process with nuclear magnetic resonance and found evidence for disappearance of vinyl bonds and the complementary formation of saturated bonds and of oxidized species such as alcohol or ketone.

Moet et al. \[65\] also showed that when using P3HT instead of MDMO-PPV, the absorption of the polymer does not change under the same conditions, indicating that P3HT is more stable towards the highly reactive diethylzinc. Photovoltaic devices made of P3HT:ZnO show a power conversion efficiency of 1.4\%, which is higher than the precursor MDMO-PPV:ZnO blends, and higher than the P3HT:ZnO blends made using presynthesized ZnO nanoparticles. \[59\]
1.4 Outline of the thesis

As shown in the previous section, there are various ways to make hybrid polymer:inorganic bulk heterojunctions for solar cells. The bulk heterojunction is needed to have a large enough surface area for charge separation. The most recent attractive way to create such a bulk heterojunction would be based on the precursors as discussed in section 1.3.4.

Filling an existing ligand-free inorganic nanoporous network is difficult due to the rigidity and size of the used polymers, in addition to the very different nature of the two materials, the inorganic hydrophilic, the organic hydrophobic.

Pre-prepared inorganic nanoparticles usually need surface ligands to make them soluble in a common solvent with the hydrophobic polymer. So-called 'naked' nanoparticles need a carefully balanced solvent to keep the particles dissolved, which induces a very small operable processing window for optimization of the morphology of the bulk heterojunction.

The advantage of the precursor method compared to pre-synthesized nanoparticles is that no capping layer is needed for the inorganic phase, which is difficult to remove. Organometallic compounds can be used as precursor for inorganic semiconductors, and these precursors are readily soluble in most organic solvents. However, not much research has been done in optimizing and analyzing hybrid bulk heterojunction solar cells made using a sol-gel method using an organometallic precursor.

The objective of this thesis is to improve the efficiency of hybrid bulk heterojunctions made using the precursor method, and to analyze and improve the morphology of these devices to gain insight in the sol-gel process. Chapter 2 will deal with various precursors to make in situ ZnO in a polymer layer. Different solvents are applied to optimize performance and morphology. The morphology is analyzed using atomic force microscopy (AFM). Various other processing parameters are tuned to gain optimum performance.

Chapter 3 deals with the morphology of ZnO:P3HT active layers. Three-dimensional images of the active layer are obtained using electron tomography. The three dimensional morphology is further analyzed, determining integrated spherical distances from P3HT to ZnO, correlation of this with the exciton diffusion length of excitons in the P3HT, and calculating the exciton quenching in different active layers. From these experiments and calculations, it becomes clear which properties limit the device performance of these hybrid polymer solar cells.

Chapter 4 deals with optimization of the morphology by means of using a poly(3-hexylthiophene) with partial side chain functionalization (P3HT-E). The functional groups in P3HT-E make the polymer more hydrophilic and the morphology of ZnO:P3HT-E is significantly different from that of ZnO:P3HT as shown by transmission electron microscopy (TEM). Calculations on three-dimensional tomography data of the active ZnO:P3HT-E
layer show significantly enhanced blending compared to the unfunctionalized ZnO:P3HT blends. This different morphology however, also brings new challenges and limitations to the performance of these hybrid polymer solar cells.

In chapter 5 a different polymer, poly(3-hexylselenophene) (P3HS), is used in hybrid polymer solar cells. The advantage of P3HS would be more light absorption, due to the extended absorption spectrum and smaller band gap of P3HS compared to P3HT. The morphology was analyzed using TEM and AFM, and the performance was optimized. Insight was gained into which part, crystalline or amorphous, of the P3HS contributes to the photocurrent.

In the last chapter, more control of the morphology is induced using ZnO nanorods and creating a precursor blend of P3HT and ZnO in between. This way, electrons in the ZnO phase would have a better pathway to the negative electrode.

References


1. Introduction


2. ZINC OXIDE PRECURSORS FOR HYBRID POLYMER SOLAR CELLS

Abstract

Different ZnO precursors (diethylzinc, dibutylzinc, ethylzinc isopropoxide) have been examined for use in a ZnO:polymer blend layer, using an in-situ sol-gel process. In this process, humidity from the environment during layer deposition and subsequent thermal annealing are used to convert the precursor into ZnO. All tested precursors are able to form ZnO and working devices when blended with poly(3-hexylthiophene). Atomic force microscopy was used to investigate the surface topology of the active layers.

Ethylzinc isopropoxide has a built-in oxygen atom and may not need water or oxygen to form ZnO. However, device performance with poly(3-hexylthiophene) appeared to be very low when processed in dry and oxygen free environment, compared to a similar device where ambient water was used for precursor conversion. Additionally, higher temperatures are needed to convert this precursor into ZnO under inert atmosphere, which are not compatible with most conjugated polymers used in polymer solar cells.

The highest performance for a ZnO:poly(3-hexylthiophene) solar cell was obtained using diethylzinc as precursor. The best cell gave a power conversion efficiency of $\sim 2.0\%$ in simulated solar light.
2. Zinc oxide precursors for hybrid polymer solar cells

2.1 Introduction

The low exciton diffusion length in organic semiconductors makes it crucial that the electron donor and acceptor are always in close contact in an organic solar cell. In order to achieve this, the donor and acceptor materials are mixed in a so-called bulk heterojunction. In such a bulk heterojunction, there are several requirements for the morphology. The mixing of the two materials should be good enough, such that the sizes of the donor and acceptor domains are always within the exciton diffusion length, but should not be mixed too well, because continuous percolating paths in both phases are required for charge transport to the electrodes.

Hybrid solar cells consist of a combination of an organic and inorganic semiconductor in the active layer of a solar cell. This type of material combination is an interesting alternative to purely organic solar cells, because the rigidity of the inorganic material stabilizes the three dimensional morphology of the bulk heterojunction. In contrast, the morphology of full-organic solar cells may change with time and temperature leading to reduced performance. Hybrid solar cells offer the advantage of a stable morphology and therefore stable performance. Various inorganic acceptor materials are available, such as CdSe, PbS, TiO$_2$, and ZnO. Here, the focus will be on ZnO because of its ease of synthesis.

There are various ways to synthesize a ZnO:polymer bulk heterojunction network. One option is deposition of a porous ZnO layer first and infiltrating a polymer or dye afterwards. Alternatively a nanocarpet of pre-synthesized ZnO nanorods may be used. Further, ZnO nanoparticles may be mixed with a polymer to make a ZnO nanoparticle network inside a polymer matrix. The method that will be explored here uses a ZnO precursor that is mixed with the polymer in solution and that is converted into ZnO when depositing the layer. This strategy is referred to as the in-situ method.

To make hybrid polymer solar cells using the in-situ method, a precursor is needed that can be easily converted into the desired n-type semiconductor, ZnO. Commercially available precursors are dimethylzinc (DMZ) and diethylzinc (DEZ). The reaction of these precursors with water from the environment (40% relative humidity) produces Zn(OH)$_2$, which can be converted into ZnO when elevated to a moderate temperature. For DMZ and DEZ it has already been demonstrated that functioning devices can be made. DMZ is less attractive as precursor, due to its volatile nature.

The aim of the research described in this chapter is to possibly identify new ZnO precursors and optimize the deposition conditions that can lead to efficient working solar cells in combination with poly(3-hexylthiophene) (P3HT). The recent work of Moet et al. on ZnO:P3HT solar cells made from DEZ as ZnO precursor served as starting point for this work. Apart from DEZ, two other precursors have been investigated. First, dibutylzinc
2.2 ZnO layers from different precursors

(ZnO) is used to investigate if a ZnO precursor with a higher boiling point than DEZ is beneficial. Because of its low boiling point, DEZ may actually partly evaporate already during spin coating such that it is not converted to ZnO in the film. Second, ethylzinc isopropoxide (EZIP) is tested. EZIP is formed by reacting DEZ with isopropanol and is less reactive towards water such that the conversion into ZnO is less vigorous. In addition, EZIP may form ZnO without using water as external source of oxygen.

The remainder of this chapter describes the formation of ZnO layers using DEZ, DBZ, and EZIP, followed by the optimization and characterization of the ZnO:P3HT blend layers that can be made using these three precursors under a variety of deposition conditions.

2.2 ZnO layers from different precursors

The conversion of a precursor like DEZ into ZnO involves two consecutive reactions. In the first step the precursor should be hydrolyzed forming Zn(OH)$_2$, which then can be converted into ZnO and water by a condensation reaction. Before exploring the formation of ZnO:P3HT blends it useful to examine the formation of pure ZnO layers from the three precursors DEZ, DBZ, and EZIP.

Spin coating DEZ from toluene under a relative humidity of 40% in an oxygen free nitrogen atmosphere results in rough, scattering layers of Zn(OH)$_2$. This roughness is undesirable because the active layer of a solar cell should not have pinholes as these may cause the evaporated top electrode to short with the bottom electrode. Adding tetrahydrofuran (THF) to the solution of DEZ in toluene enhances the layer smoothness significantly. THF coordinates to the Zn atom of DEZ and reduces the hydrolysis reaction rate, leading to smoother films.

The condensation reaction of a smooth layer of Zn(OH)$_2$ (formed using DEZ as precursor) on a glass substrate into ZnO is further illustrated in figure 2.1a. Layers have been prepared as described above, annealing has been performed in the same environment for 15 minutes. The onset of absorption of ZnO is approximately at 365 nm (Zn(OH)$_2$ shows no absorption at this wavelength). It is evident that the conversion reaction requires a minimum temperature of 90 °C to complete. A higher annealing temperature is usually undesirable, because of degradation of most polymers at high temperature.

The second precursor DBZ is chemically very similar to DEZ but has a higher boiling point. DBZ is provided as a solution in heptane by the manufacturer and forms fairly smooth layers when spin coated under a relative humidity of 40% in an oxygen free nitrogen atmosphere. Spin coating DBZ from a heptane/THF solvent mixture leads to improved layers without pinholes.

The third precursor discussed is ethylzinc isopropoxide (EZIP). The synthesis of this precursor is relatively easily achieved by reacting DEZ with isopropanol. Since this
reaction is exothermic, the reaction from EZIP to Zn(OH)$_2$ is most likely less violent compared to the reaction from DEZ to Zn(OH)$_2$. EZIP is dissolved in a 2:3 mixture of toluene:THF and spin coated onto a glass substrate under a nitrogen environment with relative humidity of 40%. This yields lightly scattering layers by eye.

Absorption spectra from ZnO layers formed using the three different precursors are shown in figure 2.1b. All layers were prepared under similar conditions and converted to ZnO at 100 °C. The absorption onset is similar in all cases, indicating successful synthesis of ZnO from all precursors. For EZIP, the spectrum shows a long tail into the visible range of the spectrum that is most likely due to scattering.

### 2.3 ZnO:P3HT blends using diethylzinc as precursor

Diethylzinc (DEZ) has previously been used in hybrid solar cells and is therefore the starting point of optimization in this chapter. DEZ is well soluble in a common organic solvents with P3HT, like chloroform, chlorobenzene, or o-dichlorobenzene. In the previous section it was shown that addition of THF was necessary to slow down the reaction of DEZ with water from the environment. THF however, is a less good solvent for regioregular P3HT and it is necessary to find a balance in adding a sufficient amount for stabilization of the DEZ and a small enough quantity to prevent the P3HT from aggregating in the solution. Because DEZ is commercially available in toluene, a toluene/THF mixture containing DEZ is used as stock solution as described in the experimental section (section 2.8). This stock solution is then added to P3HT in a solvent such as chloroform...
2.3. ZnO:P3HT blends using diethylzinc as precursor

Spin coating DEZ and P3HT from a CF/THF/toluene solvent mixture leads to rough, scattering layers and results in devices showing relatively high leakage current under reverse bias and a negligible photovoltaic effect. Using CB instead of CF still gives rise to quite rough layers by eye, but yields proper working devices. ODCB also results in working devices, but gives rougher, more scattering layers than the CB/THF/toluene solvent mixture, judging by eye. J-V curves of the devices, in dark and under illumination, are shown in figure 2.2. Since CB yielded the best device performance, other processing parameters were optimized using a CB/THF/toluene solvent mixture.

![J-V curves of ZnO:P3HT solar cells in dark and under illumination.](image)

**Fig. 2.2:** J-V curves of ZnO:P3HT solar cells in dark and under illumination. The active layers were spin coated from different solvents using DEZ as ZnO precursor and subsequently annealed at 100 °C. Apart from the solvent indicated in the legend, each solution also contained toluene and THF.

Other processing parameters that influence the device performance were explored and results are shown in table 2.1. PEDOT:PSS was used as bottom electrode for hole collection and is spin coated from an aqueous, acidic dispersion. Annealing of this PEDOT:PSS layer will remove most of the water, which is likely to influence the device performance, especially since the acidic nature of the PEDOT:PSS is potentially destructive for the ZnO. We found that annealing of the PEDOT:PSS layer at 100 °C prior to spin coating the active layer results in better device performance. We note that due to the fact that the relative humidity during spin coating is 40%, the PEDOT:PSS layer will not be completely dry. Table 2.1 further demonstrates the importance of annealing of the active layer after deposition also at 100 °C. Without annealing of the active layer the solar cell does not work. This can be expected, because at that time ZnO is not yet formed.

Additionally, it was tested whether the device would perform better when the active layer was exposed to air after annealing at 100 °C inside the glove box. Oxygen from the air is known to react with any free electrons that are present in the ZnO conduction band and effectively un-dope the materials to an intrinsic semiconductor. The efficiency was,
Tab. 2.1: Initial screening of processing parameters for preparing ZnO:P3HT solar cells using DEZ as ZnO precursor.

<table>
<thead>
<tr>
<th>active layer annealed</th>
<th>PEDOT:-PSS annealed</th>
<th>exposed to air</th>
<th>ZnO vol-%</th>
<th>P3HT (mg mL⁻¹)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA cm⁻²)</th>
<th>FF</th>
<th>MPP (mW cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>19</td>
<td>10</td>
<td>0.57</td>
<td>0.093</td>
<td>0.27</td>
<td>0.014</td>
</tr>
<tr>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>19</td>
<td>10</td>
<td>0.58</td>
<td>3.9</td>
<td>0.44</td>
<td>0.99</td>
</tr>
<tr>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>19</td>
<td>10</td>
<td>0.61</td>
<td>4.1</td>
<td>0.52</td>
<td>1.3</td>
</tr>
<tr>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>19</td>
<td>10</td>
<td>0.75</td>
<td>5.2</td>
<td>0.52</td>
<td>2.0</td>
</tr>
<tr>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>19</td>
<td>5</td>
<td>0.79</td>
<td>3.4</td>
<td>0.49</td>
<td>1.3</td>
</tr>
<tr>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>13</td>
<td>10</td>
<td>0.53</td>
<td>2.7</td>
<td>0.51</td>
<td>0.73</td>
</tr>
<tr>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>25</td>
<td>10</td>
<td>0.66</td>
<td>5.3</td>
<td>0.49</td>
<td>1.7</td>
</tr>
</tbody>
</table>

however, lower compared to the same device without air exposure, because of lower V_{oc} and J_{sc}. The origin for this decreased efficiency is unknown.

Using different concentrations of P3HT and DEZ in the spin coating solution (but keeping the same ratio) will likely lead to a different morphology. More concentrated solutions cannot be used because P3HT does not dissolve well at higher concentrations. If the solution was diluted twice, simply by adding CB, the device performance was not improved, mainly due to a lower J_{sc}. The reason is unclear, it is possible that more DEZ evaporates from the solution during spin coating, which lowers the amount of ZnO in the film.

The amount of ZnO in the blend was also adjusted to find the optimum device performance. This was adjusted by using less or more stock solution for the solvent mixture, and adjusting the correct volume by changing the amount of added CB, as described in the experimental section (section 2.8).

Reducing the amount of ZnO from 19 to 13 vol-% in the blend results in a significant decrease of J_{sc}. This is likely due to less charge generation and fewer available percolation pathways (a higher chance of isolated ZnO domains) for electrons in the ZnO phase to reach the aluminum electrode. When increasing the amount of ZnO to 25 vol-% the J_{sc} remains high, but V_{oc} and FF decrease, resulting in a lower MPP. The optimum amount of ZnO was found to result in 19 vol-% of ZnO in the blend, assuming full conversion of the precursor.

The effect of the ZnO concentration on the surface morphology was investigated using atomic force microscopy (AFM). The results are presented in figure 2.3 and show that higher precursor concentrations result in rougher layers, quantified by the significant increase in root-mean-square surface roughness (R_{RMS}). The increased roughness may explain the lower value of V_{oc} observed at 25 vol-%, because shunts between the top
2.3. ZnO:P3HT blends using diethylzinc as precursor

and bottom electrode are more likely to occur. At ZnO contents lower than 19 vol-\%, the layer is possibly even smoother, but also here the $V_{oc}$ is reduced. The reason for this reduction is not understood and there seems to be no clear trend in $V_{oc}$ when all three devices are compared. We note that even in the same device processed on a different day, the $V_{oc}$ may vary.

![AFM images](image)

**Fig. 2.3:** AFM images of ZnO:P3HT blends made using DEZ as ZnO precursor with 19 and 25 vol-% ZnO. Height scale is in nanometers.

Using the optimized parameters, the thickness of the active layer was varied by changing the spin rate in the spin coating step. The device performance in terms of $V_{oc}$, $J_{sc}$, $FF$, and $MPP$ are shown in figure 2.4. The thinnest devices ($<50$ nm) show a relatively low $FF$ and $V_{oc}$ (figure 2.4a). Above $\sim100$ nm active layer thickness, $V_{oc}$ and $FF$ are constant. The trend observed for the $J_{sc}$ in these devices is shown in figure 2.4b. $J_{sc}$ improves with increasing active layer thickness. The performance is maximized for the thickest layers, prepared at a spin rate of only 500 r.p.m. Spin coating at a slower rate would result into poor distribution of material on the PEDOT:PSS/ITO/glass substrate, and is irreproducible. Therefore 500 r.p.m. was used as minimum spin rate.

Interestingly, the efficiency of ZnO:P3HT devices keeps increasing with layer thickness, while there is a clear optimum in layer thickness in a ZnO:MDMO-PPV hybrid cell. This high efficiency at high layer thickness may be attributed to the high hole mobility in annealed, crystalline regioregular P3HT. Consequently, the electron mobility in the ZnO phase must also be high.

The $J-V$ characteristics of the best device produced using P3HT and DEZ is shown in figure 2.5 along with the external quantum efficiency ($EQE$), which shows the sensitivity of the device for the various wavelengths of visible light. The $J-V$ curve shows low leakage.
current at reverse bias, meaning that even though the layer is rough, it contains no, or very few shunts between the PEDOT:PSS and the aluminum electrode. The EQE graph shows a nearly flat conversion efficiency between 450 and 600 nm light of roughly 45%. In the EQE the vibronic features of P3HT that are usually present in the absorption spectrum are almost absent. This is a consequence of the thick (225 nm) layer that absorbs most of the incident light that has an energy above the optical band gap of P3HT.

**Fig. 2.4:** Device parameters versus layer thickness of ZnO:P3HT hybrid solar cells made with DEZ as ZnO precursor.

**Fig. 2.5:** J-V curve and EQE of the optimized ZnO:P3HT cell, using DEZ as ZnO precursor.
2.4 ZnO:P3HT blends using dibutylzinc as precursor

Dibutylzinc (DBZ) is commercially available as solution in heptane. In section 2.2 it was demonstrated that THF is not necessarily needed to prepare smooth ZnO layers on a glass substrate when DBZ was spin coated from a heptane solution.

First, DBZ was dissolved in a solvent mixture with heptane and chlorobenzene (CB), and tested with and without THF as co-solvent. AFM images of the resulting ZnO:P3HT blend layers are presented in figure 2.6. The surface roughness ($R_{RMS}$) is $\sim$20 nm for both layers, indicating that addition of THF to the solvent mixture does not result in a significant change in roughness.

![AFM images of ZnO:P3HT layers made using DBZ as ZnO precursor spin coated from CB, using heptane or heptane/THF as cosolvent.](image)

(a) From heptane, $R_{RMS} = 19$ nm

(b) From heptane/toluene, $R_{RMS} = 23$ nm

**Fig. 2.6:** AFM images of ZnO:P3HT layers made using DBZ as ZnO precursor spin coated from CB, using heptane or heptane/THF as cosolvent.

Photovoltaic devices were made and the characteristics of the devices are presented in table 2.2. It is clear that adding THF improves the device performance, mainly in $J_{sc}$ and $FF$, although no obvious difference in surface roughness is observed. It is likely that the internal distribution of ZnO is different.

Heptane is a non-solvent for P3HT. To enable a better comparison with the DEZ experiments heptane was removed from the as-received solution by evaporation at elevated temperature, and replaced with toluene (see section 2.8). It turns out that the choice for heptane or toluene has no significant effect and adding THF enhances the device performance to a similar extent when either DBZ was in heptane or toluene (table 2.2). To test the effect of the amount of ZnO for optimal performance, the amount of DBZ added to the solution was varied. The resulting amount of vol-% ZnO in the blend was varied between 15 and 23 vol-%, assuming full conversion of the precursor into ZnO. Table 2.2
Tab. 2.2: Device performance of ZnO:P3HT devices made using DBZ as ZnO precursor, using different solvents and ZnO concentration.

<table>
<thead>
<tr>
<th>Solvent: CB + vol-% ZnO</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>MPP (mW cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hex</td>
<td>19</td>
<td>0.52</td>
<td>3.9</td>
<td>0.39</td>
</tr>
<tr>
<td>hex/THF</td>
<td>19</td>
<td>0.59</td>
<td>4.5</td>
<td>0.47</td>
</tr>
<tr>
<td>tol</td>
<td>19</td>
<td>0.57</td>
<td>3.0</td>
<td>0.44</td>
</tr>
<tr>
<td>tol/THF</td>
<td>15</td>
<td>0.68</td>
<td>4.4</td>
<td>0.41</td>
</tr>
<tr>
<td>tol/THF</td>
<td>19</td>
<td>0.64</td>
<td>5.3</td>
<td>0.44</td>
</tr>
<tr>
<td>tol/THF</td>
<td>23</td>
<td>0.66</td>
<td>4.7</td>
<td>0.38</td>
</tr>
</tbody>
</table>

shows that the optimum device performance is obtained at 19 vol-% ZnO.

The $J$-$V$ curve and $EQE$ of the optimized device are shown in figure 2.7. The $J$-$V$ shows that there is negligible dark current under reverse bias, demonstrating high shunt resistance despite the rough active layer. Under illumination and reverse bias there is a small increase in photocurrent, indicating that not all photogenerated charges are collected at short circuit but that an extra (reverse) bias is needed to extract these charges. The $EQE$ is similar to the $EQE$ of the ZnO:P3HT device based on DEZ precursor, with a flat conversion efficiency between 450 and 600 nm, of about 45%.

Summarizing, DBZ is a suitable precursor to produce ZnO:P3HT hybrid solar cells. Compared with DEZ, performances and optimized processing conditions are similar.
2.5 ZnO:P3HT blends using ethylzinc isopropoxide as precursor

As is discussed in section 2.1, ethylzinc isopropoxide (EZIP) is easily synthesized from DEZ and isopropanol. Because the reaction of DEZ to EZIP is exothermic, the hydrolysis of EZIP to Zn(OH)$_2$ will be less exothermic than the reaction from DEZ to Zn(OH)$_2$ and therefore expectedly slower and more amenable to control, possibly resulting in better mixing and smoother surface morphology.

EZIP was dissolved in CB, because this is the main component of the solvent mixtures used for DEZ and DBZ. Since EZIP is less reactive than these other precursors, addition of THF to control the hydrolysis may not be necessary and a layer of ZnO:P3HT was prepared using CB without any cosolvents. An AFM image of such layer deposited is presented in figure 2.8.

