Introduction

Abstract

As the evidence of global warming continues to build-up, it is becoming clear that we will have to find ways to produce electricity without the release of carbon dioxide and other greenhouse gases. Fortunately, we have renewable energy sources which neither run out nor have any significant harmful effects on our environment. Harvesting energy directly from the sunlight using photovoltaic (PV) technology is being widely recognized as an essential component of future global energy production. In this chapter, a brief overview regarding the photovoltaic devices is given, with emphasis on the organic solar cells, ending with a short outline of the thesis.
1.1 Motivation

As the global energy demand continues to increase every year, the limiting supply of today’s main energy sources (i.e. oil, coal, uranium) and their detrimental long-term effects on the natural balance on our planet, underscore the urgency of developing renewable energy sources. Today’s plants are unable to absorb the huge amount of extra carbon dioxide that is released in the earth’s atmosphere mainly by burning of fossil fuel [1, 2]. As a result, the increased concentration of carbon dioxide in the atmosphere considerably adds to the greenhouse effect which will increase the global mean surface temperature [2]. The consequence of these chances are already seen by an increase in the frequency and severity of natural disasters [1].

Fortunately, we have renewable energy sources which neither run out nor have any significant harmful effects on the environment. Harvesting energy directly from the sunlight using photovoltaic (PV) technology is being widely recognized as an essential component of future global energy production. Provided that PV devices can be made truly economically competitive with fossil fuels and other emerging renewable energy technologies, large scale manufacturing of these devices offers a sustainable energy source which can supply a significant fraction of our daily energy needs.

1.1.1 Inorganic solar cells

The photovoltaic cells have become extensively studied since the 1950s when the first crystalline silicon solar cell, which had an efficiency of 6%, was developed at Bell Laboratories [3]. Since then, the efficiency has reached 24% for crystalline Si solar cells [4], which is already close to the theoretical predicted upper limit of 30% [5, 6]. Practically all conventional inorganic solar cells incorporate a semiconductor that is doped to form a p-n junction across which the photovoltage is generated. The p side contains an excess of the positive charges (holes), and the n side contains an excess of the negative charges (electrons). In the region near the junction an electric field is formed and the electrons and holes, which are generated through light absorption in the bulk of Si, diffuse to this junction, where they are directed by the electric field towards the proper electrode. Over the years, solar cells have been made from many other semiconductor materials with various device configuration such as single-crystal, polycrystalline, and amorphous thin-film structures. At present, crystalline Si solar cells are by far most dominant PVs used and account for more than 85% of the market. A comprehensive review on Si and other type of solar cells can be found in literature [7].

Although in the last 5 years the production of PV modules was increased steadily by an annual average of 40%, the semiconductor PV still accounts for less that 0.1% of the total world energy production. One of the major obstacles for the market implementation of PV cells is the large production costs for Si-based technology. However, despite much effort of further reducing the price, large scale production of Si-based solar cells will be limited by the availability of raw materials, such as solar-grade Si. Therefore, to ensure a sustainable tech-
nology path for PV, the development of new materials and device structures are required.

1.1.2 Organic solar cells

Organic materials bear the potential to develop a long-term technology that is economically viable for large-scale power generation based on environmentally safe materials with unlimited availability. Organic semiconductors are a less expensive alternative to inorganic semiconductors like Si; they can have extremely high optical absorption coefficients which offer the possibility for the production of very thin solar cells. Additional attractive features of organic PVs are the possibilities for thin flexible devices which can be fabricated using high-throughput, low temperature approaches that employ well established printing techniques in a roll-to-roll process [8, 9]. This possibility of using flexible plastic substrates in an easily scalable high-speed printing process can reduce the balance of system cost for organic PVs, resulting in a shorter energetic pay-back time.

The electronic structure of all organic semiconductors is based on conjugated \( \pi \)-electrons. A conjugated organic system is made of an alternation between single and double carbon-carbon bonds. Single bonds are known as \( \sigma \)-bonds and are associated with localized electrons, and double bonds contain a \( \sigma \)-bond and a \( \pi \)-bond. The \( \pi \)-electrons are much more mobile than the \( \sigma \)-electrons; they can jump from site to site between carbon atoms thanks to the mutual overlap of \( \pi \)-orbitals along the conjugation path, which causes the wave functions to delocalize over the conjugated backbone. The \( \pi \)-bands are either empty (called the Lowest Unoccupied Molecular Orbital - LUMO) or filled with electrons (called the Highest Occupied Molecular Orbital - HOMO). The band gap of these materials ranges from 1 to 4 eV. This \( \pi \)-electron system has all the essential electronic features of organic materials: light absorption and emission, charge generation and transport. Figure 1.1 shows several examples of conjugated organic moieties.