The surface roughness ($R_{RMS} = 50$ nm) is significantly higher than layers made from DEZ and DBZ using THF as cosolvent. The device performance was reasonable, but less than with the DEZ and DBZ so far (table 2.3).

To possibly enhance the device performance, different solvent mixtures were examined and the results are summarized in table 2.3. When THF is added to the CB to slow down the reaction of the precursor and make a smoother layer, the performance of the solar cells decreased, due to a lower $J_{sc}$. When toluene was tested as cosolvent the performance is improved compared to CB only, mainly via an increase of the $V_{oc}$. For cells processed from CB/tol and CB/tol/THF solvent mixtures, the power output approaches 1.0 mW cm$^{-2}$ (resulting in a power conversion efficiency close to 1%). It also shows that addition of THF does not have a positive effect for EZIP. This is consistent with the fact that EZIP is less reactive than DEZ and DBZ towards ambient water. The beneficial effect of toluene as cosolvent is presently not understood. Replacing CB by CF as main solvent
Tab. 2.3: Device performance of ZnO:P3HT devices made using EZIP as ZnO precursor, using different solvents and ZnO concentration.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>( FF )</th>
<th>( MPP ) (mW cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>0.45</td>
<td>3.6</td>
<td>0.47</td>
<td>0.78</td>
</tr>
<tr>
<td>CB/THF</td>
<td>0.47</td>
<td>2.0</td>
<td>0.52</td>
<td>0.48</td>
</tr>
<tr>
<td>CB/tol/THF</td>
<td>0.56</td>
<td>3.3</td>
<td>0.53</td>
<td>0.94</td>
</tr>
<tr>
<td>CB/tol/THF 29 vol-% ZnO</td>
<td>0.45</td>
<td>3.7</td>
<td>0.49</td>
<td>0.81</td>
</tr>
<tr>
<td>CB/tol</td>
<td>0.59</td>
<td>3.0</td>
<td>0.56</td>
<td>0.98</td>
</tr>
<tr>
<td>CF/tol/THF</td>
<td>0.38</td>
<td>0.20</td>
<td>0.52</td>
<td>0.040</td>
</tr>
</tbody>
</table>

did not lead to well-performing devices, mainly because of a very low \( J_{sc} \). All solar cells show a reasonably high \( FF \), suggesting that the layers are closed and no shunts between top (aluminum) and bottom (PEDOT:PSS) electrode are present.

The \( J-V \) curve and \( EQE \) graphs of the best ZnO:P3HT device made from EZIP are shown in figure 2.9. The \( J-V \) shows almost no leakage current under reverse bias in the dark. There is a minimal increase of photocurrent under reverse bias, implying that the collection of charges is not strongly field dependent. The \( EQE \) shows a flat response between 450 and 600 nm at around 22%, about half of what was observed using DEZ or DBZ as precursor.

![J-V curve](image-a.png)  
![EQE graph](image-b.png)

**Fig. 2.9:** \( J-V \) curve and \( EQE \) of the optimized ZnO:P3HT cell, made using EZIP as ZnO precursor.
2.6 ZnO:P3HT blends using ethylzinc isopropoxide under inert conditions

In the previous section it was shown that EZIP can be used as precursor for making ZnO:P3HT blends when ambient water is present to convert EZIP to Zn(OH)$_2$ which then forms ZnO upon thermal annealing. Because EZIP already has built-in oxygen, water may not be needed to convert it into ZnO. This reaction would then be an elimination reaction.

Figure 2.10 compares the optical absorption of an EZIP layer spin coated on glass with that of EZIP layers annealed at 200 °C, in air and under inert conditions (dry oxygen-free nitrogen). The measurements were performed in air and hence also the unannealed EZIP layer has probably (partly) reacted to Zn(OH)$_2$. The absorption spectra of the annealed EZIP layers are virtually identical and characteristic for ZnO (absorption onset at 360 nm), indicating that EZIP is indeed able to form ZnO without being exposed to water or oxygen. This observation gives the prospect of first forming the mixed precursor:P3HT layer and then applying heat to form ZnO. If successful this would also allow to adjust the morphology of the active layer by for example slow drying or solvent annealing prior to ZnO formation.

![Absorption spectra of EZIP and EZIP layers annealed in air and under inert conditions.](image)

Fig. 2.10: Absorption spectra of a pure layer of EZIP, a layer of EZIP annealed in air, and a layer of EZIP annealed under inert conditions. Annealing was performed at 200 °C.

A mixed layer of EZIP:P3HT is investigated using AFM under inert and dry conditions in a glove box (figure 2.11). The sample was not exposed to oxygen or water between deposition and the AFM measurement. Figure 2.11a shows the layer before thermal annealing and figure 2.11b after thermal annealing at 200 °C. The images and the measured surface roughness clearly show that the morphology of the layer changes upon annealing and that the surface becomes more corrugated. This is probably due to the
thermally induced conversion of EZIP into ZnO in which volatile reaction products evaporate. Further, P3HT may form larger crystalline domains during annealing because the increased temperature imparts mobility on the polymer chains.\textsuperscript{13,19}

The surface roughness of the annealed active layer is comparable to the roughness of a ZnO:P3HT layer made using DEZ as precursor, hence there is a fair chance that there are few shunts between the top and bottom electrode in a device. Initially the device performance was low, mainly due to a low $V_{oc}$ of $\sim$0.3 V, and low $J_{sc}$ of 0.1 mA cm$^{-2}$. The $FF$ was 0.3-0.4, resulting in a maximum power point close to 0.01 mW cm$^{-2}$. After optimization steps in the solvent mixture, a device could be made with a $V_{oc}$ of 0.36 V, $J_{sc}$ of 2.6 mA cm$^{-2}$, and $FF$ of 0.32, resulting in a $MPP$ of 0.3 mW cm$^{-2}$. Here, CB was used as solvent with 12 vol-% toluene as cosolvent and an amount of EZIP that results in 38 vol-% ZnO when assuming full conversion of the precursor. The $J$-$V$ curve and $EQE$ of this optimized device are shown in figure 2.12.

Although this is the best device made using EZIP as precursor under inert conditions, the device shows serious leakage current in the dark. The external quantum efficiency ($EQE$) shows a maximum value at around 450 nm, which is 23%.
2.7 Conclusions

Three different ZnO precursors to make in-situ ZnO:P3HT hybrid solar cells were investigated. Diethylzinc (DEZ), dibutylzinc (DBZ), and ethylzinc isopropoxide (EZIP) each hydrolyze with water from the environment to form Zn(OH)$_2$ which then condenses into ZnO upon heating at 100 °C.

For each precursor the deposition conditions were varied extensively and the parameters of the optimized solar cells are summarized in table 2.4. When DEZ or DBZ are used as precursor, THF is needed as a cosolvent to obtain the best ZnO:P3HT solar cells. THF coordinates with its oxygen atom to Zn and slows down the hydrolysis reaction to Zn(OH)$_2$. Using THF as cosolvent, closed layers of ZnO:P3HT can be formed that have a surface roughness of about 20 nm. When using the less reactive EZIP precursor, use of THF has no beneficial effect. Remarkably it is found that the use of toluene as a cosolvent has a beneficial effect when using EZIP. Toluene is thought not to be interacting with the precursor. For each of the three precursors the optimum amount of ZnO is 19 vol-%. When more ZnO is used the roughness of the layers further increases.

Since EZIP has a built-in oxygen atom, EZIP can be converted into ZnO by heat treatment at 200 °C without using ambient water in the reaction. Using EZIP under dry conditions working devices have been prepared but the MPP was limited to only 0.3 mW cm$^{-2}$ (table 2.4).

Table 2.4 shows that the best devices were obtained using DEZ as precursor. For DBZ the best performance is slightly less, but with EZIP it was not possible to reach similar good performance. After optimizing the ZnO contents, the solvent mixture, concentration,
2. Zinc oxide precursors for hybrid polymer solar cells

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Solvent</th>
<th>ZnO (vol-%)</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>FF</th>
<th>MPP (mW cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEZ</td>
<td>CB/THF/tol</td>
<td>19</td>
<td>0.75</td>
<td>5.2</td>
<td>0.52</td>
<td>2.0</td>
</tr>
<tr>
<td>DBZ</td>
<td>CB/THF/tol</td>
<td>19</td>
<td>0.64</td>
<td>5.3</td>
<td>0.44</td>
<td>1.5</td>
</tr>
<tr>
<td>EZIP</td>
<td>CB/tol</td>
<td>19</td>
<td>0.59</td>
<td>3.0</td>
<td>0.56</td>
<td>0.98</td>
</tr>
<tr>
<td>EZIP no H(_2)O</td>
<td>CB/tol</td>
<td>38</td>
<td>0.36</td>
<td>2.6</td>
<td>0.32</td>
<td>0.30</td>
</tr>
</tbody>
</table>

annealing temperatures of the PEDOT:PSS and the active layer, DEZ ultimately provides about 2.0% power conversion efficiency in simulated solar light. Because DEZ was the precursor that resulted in the best devices, it is used as the standard precursor throughout the remainder of the investigations described in this thesis.

### 2.8 Experimental

**Ethylzinc isopropoxide synthesis:** Ethylzinc isopropoxide (EZIP) was prepared by adding 0.5 mL of dry isopropanol dropwise to 5 mL of a 1.1 M solution of diethylzinc (DEZ) in toluene, using a Schlenk flask inside a nitrogen-filled glove box. The reaction mixture was stirred for 10 min. to ensure complete reaction of DEZ to EZIP. Then, all solvents were removed in vacuum, leaving solid EZIP in the Schlenk flask. NMR measurements indicated traces of toluene. The EZIP could then be dissolved in chloroform, chlorobenzene or toluene. The solubility of EZIP in the different solvents was moderate.

\(^1\)H NMR (CDCl\(_3\)) \(\delta\): 4.17 (septet, \(J = 6.3\) Hz, 1H), 1.22 (d, \(J = 6.3\) Hz, 6H), 1.20 (t, \(J = 8.1\) Hz, 3H), 0.28 (q, \(J = 8.1\) Hz, 2H)

**Materials:** Regioregular P3HT (\(M_n = 30\) kg mol\(^{-1}\) with a polydispersity of 2.1) was obtained from Rieke Metals. Before use, it was reduced using hydrazine and purified using soxhlet extraction with hexane and chloroform. PEDOT:PSS (Clevios P VP AL4083, H. C. Stark) comes dispersed in water. The solution is filtered by a 5 \(\mu\)m filter before use. DEZ is provided as a 1.1 M solution in toluene. 3.2 mL dry tetrahydrofuran (THF) was added to 1.8 mL DEZ solution to create a stock solution of DEZ in toluene/THF. DBZ is provided as a 1 M solution in heptane. 1 mL THF is added to 1 mL DBZ solution in heptane to create a DBZ/heptane/THF stock solution. In order to make a DBZ/toluene/THF solution, heptane was removed from the DBZ/heptane solution by evaporation, and replaced with toluene to yield a solution of 1.5 M DBZ in toluene. A stock solution of DBZ/toluene/THF is prepared by adding 1 mL of THF to 1 mL of DBZ in toluene.
**Methods:** Precursor:P3HT blend solutions were prepared by first dissolving P3HT in chlorobenzene or o-dichlorobenzene. Then, the appropriate amount of precursor solution or stock solution is added, such that assuming full conversion of the precursor, a 1:1 weight ratio of ZnO:P3HT (∼19 vol-%) is present in the final layer. Typically, 5 mg P3HT is dissolved in 350 µL chlorobenzene, followed by adding 150 µL of the DEZ stock solution in toluene/THF, leading to the final solution that was used for spin coating the active layer. The final solution contained 10 mg mL⁻¹ P3HT.

For devices, tin-doped indium oxide (ITO) substrates (Philips Research) were used. These substrates were precleaned by sonication in acetone for 15 min, followed by scrubbing thoroughly with sodium dodecyl sulfate (SDS) and sonicating in an aqueous solution with SDS for 15 min. Then, the substrates were rinsed with deionized water to remove all SDS, followed by another sonication step in isopropanol. Finally, 30 min. of UV-ozone treatment was applied to remove remaining contaminants from the ITO layer to improve the wetting properties of the substrate.

The typical layout of the solar cell is glass/ITO/PEDOT:PSS/active layer/Al, where the active layer is a blend of polymer and ZnO. After cleaning, the substrates were transferred to a nitrogen-filled glove box (< 30 ppm O₂). In case where the active layer needs to be prepared using a humid environment, the glove box was already set to control the relative humidity (at 40%).

PEDOT:PSS was first spin coated onto the glass/ITO substrate at a spin rate of 1500 r.p.m. for 60 s, subsequently 3000 r.p.m. for another 60 s, followed by annealing at 100 °C on a hot plate. This procedure leads to a ∼70 nm PEDOT:PSS layer on the glass/ITO substrate. After 10-15 min., the substrate was cooled down and the active layer was applied, at a typical spin rate of 500 r.p.m. for 60 s and subsequent drying of the sample at 3000 r.p.m. for 60 s. Then, the substrate was left in humid environment for 15 min. to finalize the reaction of precursor with water from the environment, followed by another annealing step. Regioregular P3HT ($M_n = 30$ kg mol⁻¹ with a polydispersity of 2.1) was obtained from Rieke Metals. Before use, it was reduced using hydrazine and purified using soxhlet extraction with hexane and chloroform. at 100 °C for 15 min., to finalize the condensation reaction of Zn(OH)₂ to ZnO.

The samples were then transferred to another nitrogen-filled glove box (< 1 ppm O₂, <1 ppm H₂O) where 100 nm of aluminum was evaporated at a pressure < 3·10⁻⁷ mbar. The size of the cells was 0.091 cm².

**Device characterization:** Current-voltage (J-V) characteristics were measured under inert conditions inside the glove box using a Keithley 2400 Source Meter, controlled by a computer. The device was illuminated by a 50 W tungsten-halogen lamp filtered by a Schott GG420 UV filter and a Hoya LB120 daylight filter. External quantum efficiency
(EQE) measurements were performed with respect to a calibrated silicon reference. A homebuilt set-up based on a Philips focusline 7027 light source and an Oriel monochromator were used. The monochromatic light was focused on an aperture with a diameter of 2 mm, to create a light spot smaller than the device area.

**Atomic force microscopy (AFM):** Tapping mode AFM was measured with a Veeco MultiMode and a Nanoscope III controller using PPP-NCH-50 probes from Nanosensors.

**Thickness measurements:** The thicknesses of the layers were determined using a Veeco Dektak 150 surface profiler. Part of the active layer was removed using a sharp knife, the step height difference measured using the Dektak 150 determines the layer thickness.

**References**


3. THE EFFECT OF THREE-DIMENSIONAL MORPHOLOGY ON THE EFFICIENCY OF HYBRID POLYMER SOLAR CELLS

Abstract

The efficiency of polymer solar cells critically depends on the intimacy of mixing of the donor and acceptor semiconductors used in these devices to create charges and on the presence of unhindered percolation pathways in the individual components to transport holes and electrons. The visualization of these bulk heterojunction morphologies in three dimensions has been challenging and has hampered progress in this area. Here, the morphology of 2%-efficient hybrid solar cells consisting of poly(3-hexylthiophene) as the donor and ZnO as the acceptor are spatially resolved in the nanometer range by electron tomography. The morphology is statistically analyzed for spherical contact distance and percolation pathways. Together with solving the three-dimensional exciton-diffusion equation, a consistent and quantitative correlation between solar-cell performance, photophysical data, and the three-dimensional morphology has been obtained for devices with different layer thicknesses that enables differentiating between generation and transport as limiting factors to performance.
3. The effect of 3D morphology on hybrid polymer solar cells

3.1 Introduction

Efficient organic solar cells use a bulk heterojunction of two semiconductors with offset energy levels to create charges. By intimately mixing electron donor and acceptor materials, the intrinsic limitations related to the low mobility and lifetime of excitons in organic semiconductors can be overcome, resulting in effective carrier generation at the extended donor-acceptor interface. The most efficient organic solar cells combine p-type conjugated polymers with n-type fullerenes, which have recently reached efficiencies of 8.3%.

Control over the morphology of the blend by the proper choice of processing conditions is generally essential to reach this level of performance and one of the traditional challenges in the field of organic solar cells lies in optimization of the morphology of the mixed layer. As an alternative to fully organic solar cells, hybrid solar cells use a combination of organic and inorganic materials. This concept has been demonstrated by combining semiconducting polymers as the donor with different inorganic materials, including CdSe, TiO$_2$, and ZnO as the acceptor. Potential advantages of the inorganic semiconductors are a high dielectric constant, which facilitates carrier generation processes, a high carrier mobility, and thermal morphological stability of the blended materials. Ultimately, hybrid cells offer the prospect of actual control over the morphology of the blend by first constructing the inorganic scaffold with the proper layout and dimensions but until now the best hybrid solar cells were made by simultaneous deposition of the two components. This often involves precarious processing, owing to the rather different nature of the materials involved. These drawbacks can largely be circumvented by the in situ generation of the inorganic semiconductor inside the organic material. In this process, a well-soluble organometallic precursor is deposited from solution together with the semiconducting polymer. During and after this deposition the precursor is converted, by reacting with moisture from the surrounding atmosphere, to an inorganic network inside the polymer film. This has provided 1.4%-efficient photovoltaic cells, using diethylzinc as the ZnO precursor and poly(3-hexylthiophene) (P3HT) as the semiconducting polymer. The reasons for the reduced efficiency of hybrid solar cells compared with the more efficient polymer:fullerene cells are only partly understood and need to be analyzed to further increase the performance. Here, we describe and analyze in situ ZnO:P3HT solar cells that reach a power conversion efficiency of 2%. Photoinduced absorption spectroscopy and three-dimensional (3D) electron microscopy of the active layers, combined with statistical analysis of percolation paths and solving the exciton diffusion equation are used to provide an unprecedented detailed insight into the role of the nanoscale morphology in creating and transporting charges in these bulk heterojunctions. Such analysis enables a unique and quantitative insight into the loss mecha-
nisms associated with morphology that control, and ultimately limit, the power conversion of these rather efficient ZnO:P3HT hybrid solar cells.

3.2 Device characterization

The active layer of the photovoltaic cells was applied by spin coating a blend of diethylzinc and P3HT from a mixture of chlorobenzene, toluene, and tetrahydrofuran onto a transparent electrode, consisting of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on an indium tin oxide (ITO)-covered glass substrate. During spin coating, the diethylzinc was exposed to humidity, causing hydrolysis and the formation of Zn(OH)$_2$. The subsequent condensation reaction is completed by annealing the film at 100 °C to form an interpenetrating network of ZnO inside the P3HT. Electron diffraction experiments demonstrate the presence of crystalline P3HT and ZnO domains in these active layers (figure 3.1). These mixed films do not visibly scatter light, indicating that no coarse phase separation between the organic and inorganic component takes place during the deposition process. An aluminum top electrode completes the device.

Fig. 3.1: Electron diffraction of pure P3HT and ZnO:P3HT blends. Measured with a camera length of 730 mm. Diffraction rings of P3HT and ZnO are indicated.

The optimal parameters for device performance were determined in chapter 2. A 1:1 weight ratio between polymer and ZnO was found to give the best performance. This translates into a ZnO volume fraction of about only 20%, noticeably smaller than what is commonly used in polymer:fullerene solar cell devices, where the optimal fullerene content generally exceeds 50%. In addition, the thickness of the ZnO:P3HT active layer was systematically varied between 50 and 250 nm, by adjusting the spin rate during the coating process, while keeping the same P3HT and diethylzinc concentration. Despite some spread in the results, a clear trend is observed: the performance of the devices improves with increasing photoactive layer thickness, mainly as a result of increasing
current densities. The overall best performance was obtained for a device with an active layer thickness of 225 nm. Under illumination with 100 mW cm\(^{-2}\) simulated solar light, this device delivers an open circuit voltage \((V_{oc})\) of 0.75 V, a short circuit current density \((J_{sc})\) of 5.2 mA cm\(^{-2}\) and a fill factor \((FF)\) of 0.52, resulting in an estimated device efficiency of 2.0% (figure 3.2a). Spectral response measurements (figure 3.2b) reveal a maximal external quantum efficiency \((EQE)\) of 44% at 520 nm. The broad, rather flat shape of the spectral response is related to the thickness of the device. Convolution of the \(EQE\) with the AM1.5G spectrum affords a current density of 5.6 mA cm\(^{-2}\), which is in reasonable agreement with the value obtained from current-voltage \((J-V)\) measurements.

It is quite uncommon for polymer solar cells to have an optimal layer thickness significantly larger than 100 nm, because many material combinations suffer from charge collection limitations at larger thicknesses. P3HT:PCBM [(6,6)-phenyl-C\(_{61}\)-butyric acid methyl ester) is one notable exception, demonstrating that in P3HT carrier mobilities are sufficiently high to allow thick photoactive layers. The good performance of the relatively thick ZnO:P3HT layer is a strong indication that electron collection through the ZnO phase occurs quite effectively as well, despite the relatively low ZnO content.

Thicker ZnO:P3HT cells outperform the thinner devices owing to increasing current density, while the fill factor and open circuit voltage remain constant. The increase of current density with increasing layer thickness is shown in figure 3.3a. For comparison, the number of photons absorbed by the ZnO:P3HT layer is included. The absorption was calculated by optical modeling, integrating over all wavelengths using the complex refractive index of the mixed layer \((\tilde{n} = n + i \cdot k)\), where \(n\) is the refractive index and \(k\) is the extinction coefficient) as determined by ellipsometry. The modeling was carried
out on the entire stack of layers (glass/ITO/PEDOT:PSS/ZnO:P3HT/Al) in the device and thus accounts for interference effects (see section 3.6).

Figure 3.3a shows that the increasing current density with layer thickness is noticeably larger than the absorption increase. This can be quantified with the internal quantum efficiency \((\text{IQE})\), which is the ratio between the measured \(J_{sc}\) and the number of absorbed AM1.5 photons per unit area and time. The \(\text{IQE}\) (figure 3.3b) increases significantly with layer thickness from 20\% for 50 nm thick cells up to 50\% for cells with active layer thicknesses >150 nm. Hence, in thicker layers, not only more photons are absorbed, but these photons are also more efficiently transferred into collected current. This is counterintuitive, because one would expect that charge collection becomes more difficult for thicker layers, owing to the larger distances over which the carriers need to be transported and the smaller electric field over the layer.

Fig. 3.3: Increase in current density and internal quantum efficiency versus active layer thickness.

### 3.3 Photoinduced absorption

To further investigate the observed \(\text{IQE}\) differences, photoinduced absorption (PIA) measurements were carried out on three ZnO:P3HT photovoltaic cells with different layer thicknesses (44, 54 and 151 nm). For all three samples, excitation at 488 nm (2.54 eV) results in photoinduced bleaching bands of neutral P3HT at 1.9, 2.2, and 2.35 eV (figure 3.4) normalized at the bleaching signal at 2.2 eV to correct for differences in layer thick-
ness). Moreover, the characteristic absorption bands of the polymer radical cation at 0.5 and 1.3 eV are observed, unambiguously demonstrating photoinduced charge generation in this blend. The low-energy absorption at 0.5 eV is relatively large because at this energy also electrons injected into the ZnO contribute to the PIA signal. The spectra also exhibit a peak at 1.06 eV, which is related to a P3HT triplet state. This indicates that quenching of the initially formed singlet exciton is not quantitative, leaving enough time for intersystem crossing to the triplet state for a significant fraction of the excitations. Without knowing the exact absorption coefficient and lifetime of the different photoinduced states, one cannot quantitatively assess their yields, but comparing the ratio between polaron and triplet bands does provide relevant information about the relative yields. For thicker layers, the radical cation bands increase significantly compared with the triplet absorption, suggesting a higher carrier generation efficiency, in accordance with the observed higher IQE for thicker layers. Photoluminescence spectroscopy on ZnO:P3HT films confirmed the incomplete exciton quenching. Quantitative analysis was severely hampered by the intrinsic low photoluminescence efficiency in P3HT, which is mainly determined by disordered regions and generally not representative for most excitons.