A typical organic PV cell consists of a photoactive layer sandwiched between

![Chemical structures and abbreviations of some conjugated organic molecules. From left: poly(acetylene) PA, poly(para-phenylene-vinylene) PPV, a substituted PPV (MDMO-PPV), poly(3-hexyl thiophene) P3HT, and a \( C_{60} \) derivative ([60]PCBM, called PCBM throughout this thesis). In each compound one can identify a sequence of alternating single and double bonds.](image)

Figure 1.1: Chemical structures and abbreviations of some conjugated organic molecules. From left: poly(acetylene) PA, poly(para-phenylene-vinylene) PPV, a substituted PPV (MDMO-PPV), poly(3-hexyl thiophene) P3HT, and a \( C_{60} \) derivative ([60]PCBM, called PCBM throughout this thesis). In each compound one can identify a sequence of alternating single and double bonds.
two different electrodes, one of which should be transparent in order to allow the incoming photons to reach the photoactive layer, as seen in Figure 1.2. This photoactive layer is based on a single, a bi-layer, or a mixture of two (or more) components. Upon light absorption the charge carriers are generated inside the photoactive layer and due to the presence of an electric field, provided by the asymmetrical ionization energies/work functions of the electrodes (anode and cathode)*, these charges are transported and collected into the external circuit. In this way an organic solar cell converts light into electricity.

The first investigation of an organic PV cell came as early as 1959, when an anthracene single crystal was studied. The cell exhibited a photovoltage of 200 mV with an extremely low efficiency [10]. Since then, many years of research have shown that the typical power conversion efficiency of PV devices based on single (or homojunction) organic materials will remain below 0.1%, making them unsuitable for any possible application. Primarily, this is due to the fact that absorption of light in organic materials almost always results in the production of a mobile excited state (referred to as exciton), rather than free electron-hole pairs as produced in inorganic solar cells. This occurs for the reason that organic materials are characterized by low dielectric constant (typically 2-4), compared to inorganic semiconductors, which require an energy input much higher than the thermal energy ($kT$) to dissociate these excitons [11–13]. The electric field provided by the asymmetrical work functions of the electrodes is not sufficient to break-up these photogenerated excitons. Instead, the excitons diffuse within the organic layer until they reach the electrode, where they may dissociate to supply separate charges, or recombine. Since the exciton diffusion lengths are typically 1-10 nm [14–18], being much shorter than the device thicknesses, exciton diffusion limits charge carrier generation in these devices since most of them are lost through recombination. Photogeneration is therefore a function of the available mechanisms for excitons dissociation. A major breakthrough in the cell performance came in 1986 when Tang discovered that much higher efficiencies (about 1%) are attainable when bringing an electron donor (D) and an electron acceptor (A) together in one cell [19].

*[Herein the anode was taken as the positively biased electrode and the cathode as the negatively biased electrode.]*
1.1. Motivation

the heart of all three currently existing types of organic PV cells: dye-sensitized solar cells [20–22]; planar organic semiconductor cells [19, 23–25]; and high surface area, or bulk heterojunction cells [8, 26–28]. In the following this concept is briefly reviewed together with the operation processes and limitations of the organic PV cell.

The concept of an organic (bulk) heterojunction

Most of the developments that have improved the performance of organic PV devices are based on D/A heterojunctions. The idea behind a heterojunction is to use two materials with different electron affinities and ionization potentials. At the interface, the resulted potentials are strong and may favor exciton dissociation: the electron will be accepted by the material with the larger electron affinity and the hole by the material with the lower ionization potential, provided that the differences in potential energy are larger than the exciton binding energy. In the planar heterojunction, or ‘bi-layer’ device, the organic D/A interface separates excitons much more efficient than an organic/metal interface in the single layer device. The energetic diagram of such a bi-layer device is depicted in the Figure 1.3(a). Sunlight photons which are absorbed inside the device excite the donor molecule (1), leading to the creation of excitons. However, the acceptor phase can also absorb light, but for simplicity only the photons that are absorbed by the donor phase are considered here. The created excitons start to diffuse (3) within the donor phase and if they encounter the interface with the acceptor then a fast dissociation takes place (4) leading to charge separation [29, 30]. The resulting metastable electron-hole pairs across the D/A interface may still be Coulombically bound and an electric field is needed to separate them into free charges [31, 32]. Therefore, at typical operation conditions, the photon-to-free-electron conversion efficiency is not maximal. Subsequently, the separated free electrons (holes) are transported (5) with the aid of the internal electric field, caused by the use of electrodes with different work functions, towards the cathode (anode) where they are collected by the electrodes (6) and driven into the external circuit. However, the excitons can decay (2), yielding e.g. luminescence, if they are generated far from the interface. Thus, the excitons should be formed within the diffusion length of the interface. Since the exciton diffusion lengths in organic materials are much shorter than the absorption depth of the film, this limits the width of effective light-harvesting layer.