![Fig. 3.4: Normalized PIA spectra of P3HT and ZnO:P3HT blend layers used in solar cells recorded at $T = 80$ K. In the device, the active layers had thicknesses of 151 nm (black), 54 nm (red), and 44 nm (green). Spectra were normalized at the 2.2 eV bleaching band.](image)

The observed incomplete charge generation in hybrid ZnO:polymer films makes them distinctly different from photoactive blends with fullerenes as the electron acceptor, where exciton quenching is generally quantitative, even at very low fullerene contents. This could be related to a higher miscibility for the molecular acceptors with the donor polymer, affording better dispersion of the acceptor (domains) inside the polymer matrix.
3.4  Electron tomography and exciton diffusion calculations

A suboptimal morphology is one possible cause for incomplete charge carrier generation, demonstrated by PIA measurements. To examine the morphology of the ZnO:P3HT film, transmission electron microscopy (TEM) was used. The bright-field TEM image of a cross-section of a typical complete device (figure 3.5) shows that the photoactive layer is much rougher than all layers underneath. In the image, ZnO shows up as the darker regions as a consequence of a higher electron density. Evidently, ZnO is not homogeneously dispersed inside the polymer matrix, especially at the interface with the PEDOT:PSS, where a layer of pure P3HT is present. This layer is at least 10 nm thick, causing excitons generated within the first few nanometers from the PEDOT:PSS interface not to reach a ZnO interface to create charges. Possibly, (part of) the triplets observed using PIA originate from this layer. This interface layer constitutes a larger fraction for thinner devices, which could explain the larger triplet signals in these samples. In absolute terms, however, the number of excitons that are expected to be lost in this P3HT interface layer is not large enough to completely account for the measured IQE losses, which exceed 50% for all devices.

![Figure 3.5](image)

**Fig. 3.5:** (a) Transmission electron micrograph of a cross-section of a 124 nm ZnO:P3HT photovoltaic cell. The sample was obtained using focused ion beam. The different layers present in the device are indicated in the image; the platinum layer is deposited later to allow preparation of the TEM sample. (b) 3D reconstruction of a tilt series of the same sample. The ZnO is illustrated in yellow, the polymer is transparent against a black background.

More detailed TEM analyses were carried out on freestanding films. Representative mixed films of different thicknesses (57, 100, and 167 nm) were spin coated on PEDOT:PSS and then floated on water, leaving ZnO:P3HT films that were analyzed by electron
tomography. The snapshots of the reconstructed volumes of these films are shown in figure 3.6. A threshold was applied to the raw data as obtained by electron tomography in such a way that ZnO appears yellow and P3HT looks transparent. Ostensibly, a large difference between the three films is obtained, showing finer phase-separated domains with increasing layer thickness. In particular, the thinnest film has much larger domains, both for the ZnO and the P3HT. The presence of P3HT domains that are substantially larger than the exciton diffusion lengths in P3HT is consistent with the large triplet signals in PIA measurements and the low \(IQE\) in the thin devices.

![Fig. 3.6: Reconstructed volumes of ZnO:P3HT layers, obtained by electron tomography. Three samples with thicknesses as indicated are shown, the size of all samples is 700 x 700 nm; ZnO appears yellow, P3HT transparent.](image)

To quantify the relevant morphological parameters, an extensive statistical analysis of the 3D-TEM images was carried out. Therefore, the original 3D-TEM data of the bulk of the film (about 60% of the total thickness) were binarized to decide which voxels (3D data points) are ZnO and which are P3HT. The results are summarized in table 3.1. In the two thickest layers, the estimated ZnO volume fraction is close to the expected value of 19%, on the basis of the ratio of diethylzinc and P3HT in the spin coating solution. The ZnO content in the thinnest layer is significantly lower at 13%. This is tentatively rationalized by a comparatively large fraction of the diethylzinc evaporating during spin coating with the higher spin rate applied for this thin layer. The low ZnO content of the thinnest film partially accounts for the relatively large observed P3HT domains. Next, spherical contact distances, defined as the distance from a certain voxel of one material to the nearest voxel of the other material, were determined for these three films. As under operation, excitons are primarily generated inside P3HT, we focus on the distance distribution from P3HT to ZnO. Figure 3.7 shows the probability to find P3HT at a certain shortest distance to a ZnO domain. For the 100 and 167 nm thick films, most P3HT lies well within a shortest distance of 10 nm from ZnO. On the other hand, the 57 nm thick
sample has a large amount of polymer at shortest distances as high as 25 nm from an interface with ZnO. This analysis substantiates that coarser phase separation is present in thinner layers.

**Tab. 3.1:** Calculated volume fraction, exciton quenching, and percolation connectivity of ZnO:P3HT bulk heterojunction layers inferred from electron tomography.

<table>
<thead>
<tr>
<th>Film thickness (nm)</th>
<th>57</th>
<th>100</th>
<th>167</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO volume fraction (%)</td>
<td>13±4</td>
<td>21±8</td>
<td>21±8</td>
</tr>
<tr>
<td>Without electrodes: Generation efficiency (%)</td>
<td>40±3</td>
<td>78±5</td>
<td>83±5</td>
</tr>
<tr>
<td>With electrodes: Generation efficiency by ZnO (%)</td>
<td>32±5</td>
<td>73±5</td>
<td>79±6</td>
</tr>
<tr>
<td>Quenching efficiency by electrodes (%)</td>
<td>32±1</td>
<td>7±1</td>
<td>4±1</td>
</tr>
<tr>
<td>ZnO connected to top (%)</td>
<td>96±2</td>
<td>94±5</td>
<td>92±5</td>
</tr>
<tr>
<td>ZnO monotonously connected to top (%)</td>
<td>92±2</td>
<td>85±10</td>
<td>80±12</td>
</tr>
</tbody>
</table>

(a) Distribution of the probability to find a P3HT voxel at a certain distance from a ZnO domain for mixed ZnO:P3HT films of different thicknesses, calculated from the 3D-TEM data shown in figure 3.6.

(b) Cumulative probability to have P3HT within a shortest distance to ZnO. The error margins indicated are obtained from the two most extreme thresholds possible for the binarization of the 3D-TEM data.

**Fig. 3.7:** Statistical analysis of the 3D morphology.

It is not exactly clear what governs the large morphology differences. During deposition several processes take place simultaneously: evaporation of three different solvents and diethylzinc, adsorption of water, reaction of diethylzinc with water, evaporation of condensation reaction products and gelation and/or precipitation of P3HT and the inorganic material. The relative rate of these processes will determine the final morphology. Our results suggest that these relative rates change significantly with increasing spin rate during deposition.
To quantify the effect of the coarseness of the phase separation on the charge carrier generation, exciton diffusion in the active layer has been modeled. The diffusion of excitons in the polymer phase can be described by the diffusion equation

\[
\frac{dn}{dt} = -\frac{n}{\tau} + D \nabla^2 n + g
\]

(3.1)

where \( D \) is the diffusion constant, \( n \) is the exciton density, \( \tau \) is the exciton lifetime, and \( g \) is the rate of exciton generation. The exciton lifetime and exciton diffusion rate constant in P3HT are taken from the literature: \( \tau = 400 \) ps and \( D = 1.8 \cdot 10^7 \) m\(^2\) s\(^{-1}\). The actual diffusion rate constant may be lower, because the P3HT is possibly more disordered when blended with ZnO than in the pure material. It is assumed that at an interface with ZnO, excitons are efficiently quenched, that is, \( n = 0 \). These assumptions cause the calculated quenching to be an upper limit to actual charge generation efficiency. In this respect, we note that exciton quenching at the ZnO:P3HT interface has been questioned, but we stress that the alternative explanation, that is, that free charges are directly generated in P3HT with a quantum yield of 1.7% and ZnO just acts to collect the electrons, is not compatible with the \( IQE \approx 50\% \) observed here. Figure 3.8 shows the calculated exciton quenching efficiency \( \eta_Q \) for different layer thicknesses in bulk material obtained by solving the diffusion equation using cyclic boundary conditions and reveals that exciton quenching is far more efficient in the thicker layers as a consequence of their finer morphology.

However, with active layers as thin as 60 nm, the effect of the electrodes cannot be ignored. It is well established that excitons in conjugated polymers can be quenched at both PEDOT:PSS and LiF/Al electrodes. The quenching is associated with long range energy transfer of excitons to the electrode interface assisted by exciton diffusion. Exciton quenching at the electrodes will not contribute to the photocurrent generation. To emulate the effect of electrodes, two perfectly quenching planes were used as boundary conditions, instead of imposing cyclic boundary conditions. The effect of introducing electrodes is especially striking for the thinnest layer (table 3.1): 32\% of excitons are quenched by the electrodes and do not contribute to the current. The presence of electrodes also affects the efficiency of quenching by ZnO: as a sizeable fraction of excitons diffuses towards the electrodes, fewer excitons will be quenched by ZnO and contribute to the photocurrent. For the thicker layers (100 and 167 nm), these effects are far less pronounced. This is in part due to the much finer morphology and in part due the larger layer thickness, as both these factors result in most excitons being generated closer to ZnO than to an electrode. Figure 3.8d shows vertical cross-sections of the quenching efficiency in the presence of the electrode.

Besides charge carrier generation, also carrier collection is essential for solar cell
operation. Efficient collection relies on continuous pathways for both carriers. In view of the large volume excess of polymer in the blend, connectivity of this material will not be a limiting factor. The fraction of ZnO voxels that is interconnected through other ZnO voxels to the top of the investigated slab is quite high, at values well over 90% for all three layers, despite the low ZnO content (table 3.1). The connectivity is smaller for thicker layers, probably because larger distances have to be crossed. However, mere continuity may not be enough to effectively collect the charges. Within a continuous phase, pathways may exist that do not continue in the direction towards the collecting electrode. Owing to the macroscopic electric field over the active layer of the device, carriers may be trapped inside those cul-de-sacs and cannot be collected. Therefore, we also determined the fraction of ZnO connected to the top through a strictly rising path. The calculated unidirectionally connected fraction of ZnO is still very high (93%) for the 57 nm thin layer, but reduces for thicker layers, reaching 80% for the 167-nm-thick film.
3.5 Conclusions

Looking at the combined effects of charge carrier generation and collection, we can conclude that the relatively poor performance of thin ZnO:P3HT solar cells is related to inefficient charge generation as a result of the low ZnO content and the coarse phase separation, as well as the exciton losses impaired by the electrodes and possibly incomplete exciton dissociation. For thicker photoactive layers, charge generation is much more efficient, owing to a much more favorable phase separation. These devices show superior efficiencies, but owing to increasing difficulty to collect the generated electrons the IQE does not exceed about 50%. Further improvement can be anticipated if better control over the morphology of the photoactive blend can be gained.

3.6 Experimental

Materials: Regioregular P3HT ($M_n = 30$ kg mol$^{-1}$ with a polydispersity of 2.1) was obtained from Rieke Metals, and was reduced and purified before use. PEDOT:PSS (Clevios P VP Al 4083) was purchased from H.C. Stark and filtered with a 4.5 µm filter before use. Aluminum wire (99.999%) was obtained from Engelhard-Clal, and diethylzinc (1.1 M solution in toluene) from Aldrich.

Methods: Substrates for device preparation were glass plates covered with patterned ITO. These substrates were thoroughly cleaned by sonication in acetone and aqueous dodecyl sulphate solution, followed by rinsing with water and sonication in isopropanol and applying ultraviolet-ozone for 30 min. The substrates were then transferred to a nitrogen-filled glove box with a controlled humidity (relative humidity) of 40%. PEDOT:PSS was applied by spin coating at 1500 r.p.m. for 1 min., and subsequent drying for 1 min. at 3000 r.p.m., followed by heating on a hot-plate at 100 °C for 15 min. The active layer was deposited by spin coating the mixed solution of diethylzinc and P3HT. Diethylzinc/P3HT solutions were prepared by mixing 350 µL of P3HT in chlorobenzene (14.3 mg mL$^{-1}$) with 150 µl of a diethylzinc solution (0.4 M, obtained by mixing 1.8 mL of a 1.1 M diethylzinc solution in toluene with 3.2 mL of tetrahydrofuran). The final solution contained 10 mg mL$^{-1}$ P3HT. Assuming full conversion of the diethylzinc to ZnO, this would afford a 1:1 (w/w) ratio of ZnO:P3HT in the mixed film.

Devices were all spin coated from the same solution at different spin rates. The blends were aged for 15 min. and then annealed for 15 min. at 100 °C in nitrogen. After heating, the samples were transferred to a glove box with an inert nitrogen atmosphere ($<$1 ppm H$_2$O and $<$1 ppm O$_2$) using an air-tight container. The back electrode consisted of 100
nm of aluminum and was evaporated under high vacuum (<3 \cdot 10^{-7} \text{ mbar}). All handling and analysis of the cells was carried out under an inert atmosphere.

For TEM investigations, the ZnO:P3HT films were floated from the water-soluble PEDOT:PSS substrate onto the surface of demineralized water and picked up with 200-mesh copper TEM grids. Bright-field TEM morphology observation and acquisition of tilt series for electron tomography were carried out on a Technai G² 20 TEM (FEI) operated at 200 kV. All tilt series were obtained in an automatic fashion by using EXPLORE 3D software (FEI), in the tilt range of ±70° with a saxton tilt scheme with a 0° tilt step of 1.5°. The alignment and simultaneous iterative reconstruction of the data series was carried out by using INSPEC 3D (FEI) and visualization of the 3D reconstructed volume was done with Amira 4.1 (Mercury Computer Systems). Cross-sectional specimen preparation from a complete device was carried out by focused-ion-beam (FIB) machine applying a Quanta 3D FEG (FEI).

For the statistical analysis and exciton diffusion modelling the electron tomography data were binarized. The threshold for this binarization has a major impact on the final outcome and hence error margins were estimated by applying the two extremes for this threshold. These margins indicate the uncertainty within this particular sample. Larger differences can be expected between samples.

For the statistical analysis and exciton diffusion modelling, only the homogeneous part of the morphology was used, leaving out the ill-defined interfaces with PEDOT:PSS and aluminum. This part constitutes 60% of the total local ZnO:P3HT layer. To avoid overestimating edge effects in the diffusion modelling, the data set is extended by mirroring part of the morphology until the correct thickness is obtained. The connectivity of the ZnO network was calculated for the reduced data set and extrapolated to the correct thickness. The diffusion equation is solved numerically by using a fully explicit scheme: 

\[
n(t + \Delta t) = n(t) + \Delta t \left( \frac{dn}{dt} \right),
\]

with the last term given by equation 3.1. When the steady-state is reached, that is, when \( \frac{dn}{dt} \) is smaller than a pre-set tolerance, the exciton density throughout the polymer phase is known. By comparing this with the exciton density in the absence of a quencher (\( \tau_g \)), the quenching efficiency \( \eta_Q \) is obtained from 

\[
\eta_Q = 1 - n/(\tau_g).
\]

**Device characterization:** Current density-voltage (J-V) measurements were carried out at room temperature with a computer-controlled Keithley 2400 Source Meter in the dark or under simulated solar light (100 mW cm\(^{-2}\)) from a Philips Brilliantline Pro 50 W tungsten-halogen lamp, filtered by a Schott GG420 UV filter and Hoya LB120 daylight filter. External quantum efficiency (EQE) measurements were performed without bias illumination with respect to a calibrated silicon reference diode (Hamamatsu S1226-8BQ). A home-built set-up, utilizing a Philips focusline 7027 light source and an Oriel monochromator
was used. The monochromatic light was focused on an aperture (\( \varphi \leq 2 \) mm) to create a light spot smaller than the device area. The results were corrected for the light intensity dependence of the short circuit current density (\( J_{sc} \propto \text{Intensity}^\alpha \), with \( \alpha \approx 0.95 \), determined separately). The EQE was convoluted with the AM1.5G spectrum to yield the \( J_{sc} \), and the efficiency was calculated by multiplying this value with the \( V_{oc} \) and \( FF \) from the \( J-V \) measurements. The film thickness was measured on a Veeco Dektak 150 surface profiler.

**Optical Modeling:** The optical modeling calculations for determination of the internal quantum efficiency of the devices were performed with the ESSENTIAL MACLEOD software package (Thin Film Center, Inc., Tucson, USA). The optical constants of glass and ITO were provided by Thin Film Center, the value of PEDOT:PSS and Al were obtained from the literature.\(^{[29,30]}\) The optical constants of ZnO:P3HT were obtained by ellipsometry measurements using a Woollam WVASE32 ellipsometer.

**Electron diffraction:** Electron diffraction (ED) experiments were performed on ZnO:-P3HT films of 45 and 100 nm thickness and on pure P3HT. For the pure P3HT film the brightest diffraction ring corresponds to a \( d \)-spacing of 0.39 nm. This ring is attributed to the (020) reflection of P3HT crystals associated with the typical \( \pi-\pi \) stacking distance of P3HT chains.\(^{[31]}\) For the blend films we observe the same diffraction ring of P3HT together with new diffraction rings at larger angles. More specifically we see one narrow and a broad ring that can be attributed to the (100) and a combination of the (002) and (101) diffractions of wurtzite ZnO, respectively.\(^{[32]}\) These rings correspond to a \( d \)-spacing of about 0.25 nm. The ED of the bulk heterojunction layers evidences the presence of crystalline P3HT and ZnO.

**References**


4. CONTROLLING THE MORPHOLOGY AND EFFICIENCY OF HYBRID ZNO:POLYTHIOPHENE SOLAR CELLS VIA SIDE CHAIN FUNCTIONALIZATION

Abstract

The efficiency of polymer - metal oxide hybrid solar cells depends critically on the intimacy of mixing of the two semiconductors. The effect of side chain functionalization on the morphology and performance of conjugated polymer:ZnO solar cells is investigated. Using an ester-functionalized side chain poly(3-hexylthiophene) derivative (P3HT-E), the nanoscale morphology of ZnO:polymer solar cells is significantly more intimately mixed compared to ZnO:poly(3-hexylthiophene) (ZnO:P3HT), as evidenced experimentally from a 3D reconstruction of the phase separation using electron tomography. Photoinduced absorption reveals nearly quantitative charge generation for the ZnO:P3HT-E blend but not for ZnO:P3HT, consistent with the results obtained from solving the 3D diffusion equation for excitons formed in the polymer within the two experimental ZnO morphologies. For thin ZnO:P3HT-E active layers (±50 nm) this yields a significant improvement of the solar cell performance. For thicker cells, however, the reduced hole mobility and a reduced percolation of ZnO pathways hinders charge carrier collection, limiting the power conversion efficiency.
4.1 Introduction

By combining considerable power conversion efficiencies with desirable properties such as low weight and mechanical flexibility, thin film organic polymer photovoltaic devices are an attractive approach for generating renewable energy. The use of roll-to-roll solution processing of devices adds to the prospects of obtaining efficient and low-cost devices. Moreover, the optical and electrical properties of the materials can be tuned by changing the molecular structure. This has resulted in a substantial increase in efficiency of polymer solar cells in the last few years,\textsuperscript{1–7} where first applications are emerging.\textsuperscript{8,9}

Photoexcitation in organic semiconductors does not lead to free charge carriers which are required for a photovoltaic effect. Instead, strongly bound electron-hole pairs (excitons) are created that will only separate into free carriers at an interface between an electron donor (p-type) and electron acceptor (n-type) material. The distance that such an exciton is able to cover is very limited, dependent on the diffusion constant of the exciton and its intrinsic lifetime. Ideally, an exciton is created within a few nanometers of the donor-acceptor interface to ensure a high quantum efficiency of charge generation and consequently most organic solar cells are based on a bulk heterojunction in which the n-type and p-type materials are intimately mixed. Today, the most efficient organic solar cells combine p-type conjugated polymers with n-type fullerenes, reaching efficiencies up to 8.3%.\textsuperscript{10}

An alternative to full-organic solar cells are so-called hybrid solar cells. These devices combine the solution processability of organic compounds with the morphological stability of inorganic materials, such as CdSe,\textsuperscript{11–13} TiO\textsubscript{2},\textsuperscript{14–17} or ZnO.\textsuperscript{18–23} Recently, we achieved a power conversion efficiency (PCE) of 2.0% for a ZnO:poly(3-hexylthiophene) (ZnO:P3HT) blend, which was prepared by spin coating a mixture of P3HT and diethylzinc (DEZ) as a ZnO precursor from a common solvent.\textsuperscript{chap3} During spin coating, DEZ reacts with ambient moisture to form Zn(OH)_2, while the solvent evaporates. By subsequent annealing of the Zn(OH)_2:P3HT layer to 100 °C it is possible to complete the condensation reaction of Zn(OH)_2 into ZnO and to form a hybrid ZnO:P3HT bulk heterojunction active layer. Due to the large polarity difference between the organic and inorganic components, phase separation occurs. For thin layers, this process affords coarsely phase separated films that limit charge generation. Thicker films obtained by spin coating at lower speed, on the other hand, are better mixed, but here charge extraction becomes limiting, because an increasing part of the ZnO is no longer connected to the electron collecting electrode, disabling part of the charges formed to contribute to the photocurrent (see chapter\textsuperscript{3}).

The challenge now, is to make hybrid layers that feature both high generation efficiency and high charge collection. This is expected to lead to higher efficiencies in
ZnO:polymer hybrid solar cells. To achieve this goal we have investigated a more hydrophilic polythiophene derivative with ester-functionalized side chains. The ester functions in poly[(3-hexylthiophene-2,5-diyl)-co-(3-(2-acetoxyethyl)thiophene-2,5-diyl)] (7:3 ratio) (P3HT-E, figure 4.1) are more compatible with the polar ZnO surface. We expect it to yield more finely dispersed ZnO in the polymer matrix and, hence, an improved charge carrier generation and power conversion efficiency.

![Molecular structures of P3HT and P3HT-E.](image)

**Fig. 4.1:** Molecular structures of P3HT and P3HT-E.

### 4.2 Microscopic analysis

ZnO:P3HT and ZnO:P3HT-E films were prepared by spin coating a mixture of the polymer and DEZ from a chlorobenzene:toluene:tetrahydrofuran solvent mixture in a N₂ atmosphere with a relative humidity of 40%, followed by annealing at 100 °C as described in detail in the experimental section 4.9. The mixed films were made with a ZnO:-polymer ratio that is optimal for the performance of the solar cell (vide infra). This implies a somewhat larger ZnO content in the ZnO:P3HT-E compared to the ZnO:P3HT film.

The surface topographies of thin (<50 nm) ZnO:polymer films were investigated with tapping mode atomic force microscopy (TM-AFM). The spin coated and annealed ZnO:-P3HT blends shows a rough topography with a RMS surface roughness of approx. 25 nm, which indicates a coarse phase separation (figure 4.2a, see also chapter 3). Using P3HT-E instead of P3HT (figure 4.2b), the layer shows a much smoother surface with a RMS surface roughness of only 4.7 nm, implying a better miscibility of P3HT-E and ZnO. Transmission electron microscopy (TEM) affords information about the bulk of the active layer. Owing to the high electron density in ZnO, there is a large contrast between polymer and ZnO, which makes TEM an excellent imaging technique to investigate this type of layers. The TEM image of the 50 nm thin film of ZnO:P3HT clearly shows large
ZnO clusters and large pure polymer domains (figure 4.3a). As P3HT is the only absorber of visible light in the active layer, these large P3HT domains are unfavorable because the excitons created in such domain cannot diffuse towards the interface with ZnO during their lifetime and decay before being able to form charges. In the 50 nm film of ZnO:P3HT-E, however, ZnO is much more evenly dispersed inside the polymer matrix (figure 4.3b). This more intimate mixing is favorable for charge generation.