A revolutionary development in organic PVs came in the mid 1990s with the introduction of the dispersive (or bulk) heterojunction, where the donor and acceptor material are blended together. If the length scale of the blend is similar to the exciton diffusion length, the exciton decay processes (2) is dramatically reduced since in the proximity of every generated exciton there is an interface with an acceptor where fast dissociation takes place (4). Hence, charge generation takes place everywhere in the active layer, as is schematically represented in Figure 1.3(b). Provided that continuous pathways exist in each material from the interface to the respective electrodes, the photon-to-electron conversion efficiency and, hence, the photosensitivity is dramatically increased. The observation of improved device performance using bulk heterojunctions represents
the departure from the device physics of conventional inorganic PV cells and has led to new device and materials designs. Nowadays, the bulk heterojunction is the most promising concept for all-organic PV cells. Dye-sensitized solar cells, as developed in 1990s by Grätzel, however, function on similar principles [20–22].

One class of organic materials used as photoactive layer in bulk heterojunction PV cells that have received considerable attention in the last few years are semiconducting polymers and molecules. They combine the opto-electronic properties of conventional semiconductors with the excellent mechanical and processing properties of ‘plastic’ materials. Additionally, they possess an unprecedented flexibility in the synthesis, allowing for alteration of a wide range of properties, such as bandgap, molecular orbital energy level, wetting and structural properties, as well as doping. This ability to design and synthesize polymers and molecules that can be casted from solution using wet-processing techniques such as spin-coating, ink jet printing, and screen printing, represents an enormous attractive route for cheap production of large-area PV cells that can be applied to systems that require flexible substrates. Since ultrafast photoinduced electron transfer from a conjugated polymer as donor to buckminsterfullerene (C\textsubscript{60}) or its derivatives as acceptor was first observed in 1992 by Sariciftci et al. \[29\], this material combination has been extensively studied in bulk heterojunction PV cells. In 1995 Yu et al. \[27\] fabricated the first fully organic bulk heterojunction cell based on a mixture of soluble PPV derivative with a fullerene acceptor [such as C\textsubscript{60} derivative PCBM \[33\]; Figure 1.1(e)]. In 2001 Shaheen et al. \[34\] obtained the first truly promising results for bulk heterojunction solar cells when mixing a conjugated polymer [such as MDMO-PPV, Figure 1.1(c)] with PCBM in a 20:80 weight percentage and optimizing the nanoscale morphology of the film, yielding a power conversion efficiency of 2.5%. Recently, power conversion efficiencies of >3.5% have been achieved for polymer:fullerene (PCBM) bulk heterojunction solar cells based on polythiophene derivatives [such as regioregular P3HT; Figure 1.1(d)] as absorbing and electron-
1.1. Motivation

Figure 1.4: Typical $J$-$V$ characteristics of an organic PV cell in the dark (dashed line) and illumination (solid line) conditions. The short-circuit current density ($J_{SC}$) and open-circuit voltage ($V_{OC}$) are shown. The maximum output power ($P_{max}$) is given by the rectangle $J_{max} \times V_{max}$.

donating material [35–39].

Characterization of organic bulk heterojunction PV cells

Bulk heterojunction solar cells with a photoactive layer prepared from a conjugated polymer and fullerene molecules, are fabricated by depositing (i.e. spin-coating) the active layer from a solution on a transparent bottom electrode, normally indium-tin-oxide (ITO), which forms the anode. To enhance the reproducibility and the performance of the devices, a thin conductive organic layer is typically applied from solution on top of ITO, before the actual active layer is deposited. The most widely used cover layer on ITO is a transparent composite PEDOT:PSS [40–42], consisting of oxidized polyethylenedioxythiophene (PEDOT) and impartially anionic form polystyrenesulfonate (PSS). A low work function metal (calcium, barium, or a thin layer of lithium fluoride; all topped with aluminum) is evaporated under high vacuum on top of the photoactive layer and serves as cathode, as shown schematically in Figure 1.2. Under illumination (at short-circuit condition), the main processes that govern the operation of these devices are depicted in Figure 1.3(b).