![AFM height images of ZnO:P3HT and ZnO:P3HT-E active layers. Height scale is in nanometers.](image)

**Fig. 4.2:** AFM height images of ZnO:P3HT and ZnO:P3HT-E active layers. Height scale is in nanometers.

![TEM images of blend ZnO:polymer layers](image)

**Fig. 4.3:** TEM images of blend ZnO:polymer layers
To obtain a more detailed insight into the morphologies, electron tomography was performed on the 50 nm thin layers of ZnO:P3HT and ZnO:P3HT-E. The images of the reconstructed volumes are shown in figure 4.4, ZnO being yellow and the polymer being transparent against a black background. Note that the ZnO:P3HT-E image (figure 4.4b) is shown at slightly higher magnification. The images clearly confirm that ZnO disperses much better in P3HT-E than in P3HT. The volume fraction of ZnO calculated from the three dimensional morphologies that is present differs for the two films; 13 vol-% ZnO present in ZnO:P3HT and 17 vol-% in ZnO:P3HT-E. We note that the composition of both films had been optimized for the solar cell performance at this layer thickness. For both films there is less ZnO present then expected based on the amount of DEZ in the solution. Assuming full conversion of all added DEZ, the ZnO content would have been 20 and 25 vol-%, respectively. In both cases, part of the DEZ evaporates during spin coating.

**Fig. 4.4:** Reconstructed volumes from electron tomography of ZnO:polymer blend layers.

### 4.3 Spectroscopic analysis

UV-vis absorption spectra of pure films of P3HT and P3HT-E are virtually identical (figure 4.5), indicating a similar degree of crystallization and a comparable optical band gap. In sharp contrast, the absorption spectra of the mixed ZnO:polymer films differ substantially. The ZnO:P3HT film displays an absorption spectrum that closely resembles that of the pure polymer, but the ZnO:P3HT-E film exhibits a significantly blue-shifted absorption, suggesting less pronounced polymer crystallization. This difference can be explained by an increased interaction between this polymer and ZnO and by smaller polymer domains, impeding effective aggregation.
Photoinduced absorption (PIA) spectroscopy was performed on the active layers to investigate the efficiency of charge generation. Figure 4.6 shows PIA spectra of blends of P3HT and P3HT-E with ZnO recorded with photoexcitation at 488 nm. The PIA spectrum of ZnO:P3HT shows a bleaching band from 1.9-2.5 eV, in correspondence with its neutral absorption spectrum. For ZnO:P3HT-E the bleaching band has a less well resolved vibronic progression and is located at slightly higher energy (the onset has shifted by 0.07 eV), characteristic for less crystalline polythiophene. The signals at 0.4, 1.25, and 1.8 eV in the ZnO:P3HT can be attributed to polarons (radical cations) in P3HT. The signal at 0.4 eV is overlapping with that of conduction band electrons in ZnO (see chapter 3). Importantly, the ZnO:P3HT blend shows a significant peak at 1.06 eV which can be attributed to a triplet-triplet absorption. Triples are indicative for incomplete charge generation.
4.4 Charge carrier generation

To quantify the effect of the coarseness of the phase separation on the charge carrier generation, the exciton diffusion in the active layers has been modeled using the three dimensional electron tomography ZnO morphology datasets (see also chapter 3). The diffusion of the excitons in the polymer phase can be modeled by solving the diffusion equation for steady state:

\[
\frac{dn}{dt} = -\frac{n}{\tau} + D \nabla^2 n + g = 0
\]  

(4.1)

where \(D\) is the diffusion constant, \(n\) is the exciton density, \(\tau\) is the exciton lifetime and \(g\) is the rate of exciton generation. The exciton lifetime and diffusion rate constant in P3HT are taken from the literature, and assumed to be equal for both P3HT and P3HT-E: \(\tau = 400\) ps and \(D = 1.8 \cdot 10^{-7}\) m\(^2\) s\(^{-1}\). While there is no proof for this assumption we note that the exciton diffusion length in conjugated polymers is usually in the 5-6 nm region, as a consequence of a balance of \(\tau\) and \(D\). Furthermore, it is assumed that ZnO is a perfect quencher, consequently, \(n = 0\) at the ZnO:polymer interface. Disregarding the effect of electrodes, using cyclic boundary conditions, this leads to a charge carrier generation efficiency of 40% in the ZnO:P3HT blend, and to 96% in the ZnO:P3HT-E blend. This is illustrated in figure 4.7 and summarized in table 4.1.

It has been reported that the excitons can also be quenched at electrodes like PEDOT:PSS and Al. This quenching, however, will not contribute to the photocurrent. When
quenching at the electrodes is taken into account in the exciton diffusion modeling, ca. 32% of the excitons in ZnO:P3HT are quenched at the electrodes and only ca. 32% of the excitons afford charge carriers (table 4.1). The remaining excitons are lost via intrinsic decay. For ZnO:P3HT-E, still 90% of the excitons yield charge carriers, while only 5.8% are quenched at the electrodes. This clearly demonstrates that the significantly improved charge carrier generation obtained for a finer phase separation also decimates possible exciton losses at the electrodes.

**Tab. 4.1:** Exciton quenching and ZnO connectivity data for 50 nm films.

<table>
<thead>
<tr>
<th></th>
<th>ZnO:P3HT</th>
<th>ZnO:P3HT-E</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO volume fraction (%)</td>
<td>13</td>
<td>17</td>
</tr>
<tr>
<td>Without electrodes: Generation efficiency by ZnO (%)</td>
<td>40</td>
<td>96</td>
</tr>
<tr>
<td>With electrodes: Generation efficiency by ZnO (%)</td>
<td>32</td>
<td>90</td>
</tr>
<tr>
<td>Quenching efficiency by electrodes (%)</td>
<td>32</td>
<td>6</td>
</tr>
<tr>
<td>ZnO connected to top (%)</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>ZnO monotonously connected to top (%)</td>
<td>93</td>
<td>81</td>
</tr>
</tbody>
</table>

### 4.5 Percolation pathways in ZnO

Besides charge carrier generation, also charge collection is essential. This may be limited, especially by discontinuities in the ZnO percolation network which has a volume percentage of less than 20% (chapter 3). The three dimensional electron tomography data
were analyzed to determine the fraction of ZnO connected to the aluminum top electrode where electrons are collected and the fraction of ZnO connected via a monotonously rising path. The latter excludes pathways that do not continue in the direction towards the collecting electrode where electrons may become trapped and recombine before being collected. The results are summarized in table 4.1. The fraction of ZnO connected to the aluminum electrode is near unity for both ZnO:polymer active layers. The fraction connected via monotonously rising path is significantly lower for the ZnO:P3HT-E film, but still quite high at 81%. Looking at the combined effects of charge carrier generation and connectivity we would expect larger currents in ZnO:P3HT-E compared to ZnO:P3HT.

4.6 Solar cell performance

Photovoltaic devices have been fabricated by sandwiching a 50 nm thick ZnO:polymer layer between glass/ITO/PEDOT:PSS and evaporated aluminum contacts. The ZnO content of the active layer was varied to gain optimum power conversion efficiency, leading to 13 vol-% ZnO in the ZnO:P3HT layer, whereas the ZnO:P3HT-E devices exhibited this maximum at 17 vol-%, as determined by electron tomography on the photoactive layers of actual devices.

Current density-voltage (J-V) characteristics and external quantum efficiency (EQE) measurements are shown in figure 4.8a. Typical parameters are summarized in table 4.2. Comparing the two 50 nm layer devices, the cell with P3HT-E has a higher open circuit voltage (\(V_{oc}\)) and short circuit current (\(J_{sc}\)) than the P3HT device, while the fill factor (FF) is lower. The high \(V_{oc}\) for P3HT-E is attributed to the larger optical band gap, as shown in the absorption (figure 4.5b) and EQE (figure 4.8b) onset, while the comparatively low \(V_{oc}\) for thin P3HT is likely caused by the presence of shunts that arise when the layer roughness (25 nm RMS, see section 4.2) is on the order of the layer thickness (50 nm). These shunts also cause the strongly increased (dark) current for the 50 nm ZnO:P3HT below -0.5 V (figure 4.8a). The larger current for P3HT-E is ascribed to the increase in charge carrier generation in the active layer resulting from the more intimate mixing.

<table>
<thead>
<tr>
<th>Device</th>
<th>(d) (nm)</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:P3HT</td>
<td>124</td>
<td>0.75</td>
<td>4.3</td>
<td>0.53</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.44</td>
<td>1.3</td>
<td>0.39</td>
<td>0.2</td>
</tr>
<tr>
<td>ZnO:P3HT-E</td>
<td>117</td>
<td>0.80</td>
<td>2.2</td>
<td>0.38</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.02</td>
<td>2.1</td>
<td>0.40</td>
<td>0.8</td>
</tr>
</tbody>
</table>

ZnO:P3HT devices significantly improve by increasing the active layer thickness to
4. Controlling the morphology via side chain functionalization

120 nm (table 4.2), resulting from fewer shunts and thus a higher $V_{oc}$, and improved currents, owing to a better mixing (see chapter 3). On the other hand, when a thicker ZnO:P3HT-E active layer (~120 nm) is produced, the $J_{sc}$ does not increase, despite the increased absorption of light. Charge carrier generation calculations were not available for this layer, because three dimensional electron tomography was not possible due to the fine phase separation. However, in the PIA spectrum of a thick ZnO:P3HT-E layer (not shown) no triplets were observed, indicating quantitative charge carrier generation. Therefore, charge collection must be a serious loss factor for these devices. Also at reverse bias (-2 V) the photocurrent of the 120 nm ZnO:P3HT-E cell remains less than that of the ZnO:P3HT cell, showing that at higher reverse electric fields the additional carriers are not yet collected.

A critical parameter for collection is the charge carrier mobility. The hole mobilities in the pure polymers and ZnO:polymer blends were determined in hole-only devices which were fabricated by sandwiching a neat polymer or ZnO:polymer layer between PEDOT:-PSS and gold electrodes. In these devices, the space charge limited current can be described by the Mott-Gurney law:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \exp(0.891 \gamma \sqrt{\frac{V}{L}})$$

(4.2)

Where the applied voltage $V_{app}$ has been corrected for the built-in voltage ($V_{bi}$) originating from the work function difference between the electrodes and for the series resistance ($V_{rs}$), which is mainly the resistance over the ITO contact such that $V = V_{app} - V_{bi} - V_{rs}$. Further, $\mu$ is the hole mobility in the sandwiched layer, $\varepsilon_0$ the permittivity of vacuum, $\varepsilon_r$ the weighted average dielectric constant of the two components, and $\gamma$ the field activa-
4.7 Other functionalized polymers

By fitting the experimental $J-V$ curve, the hole mobility was determined. The results are summarized in table 4.3. The hole mobility found for P3HT was $2 \cdot 10^{-8} \text{m}^2 \text{V}^{-1} \text{s}^{-1}$, which is consistent with literature values. The hole mobility found for neat P3HT-E is in the same order of magnitude. When P3HT is blended with ZnO, the mobility decreases with about one order of magnitude. This effect is strongly enhanced in blends of P3HT-E with ZnO where hole mobilities are 3 to 5 orders of magnitude lower than in the pure P3HT-E. We note that the hole-only devices of the blends exhibited a noticeable built-in voltage (0.5 V for ZnO:P3HT-E and 0.3 V for ZnO:P3HT), therefore injection of electrons into the LUMO of the ZnO cannot completely be excluded. Consequently, the measured values for the hole mobility of blends are maximum values.

**Tab. 4.3:** Hole mobilities ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$) of pure polymers and blends ($\pm 1$ order of magnitude).

<table>
<thead>
<tr>
<th></th>
<th>P3HT</th>
<th>P3HT-E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure polymer</td>
<td>$2 \cdot 10^{-8}$</td>
<td>$5 \cdot 10^{-8}$</td>
</tr>
<tr>
<td>Thick blend (~120 nm)</td>
<td>$8 \cdot 10^{-10}$</td>
<td>$2 \cdot 10^{-11}$</td>
</tr>
<tr>
<td>Thin blend (~50 nm)</td>
<td>$4 \cdot 10^{-8}$</td>
<td>$9 \cdot 10^{-13}$</td>
</tr>
</tbody>
</table>

It has been demonstrated before that the morphology affects hole mobility. A finer morphology leads to lower mobilities and solar cell efficiencies, because of more complicated pathways for charges. Besides the morphology, also crystallinity is of importance, as polythiophenes are known to have higher hole mobility in the crystalline state with a lamellar organization of polymer chains. Crystallinity is indicated by a red-shift in absorption compared to the amorphous material. The blue-shifted absorption for ZnO:P3HT-E indicates a lower crystallinity for this polymer when mixed with ZnO (figure 4.5b). This is likely due to interaction with the ZnO surface and/or the extended interface area between the two materials.

4.7 Other functionalized polymers

Other polythiophenes with different functional groups, or a different ratio of functional groups on the side chain, were also used in a ZnO:polymer blend, in order to change the morphology and to enhance the performance. The first other polymer is poly[(3-hexylthiophene-2,5-diyl)-co-(3-(2-acetoxyethyl)thiophene-2,5-diyl)] (9:1 ratio) (P3HT-E10, figure 4.9), and is similar to P3HT-E but only 10% of the side chains have the functional ester group, instead of 30% in the P3HT-E case. The other polymer, poly[(3-hexylthiophene-2,5-diyl)-co-(3-(hydroxyethyl)thiophene-2,5-diyl)] (9:1 ratio) (P3HT-OH, figure 4.9) has an alcohol functional group instead of an ester. The P3HT-E10 is similar to
### Controlling the morphology via side chain functionalization

P3HT-E, but has less functionalized side chains, consequently the morphology is expected to change in a similar way, but lesser degree, as with the P3HT-E, which might result into a higher exciton quenching compared to the ZnO:P3HT blend, but with higher hole mobility compared to the ZnO:P3HT-E blend.

AFM imaging (figure 4.10) shows that smooth layers have been obtained and that indeed, the polymers are able to change the topology of the blend layers. With less functional groups compared to P3HT-E, P3HT-E10 and P3HT-OH give very similar values for $R_{RMS}$ (6.1 and 2.7 nm) as P3HT-E (4.7 nm) when blended with ZnO. P3HT-OH is able to change the topology by a larger degree, indicating that OH groups have a stronger interaction with the ZnO than ester groups have.

![Molecular structures of modified polythiophenes](image)

**Fig. 4.9:** Molecular structures of modified polythiophenes.

![AFM height images](image)

**Fig. 4.10:** AFM height images of ZnO:P3HT-E10 and ZnO:P3HT-OH active layers. Height scale is in nanometers.
This is further illustrated using TEM imaging (figure 4.11). Both ZnO:P3HT-E10 and ZnO:P3HT-OH blend films of ~50 nm thickness show similar morphology, compared to a ZnO:P3HT-E blend (figure 4.3b). From these data it is not clear whether or not the morphology is significantly different between the ZnO:P3HT-E, ZnO:P3HT-E10, or ZnO:P3HT-OH blends (figure 4.3b, 4.11a and 4.11b), while in all cases, it is clear the ZnO is finer dispersed compared to the ZnO:P3HT blend (figure 4.3a) and hence, would lead to a higher exciton quenching by the ZnO.

![TEM images of ZnO:P3HT-E10 and ZnO:P3HT-OH active layers.](image)

**Fig. 4.11:** TEM bright-field images of ZnO:P3HT-E10 and ZnO:P3HT-OH active layers.

Photoinduced absorption was performed on these blend layers, in order to investigate whether P3HT-E10 and P3HT-OH are able to donate charges to the ZnO electron acceptor (figure 4.12). The photoinduced bleaching band for the ZnO:P3HT-E10 blend was shifted 0.04 eV for a 59 nm thick layer, compared to the ZnO:P3HT blend (figure 4.6). There was no triplet (T_n ← T_1) peak measured at 1.06 + 0.04 = 1.1 eV for this blend layer, while the polaron bands at 0.4 eV for ZnO and 1.28 eV for P3HT-E10 are present, indicative for charge generation.

The ZnO:P3HT-OH layer shows a 0.08 eV shift in bleaching onset, and analogous to the other functionalized polymers this layer shows no triplet absorption at 1.14 eV. Polaron bands are clearly present also in this blend layer, indicating charge separation between ZnO and P3HT-OH. From the PIA spectra, it is expected that these blend layers are able to produce a significant number of charge carriers under illumination and that exciton dissociation is close to unity in photovoltaic devices.

Photovoltaic devices were prepared from these ZnO:P3HT-E10 and ZnO:P3HT-OH blends. The optimum ZnO content in the blend layer was 25 and 30 vol-%, respectively. The device parameters are shown in table 4.4 along with the calculated hole mobility for a similar active layer sandwiched between a PEDOT:PSS and gold contact. The $V_{oc}$
is higher for all functionalized polymers compared to the P3HT. The $\text{FF}$ is only able to reach $\sim 0.5$ when a thick ZnO:P3HT or thin ZnO:P3HT-E10/ZnO:P3HT-OH layer is used. In the thin ZnO:P3HT blend, the low fill factor is ascribed to shunts between the top and bottom electrode (section 4.6), while the other low fill factors are ascribed to a lower hole mobility in the polymer. One notable exception is the large fill factor for the thin ZnO:P3HT-OH blend, which shows a $\text{FF}$ of 0.5 at $\mu_h = 1.0 \cdot 10^{-13}$ m$^2$ V$^{-1}$ s$^{-1}$. Additionally, the $J_{sc}$ of this blend is highest for a thin active layer, resulting in a relatively high power conversion efficiency of 1.5%. The reason for the high $\text{FF}$ is unclear, but it is clear that charge separation between these polymers and ZnO is efficient.

**Tab. 4.4:** Device parameters for selected ZnO:polymer solar cells. The ZnO contents are based on the amount of DEZ in the solution used for spin coating, mobility values are $\pm 1$ order of magnitude.

<table>
<thead>
<tr>
<th>Device</th>
<th>ZnO vol-%</th>
<th>$d$ (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$\text{FF}$</th>
<th>PCE (%)</th>
<th>$\mu_h$ (m$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:P3HT</td>
<td>20</td>
<td>124</td>
<td>0.75</td>
<td>4.3</td>
<td>0.53</td>
<td>1.7</td>
<td>$8.0 \cdot 10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>50</td>
<td>0.44</td>
<td>1.3</td>
<td>0.39</td>
<td>0.2</td>
<td>$4.0 \cdot 10^{-8}$</td>
</tr>
<tr>
<td>ZnO:P3HT-E</td>
<td>25</td>
<td>117</td>
<td>0.80</td>
<td>2.2</td>
<td>0.38</td>
<td>0.7</td>
<td>$2.0 \cdot 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>50</td>
<td>1.02</td>
<td>2.1</td>
<td>0.40</td>
<td>0.8</td>
<td>$9.0 \cdot 10^{-13}$</td>
</tr>
<tr>
<td>ZnO:P3HT-E10</td>
<td>25</td>
<td>117</td>
<td>0.84</td>
<td>3.2</td>
<td>0.46</td>
<td>1.2</td>
<td>$7.7 \cdot 10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>59</td>
<td>0.92</td>
<td>2.3</td>
<td>0.50</td>
<td>1.1</td>
<td>$1.4 \cdot 10^{-10}$</td>
</tr>
<tr>
<td>ZnO:P3HT-OH</td>
<td>30</td>
<td>126</td>
<td>0.88</td>
<td>3.8</td>
<td>0.33</td>
<td>1.1</td>
<td>$1.2 \cdot 10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>53</td>
<td>0.92</td>
<td>3.2</td>
<td>0.50</td>
<td>1.5</td>
<td>$1.0 \cdot 10^{-13}$</td>
</tr>
</tbody>
</table>
In order to obtain a higher mobility while having a better mixed morphology, a mixture of P3HT and P3HT-OH (4:1 ratio) with ZnO (20 vol-%) was also prepared. PIA spectroscopy shows that the mixed blend layers still lead to incomplete quenching in thin layers, but the quenching in thicker layers is enhanced, as is observed in the lower triplet absorption (figure 4.13). However, the device performance was not enhanced, mainly due to a lower $J_{sc}$ compared to devices with a ZnO:P3HT active layer, while the $V_{oc}$ and $FF$ were comparable.

Fig. 4.13: Photoinduced absorption spectra of a ZnO:P3HT blend, and ZnO:polymer blends, where the polymer is a mixture of 4:1 P3HT:P3HT-OH.

4.8 Conclusions

Using functionalized P3HT-based polymers that have a better compatibility towards the hydrophilic ZnO a dramatic change in the morphology of the mixed bulk-heterojunction ZnO:polymer film has been obtained compared to P3HT that lacks these functional groups. The use of P3HT-E leads to a much finer phase separation when blended with ZnO, and hence, a higher surface area for exciton dissociation and charge carrier generation between the two materials. The fraction of large polymer domains has decreased significantly using P3HT-E compared to P3HT, leading to nearly quantitative charge carrier generation within the blend. The more intimate mixing in ZnO:P3HT-E, however, seems to reduce the ZnO connectivity and due to a lower degree of crystallinity the hole mobility decreases compared to the reference compound, P3HT. P3HT-E10 and P3HT-OH gave similar results. Only in thin devices, the current and power conversion efficiency is enhanced.
4.9 Experimental

**Materials:** Regioregular P3HT ($M_n = 30$ kg mol$^{-1}$ with a polydispersity of 2.1) was obtained from Rieke Metals. Before use, it was reduced using hydrazine and purified using soxhlet extraction with hexane and chloroform. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was purchased from H.C. Stark (Clevios P VP.AI 4085) and filtered over a 5 µm filter before use. Aluminum wire was used for evaporation and purchased from Alfa Aesar, DEZ was purchased from Sigma-Aldrich (1.1 M solution in toluene).

**Methods:** Regioregular P3HT-E ($M_n = 21$ kg mol$^{-1}$ with a polydispersity of 2.1) was prepared following the Rieke method.$^{[24]}$ P3HT-E10 was prepared in a similar way, P3HT-OH was prepared from P3HT-E10 using post-polymerization reactions.$^{[24]}$

Polymer:DEZ solutions were prepared by mixing a known amount of polymer with the appropriate amount of chlorobenzene and DEZ stock solution (0.4 M, obtained by the addition of a 1.1 M DEZ solution (1.8 mL) in toluene dry tetrahydrofuran (to 3.2 mL)). The correct amount of stock solution, leading to the desired vol-% ZnO in the active layer, assuming full conversion of the DEZ into ZnO, was added and chlorobenzene was added to yield an overall polymer concentration of 10 mg mL$^{-1}$.

Substrates for device preparation were glass plates covered with patterned tin-doped indium oxide (ITO). These substrates were thoroughly cleaned by sonication in acetone and aqueous dodecyl sulfate solution, followed by rinsing with water and sonication in isopropanol. Finally UV-ozone was applied for 30 min. After this step, the substrates were transferred to a nitrogen-filled glove box with a controlled relative humidity of 40%. PEDOT:PSS was spin coated at a spin speed of 3000 r.p.m. for one minute, followed by annealing on a hot plate for 15 min. at 100 °C. Then, the active layer was spin coated from the solution described above; with the spin speed adjusted to the desired layer thickness for one minute, and was subsequently dried at 3000 r.p.m. for one minute. The layer was aged for 15 min. and heated at 100 °C for 15 min. to form the ZnO and anneal the polymer. The substrates were then transferred to a glove box with an inert nitrogen atmosphere (<1 ppm H$_2$O and <1 ppm O$_2$) using an airtight container. The back electrode, consisting of 100 nm aluminum, was evaporated under high vacuum (<3 × 10$^{-7}$ mbar). For hole-only devices a layer of 80 nm gold was evaporated instead. All subsequent handling and analysis of the cells was carried out under an inert atmosphere.

**Device characterization:** J-V characteristics were measured using a Keithley 2400 Source Meter, controlled by a computer. The device was illuminated by a 50 W tungsten-halogen lamp filtered by a Schott GG420 UV filter and a Hoya LB120 daylight filter. Exter-
nal quantum efficiency measurements were performed with respect to a calibrated silicon reference. A homebuilt set-up utilizing a Philips focusline 7027 light source and an Oriel monochromator was used. The devices were exposed to bias illumination during the $EQE$ measurement, using a 530 nm laser, to emulate the charge carrier density in the device that would occur at 1000 W m$^{-2}$ AM 1.5 conditions. The monochromatic and laser light was focused on an aperture with a diameter of 2 mm, to create a light spot smaller than the device area. Convoluting the $EQE$ spectrum with the AM1.5 spectrum yields the $J_{sc}$, which was in good correspondence (within 20%) of the $J_{sc}$ measured using the tungsten-halogen lamp.

**Atomic force microscopy (AFM):** AFM was applied on the devices using a Veeco MultiMode with a Nanoscope III controller, in tapping mode. The used probes were PPP-NCH-50 from Nanosensors. The thicknesses of the layers were determined using a Veeco Dektak 150 surface profiler.

**Transmission electron microscopy (TEM):** For TEM investigations, the ZnO:polymer films were floated from the water soluble PEDOT:PSS substrate onto the surface of demineralized water and picked up with 200-mesh copper TEM grids. Bright-field TEM morphology observation and acquisition of tilt series for electron tomography were performed on a Technai G$^2$ 20 TEM (FEI Co.) operated at 200 kV. All tilt series were obtained in an automatic fashion by using EXPLORE 3D software (FEI Co.), in the tilt range of $\pm 70^\circ$ with a saxton tilt scheme with a 0$^\circ$ tilt step of 1.5$^\circ$. The alignment and (SIRT-) reconstruction of the data series was performed by using INSPEC 3D (FEI Co.) and visualization of the 3D reconstructed volume was done with Amira 4.1 (Mercury Computer Systems, Inc.). For the statistical analysis with GeoStoch (Institute of Stochastics, Ulm University) and exciton diffusion modeling the electron tomography data were binarized.

**Photoinduced absorption (PIA):** PIA was carried out using a homebuilt setup, by exciting a part of the device where no ITO or metal electrode is present, inside a continuous flow cryostat at 80 K with mechanically modulated (275 Hz) Ar-ion laser (Spectra Physics 2025) pump beam at 488 nm (25 mW, beam diameter of 2 mm). The resulting change in transmission of a tungsten-halogen white-light probe beam was monitored after dispersion by a triple-grating monochromator, using Si, InGaAs, and a cooled InSb detector using lock-in amplifiers.
4. Controlling the morphology via side chain functionalization

References


5. HYBRID POLYMER SOLAR CELLS FROM ZINC OXIDE AND A SMALL BAND GAP POLYMER

Abstract

Poly(3-hexylselenophene) (P3HS) is used in combination with zinc oxide (ZnO) to make hybrid polymer - metal oxide solar cells with a photoresponse up to 740 nm. Intimately mixed ZnO:P3HS layers were prepared by casting P3HS and diethylzinc as reactive precursor from a common solvent mixture in a moist atmosphere, followed by conversion to ZnO in the film. Photoinduced absorption spectroscopy was used to identify the electron transfer reaction occurring from P3HS to ZnO under illumination. The performance of ZnO:P3HS solar cells was optimized for composition, layer thickness, and conversion temperature to a final power conversion efficiency of 0.4% in simulated solar light. The performance is primarily limited by a low short circuit current. By comparing the spectrally resolved external quantum efficiency with the optical absorption, we find that the abundant semi-crystalline phase of P3HS gives a negligible contribution to the photocurrent which is dominated by the scarce amorphous P3HS regions in direct contact with the ZnO.
5. Hybrid polymer solar cells from zinc oxide and a small band gap polymer

5.1 Introduction

Hybrid solar cells comprise a combination of an organic and inorganic semiconductor in the active layer and form a potentially interesting alternative to purely organic or polymer solar cells. In most hybrid solar cells the organic or polymer semiconductor serves as the electron donor and transports the photogenerated holes while the inorganic semiconductor accepts and transports electrons. The salient advantage, compared to all organics cells, would be that the rigidity of the inorganic component stabilizes the three dimensional morphology of the active layer. For molecular and polymer bulk heterojunction solar cells the donor and acceptor components are usually mixed while depositing the photoactive layer, but the obtained morphology may change with time and temperature. Because the extent of phase separation, the degree of intermixing, and the size and interconnectivity of the domains are crucial to charge generation and charge transport a change of morphology will generally deteriorate the carefully optimized device performance.

Three different strategies have been explored for making hybrid solar cells, all leading to working devices. In the first approach the organic molecule or polymer is filled into a nanoporous inorganic template. This has the advantage that it is possible to utilize carefully designed three-dimensional interconnected inorganic structures, but it turns out to be challenging to effectively fill the small pores that are ultimately needed to ensure that all excitons generated in the polymer reach the interface with the inorganic. The second strategy overcomes this limitation and uses the mixing of the polymer with inorganic nanoparticles, nanorods, or tetrapods to spontaneously form a hybrid bulk heterojunction. The challenge in this approach is to effectively remove (part) of the organic ligands that solubilize the particles to create sufficient interparticle contacts that enable charge transport while maintaining the processability of these particles in a common solvent with the polymer. The third method involves the use of a molecular precursor to the inorganic semiconductor that can be dissolved together with the polymer in a common solvent to cast the layer that is simultaneously or subsequently converted into the inorganic phase by applying heat. One of the challenges here is to find a semiconductor that can crystallize at sufficiently low temperatures to preserve the integrity of the organic semiconductor during the conversion. We have shown that zinc oxide (ZnO) formed from diethylzinc as reactive precursor can fulfill this role when combined with poly(\(\rho\)-phenylene vinylene) and polythiophene derivatives, leading to a cell performance of about 2% under simulated solar light.

Although the precursor method to hybrid polymer metal oxide solar cells provides some advantages over the two other strategies, it is not without its own challenges. The first of these is controlling the morphology. We found that the size of the phase separated
domains in ZnO:polymer blend changes with the layer thickness of the film and that it can be adjusted by functionalizing the polymer with polar moieties in the solubilizing side chains. Nevertheless, it has not been possible to create bulk heterojunction morphologies that provide external quantum efficiencies (EQE) for photon to electron conversion of 50% or higher. At least in part the EQE is limited by the fact that it is difficult to achieve the optimal balance between intimate mixing to achieve good charge generation and forming larger interconnected domains for charge separation and transport.

Another issue, that we address here, is that ultimately a large part of the solar spectrum must be covered to be able to reach high efficient solar cell. The diethylzinc precursor method has been used in combination with poly(p-phenylene vinylene) and polythiophene derivatives that provide optical band gaps of 2.1 and 1.9 eV respectively. The high reactivity of the precursor limits the choice of polymers that can be used with this method. In fact, some degradation was already observed when using MDMO-PPV in combination with diethylzinc. We found that the precursor method cannot be applied for the many of the novel small band gap polymers that have been developed in recent years for bulk heterojunction solar cells in combination with fullerences. The reason for this is that the electron deficient units that are generally incorporated in these small band gap polymers to control the optical gap are reactive towards diethylzinc due to their low reduction potential. As a result the polymers rapidly degrade when mixed with diethylzinc in solution. Using the less reactive ethylzinc isopropoxide, degradation is slowed down but not prevented. ZnO precursors such as zinc acetylacetonate or zinc acetate are much less reactive but the temperatures needed for thermal conversion into crystalline ZnO are much higher.

Because poly(3-hexylthiophene) (P3HT) does not deteriorate in combination with diethylzinc, we expected that poly(3-hexylselenophene) (P3HS) is an interesting alternative. P3HS has a lower optical gap (1.67 eV) than P3HT (1.91 eV), especially in the aggregated state. The lower gap mainly results from a lower reduction potential. In this chapter we demonstrate normal and inverted ZnO:P3HS solar cells fabricated via the precursor method. We will show that the morphology and performance depend on layer thickness as previously observed for ZnO:P3HT cells prepared in a similar way. Surprisingly we find that the aggregated P3HS gives only a small contribution to the photocurrent.

5.2 Photoinduced charge transfer

First, photoinduced absorption (PIA) measurements were performed to investigate whether or not P3HS is capable of transferring an electron to ZnO under illumination. Figure
5.1 shows the PIA spectra of pure P3HS and mixed ZnO:P3HS films on a quartz substrate recorded at 80 K. The mixed ZnO:P3HS films were prepared by dissolving P3HS in chlorobenzene (CB) and adding a solution of diethylzinc in a mixture of toluene and tetrahydrofuran (THF), followed by spin coating in moist nitrogen atmosphere, ageing and thermal conversion to ZnO at 100 °C. In a separate experiment we verified that P3HS is stable in solution (ODCB) towards the presence of diethylzinc by monitoring the UV-visible-near-IR spectrum, which did not change over at least 1 h, even after warming the solution. The intensity of the PIA spectrum of the pristine film was about one order of magnitude less than that of the blend film as can be seen from the different scale of the left and right vertical axis.

![Fig. 5.1: Photoinduced absorption spectra of a pure P3HS film (120 nm), and a ZnO:P3HS blend layer (140 nm). The measurement was performed at 80 K.](image)

In pristine P3HS two PIA signals are observed, one at 1.00 eV and one that possibly has maximum below 0.4 eV. The <0.4 eV signal is characteristic for radical cations in conjugated polymers and is assigned to the low-energy \((D_1 \leftarrow D_0)\) absorption band originating from a transition of an electron from the highest doubly occupied molecular orbital to the singly occupied level in the P3HS radical cation\[^{[24]}\]. In consequence, the 1.00 eV is probably the corresponding high-energy transition \((D_2 \leftarrow D_0)\) involving excitation from the singly occupied level to the lowest unoccupied molecular orbital. In this assignment the \(D_2 \leftarrow D_0\) transition in P3HS at 1.00 eV is shifted by 0.24 eV compared to the \(D_2 \leftarrow D_0\) transition in P3HT at 1.24 eV\[^{[17,3]}\]. This shift is exactly the same as the difference in optical gap \((S_1 \leftarrow S_0)\) between P3HS (1.66 eV) and P3HT (1.91 eV), which corroborates the assignment. Alternatively, the P3HS triplet absorption \((T_n \leftarrow T_1)\) might also be expected to contribute to the PIA spectrum. In P3HT the \(T_n \leftarrow T_1\) band is found at 1.06 eV\[^{[23]}\] and hence, tentatively, in P3HS the \(T_n \leftarrow T_1\) band would be expected at 1.06 - 0.24 \(\approx 0.82\) eV. The fact that no signal is observed at this photon energy, argues against triplet states being formed in P3HS. The result that pure P3HS forms charges under illumination
can be due the formation of polaron pairs (radical cations and anions) or can be due to electron transfer to an unintentional dopant, e.g. molecular oxygen.

In the ZnO:P3HS blends, the PIA signal is ± 10 times stronger. The increase of the signal at 1.10 eV leaves little doubt that this is indeed due to the D$_2$ ← D$_0$ transition in P3HS radical cations, since more P3HS$^+$ is created due to charge transfer between P3HS and ZnO. The PIA signal at 0.4 eV has increased even more. In ZnO:P3HS the 0.4 eV band is a superposition of the low-energy (D$_1$ ← D$_0$) absorption of P3HS radical cations and the PIA signal of electrons injected into the ZnO that are known to contribute in this region.$^{26}$ Also the plateau in the region 1.2-1.6 eV that maximizes at the optical gap is characteristic of charge carriers in a conjugated polymer. In analogy with studies on P3HT and P3HT:fullerene blends the peak at 1.6 eV, i.e. just below the optical band gap of P3HS, can be ascribed to charges in aggregated conjugated chains$^{27}$ or to a contribution of electroabsorption (EA) to the PIA. In the latter case the modulated space-charge field created by photoinduced charges results in a PIA spectrum that exhibits EA$^{28}$ similar to EA caused by externally applied electrical fields.$^{29}$ The fact that peak at 1.6 eV is less intense for P3HS than for ZnO:P3HS is consistent with the explanation of an EA contribution and matches with the experimental result of similar signal intensity differences observed at 1.8 eV in P3HT and P3HT:fullerene blends.$^{29}$ In the PIA spectrum of ZnO:P3HS further a vibronic progression of bleaching signals of the S$_1$ ← S$_0$ band can be observed at 1.70, 1.86, 2.02, and 2.16 eV.

The PIA spectra demonstrate that photoexcitation of ZnO:P3HS blends leads to formation radical cations in P3HS and electrons in ZnO upon illumination.

### 5.3 Processing conditions

The first step towards ZnO:P3HS solar cells is establishing the optimized processing conditions that allow making bulk heterojunction solar cells. P3HT and P3HS have similar properties and hence the starting point for fabrication of ZnO:P3HS devices is the procedure that has been developed for ZnO:P3HT devices as detailed in section 5.10.$^{16,17,3}$ In short, this involves dissolving the polymer in chlorobenzene (CB) and adding a solution of diethylzinc in a mixture of toluene and tetrahydrofuran (THF), followed by spin coating in moist nitrogen atmosphere, ageing and thermal annealing at 100 °C as detailed in the Experimental Section 5.10. Solar cells were fabricated by applying a ZnO:P3HS active layer in between a glass/ITO/PEDOT:PSS substrate and aluminum top electrode. Both CB and o-dichlorobenzene (ODCB) were tested as they are good solvents for P3HS at elevated temperature$^{22,23}$ and compatible with the standard procedure. In addition, we investigated the effect of the temperature (room temperature or ∼100 °C) of the solution used during spin coating and the temperature of the substrate (room temperature or ∼100
Results of these experiments in terms of the solar cell performance parameters as measured under simulated solar light are summarized in table 5.1.

Devices processed using CB exhibited better performance than devices processed using ODCB. The devices were slightly better if the glass/ITO/PEDOT:PSS substrate was cooled down to room temperature after annealing the PEDOT:PSS layer, and the spin coating was done from hot solution. An AFM image of the ZnO:P3HS layers (Figure 5.2) processed using CB shows the difference in surface roughness obtained when spin casting from hot (∼100 °C) or room temperature CB/toluene/THF solution. After conversion, the layer cast from the hot solution is much smoother (rms roughness 12.5 nm) than the layer deposited at room temperature (rms roughness 23.3 nm). Based on these initial results, all devices discussed in the next sections are processed from a hot solvent mixture using CB, spin coated onto a substrate at room temperature.

**Tab. 5.1:** Initial results exploring the effects of solvent mixture and solvent temperature on the device performance.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA cm^{-2})</th>
<th>FF</th>
<th>MPP (mW cm^{-2})</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CB</td>
<td>20</td>
<td>0.50</td>
<td>1.1</td>
<td>0.39</td>
<td>0.21</td>
<td>208</td>
</tr>
<tr>
<td>2</td>
<td>CB</td>
<td>100</td>
<td>0.60</td>
<td>1.5</td>
<td>0.39</td>
<td>0.35</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>CB</td>
<td>100</td>
<td>0.60</td>
<td>1.3</td>
<td>0.40</td>
<td>0.31</td>
<td>320</td>
</tr>
<tr>
<td>4</td>
<td>ODCB</td>
<td>100</td>
<td>0.40</td>
<td>0.65</td>
<td>0.42</td>
<td>0.11</td>
<td>210</td>
</tr>
<tr>
<td>5</td>
<td>ODCB</td>
<td>100</td>
<td>0.42</td>
<td>0.64</td>
<td>0.41</td>
<td>0.11</td>
<td>190</td>
</tr>
</tbody>
</table>

5.4 **ZnO contents and layer thickness**

One parameter that influences morphology and efficiency in ZnO:polymer solar cells is the ZnO volume contents. With more ZnO present, more excitons in the polymer have a chance to dissociate at the interface, leading to higher currents and efficiencies. However, when more ZnO is introduced, the layer becomes usually rougher and shunts between the hole- and electron collecting contact may start to appear (see chapter 2). This roughness is also observed for the ZnO:MDMO-PPV system.

The effect of vol-% ZnO in the blend layer on the device performance is shown in figure 5.3. The thickness of these layers is 145 ± 17 nm and the surface roughness 15 ± 5 nm, which is less than that of ZnO:P3HT devices that have a surface roughness of 25 ± 5 nm (chapter 3). Figure 5.3 shows that the fill factor (FF) increases slightly with ZnO contents, while the open circuit voltage (V_{oc}) decreases. The FF likely signifies better transport of electrons in the ZnO phase to the aluminum electrode, because
5.4. ZnO contents and layer thickness

more pathways for electrons exist. Considering that the FF increased, it is unlikely that the reduced $V_{oc}$ is due to formation of shunts and a tentative explanation would be that the higher space-average dielectric constant with increasing ZnO contents reduces the energy of the charge transfer state and thereby the resulting $V_{oc}$.\textsuperscript{25} We note that a similar behavior of FF and $V_{oc}$ with increasing ZnO contents has previously been observed in nanoparticle-ZnO:MDMO-PPV blends.\textsuperscript{32}

![AFM images of ZnO:P3HS blend layers processed from a solvent mixture containing chlorobenzene.](image)

**Fig. 5.2:** AFM images of ZnO:P3HS blend layers processed from a solvent mixture containing chlorobenzene.

The short circuit current ($J_{sc}$) does not show a straightforward relation with the ZnO content. For higher ZnO contents, more charge generation can be expected, when there is a larger interface between the polymer and ZnO, but at the same time the amount of the
absorber, P3HS, decreases. Transmission electron microscopy (TEM) imaging has been performed on the active layers with 15 and 30 vol-% as shown in figure 5.4. Because ZnO has a higher electron density than the polymer, it appears dark and the polymer appears light in the grayscale images. The two images show, however, more or less similar phase separation, judging by the eye, and do not easily explain the difference in $J_{sc}$.

**Fig. 5.4:** TEM images of two active layers, with low and high ZnO concentration.

For the optimum ZnO concentration, 19 vol-%, the layer thickness was optimized for maximum performance. Figure 5.5a shows a constant $V_{oc}$, except for the thinnest layer. The $FF$ decreases slightly with active layer thickness. This is characteristic for organic solar cells and finds its origin in the fact that thicker layers enhance the probability for bimolecular charge recombination due to the longer distance charges need to migrate before being collected and also reduce the electric field that is required for charge drift.

The $J_{sc}$ of ZnO:P3HS solar cells increases with layer thickness (figure 5.5b). In chapter 3, it was shown that for ZnO:P3HT cells made in a similar procedure, $J_{sc}$ increased more than linearly with layer thickness and number of absorbed photons. The explanation for this unexpected behavior was found in the morphology of the active layer changed that became more intimately mixed for thicker layers. To determine whether a similar morphology effect occurs in ZnO:P3HS layers, TEM was performed on the thinnest (46 nm) and thickest (167 nm) ZnO:P3HS layers. Figure 5.6 shows that the thin ZnO:P3HS layer has a coarser phase separation than the thick layer. The coarser morphology observed for the thinner film is not a projection artifact, i.e. three stacked images of the thin film (not shown) still appear coarser than the thick film and the observation for ZnO:P3HS is consistent with results from electron tomography on ZnO:P3HT films (chapter 3 and 4).
5.4. ZnO contents and layer thickness

![Graphs showing device parameters versus active layer thickness of ZnO:P3HS devices.](image)

**Fig. 5.5:** Device parameters versus active layer thickness of ZnO:P3HS devices.

The morphology difference leads to less exciton dissociation and charge formation in thin layers than in thick films. Electron tomography on ZnO:P3HT has shown that for thin layers the ZnO vol-% is actually less than based on the amount of diethylzinc added (chapter 3). Judging by eye, Figure 5.6 also shows that for ZnO:P3HS the amount ZnO (dark regions) is less in the thinnest layer.

![TEM images of a thin and thick active layer.](image)

**Fig. 5.6:** TEM images of a thin and thick active layer.
5.5 Normal and inverted devices

The current density-voltage characteristics (J-V curve) of the optimized ZnO:P3HS cell in dark and under simulated solar light are shown in figure 5.7 and the parameters are collected in table 5.2. The performance is modest and mainly limited by a rather low $J_{sc}$. The $EQE$ of the optimized device and the optical absorption spectrum of the active layer give some indication on the origin of the low $J_{sc}$ (figure 5.7). The $EQE$ shows a maximum of $\sim$10%. Remarkably, a comparison of the $EQE$ with the absorption spectrum of the ZnO:P3HS the layer reveals considerable differences. While the onsets of the $EQE$ and the absorption spectrum both occur at $\sim$740 nm (1.67 eV), the maximum in the $EQE$ is significantly blue-shifted compared to the maximum in the absorption. Because the optical absorption represents the entire sample, any deviation from that in the $EQE$ implies that not the entire sample contributes to the photocurrent. In this particular example, the $EQE$ of the ZnO:P3HS films shows that the dominant contribution to the photocurrent comes from the amorphous part of P3HS and that the semi-crystalline part that is associated with the more red-shifted and fine structured absorption is hardly contributing to the current. Possibly, the P3HS domains that are in direct contact with the ZnO are amorphous while the semi-crystalline P3HS is further away from the interface. This would rationalize that excitons created in the semi-crystalline P3HS cannot reach the interface with ZnO because they would need to cross a region with higher energy gap.

At this point it is interesting to compare the $EQE$ data with the PIA spectrum. While the $EQE$ data clearly show that the aggregated P3HS has only a small contribution to the photocurrent, the bleaching signal in the PIA spectrum is clearly associated with the aggregated fraction meaning that photogenerated charges are present in the semi-crystalline phase. While at first sight this may seem contradictory, it can be easily rationalized by considering that the long lived charges formed in P3HS move away from the interface with the ZnO and are stabilized in the aggregated P3HS phase.

Using the optimized processing conditions for the photoactive layer we also prepared devices in which the polarity of the electrodes is reversed. To make these inverted devices, the diethylzinc - P3HS mixture was spin coated on an ITO/ZnO bottom electrode, aged, and converted at 100 °C. A MoO$_3$/Al layer was deposited by thermal evaporation in high vacuum on top of the photoactive layer to complete the device. The inverted devices performed less than the normal device, the losses were mainly due to $V_{oc}$ and $J_{sc}$, and show the same discrepancy of the $EQE$ and the absorption spectrum.
5.6 Annealing temperature

Ballentyne et al. have shown that bulk heterojunction solar cells of P3HS with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as acceptor show better performance when annealed at high temperature (150 °C). The higher annealing temperature can also possibly convert more of the amorphous P3HS into a semi-crystalline phase, leading to an enhanced red-shift in absorption, as well as in the EQE.

Results are displayed in figure 5.8 for the normal and inverted device architecture. For the normal device configuration annealing at 100 or 150 °C gives rather similar performance, while at 175 °C the $V_{oc}$ and $J_{sc}$ decrease considerably. The EQE (figure 5.9a) confirms the lower currents measured on the device annealed at the highest temperature and reveal no clear shift in the EQE maximum. The absorption spectrum shows no significant change with annealing temperature although the long wavelength shoulder at 685 nm becomes slightly more pronounced, consistent with the expected morphological change.