In order to investigate the PV performance of a cell, as well as its electric behavior, the current density-voltage ($J$-$V$) characteristics in the dark and under illumination are considered. Figure 1.4 shows a typical $J$-$V$ curve of a PV device in the dark (dashed line) and under illumination (solid line). When the cell is illuminated, the $J$-$V$ curve is shifted down by the amount of photocurrent ($J_{ph}$) generated. The open-circuit voltage, $V_{OC}$, is the maximum photovoltage that can be generated in the cell and corresponds to the voltage where current under illumination is zero. The maximum current that can run through the cell at zero applied voltage is called the short-circuit current, $J_{SC}$. The maximum of the obtained electrical power $P_{max}$ is located in the fourth quadrant where the product of current density $J$ and voltage $V$ reached its maximum value ($J_{max} \times V_{max}$); as
seen in Figure 1.4). It is observed from the Figure 1.4 that $P_{\text{max}}$ is bigger when the $J$-$V$ curve resembles a rectangular with the area $J_{\text{SC}} \times V_{\text{OC}}$. The ratio between (the rectangle of) $P_{\text{max}}$ and the product of (or a rectangle defined by) $J_{\text{SC}}$ and $V_{\text{OC}}$ measures the quality of the shape of the $J$-$V$ characteristics, and is defined as the fill factor (FF):

$$ FF \equiv \frac{J_{\text{max}} \cdot V_{\text{max}}}{J_{\text{SC}} \cdot V_{\text{OC}}} $$

(1.1)

thus $P_{\text{max}} = J_{\text{SC}} \cdot V_{\text{OC}} \cdot FF$. The power conversion efficiency $\eta$ of a solar cell is the ratio between the maximum output power $P_{\text{max}}$ and the power of the incident light $P_{\text{light}}$:

$$ \eta \equiv \frac{P_{\text{max}}}{P_{\text{light}}} = \frac{J_{\text{SC}} \cdot V_{\text{OC}} \cdot FF}{P_{\text{light}}} $$

(1.2)

Because of the wavelength and intensity dependence of $P_{\text{max}}$, the power conversion efficiency $\eta$ should be measured under standard test conditions. Equation 1.2 shows that in order to increase $\eta$, for the same incident light power $P_{\text{light}}$, either $J_{\text{SC}}$, $V_{\text{OC}}$, or FF (or all) need to be increased. For organic solar cells based on polymer:fullerene bulk heterojunctions, the magnitude of $J_{\text{SC}}$, $V_{\text{OC}}$, and FF depends on parameters such as: light intensity [43], temperature [44, 45], composition of the components [46], thickness of the active layer [47], the choice of electrodes used [48, 49], as well as the solid state morphology of the film [34]. Their optimization and maximization require a clear understanding of the device operation and photocurrent, $J_{\text{ph}}$, generation and its limitations in these devices. The relation between the experimental $J_{\text{ph}}$ and material parameters (i.e., charge-carrier mobility, bandgap, molecular energy levels, or relative dielectric constant) needs to be understood and controlled in order to allow for further design of new materials that can improve the efficiency of this type of solar cells.

A first attempt to understand the physics behind the organic bulk heterojunction solar cells was done by using numerical models and concepts that are well established for inorganic solar cells, such as the $p$-$n$ junction model. To improve the agreement of the classical $p$-$n$ model with the experimental $J_{\text{ph}}$ of an organic bulk heterojunction cell, an expanded replacement circuit has been introduced [38, 50, 51]. This model replaces the photoactive layer by an ideal diode and a serial and a parallel resistance, which have an ambiguous physical meaning for an organic cell. However, different to classical $p$-$n$ junction cells with spatially separated $p$- and $n$-type regions of doped semiconductors, bulk heterojunction cells consist of an intimate mixture of two un-doped (intrinsic) semiconductors that are nanoscopically mixed and that generate a randomly oriented interface. Moreover, due to the different charge generation, transport and recombination processes in bulk heterojunctions, the classical $p$-$n$ junction

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*To allow meaningful comparisons of solar cell performances all over the world, the PV cells are rated at a well-defined set of conditions known as Standard Test Conditions (STC). These conditions include the temperature of the PV cells (25 °C), the intensity of radiation (1000 W/m²), and the spectral distribution of the light (air mass 1.5 or AM1.5, which is the spectrum of sunlight that has been filtered by passing through 1.5 thicknesses of the earth’s atmosphere).
model is not applicable to describe the $J_{ph}$ of these solar cells [52]. An alternative approach is to use the metal-insulator-metal (MIM) concept [28], where a homogenous blend of two unipolar semiconductors (donor/acceptor) is described as one semiconductor with properties derived from the two materials. This means that the photoactive layer is described as one ‘virtual’ semiconductor assuming that its conduction band is given by the LUMO of the acceptor and its valence band is determined by the HOMO of the donor-type material [see Figure 1.3(b)]. Under PV operation mode (at short-circuit condition), the potential difference available in the MIM device, that drives the photogenerated charge carriers towards the collection electrodes, is caused by the difference between the work functions of the metal electrodes. The applicability of MIM model to organic bulk heterojunction cells is demonstrated through the work presented in this thesis.