For the inverted cells increasing the annealing temperature does have a beneficial effect. The power conversion efficiency increases by 50% when the annealing temperature increases from 100 to 200 °C as a result of an increased $J_{sc}$ and FF (see figure 5.8c and 5.8d). The increase in $J_{sc}$ and FF can be ascribed to an enhanced crystallinity of the P3HS when annealed at higher temperature. Consistently, the optical absorption shows a more pronounced shoulder at 685 nm when the device is annealed above 150 °C. The EQE of the inverted devices and the optical absorption of the same layers is displayed in figure 5.9b. There is a small shift of the maximum EQE and the whole EQE spectrum increases, while the shape remains more or less similar. This implies that the increased $J_{sc}$ is probably due to a better transport of holes in the P3HS phase, rather than increased exciton dissociation and charge formation. The increased FF for higher

---

**Tab. 5.2:** Performance of optimized ZnO:P3HS and PCBM:P3HS solar cells in normal and inverted device configurations.

<table>
<thead>
<tr>
<th>Blend</th>
<th>architecture</th>
<th>Annealing temperature (°C)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>MPP (mW cm$^{-2}$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:P3HS</td>
<td>Normal</td>
<td>100</td>
<td>0.60</td>
<td>1.8</td>
<td>0.38</td>
<td>0.42</td>
<td>135</td>
</tr>
<tr>
<td>ZnO:P3HS</td>
<td>Normal</td>
<td>175</td>
<td>0.30</td>
<td>0.57</td>
<td>0.43</td>
<td>0.074</td>
<td>145</td>
</tr>
<tr>
<td>ZnO:P3HS</td>
<td>Inverted</td>
<td>100</td>
<td>0.47</td>
<td>0.85</td>
<td>0.36</td>
<td>0.14</td>
<td>135</td>
</tr>
<tr>
<td>ZnO:P3HS</td>
<td>Inverted</td>
<td>200</td>
<td>0.35</td>
<td>1.5</td>
<td>0.40</td>
<td>0.21</td>
<td>113</td>
</tr>
<tr>
<td>PCBM:P3HS</td>
<td>Normal</td>
<td>160</td>
<td>0.58</td>
<td>5.7</td>
<td>0.45</td>
<td>1.5</td>
<td>110</td>
</tr>
</tbody>
</table>
annealed devices supports this reasoning. Despite the beneficial effect of temperature in the inverted device, the overall power conversion efficiency remains lower than in the normal device architecture.

To rationalize the different effect of temperature on device performance for normal and inverted architecture, we surmise that at temperatures above 150 °C the acidic PEDOT:PSS employed in the normal devices degrades the acid sensitive ZnO. In an attempt to confirm this proposition, devices with MoO₃ on ITO instead of PEDOT:PSS in the normal configuration were made. Unfortunately these devices did not provide any reasonable photovoltaic effect for active layers of ZnO:P3HS or ZnO:P3HT. We did not investigate the reasons for this failure, but possibly the reactive diethylzinc affects the integrity of the MoO₃ layer. Normal devices in which PEDOT:PSS was replaced by MoO₃ worked well when the active layer was a P3HT:PCBM blend.
5.6. Annealing temperature

Fig. 5.8: Device parameters of ZnO:P3HS devices versus annealing temperature, normal and inverted devices.

Fig. 5.9: External quantum efficiency (EQE) of ZnO:P3HS devices, annealed at different temperatures (symbols), and corresponding optical densities (lines).
5.7 Comparison with PCBM:P3HS

To better understand the differences between EQE and absorption for the ZnO:P3HS cells, we fabricated and characterized PCBM:P3HS cells in the normal cell configuration, following the work of Ballantyne et al.\textsuperscript{22,23} The solar cell parameters of the PCBM:P3HS versus annealing temperature (figure 5.10) show that the $V_{oc}$ decreases with increasing annealing temperature, but an increase in $FF$ and especially in $J_{sc}$. The reduction of the $V_{oc}$ is explained by the higher HOMO level of the more crystalline polymer. The increased $FF$ and $J_{sc}$ evidence a better charge collection, likely enhanced by the increased hole transport in the P3HS phase and electron transport in PCBM higher crystallinity.\textsuperscript{23} As a result, the device performance almost triples when going from the as-cast device to the one annealed at 160 °C.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_10.png}
\caption{Device parameters of a PCBM:P3HS device versus annealing temperature.}
\end{figure}

The red shift in the absorption spectrum and the relative increase of the long wavelength shoulder at 685 nm, confirm that annealing results in more crystalline P3HS. Both for the as-cast device and the device annealed at 160 °C the EQE (figure 5.11) corresponds fairly well to optical absorption of the active layer. Hence we conclude that that the crystalline P3HS domains that form upon annealing remain in direct contact with PCBM domains, such that both amorphous and crystalline P3HS contribute to the photocurrent as suggested by the EQE (figure 5.11). The important conclusion is that the aggregated phase of P3HS is capable of generating charges when in contact with PCBM.
5.8 Comparing absorption and EQE

In P3HS the long wavelength absorption and the presence of vibronic structure with a long-wavelength shoulder at $\sim 685$ nm indicate the presence of ordered, semi-crystalline domains in thin films.\textsuperscript{21,23} Comparison of the absorption spectra and the $EQE$ data for the normal and inverted ZnO:P3HS cells reveals that the wavelength of maximum absorption (575 nm) is higher than that of the maximum in the $EQE$ (500-520 nm) and that the low energy shoulder present in the absorption at 685 nm is much less pronounced in the $EQE$ (figure 5.9). A similar blue shift between absorption and $EQE$ and concomitant partial loss of the vibronic features has previously been observed in nanoparticle-ZnO:P3HT solar cells.\textsuperscript{33} Both experiments indicate that, in these particular systems, the photocurrent largely results from photon absorption in disordered and amorphous domains of the films and that the desired contribution from the semi-crystalline domains featuring the long-wavelength absorption is smaller. Interestingly, the blue shift and loss of low energy features was also observed in the absorption spectrum of very thin ($< 10$ nm) P3HT films on ZnO.\textsuperscript{34} This indicates that at the immediate contact with ZnO, the P3HT is disordered and not semi-crystalline. Because the exciton diffusion length in conjugated polymers is generally less than 10 nm, only excitons created within such distance can reach the interface with ZnO to generate charge carriers and contribute to the photocurrent. Hence, if disordered polymer chains prevail within 10 nm of the hybrid interface in the nanoparticle-ZnO:P3HT blends studied previously,\textsuperscript{33} and ZnO:P3HS films described here, the observed shifts between $EQE$ and absorption maxima can be easily rationalized. In such case, the wider band gap of the amorphous polymer chains blocks excitons generated in the semi-crystalline smaller band gap domains from reaching the interface.
with ZnO. Of course this is not a favorable situation for creating efficient solar cells because it excludes the desired contribution of low-energy photons to the photocurrent. The experiments shown in figure 5.9 reveal that annealing to higher temperatures does not improve the low-energy contribution and causes minimal changes in the absorption. One possible way to create more ordered polymer chains at the interface has been suggested by Hsu et al. who found that long alkanethiols absorbed at the ZnO surface can increase the ordering of P3HT chains at the interface.\footnote{34}

Apart from the above cause, a second effect may explain -or contribute to- the reduced \textit{EQE} in the long wavelength region of the ZnO:P3HS films. Excitons in the semi-crystalline P3HS domains likely have a shorter lifetime than excitons in the amorphous phase, similar to P3HT\footnote{35} and are therefore more likely to decay before reaching the ZnO interface. On other hand, comparing the absorption with the \textit{EQE} of annealed PCBM:P3HS cells (figure 5.11) reveals that both crystalline and amorphous P3HS domains contribute to the photocurrent. This suggests that the first explanation prevails, but we note that PCBM might be better dispersed in the P3HS than ZnO in P3HS such that exciton diffusion is less important for PCBM:P3HS cells than for ZnO:P3HS cells. In this respect it must be noted that for annealed PCBM:P3HS films the absorption maximum at 551 nm is considerably blue shifted compared to the maximum of 575 nm for annealed ZnO:P3HS. This confirms that PCBM is more finely dispersed in P3HS than ZnO such that in the latter blend purer and possibly larger acceptor-free P3HS regions exist. This conclusion is consistent with XRD measurements showing that PCBM:P3HS blend films show a lower degree of crystallinity than PCBM:P3HT films and have larger fractions of PCBM dissolved in P3HS as deduced from optical microscopy, Raman, and fluorescence mapping.\footnote{23}

\section*{5.9 Conclusions}

Small band gap P3HS was successfully used in hybrid solar cells in combination with ZnO in normal and inverted device configurations. The active layer was prepared via an in-situ sol-gel method using diethylzinc as a precursor and thermal annealing. The device performance was optimized by changing the solvent mixture, ZnO contents, active layer thickness and annealing temperature. The maximum power conversion efficiency was achieved for the normal device configuration by spin coating the diethylzinc-P3HS mixture from a hot chlorobenzene/toluene/THF solution, to give 19 vol-% ZnO in the blend at a layer thickness of 135 nm.

Having a power conversion efficiency of \(~0.4\%\), the performance of the cells is modest. Compared to the 2\% ZnO:P3HT cells prepared previously via a similar method, the $V_{oc}$ of the ZnO:P3HS cell (0.60 V) is lower than that of the ZnO:P3HT cell (0.75 V) de-
spite the fact that the HOMO levels of P3HS and P3HT are similar and no significant differences would be expected. The $J_{sc}$ (1.8 mA cm$^{-2}$) of the optimized ZnO:P3HS cell is significantly lower than that of ZnO:P3HT (5.2 mA cm$^{-2}$), even though the small band gap of P3HS enables absorbing more photons. The low $J_{sc}$ is due to a low EQE that maximizes at only 10% compared to 44% for ZnO:P3HT. Remarkably, we find that the EQE of the ZnO:P3HS is blue-shifted compared to the optical absorption of the active layer. This blue shift indicates that mainly the non-aggregated (amorphous) P3HS part of the film contributes to the photocurrent and that the major, aggregated (semi-crystalline), domains are not photoactive. As tentative explanation for this phenomenon we consider that at the interface with ZnO, P3HS is disordered, similar to the disorder observed for P3HT chains at ZnO-P3HT interfaces. The wider band gap disordered P3HS domains block low energy excitons generated in the semi-crystalline parts of the film to reach the interface.

5.10 Experimental

Materials: The poly-3-hexylselenophene (P3HS) used had a molecular weight of $M_w$ 94 kg mol$^{-1}$ and polydispersity index 1.87, and a regioregularity of 97% based upon $^1$H NMR integration of the methylene region. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was purchased from H.C. Stark (Clevios P VP Al 4085) and filtered over a 5 µm filter before use. Aluminum wire was used for evaporation and purchased from Alfa Aesar. Diethylzinc (DEZ) was purchased from Sigma-Aldrich. Blends of P3HS and DEZ were prepared by creating a stock solution of 0.216 mL DEZ in 1.58 mL toluene and 3.20 mL tetrahydrofuran, and adding the appropriate amount to a solution of P3HS in $o$-dichlorobenzene (ODCB) or chlorobenzene (CB), resulting in a 10 mg mL$^{-1}$ P3HS solution. The amount of DEZ solution was such that, assuming full conversion, it would lead to 19 vol-% ZnO in the blend. For the devices made using different ZnO contents, the amount CB was reduced or increased, and the amount DEZ solution adjusted to get the desired ZnO vol-% in the blend layer.

Photovoltaic devices: Substrates used for devices were glass substrates covered with tin-doped indium oxide (ITO). These substrates were thoroughly cleaned by sonication in acetone and aqueous dodecyl sulfate solution, followed by rinsing with water and sonication in isopropanol. Then, UV-ozone was applied for 30 min. After this step, the substrates were transferred to a nitrogen-filed glove box with a controlled relative humidity of 40%. PEDOT:PSS was spin coated a spin speed of 3000 r.p.m. for 1 min., followed by annealing on a hot plate for 15 min. at 100 °C. Then the active layer was spin coated from the solution described above, at 500 r.p.m. for 1 min. (or at higher spin speed for the layer
thickness experiment) and subsequent drying for 1 min. at 3000 r.p.m. The layer was aged in the glove box for 15 min. and then heated at 100 °C for 15 min. to form the ZnO and anneal the polymer. The substrates were then transferred to a glove box with an inert nitrogen atmosphere (<1 ppm H$_2$O and <1 ppm O$_2$) using an air-tight container. The back electrode, consisting of 100 nm aluminum, was evaporated under high vacuum (<3·10^{-7} mbar). All subsequent handling and analysis of the cells were carried out under an inert atmosphere.

**Current-voltage measurements:** $J$-$V$ characteristics were measured using a Keithley 2400 Source Meter, controlled by a computer. The device was illuminated by a 50 W tungsten-halogen lamp filtered by a Schott GG420 UV filter and a Hoya LB120 daylight filter. External quantum efficiency measurements were performed with respect to a calibrated silicon reference. A homebuilt setup utilizing a Philips focusline 7027 light source and an Oriel monochromator was used. The devices were exposed to bias illumination during the $EQE$ measurement, using a 530 nm laser, to emulate the charge carrier density in the device that would occur at 1000 W m$^{-2}$ AM1.5 conditions. The monochromatic and laser light was focused on an aperture with a diameter of 2 mm, to create a light spot smaller than the device area. Convoluting the $EQE$ spectrum with the AM1.5 spectrum yields the $J_{sc}$, which was in good correspondence (within 20%) of the $J_{sc}$ measured using the tungsten-halogen lamp.

**Atomic force microscopy (AFM):** AFM was applied on the devices using a Veeco MultiMode with a Nanoscope III controller, in tapping mode. The used probes were PPP-NCH-50 from Nanosensors. The thicknesses of the layers were determined using a Veeco Dektak 150 surface profiler.

**Transmission electron microscopy (TEM):** For TEM investigations, the P3HT:ZnO films were floated from the water soluble PEDOT:PSS substrate onto the surface of demineralized water and picked up with 200-mesh copper TEM grids. Bright-field TEM morphology observation was performed on a Technai G$^2$ 20 TEM (FEI Co.) operated at 200 kV.

**Photoinduced absorption (PIA):** PIA measurements were carried out using a homebuilt setup, by exciting a representative film on a quartz substrate, inside a continuous flow cryostat at 80 K with a mechanically modulated (275 Hz) Ar-ion laser (Spectra Physics 2025) pump beam at 488 nm (25 mW, beam diameter of 2 mm). The resulting change in transmission of a tungsten-halogen white-light probe beam was monitored after dispersion by a triple-grating monochromator, using Si, InGaAs, and a cooled InSb detector using lock-in amplifiers.
References


6. ZINC OXIDE NANORODS AS TEMPLATE FOR HYBRID POLYMER SOLAR CELLS

Abstract

A ZnO nanorod template layer has been infiltrated with a ZnO/poly(3-hexylthiophene) (P3HT) blend to create a hybrid polymer - metal oxide solar cell that features a hierarchically built inorganic phase, with 300 nm ZnO nanorods for charge collection connected to a fine ZnO network for charge generation throughout the bulk. These hierarchical ZnO:P3HT layers were prepared by casting P3HT and diethylzinc (as reactive ZnO precursor) from a common solvent mixture in moist atmosphere on a ZnO nanorod carpet grown from a compact ZnO nucleation layer, followed by thermal conversion. Atomic force microscopy and scanning electron microscopy confirmed the infiltration of the ZnO:P3HT blend in between the ZnO nanorods. Photoinduced absorption spectroscopy revealed that the relative efficiency of charge generation in the ZnO:P3HT blend layers is not influenced by connecting to the ZnO nanorod carpet. We find that the performance of the combined ZnO nanorod ZnO:P3HT blend solar cells is not improved compared to ZnO:P3HT blend cells and, actually, somewhat less. This is interpreted as being due to a poor contact between the ZnO network in the ZnO:P3HT blend and the ZnO nanorods.
6. Zinc oxide nanorods as template for hybrid polymer solar cells

6.1 Introduction

Hybrid solar cells use a combination of organic polymer and inorganic semiconductor materials with offset energy levels to create and collect charges under illumination. Because of the small exciton diffusion length in semiconducting polymers (2.6–12 nm), hybrid solar cells preferably use an interpenetrating network of the electron donor and the electron acceptor materials with a phase separation in the nanometer range to generate charges efficiently and having continuous pathways for charge collection.

In chapter 3 it was shown that for hybrid films based on ZnO as electron acceptor and poly(3-hexylthiophene) (P3HT) as donor prepared via a ZnO-precursor method, the phase separation between P3HT and ZnO was rather coarse when the films are thin. Consequently, part of the photogenerated singlet excitons in the P3HT were lost by recombination and triplet formation before reaching the interface with ZnO to create charges.

In thicker layers, the phase separation was finer and charge generation was better, but these layers had a larger fraction of ZnO not connected to the electrode. Charges formed in these ZnO domains cannot contribute to the photocurrent and must recombine eventually, contributing to conversion losses. By increasing the polarity of the side chains in a modified P3HT, a finer phase separation and nearly quantitative charge generation was achieved in thin films (see chapter 4), but charge collection became increasingly more difficult because the mobility is reduced in systems with fine phase separation.

An alternative method to create an interpenetrating network of the two materials in hybrid polymer solar cells is using pre-defined inorganic template structures or nanorods that are infiltrated with the photoactive polymer (see also section 1.3.2). Because the inorganic template is directly deposited onto the electrode, all material is connected to the respective electrode by definition. Limitations in photovoltaic efficiency occur when the pores in the template are too large, such that part of the photoactive material is too far away from the donor-acceptor interface for photogenerated excitons to reach this interface and generate charges.

To enhance the charge collection in the first type of hybrid solar cells (thick (∼300 nm) ZnO:P3HT layers with randomly distributed ZnO) and to improve the charge generation in the second type (with a well-defined pre-fabricated ZnO template), a combination of both methods may give rise to the advantages of both worlds; good exciton generation due to intimate mixing of the electron donor and acceptor and good charge transport as soon as the short distance to the nanorods has been covered.

This chapter describes the fabrication of a ZnO nanorod carpet on top of a ZnO nucleation layer that is infiltrated with a ZnO:P3HT blend to achieve a such hierarchically structured ZnO:P3HT layer. Despite of evidenced infiltration of a ZnO:P3HT blend in
between the ZnO nanorods, we find that the performance of hybrid solar cells based on a randomly generated network of ZnO during the layer deposition is not enhanced by inserting this ZnO:P3HT blend in a pre-prepared ZnO nanorod template. It seems that the contact between the two ZnO structures is not optimal.

6.2 Nanorod growth

To grow nanorods, first a layer of ZnO is applied onto a glass/ITO substrate by spin coating zinc acetate, followed by thermal conversion. This closed ZnO layer improves charge collection by acting as hole blocking layer, and serves as nucleation layer to template ZnO nanorod growth. Nanorods are formed because the growth rate of ZnO crystals is the highest on the polar top (0001) face.17

Various techniques of growing ZnO nanorods on top of ZnO nucleation layer have been reported. Here, the route of Peterson et al. was adapted,17,18 which uses a supersaturated solution of Zn$^{2+}$ ions in a basic hydrous environment (see section 6.8). This way, there is good control of the growth rate and the final length of the ZnO nanorods. A rod length of $\sim300$ nm is used, because exciton quenching in mixed ZnO:P3HT layers is best in thick layers, and thick ZnO:P3HT layers can benefit more from the charge collection enhancement than thin layers (see table 3.1).

Scanning electron microscopy (SEM) images of ZnO nanorods grown on a ZnO nucleation layer are shown in figure 6.1. From the top view it is clear that the nanorods do not grow perfectly perpendicular to the surface of the glass/ITO/ZnO substrate. The tops of the ZnO nanorods seem to cluster, while the rods near the bottom appear to have a more equal distribution. The distance between nanorods at the top is $100\sim300$ nm. The observed open structure should allow for infiltrating P3HT or ZnO:P3HT blends.14,15,18

6.3 Polymer infiltration into a ZnO nanorod carpet

Previously it has been shown that P3HT can be applied on top of (and in between) ZnO nanorods by spin coating.14,15 Here, P3HT is applied by spin coating from a solution in a mixture of chlorobenzene, toluene, and tetrahydrofuran (THF), in order to enable direct comparison with spin coating ZnO:P3HT precursor blends from the same solvent mixture (section 6.4).

After spin coating a thick layer of P3HT onto a ZnO nanorod carpet, atomic force microscopy (AFM) and SEM were used to investigate the surface of the layer (figure 6.2). Figure 6.2a shows the AFM image of such a layer. Clearly, the ZnO nanorods are protruding through the top of the P3HT layer, as evidenced from the significant height difference. The SEM image (figure 6.2c) confirms the protrusion of the ZnO nanorods.
through the P3HT layer. The inset in the figure is the top view of the layer, which looks nearly identical to a neat ZnO nanocarpet on a ZnO layer (figure 6.1a). Optical absorption leaves no doubt that P3HT is present in between the nanorods.

The protruding ZnO nanorods are of course not desired and resulted in electrical shunts between the bottom and the top electrode in photovoltaic devices made from these layers. To cover the long ZnO nanorods completely and thereby avoid shunting between bottom and top electrodes an additional layer of P3HT was applied on top of the first P3HT layer. This extra P3HT layer was applied by spin coating from a fast evaporating solvent, chloroform, in order to ensure a thick P3HT layer. By eye, chloroform does not wash away the P3HT layer already present in the ZnO nanorod carpet. This was confirmed by immersing a ZnO nanorod carpet with the first P3HT layer in chloroform for a prolonged time.

The AFM and SEM images after deposition of the second P3HT layer are shown in figure 6.2b and 6.2d. Compared to the single layer of P3HT the differences are substantial. The AFM image shows a very smooth top layer, where nanorods are no longer protruding. The SEM image also shows a smooth top layer, under which the ZnO nanorods are visible. In conclusion, the additional P3HT layer can be used to prevent shunts between the top electrode and the bottom ZnO electrode in a final device.

To check whether P3HT is able to generate charges in the nanorod-ZnO:P3HT junction, steady state photoinduced absorption (PIA) spectroscopy at $T = 80$ K was performed on several layer configurations (figure 6.3). Excitation at 488 nm (2.54 eV) of pure P3HT on a quartz substrate results in a strong PIA signal at 1.06 eV of the triplet-triplet absorption ($T_1 \leftarrow T_0$, $^3$) accompanied by the corresponding bleaching band ($S_1 \leftarrow S_0$) near
Fig. 6.2: AFM and SEM images of P3HT on a ZnO nanorod carpet. The single layers show that nanorods are protruding through the top of the P3HT layer, the images of the double layers show a smooth layer of P3HT on top of the rods. Tilted SEM images are taken using an angle of 52°.
the optical band gap of 1.96 eV. All spectra in figure 6.3 are normalized to this bleaching band. The long-lived triplet excited state in pure P3HT is formed from the singlet excited state via intersystem crossing.

The PIA spectrum of a thin (∼38 nm) layer of P3HT on a flat ZnO layer without nanorods shows no triplet-triplet absorption. The PIA signals observed at 0.4, 1.24 and 1.8 eV originate from positively charged P3HT and indicate that photoexcitation produces charges. ZnO acts as electron acceptor and charge separation occurs at the ZnO/P3HT interface, leaving positively charged P3HT and negatively charged ZnO. The free electrons in the negatively charged ZnO contribute to the PIA signal <0.5 eV.

The absence of the triplet-triplet absorption suggests that charge formation is significantly faster than intersystem crossing. Based on the layer thickness of the P3HT (∼38 nm) and the singlet exciton diffusion length (2.6-12 nm) this is surprising and in fact one would expect the triplet-triplet absorption to be observed, because part of the P3HT is further away from the interface with ZnO than the exciton diffusion length. As a possible explanation for this result, we conjecture that long-lived P3HT triplet states formed in the layer diffuse to the crystalline-ZnO/P3HT interface and generate charges. The triplet energy of P3HT at 1.2-1.4 eV is likely to be slightly higher in energy than the energy of the charge transfer state (e·V_{oc} + 0.5 eV ≈ 1 eV), which makes this process energetically possible. If this mechanism is indeed operative, it would imply that the triplet exciton diffusion length in P3HT is ∼38-12≈26 nm or longer.