1.2 Outline of the thesis

In 2001 bulk heterojunction solar cells prepared from conjugated polymers and fullerene molecules made a significant step in power conversion efficiency from 1% to 2.5%. Despite this enhancement, resulting mostly from an improved solid state morphology of the film, there was not much known about charge transport and photogeneration mechanisms that govern the efficiency of these type of PV cells. Questions that need to be answered are: what are the charge-carrier mobilities in the polymer, fullerene, and in their mixture? How efficient and through which mechanisms do the charge carriers dissociate at the polymer/fullerene interface? What is the role of the electrodes, or what limits the efficiency at lower fullerene fractions? This thesis discusses and underlines the fundamental processes behind the operation of these solar cells, which are absolutely necessary to further improve the device performance.

To understand the photocurrent generation in bulk heterojunction solar cells based on conjugated polymer and fullerene molecules, in Chapter 2 the transport of charge carriers in the pristine fullerene and polymer:fullerene films is investigated and interpreted, using a phenomenological model for the charge carrier mobility. The experimental results for charge carrier mobilities are further discussed on the basis of energetic disorder of the system and molecular packing of the components in the film.

The photocurrent generation in polymer:fullerene blends is discussed in Chapter 3, with emphasis on the mechanism of charge dissociation at the polymer/fullerene interface and the consequences that an unbalanced transport of electrons and holes has on the photocurrent and device performance. A fundamental electrostatic limit for the photocurrent in the polymer:fullerene blends is discussed and experimentally proved.

The metal electrode dependence of the performance of polymer:fullerene solar cells is treated in Chapter 4. First, the open-circuit voltage of the solar cell is investigated by using metal electrodes with different work functions. A relation between open-circuit voltage and metal work function is established. Subsequently, the effect of metal work function on other solar cell parameters, such as
short-circuit current, fill factor, and maximum output power, is discussed.

In Chapter 5, the dependence of the performance of polymer:fullerene cells on their composition is addressed. The charge carrier mobilities of electrons and holes, as a function of fullerene fraction, is measured independently in the blend using the current-voltage technique. The obtained mobilities are used to study the photocurrent in these blends, as a function of their composition, and identify the parameters that limit the device performance at lower fullerene fractions where light absorption is more effective.

Finally, Chapter 6 describes the charge transport and photocurrent generation in composite films of regioregular poly(3-hexylthiophene) and PCBM molecules. The improved performance by applying a post production heat treatment to the devices is discussed in terms of charge carrier mobility, optical absorption spectroscopy, and photocurrent generation.

1.3 Abbreviations

For clarity, we have used abbreviations which are most common in the field. Table 1.1 summarizes the most common abbreviations used throughout this thesis.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AM1.5</td>
<td>Air mass 1.5</td>
</tr>
<tr>
<td>BEHBMB-PPV</td>
<td>Poly[(2,5-bis(2'-ethylhexyloxy))-co-(2,5-bis(2’-methylbutyloxy))-para-phenylenevinylene]</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>G</td>
<td>Generation rate of bound electron-hole pairs</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium-tin-oxide</td>
</tr>
<tr>
<td>J_D</td>
<td>Current density in the dark</td>
</tr>
<tr>
<td>J_L</td>
<td>Current density under illumination</td>
</tr>
<tr>
<td>J_ph</td>
<td>Net photocurrent</td>
</tr>
<tr>
<td>J_SC</td>
<td>Short-circuit current</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>Poly(2-methoxy-5-(3’,7’-dimethoxyctloxy)-para-phenylene vinylene)</td>
</tr>
<tr>
<td>P3HT</td>
<td>regioregular Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PCBM</td>
<td>Phenyl-C_{61}-butyric acid methyl ester</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Polyethylene dioxythiophene:polystyrenesulfonate</td>
</tr>
<tr>
<td>PPV</td>
<td>Poly(para-phenylene vinylene)</td>
</tr>
<tr>
<td>V_0</td>
<td>Compensation voltage</td>
</tr>
<tr>
<td>V_{BI}</td>
<td>Built-in voltage</td>
</tr>
<tr>
<td>V_{RS}</td>
<td>Voltage drop on series resistance</td>
</tr>
<tr>
<td>V_{OC}</td>
<td>Open-circuit voltage</td>
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Chapter 1: Introduction


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