As can be expected the triplet-triplet absorption reappears when a thick layer of P3HT (∼260 nm) is applied onto a compact ZnO layer (without nanorods), although the relative intensity has decreased slightly compared to a pure P3HT layer on quartz. The spectrum was recorded with illumination from the P3HT side and only a fraction of the light penetrates the P3HT far enough to create singlet excitons in the vicinity (<12 nm) of ZnO. Nevertheless, the spectral signatures of charges can be discerned. The signal at 0.4 eV is somewhat less intense than expected compared to the signal at 1.24 eV which is due to charges and the high-energy shoulder of the triplet-triplet absorption.

A single P3HT layer on top of a ZnO layer with a ZnO nanorod carpet shows little to no triplet-triplet absorption at 1.06 eV. The PIA signals observed at 0.4, 1.25, and 1.8 eV from P3HT polarons and electrons in ZnO polarons evidence charge formation. Consequently, P3HT present in between the ZnO rods is in sufficient close contact with the ZnO nanorods to create charges directly via the singlet state or indirectly via the triplet state.

When a second P3HT layer is applied onto the ZnO nanorod carpet to cover the nanorods completely as shown in figure 6.2b and 6.2d, the triplet-triplet absorption is again present in the PIA spectrum. Also P3HT polaron bands at 0.4, 1.25, and 1.8 eV are observed, indicating that charges are formed at the ZnO/P3HT interface. In the extra
P3HT layer, however, a significant part of the excitons is generated too far away from the ZnO interface to contribute to generation. Hence, to enhance charge generation and maximize the short circuit current of solar cells based on a ZnO nanorod carpet, it is beneficial to apply a ZnO:P3HT blend instead of pure P3HT in between the ZnO nanorods.

6.4 Infiltration of a ZnO:P3HT blend into a ZnO nanorod carpet

A ZnO:P3HT blend was deposited onto a ZnO nanorod carpet in a similar fashion as the pure P3HT layer described in the previous section. A solution of ZnO precursor, diethylzinc, and P3HT in a solvent mixture of chlorobenzene, toluene, and THF is spin coated at 500 r.p.m. on top of the ZnO nanorod carpet. The amount of diethylzinc in the solution would yield 8 vol-% ZnO in the blend layer, instead of the 20 vol-% ZnO used in previous chapters. This lower ZnO content in the blend was chosen because ZnO will also be present in the form of ZnO nanorods in the final device, and it can be expected that less ZnO in the blend is needed. As stated in section 6.1, ZnO in the blend is mainly intended to dissociate the excitons in P3HT, and the ZnO nanocarpet mainly serves as electron transporter.

AFM and SEM were used to characterize the layers (figure 6.4). Depositing the ZnO:P3HT blend layers on top of the ZnO nanorod carpet results in very similar features compared to depositing a pure P3HT layer. The AFM image of a single layer of ZnO:P3HT on a ZnO nanorod carpet (figure 6.4a) shows a rough surface where ZnO nanorods are protruding through the ZnO:P3HT blend layer. This is confirmed with SEM (figure 6.4c) that clearly shows how ZnO nanorods are sticking out above the ZnO:P3HT layer. When a top electrode is evaporated this resulted in shunted devices.
6. Zinc oxide nanorods as template for hybrid polymer solar cells

(a) AFM image of a single ZnO:P3HT blend layer on ZnO nanorods, $R_{RMS}=11.5$ nm.

(b) AFM image of a double ZnO:P3HT blend layer on ZnO nanorods, $R_{RMS}=9.6$ nm.

(c) SEM image of a single ZnO:P3HT blend layer on ZnO nanorods.

(d) SEM image of a double ZnO:P3HT blend layer on ZnO nanorods.

**Fig. 6.4:** AFM and SEM images of a ZnO:P3HT blend on a ZnO nanorod carpet. The single layers show that nanorods are protruding through the top of the ZnO:P3HT layer, the images of the double layers show a smooth layer of ZnO:P3HT on top of the rods.
Comparing these SEM images with the SEM images of a single layer of pure P3HT on ZnO nanorods (figure 6.2c), it seems that the blend layer is infiltrated to a lesser extent between the ZnO nanorods. It is not clear how deep the infiltration of the ZnO:P3HT blend layer into the ZnO nanorod structure is.

In order to suppress the effect of nanorods protruding the ZnO:P3HT layer, inducing shunts in the photovoltaic devices, another layer of a ZnO:P3HT blend is spin coated on top of the first ZnO:P3HT blend layer using the same solution for spin coating as is used for the first layer. The solvent will not wash away the first layer, since the P3HT is fixed because of the surrounding ZnO network. This has been confirmed by immersion of a ZnO:P3HT layer in chloroform, where by eye the color of the layer did not change and hence, no or little P3HT was removed. AFM imaging (figure 6.4b) shows that the surface of the layer is smoother than the surface of a ZnO nanorod carpet with only one ZnO:P3HT layer. SEM imaging (figure 6.4d) confirms that the top of these samples show a smooth surface, and ZnO nanorods do not extend beyond the top of the ZnO:P3HT layer.

Figure 6.5 shows the PIA spectra of ZnO:P3HT blend layers. The red line shows the PIA spectrum of a single layer of ZnO:P3HT blend on top of a ZnO nanorod carpet. The spectrum is normalized to the bleaching of P3HT at 1.96 eV. The absorption bands of P3HT polarons (<0.5, 1.25, and 1.8 eV) and free electrons in ZnO (<0.5 eV) are clearly present, indicating photoinduced charge separation between the two materials. The triplet-triplet absorption of P3HT at 1.06 eV indicates that not all singlet excitons are quenched by the ZnO present in the layer, which may be ZnO from nanorods or ZnO originating from the ZnO precursor in the blend layer. Probably, part of the P3HT is too far away from the ZnO:P3HT interface to effectively charge separate (see also chapter 3). When an extra ZnO:P3HT layer is applied onto the first ZnO:P3HT layer to avoid ZnO nanorods protruding the top of the layer a similar spectrum is obtained (green line), indicating incomplete charge generation. Although the upper part of the layer should have lower ZnO contents, the triplet-triplet absorption strength is similar for both layers, indicating a similar degree of charge generation in the two samples. For comparison, also a double ZnO:P3HT layer on top of a compact ZnO layer (without ZnO nanorods) is displayed (black line). Also this graph is nearly identical to the other two graphs, indicating that the addition of ZnO nanorods to a double ZnO:P3HT layer does not enhance the charge generation significantly.

The observation of triplets in the ZnO:P3HT layer implies that the ZnO in this phase is not able to dissociate the triplet excitons into charges effectively, in contrast to what we proposed above for the ZnO nucleation layer. Of course the nature (e.g. crystallinity, surface chemistry, defect states) of the various ZnO phases differ in these cases and we tentatively ascribe the observed differences to be caused by differences in the ZnO.

At this point it must also be noted that for a single P3HT layer infiltrated in the ZnO
nanorods no triplet states were observed in the PIA spectrum, while they are clearly present when a ZnO:P3HT layer is deposited on the nanorod carpet. This is a remarkable difference that is hard to understand. For pure P3HT we conjectured that triplets could dissociate into charges at the ZnO nanorod surface. Apparently this quenching does not occur for P3HT triplets present in the ZnO:P3HT blends. This would imply that there is no intimate contact of P3HT inside the ZnO:P3HT blends with the ZnO nanorod surface. One possible explanation for this observation is that the nanorods are preferentially covered by ZnO from the precursor, preventing P3HT to interact directly with the nanorods.

Comparing the top view of the bare ZnO nanorods (figure 6.1a) with the nanorods infiltrated with pure P3HT (inset in figure 6.2c), the images are nearly identical, but comparing these images with the infiltrated ZnO:P3HT blend (figure 6.4c), the blend layer is visible in the image. This may indicate that the solution used for spin coating the ZnO:P3HT blend is more viscous than the solution used for spin coating the pure P3HT, consequently, the infiltration between the ZnO nanorods may to some extent be hindered. In this case, there would be no intimate contact between the P3HT and the ZnO nanorod surface, as the presence of triplet states suggests.

6.5 Photovoltaic performance of inverted devices

As a consequence of the ZnO nucleation layer on top of the glass/ITO substrate, the ITO will be the negative contact of the solar cell, and the top electrode will then be the positive contact. Compared to the traditional device, which utilizes a ITO/PEDOT:PSS layer as positive electrode, and an aluminum electrode as negative electrode, the device polarity is inverted.

Commonly used materials for the negative electrode of photovoltaic devices with in-
6.5. Photovoltaic performance of inverted devices

Verted polarity are TiO$_2$ or ZnO. Here, ZnO is already present because a ZnO nucleation layer was used for nanorod growth. For the positive electrode, several materials have been reported such as silver, gold, PEDOT:PSS, or MoO$_3$. In this study, MoO$_3$/aluminum (10/100 nm) was used as top electrode.

Before studying the effects of the nanorods, inverted devices were fabricated in which the active ZnO:P3HT layer is sandwiched between ITO/ZnO and MoO$_3$/Al electrodes. For the fabrication first a compact ZnO layer was applied onto a glass/ITO substrate as described in section 6.8. On top of the ZnO layer, an active layer was spin coated using the standard method developed in section 2.3 and used in chapter 3. In short, diethylzinc (DEZ) and P3HT were spin coated from a common solvent onto the substrate, where the DEZ reacts with moisture to form Zn(OH)$_2$ during the spin coating step. After spin coating, the substrate was heated in order to convert the Zn(OH)$_2$ into ZnO.

Various processing parameters in the fabrication procedure for inverted devices were optimized again compared to the standard procedure described in chapter 3. The reasons are twofold. First, because the inverted device architecture may require different procedures compared to the normal device. Second, because the P3HT (Plexcore) used in this study was obtained from a different manufacturer (Plextronics supplied by Sigma-Aldrich) than the P3HT used in the previous chapters (manufactured and supplied by Rieke Metals). Ultimately, the procedure was changed in only one parameter compared to the procedure described in chapter 3; the annealing temperature after film deposition. Device parameters of inverted devices annealed at different temperatures are shown in figure 6.6. The optimum annealing temperature for obtaining the highest device performance is 175 °C, compared to only 100 °C for the normal, non-inverted devices. A possible cause for this difference is the absence of a PEDOT:PSS layer, which is slightly acidic and may affect part of the acid sensitive ZnO in the active layer (see also section 5.5).

The best inverted hybrid ZnO:P3HT cell fabricated using Plexcore P3HT shows an open circuit voltage ($V_{oc}$) of 0.57 V, a short circuit current ($J_{sc}$) of 3.8 mA cm$^{-2}$, a fill factor ($FF$) of 0.51 and a maximum power point ($MPP$) of 1.1 mW cm$^{-2}$, resulting in a power conversion efficiency $\eta = 1.1 \pm 0.15 \%$. Comparing this performance to the performance of a similar device in the normal configuration (annealed at 100 °C in between ITO/PEDOT:PSS and aluminum electrodes), especially the $FF$ is higher (see figure 6.7 and table 6.1). The $MPP$ of this device in the normal architecture is 0.9 mW cm$^{-2}$, resulting in a $\eta = 0.9 \pm 0.15 \%$. Compared to the Rieke P3HT used in chapters 2 and 3, all device characteristics ($J_{sc}$, $V_{oc}$, and $FF$) of the cells with Plexcore P3HT are significantly reduced, resulting in a much lower device performance. The new Plexcore P3HT is more regioregular and crystalline than the Rieke P3HT used previously and, apparently, less suited for creating efficient ZnO:P3HT cells via the precursor method.
6.6 Photovoltaic performance of devices utilizing a ZnO nanorod carpet

The goal of using a ZnO nanorod carpet in combination with an infiltrated ZnO:P3HT layer is to enhance the collection of charges as compared to an inverted hybrid ZnO:P3HT solar cell and to enhance charge generation as compared to a hybrid nanorod-ZnO:P3HT device that uses pure P3HT (see section 6.1). The morphology and spectroscopic characterization of the ZnO:P3HT blend layer infiltrated into a ZnO nanorod carpet have been described in section 6.4 and here we compare the performance of the various configurations in photovoltaic devices.

The device parameters of different devices are summarized in table 6.2. Current density-voltage (J-V) characteristics of selected devices are shown in figure 6.8. In its most simple configuration, the device is a bilayer ZnO/P3HT junction (device 1), i.e. without ZnO nanorods or ZnO from precursor present. The MPP of this device is $\pm 0.21$ mW cm$^{-2}$, leading to an efficiency of $\pm 0.2\%$. When ZnO nanorods are added to the device structure, the performance is similar, $\pm 0.2\%$ (device 2). A device with shorter ZnO nanorods ($\sim 100$ nm) gave slightly better performance ($\pm 0.3\%$, not shown). It is noted

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|l|}
\hline
Device type & P3HT manufacturer & $V_{oc}$ (V) & $J_{sc}$ (mA cm$^{-2}$) & FF & MPP (mW cm$^{-2}$) \\
\hline
Normal & Rieke & 0.75 & 5.2 & 0.52 & 2.0 \\
Normal & Plexcore & 0.58 & 3.7 & 0.41 & 0.9 \\
Inverted & Plexcore & 0.57 & 3.8 & 0.51 & 1.1 \\
\hline
\end{tabular}
\caption{Device parameters of reference normal and inverted devices using different P3HT batches.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6_6}
\caption{Device performance of inverted ZnO:P3HT solar cells annealed at different temperatures.}
\end{figure}
that higher efficiencies for similar devices have been published in the literature.\textsuperscript{[14,15]} The reason for the lower efficiency observed here can be manifold, such as different ZnO nucleation layer fabrication method, ZnO nanorod growth method, P3HT batch, manufacturer, infiltration, and top electrode used. This was not investigated in further detail.

Inserting an 8 vol-% ZnO:P3HT blend into the nanorod carpet instead of pure P3HT, improves the device performance up to ±0.4% (device 5). This is mainly due to a higher $J_{SC}$, but $V_{OC}$ and $FF$ are also improved. In order to identify the origin of the improvement, device 5 can be compared to device 4, which lacks the ZnO nanorods. Compared to device 4, the efficiency of device 5 has decreased, mainly due to a lower $V_{OC}$ and $FF$. The reason for the lower $V_{OC}$ and $FF$ is unclear at this moment. Possibly, the surface chemistry of ZnO plays a large role, which is determined by the synthetic route towards ZnO. The ZnO made using the diethylzinc as precursor, and the ZnO nanorods grown on top of the ZnO nucleation layer have a different synthetic history. A similar difference in $V_{OC}$ has been found for ITO/PEDOT:PSS/ZnO:P3HT/Al hybrid polymer solar cells where the ZnO was prepared by pre-prepared ZnO nanoparticles\textsuperscript{[27]} compared to using a ZnO precursor and making the ZnO during film deposition\textsuperscript{[28,chap.2]} where the precursor method yields the larger $V_{OC}$.

When comparing device 5 with device 2, it can be concluded that the extra ZnO added using a ZnO precursor in the P3HT in between ZnO nanorods indeed enhances charge generation. On the other hand, ZnO nanorods do not enhance the charge transport in ZnO:P3HT photovoltaic devices, because the $J_{SC}$ and $FF$ are similar in devices 4 and 5. Because the introduction of ZnO nanorods has a significant detrimental effect on the $V_{OC}$, the efficiency is reduced compared to the ZnO:P3HT blends.
**Tab. 6.2:** Comparison of device parameters of devices with and without ZnO nanorods, using pure P3HT (ZnO vol-% = 0) or a mixed ZnO:P3HT blend as photoactive material.

<table>
<thead>
<tr>
<th>Device</th>
<th>Rods?</th>
<th>ZnO vol-%</th>
<th>No. active layers</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>MPP (mW cm$^{-2}$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No</td>
<td>0</td>
<td>1</td>
<td>0.33</td>
<td>1.4</td>
<td>0.46</td>
<td>0.21</td>
<td>38</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>0</td>
<td>2</td>
<td>0.43</td>
<td>1.2</td>
<td>0.43</td>
<td>0.22</td>
<td>610</td>
</tr>
<tr>
<td>3</td>
<td>No</td>
<td>8</td>
<td>1</td>
<td>0.56</td>
<td>1.9</td>
<td>0.46</td>
<td>0.48</td>
<td>113</td>
</tr>
<tr>
<td>4</td>
<td>No</td>
<td>8</td>
<td>2</td>
<td>0.54</td>
<td>2.2</td>
<td>0.45</td>
<td>0.53</td>
<td>190</td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>8</td>
<td>2</td>
<td>0.40</td>
<td>2.4</td>
<td>0.41</td>
<td>0.39</td>
<td>270</td>
</tr>
<tr>
<td>6</td>
<td>No</td>
<td>20</td>
<td>1</td>
<td>0.54</td>
<td>3.7</td>
<td>0.45</td>
<td>0.89</td>
<td>170</td>
</tr>
<tr>
<td>7</td>
<td>No</td>
<td>20</td>
<td>2</td>
<td>0.56</td>
<td>3.7</td>
<td>0.39</td>
<td>0.83</td>
<td>280</td>
</tr>
<tr>
<td>8</td>
<td>Yes</td>
<td>20</td>
<td>2</td>
<td>0.50</td>
<td>2.6</td>
<td>0.38</td>
<td>0.50</td>
<td>465</td>
</tr>
</tbody>
</table>

**Fig. 6.8:** $J$-$V$ curves of hybrid photovoltaic devices, with and without ZnO nanorods, and with and without ZnO precursor in the polymer layer.

To have more of the precursor-ZnO connected to the ZnO nanorod carpet, a higher volume content of ZnO in the ZnO:P3HT blend (20%) has been applied. A single layer of this blend without rods is identical to the inverted device discussed in section 6.5 (device 6 in table 6.2). Using two ZnO:P3HT blend (20%) layers on top of a ZnO nanorod carpet (device 8) leads to a performance of $\pm 0.5\%$, which is significantly lower than the ZnO:P3HT inverted device without the nanorods, mainly due to a reduced $J_{sc}$. The lower performance cannot be attributed to the second ZnO:P3HT blend (20%) layer alone, because device 7 with two ZnO:P3HT blend (20%) layers on top of each other without nanorods shows the same $J_{sc}$ as device 6, which has a single layer.

The reason for a lower $J_{sc}$ may be the poor contact of the ZnO:P3HT blend with the ZnO nanorods. As shown above from SEM and PIA, the infiltration of the ZnO:P3HT blend layer is not complete, and the contact to the nanorods is not optimal, hindering charge transport to the respective electrodes.
6.7 Conclusions

Combining two types of hybrid solar blend layers, the first being a pre-prepared ZnO nanorod carpet with infiltrated P3HT featuring high charge collection efficiency but a deficiency in charge generation, with another blend layer based on a spontaneously, randomly generated ZnO network in a P3HT layer with high charge generation efficiency but deficiency in charge collection, has the potential of bringing the advantages of both approaches into a single device.

AFM and SEM imaging confirmed that a ZnO:P3HT blend can be infiltrated in between ~300 nm ZnO nanorods to create the desired hybrid device. An extra blend layer on top of the first ZnO:P3HT blend layer was needed to prevent shunts between the top and bottom electrode, since nanorods are protruding the first blend layer creating a shunt with the top MoO$_3$/Al electrode. Photoinduced absorption spectroscopy showed that charge generation is not complete in ZnO:P3HT blend layers and likewise in nanorod/ZnO:P3HT blend layers as evidenced from the signatures of P3HT triplet states. Surprisingly, long-lived triplet states were not found in thin ZnO nanorod/P3HT layers. This has, tentatively, been interpreted as being due to charge dissociation of P3HT triplet excitons by the ZnO nanorods.

The envisioned advantage of the combination of the two different layer configurations, i.e. improved charge collection using the ZnO nanorods connected to the bottom electrode, could not be confirmed experimentally. The $J_{sc}$ and $FF$ were not enhanced when the ZnO:P3HT blend layer was infiltrated between ZnO nanorods compared to a layer without the nanorods. The origin for this negative result is not fully understood, but it seems that the (electrical) contact of the ZnO nanorods with the ZnO:P3HT blend is not optimal. This observation is consistent with the observation that P3HT triplets in pure P3HT can be quenched by the ZnO nanorods, in contrast to P3HT triplets in the ZnO:P3HT blend. Future research should focus on controlling the infiltration of ZnO:P3HT blend inside the ZnO nanorod template layer and creating an improved contact between the ZnO nanorods and the ZnO network created in the P3HT matrix. At present this seems to be the largest hurdle.

6.8 Experimental

Materials: Regioregular P3HT, Plexcore® OS 2100 ($M_n = 30-60$ kg mol$^{-1}$ with a polydispersity of 2.5) was obtained from Sigma-Aldrich. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was purchased from H.C. Stark (Clevios P VP.Al 4085) and filtered over a 5 $\mu$m filter before use. Aluminum wire was used for evaporation and purchased from Alfa Aesar. Molybdenum oxide (MoO$_3$) was purchased from
Sigma-Aldrich and used as received. Diethylzinc (DEZ) solution in toluene (1.1 M) was purchased from Sigma-Aldrich. Zinc acetate dihydrate (Acros), zinc nitrate hexahydrate (Sigma-Aldrich), and sodium hydroxide (Acros) were used as received.

**Substrate preparation:** Substrates for device preparation were glass plates covered with patterned tin-doped indium oxide (ITO). These substrates were thoroughly cleaned by sonication in acetone and aqueous dodecyl sulfate solution, followed by rinsing with water and sonication in isopropanol. Finally UV-ozone was applied for 30 min. A ZnO nucleation layer was applied by spin coating a 157 mg mL⁻¹ solution of zinc acetate dihydrate in a methoxyethanol:ethanolamine (24:1) solvent mixture at 2000 r.p.m. for 60 s, followed by thermal annealing on a hot plate at 300 °C for 5 min. These glass/ITO/ZnO substrates were stored in air in the dark until needed for further processing.

**ZnO nanorod growth:** The glass/ITO/ZnO substrates were heated to 150 °C for at least 30 min. and blow-cooled with a nitrogen gun before use. Glassware was cleaned using a HCl solution and thoroughly rinsed with deionized water prior to use. The nanorods were grown using a 200 mL aqueous solution of 1.0 mM zinc nitrate and 0.010 M NaOH. The ITO/ZnO substrates were immersed in the solution at 70 °C for 30 min. After nanorod growth, the substrates were rinsed with deionized water thoroughly, blow-dried using a nitrogen gun, and subsequently heated to 150 °C for another 10 min. The total thickness of the ZnO nucleation layer and ZnO nanorods was measured using a Veecko Dektak 150 surface profiler. Samples were stored in the dark in ambient air until needed for further processing.

**P3HT and ZnO:P3HT blend layer deposition:** The glass/ITO/ZnO/nanorod substrates were heated to 150 °C for at least 30 min. and blow-cooled with a nitrogen gun before use. The samples were transferred to a nitrogen-filled glove box with a controlled relative humidity of 40%. The P3HT or ZnO:P3HT blend layer was applied by spin coating at 500 r.p.m. for 1 min., and subsequent drying for 1 min. at 3000 r.p.m. The solutions used were 10 mg mL⁻¹ P3HT in a chlorobenzene/toluene/tetrahydrofuran (CB/tol/THF) solvent mixture in a 22:1:2 volume ratio for the pure P3HT layer. The pure P3HT layer that was used as second layer was spin coated from a 20 mg mL⁻¹ P3HT solution in chloroform.

ZnO:P3HT blend layers were spin coated from mixed solution of P3HT and diethylzinc. Diethylzinc/P3HT solutions were prepared by dissolving P3HT in the appropriate amount of CB, with the appropriate amount of a diethylzinc solution (0.4 M, obtained by mixing 1.8 mL of a 1.1 M diethylzinc solution in toluene with 3.2 mL of THF). The final solution contained 10 mg mL⁻¹ P3HT.
After deposition of the P3HT or ZnO:P3HT layer, the sample was stored in the glove box at 40% relative humidity for at least 10 min., followed by annealing at 175 °C for 5 min. Then, if multiple layers were spin coated, the next layer was deposited, followed by another annealing step of 5 min. Devices with only one deposited layer were annealed two times. After the final heating step, the samples were transferred to a glove box with an inert nitrogen atmosphere (<1 ppm H₂O and <1 ppm O₂) using an air-tight container.

Deposition of the top electrode: The back electrode consisted of 10 nm MoO₃ and 100 nm of aluminum and was evaporated under high vacuum (<3 · 10⁻⁷ mbar). All handling and analysis of the cells was carried out under an inert atmosphere.

Device characterization: Current density-voltage (J-V) measurements were carried out at room temperature with a computer-controlled Keithley 2400 Source Meter in the dark or under simulated solar light (100 mW cm⁻²) from a Philips Brilliantline Pro 50 W tungsten-halogen lamp, filtered by a Schott GG420 UV filter and Hoya LB120 daylight filter.

Atomic force microscopy (AFM): AFM was performed on the active layers of the devices using a Veeco MultiMode with a Nanoscope III controller, in tapping mode. The used probes were PPP-NCH-50 from Nanosensors.

Scanning electron microscopy (SEM): SEM was performed using a FEI Quanta 3D FEG scanning electron microscope. Devices were cut into small pieces suitable for SEM imaging, by first making a scratch on the back side where the cut is desired using a diamond pen, immersing the sample in liquid nitrogen for 20 seconds and breaking the sample mechanically. This was done several times to achieve the desired sample size for SEM measurement.

Photoinduced absorption (PIA): PIA was carried out using a homebuilt setup, by exciting a part of the device where no metal electrode is present, inside a continuous flow cryostat at 80 K with mechanically modulated (275 Hz) Ar-ion laser (Spectra Physics 2025) pump beam at 488 nm (25 mW, beam diameter of 2 mm). The resulting change in transmission of a tungsten-halogen white-light probe beam was monitored after dispersion by a triple-grating monochromator, using Si, InGaAs, and a cooled InSb detector using lock-in amplifiers.
References


SUMMARY

Hybrid polymer solar cells based on ZnO

With the increasing demand for energy and the limited availability of fossil fuels there is a need for a renewable, sustainable energy source. One source that always will be available is the energy of the sun. Sunlight energy may be captured in roughly three ways: as heat, electricity, or chemical energy. Heat may be used directly or used to power for example an electricity generator. Sunlight may be used to drive chemical reactions, where energy is stored in chemical bonds. Finally, sunlight can be converted directly into electricity using photovoltaic solar cells. Since electricity is possibly the most valuable and versatile form of energy, the direct conversion deserves attention.

By increasing the efficiency and lowering cost of solar cells, a more sustainable global energy society may be achieved. At present, the photovoltaic solar energy market is dominated by solar cells based on high-purity silicon. Producing this high-purity material takes considerable effort and cost, and therefore cheaper, more environmentally friendly alternatives are being explored. Polymer solar cells are an option, but the morphological stability of this type of devices is currently one of the issues that hinders commercialization. Hybrid polymer solar cells, using an inorganic material combined with an organic polymer, overcome this issue due to the morphological stability of the inorganic component, and combine this stability with the advantages of solution processing of organic materials. This thesis focuses on characterizing the morphology of hybrid ZnO:polymer solar cells, and altering the morphology to enhance the power conversion efficiency of these devices.

Chapter 2 describes the use of an in-situ sol-gel precursor method to make hybrid ZnO:polymer solar cells and strategies to obtain maximum power conversion efficiency. Organic ZnO precursors with different reactivity have been tested in combination with poly(3-hexylthiophene) (P3HT) to create the photoactive layers. Power conversion efficiency (PCE) and external quantum efficiency (EQE) were measured on the devices. The morphology and surface roughness of the active layers was investigated using atomic force microscopy (AFM). From these studies diethylzinc emerged as the best working ZnO precursor in combination with P3HT.
The efficiency of polymer solar cells critically depends on the intimacy of mixing of the donor and acceptor semiconductors used in these devices to create charges and on the presence of unhindered percolation pathways in the individual components to transport holes and electrons. Therefore, the effect of three-dimensional morphology of the active layer on the efficiency was investigated in chapter 3. For ZnO:P3HT cells the internal quantum efficiency (IQE) improves with increasing layer thickness. Photoinduced absorption measurements indicated less triplet state formation in thick layers, meaning that excitons created in these thick layers are better separated into free charges compared to thin films. Three-dimensional transmission electron microscopy (3D-TEM) tomography revealed the 3D morphology in great detail and allowed to determine the probability to find P3HT domains at a certain distance from a ZnO domain with nanometer resolution. From these data the exciton dissociation efficiency of the layers was calculated by solving the 3D exciton diffusion equation in three dimensions, and the percolation pathways for electrons in the ZnO phase were analyzed. Exciton dissociation was higher in thicker blends, explaining the higher IQE for these layers, while the available percolation pathways for electrons in the ZnO were reduced with increasing layer thickness.

In chapter 4 it is shown that the morphology of the active layer can be controlled by introducing polar side groups in the polymer. Carboxylic acid esters and alcohols introduce hydrophilicity into the polymer, making it more compatible with the hydrophilic ZnO. 3D TEM analyses have shown that the intimacy of mixing and the extent of exciton dissociation are indeed improved significantly for thin active layers. Device performance was still limited due to the lower amount of ZnO connected to the respective electrode hindering charge collection, and lower hole mobility of the polymer, which is not able to form a crystalline phase as observed in the optical absorption due to the very intimate mixing with ZnO.

To absorb more light, poly(3-hexylselenophene) (P3HS) was tested with ZnO in solar cells as described in chapter 5. The advantage of P3HS is a smaller optical band gap than P3HT, such that more photons from the solar spectrum can be absorbed, leading to higher current and efficiency. Device optimization was performed and active layers were analyzed using TEM. Eventually, the device performance was less compared to ZnO:P3HT blends. This could be ascribed to a lower exciton dissociation from excitons in the crystalline part of P3HS, judging from the difference in shape of absorption compared to the shape of the EQE. Probably, the lifetime and/or exciton diffusion length in crystalline P3HS is shorter than in amorphous P3HS.

Chapter 6 describes the use of a ZnO nanorod template layer, infiltrated with a ZnO:P3HT blend to create a hybrid ZnO-polymer solar cell that features a hierarchically built inorganic phase, with 300 nm ZnO nanorods for charge collection connected to a fine ZnO network for charge generation throughout the bulk. These hierarchical ZnO:P3HT
layers were prepared by casting P3HT and diethylzinc (as reactive ZnO precursor) from a common solvent mixture in moist atmosphere on a ZnO nanorod carpet grown from a compact ZnO nucleation layer, followed by thermal conversion. AFM and scanning electron microscopy confirmed the infiltration of the ZnO:P3HT blend in between the ZnO nanorods. Photoinduced absorption spectroscopy revealed that the relative efficiency of charge generation in the ZnO:P3HT blend layers is not influenced by connecting to the ZnO nanorod carpet. We find that the performance of the combined ZnO nanorod ZnO:P3HT blend solar cells is not improved compared to ZnO:P3HT blend cells without nanorods and, actually, somewhat less. This is interpreted as being due to a poor contact between the ZnO network in the ZnO:P3HT blend and the ZnO nanorods.

In conclusion, the research described in this thesis provides a first, detailed insight in the relation between the active layer morphology and the performance of hybrid metal oxide - polymer bulk heterojunction solar cells. The morphology can be controlled by changing the deposition conditions (e.g. spin rate), the nature of the polymer (e.g. presence of polar side chains), and using metal oxide template structures (e.g. nanorod carpet). In the best devices power conversion efficiencies of 2% in simulated solar light have been obtained. The thesis demonstrates that the main challenge toward more efficient solar cells is creating a morphology that is fine enough for efficient exciton dissociation and coarse enough to maintain a high mobility of charge carriers and short percolation pathways to the electrodes. A first attempt to achieving such a morphology has been described in the last chapter.
SAMENVATTING

Hybride polymere zonnecellen gebaseerd op ZnO

Door de toenemende vraag naar energie en de gelimiteerde beschikbaarheid van fossiele brandstoffen is er een behoefte naar een duurzame, hernieuwbare bron van energie. Een energiebron die altijd beschikbaar zal zijn, is de zon. Zonne-energie kan gecollecteerd worden op ruwweg drie manieren: als thermische, elektrische, of chemische energie. Warmte kan direct gebruikt worden, of indirect, bijvoorbeeld voor het aandrijven van een elektriciteitsgenerator. Zonlicht kan ook gebruikt worden om chemische reacties van energie te voorzien, waarbij energie opgeslagen wordt in chemische bindingen. Tot slot kan zonlicht ook direct worden omgezet in elektrische energie door gebruik te maken van fotovoltaïsche zonnecellen. Omdat elektriciteit waarschijnlijk de meest waardevolle en veelzijdige vorm van energie is, verdient deze directe manier van conversie onze aandacht.

Door de efficiëntie van zonnecellen te verhogen en de productiekosten te verlagen kan wereldwijd een duurzame energiehuishouding worden gerealiseerd. Op dit moment wordt de fotovoltaïsche energiemarkt gedomineerd door zonnecellen gebaseerd op siliconium, dat zeer zuiver dient te zijn. Het produceren van siliconium met zuiverheid vergt veel inspanning, is duur en daarom vindt er onderzoek plaats naar goedkopere en milieu-vriendelijker alternatieven. Polymere zonnecellen zijn een mogelijk alternatief, maar de stabiliteit van de morfologie laat op dit moment nog te wensen over en belemmert commerciële toepassing van deze technologie. In hybride polymere zonnecellen, waarin een anorganisch materiaal wordt gecombineerd met een organisch polymeer, is de morfologische stabiliteit hoger. Deze verhoogde morfologische stabiliteit wordt gecombineerd met de voordelen van nat-chemisch verwerken van organische materialen. Dit proefschrift is gericht op het karakteriseren van de morfologie van ZnO:polymeer zonnecellen en het veranderen van deze morfologie met als doel de efficiëntie te verhogen.

Hoofdstuk 2 beschrijft de sol-gel precursor methode om hybride ZnO:polymeer zonnecellen te fabriceren, en strategieëen om het maximale vermogen omzettingsrendement te behalen. Organische ZnO precursors met verschillende mate van reactiviteit zijn getest in combinatie met poly(3-hexylthiofeen) (P3HT) voor het maken van fotoactieve lagen.
Het rendement voor de conversie van zonlicht in elektrisch vermogen (PCE) en de externe quantum efficiëntie (EQE) werden gemeten. De morfologie en ruwheid van het oppervlak van de actieve lagen werden onderzocht met atomaire kracht microscopie (AFM). Uit deze studie bleek dat diethylzink de beste ZnO precursor is in combinatie met P3HT als elektron donor.

De efficiëntie van polymere zonnecellen hangt sterk af van de mate van menging van de donor- en acceptorhalfgeleiders die gebruikt worden om ladingen te maken, en van de beschikbaarheid van percolatiepaden in de individuele componenten waardoor elektronen en gaten zich ongehoor of kunnen voortbewegen. Daartoe is het effect van de driedimensionale morfologie van de actieve laag op de efficiëntie onderzocht, waarvan de resultaten zijn beschreven in hoofdstuk 3. De interne kwantum efficiëntie (IQE) voor ZnO:P3HT zonnecellen wordt steeds beter naarmate de actieve laag dikker is. Fotogene induceerde absorptiemetingen laten zien dat er relatief minder triplettoestanden aanwezig zijn in dikke lagen. Dit betekent dat excitonen in dikke lagen efficiënter worden gesplitst in vrije ladingen dan dunne lagen. Met driedimensionale (3D-) elektron tomografie bleek het mogelijk de morfologie in groot detail te meten waarmee, met nanometer resolutie, de waarschijnlijkheid om een P3HT domein te vinden op een arbitraire afstand van ZnO kon worden vastgesteld. De efficiëntie voor exciton dissociatie is berekend met deze elektron tomografie data berekend door de exciton diffusievergelijking in drie dimensies op te lossen. Tevens zijn de percolatiepaden voor elektronen in de ZnO fase geanalyseerd. Excitondissociatie bleek hoger in dikkere actieve lagen, wat de hogere IQE voor deze lagen verklaart, terwijl de beschikbare percolatiepaden voor elektronen in de ZnO verminderden met toenemende laagdikte.

Hoofdstuk 4 toont aan dat de morfologie van de actieve laag beïnvloed kan worden door polaire zijstaarten in het polymeer te introduceren. Carbonzure esters en alcoholen maken het polymeer hydrofieler, en daarmee meer compatibel met het hydrofiele ZnO. 3D-elektron tomografie laat zien dat de mate van menging en excitondissociatie signifcant hoger zijn voor dunne actieve lagen, in vergelijking met ongemodificeerd P3HT. De efficiëntie van deze actieve lagen bleek gelimiteerd door de lagere hoeveelheid ZnO die met de aluminium elektrode verbonden is, waardoor er minder percolatiepaden zijn voor elektronen, en ook door de lagere gatenmobiliteit in het polymeer, dat geen semikristallijnse structuur kan aannemen, zoals afgeleid kon worden uit optische absorptiemetingen. De afgenomen kristalliniteit is het gevolg van de zeer fijne fasescheiding tussen het polymeer en ZnO.

In een poging om meer licht te absorberen en daarmee de stroom en dus efficiëntie van deze zonnecellen te verhogen, is in hoofdstuk 5 poly(3-hexylselenofeen) (P3HS) getest als elektron donor in ZnO:polymeer zonnecellen. De kleinere optische bandafstand van P3HS is een voordeel in vergelijking met P3HT omdat er dan meer fotonen
van het zonnespectrum geabsorbeerd kunnen worden. De fabricatie van de zonnecellen werd geoptimaliseerd en actieve lagen werden gekarakteriseerd met transmissie-elektronenmicroscopie (TEM). Uiteindelijk bleek de maximale efficiëntie lager dan bij ZnO:P3HT systemen. Het verschil in vorm van golflengteafhankelijke absorptie en EQE doet vermoeden dat deze lagere efficiëntie, die voornamelijk afkomstig is van een reductie in kortsluitstroom, het gevolg is van een lagere bijdrage van excitonen gegenereerd in het kristallijne deel van P3HS.

Hoofdstuk 6 beschrijft het gebruik van een ZnO nanopaal tapijt, die geïnfiltreerd wordt met een ZnO:P3HT mengsel om een hybride ZnO:polymeer zonnecel te maken die een hiërarchisch opgebouwde anorganische fase heeft, met 300 nanometer hoge ZnO nanopaaltjes voor ladingscollectie, die verbonden is met een willekeurig, fijn verdeeld ZnO netwerk voor ladingsgeneratie in de bulk van de zonnecel. Deze hiërarchische ZnO::P3HT lagen werden gemaakt door depositie van P3HT en diethylzink (als reactieve ZnO precursor) vanuit een gemeenschappelijke oplosmiddelmengsel in een vochtige omgeving op een ZnO nanopaaltapijt die gegroeid is op een ZnO nucleatielaag, gevolgd door thermische conversie. AFM en scanning elektronen microscopie (SEM) bevestigden de infiltratie van de ZnO:P3HT gemengde laag tussen de ZnO nanopaaltjes. Fotogefundeerde absorptie liet zien dat de relatieve efficiëntie van ladingsgeneratie in de ZnO::P3HT gemengde laag niet wordt beïnvloed door het gebruik van de ZnO nanopaaltjes. De efficiëntie van de gecombineerde ZnO nanopaaltjes - ZnO:P3HT mix is niet verbe- terd in vergelijking met ZnO:P3HT zonnecellen zonder ZnO nanopaaltjes, maar is feitelijk zelfs iets minder efficiënt. Dit is waarschijnlijk het gevolg van een slecht contact tussen het ZnO netwerk in de ZnO:P3HT gemengde laag en de ZnO nanopaaltjes.

Concluderend beschrijft dit proefschrift een gedetailleerd onderzoek naar de relatie tussen de morfologie van de actieve laag en de efficiëntie van een hybride metaaloxide - polymeer zonnecellen. De morfologie kan worden aangepast door de condities tijdens depositie aan te passen (bijv. spinsnelheid), de eigenschappen van het polymeer (bijv. de aanwezigheid van polaire zijstaarten) en het gebruik van voorgevormde metaaloxide structuren (bijv. nanopaaltapijt). In de beste zonnecellen wordt een rendement voor de conversie van gesimuleerd zonlicht in elektrisch vermogen van ongeveer 2% gehaald. Dit proefschrift laat zien dat een van de belangrijkste uitdagingen om efficiëntere zon- necellen te maken, het maken van een morfologie is die fijn genoeg verdeeld is om efficiënte exciton dissociatie te hebben maar tegelijkertijd grof genoeg verdeeld is om een hoge mobiliteit van ladingsdragers en korte percolatiepaden naar de elektroden te behouden. Een eerste poging om een dergelijke morfologie te produceren is beschreven in het laatste hoofdstuk.
CURRICULUM VITAE

Stefan Oosterhout is born on 11 July 1982 in Sas van Gent, The Netherlands. After finishing secondary school in 2001 in Amersfoort, he studied Chemistry at Utrecht University. His graduation project was conducted in the "Condensed Matter and Interfaces" group under supervision of prof. dr. D.A.M. Vanmaekelbergh and dealt with the photovoltaic effect of a semiconductor-gold contact. The graduation was completed with an internship at the Energy research Centre of the Netherlands, with research project on charge transport in porous layers, supervised by dr. F.O. Lenzmann. After finishing his studies in 2007 he started his PhD in the "Molecular Materials and Nanosystems" group under supervision of prof. dr. ir. R.A.J. Janssen. The most important results are described in this thesis.
"The effect of three-dimensional morphology on the efficiency of hybrid polymer solar cells"

"Controlling the morphology and efficiency of hybrid ZnO:polythiophene solar cells via side chain functionalization"
*Advanced Energy Materials* **2011**, *1*, 90

"A multiscale approach to the representation of 3D images, with application to polymer solar cells"

"Hybrid polymer solar cells, from zinc oxide and poly(3-hexylselenophene)"

"Spatial modeling of the 3D morphology of hybrid polymer-ZnO solar cells, based on electron tomography data"
"A New Approach to Model-Based Simulation of Disordered Polymer Blend Solar Cells"

Other publications

"Thermodynamic stability of clusters of Molybdenum oxide"
Validzic, I. Lj.; Van Hooijdonk, G.; Oosterhout, S.; Kegel, W.K.
Langmuir 2004, 20, 3435

"Chemisorption determines the photovoltage of a Ti/TiO$_2$/Au/dye internal electron emission photovoltaic cell"
Koole, R.; Liljeroth, P.; Oosterhout, S.; Vanmaekelbergh, D.
Journal of Physical Chemistry B 2005, 109, 9205

"Fabrication of PEDOT-OTS-patterned ITO substrates"
Journal of Materials Chemistry 2010, 20, 6618
Ook voor mij nadert nu het einde van het promoveren. Vaak zie je je collega’s behoorlijk stressen, de een wat meer dan de ander, en ook voor mij is het een bewogen promotie geweest, met vallen en opstaan. Toch vond ik het erg fijn om hier in deze groep mijn promotie te mogen doen.

Een promotie doe je niet alleen, dat blijkt ook uit de lange lijst met namen die bij de publicaties staan. Allereerst wil ik René enorm bedanken voor zijn goede steun en begeleiding gedurende mijn promotie. René, zelfs mijn sollicitatiegesprek met jou vond ik al gezellig, ik denk niet dat er een betere begeleider zou kunnen zijn. Gedurende alle momenten tijdens mijn promotie was je beschikbaar; ook als je even niet op je kamer was, of tijdens je vakantie, je was toch bereikbaar. Samen met Martijn zijn jullie een geweldig duo in het verzinnen van razend interessante experimenten, en kunnen jullie met wat in het begin een merkwaardige conclusie lijkt, met iets op de proppen komen wat verder niemand kan verzinnen. Martijn, ook jij bent essentieel geweest in mijn groei tijdens de promotie. Met jou had ik gesprekken die me op een andere manier naar data laten kijken. Bedankt voor alle praktische hulp en het leren schrijven van artikelen.

I would like to thank Sean Shaheen, Jean Manca, Erik Bakkers, Jan Kroon and Albert Schenning for taking part in the reading and defense committee.

Veel van wat er in dit proefschrift staat is gedaan in samenwerking met verschillende mensen in verschillende disciplines. Svetlana, zonder jouw fantastische vaardigheden met de TEM hadden we nooit zulke mooie figuren kunnen krijgen en een duidelijk inzicht kunnen vergaren in de morfologie van deze zonnecellen. Jouw werk draagt voor een groot deel bij aan de totstandkoming van hoofdstukken 3 en 4. Jan, heel erg bedankt voor de optische modellering die heeft bijgedragen aan de IQE berekeningen in hoofdstuk 3. Ralf, Ole, and prof. Volker Schmidt from the Institute of Stochastics of Ulm University in Germany, your outstanding calculations on the morphology data have had a great impact on the way we looked at our data. Jan Anton, jouw berekeningen aan excitondiffusie waren geweldig, en leverden ook nog eens de kleurrijkste plaatjes op!

De samenwerking met Bert Campo van de Universiteit van Hasselt leverde de basis voor hoofdstuk 4 wat een heel bijzonder hoofdstuk is geworden met aspecten die voor de hand liggen, maar ook aspecten die we niet hebben voorzien. Dit heeft een heel mooi
resultaat opgeleverd en een publicatie.

With the material from Mohammed Al-Hashimi from Imperial College London it may not have been possible to enhance device performance of ZnO:polymer solar cells yet, but it has lead to the discovery of a phenomenon that we couldn’t foresee and is described in chapter 5. Thank you very much for your contribution.

Het kantoor, STO 4.27, is het grootste kantoor in onze groep. Niet alleen qua oppervlak van de kamer en afmetingen van de bureaus, maar ook qua aantal personen. Voor de gezelligheid en leuke filmavondjes wil ik graag Martin, Marie-France, Bram, Dirk, Girish, Jeroen, Robert, Irén, Daniele, Aranxa, Jan Anton, Dominique, Gijs, Ratheesh en Dhritiman bedanken.

I supervised three students in research projects who helped me to make the basis for chapter 6. Corné, Maikel and Rajini, thank you for you contributions.

Vooral in het begin heb ik veel hulp gekregen bij praktische zaken in het lab. Hiervoor, en voor hun gezelligheid in het lab, wil ik Frank V., Jan G., Klara, Dirk, Bram, Johan, Wiljan, Daniele, Martijn K., Peter T. en Paul B. bedanken. Daarnaast had ik ook gezellige momenten in het lab met Patrick, Arjan, Tonggang, Serkan, Alice, Benjamin, Mindaugas, Rafa, Kevin, Erwin, Erik, Zuhal, Paul J., Francisco en Wiebe.

Tijdens mijn promotie heb ik eenmaal deelgenomen aan het organiseren van het groepsuitje. Dit was erg gezellig en leuk om te doen samen met Johan, Carel, Michel en Wencke.

In het bijzonder bedank ik Sandra, Veronique, Dominique en Lotte voor alle gesprekken die we hebben gevoerd.

Naast het werk zijn directe vrienden en familie heel belangrijk voor mij. Daniëlle, Thomas, Iris, heel erg bedankt voor jullie steun de afgelopen jaren. Hoewel jullie niet altijd directe steun kunnen bieden met mijn werk zelf, is de vriendschap met jullie voor mij essentieel. Daphne, Ronan, Ciaran, Trevor, mam en pap heel erg bedankt voor de steun die jullie mij de afgelopen jaren hebben gegeven.

Het laatste stukje van mijn proefschrift is voor mijn vriendin. Bente, jij staat altijd voor me klaar, jij bent mijn steun en toeverlaat. Jij weet me altijd weer met twee benen op de grond te zetten als ik even de weg kwijt ben. Ik hou van je.

Stefan