Efficiency and Stability Studies for Organic Bulk Heterojunction Solar Cells

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EFFICIENCY AND STABILITY STUDIES FOR ORGANIC BULK HETEROJUNCTION SOLAR CELLS

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Abstract

The qualitative and quantitative characteristics of each component layer constituting the structure of organic bulk heterojunction solar cells (OSC-BHJ) contribute significantly towards its overall performance. One of the prevalent issues resulting in reduced device efficiency is due to the conformational inhomogeneities in the active and buffer layers. The mechanical stress, extended thermal exposure and presence of mutually reactive component layers etc., affects negatively on the device stability. Effective methods to address these issues will be extensively benefited by the industry since the current commercialisation of the technology is hindered owing to the lower efficiency and stability of these devices.

This dissertation focuses on methods to coherently enhance the performance and longevity of the OSC-BHJ devices. The efficiency enhancements of the devices in this work were achieved through two main routes. The first route was through morphological improvement of the active layer. The second route was through boosting the electrical characteristics of hole transporting conducting polymer layer (HTL) by controlled annealing conditions. The introduction of a suitable additive in the active layer was found to reduce unfavourable phase segregation thus resulting in enhanced morphology. Further, the annealing conditions in different atmospheres (air, nitrogen and vacuum) were found to have a clear influence on the optimum functioning of the HTL in the device. Regarding the stability improvement study done in this work, a method of employing suitable interlayer was developed to effectively abate the internal degradation occurring in the device due to etching reaction on the indium tin oxide (ITO) anode by the HTL. Moreover, experimental investigations were carried out for drawing fundamental understanding of stability degenerating issues such as the influence of mechanical defects on transparent conducting metal oxide (ITO) anode on the performance of the device and heat induced degradations in the low band gap polymer-fullerene active layer.

The highlight of this research is that the discovered methods are inexpensive, efficient, and easy to adopt. The results of the study could help the technology to overcome some of its limitations and accelerate its progress towards commercialisation.

Keywords: active layer, additive, annealing, cracks, excessive crystallisation, hole transporting layer, interlayer, power conversion efficiency, prolonged thermal exposure, transparent conducting metal oxide
Augustine, Bobins, Organisten heteroliitosaurinkokennojen hyötysuhte- ja stabilisuustutkimuksia.
Oulun yliopiston tutkijakoulu; Oulun yliopisto, Tieto- ja sähköteknikan tiedekunta
Oulun yliopisto, PL 8000, 90014 Oulun yliopisto

Tiivistelmä

Organisten heteroliitosaurinkokennojen kerrosrakenteen ominaisuudet ja laatu vaikuttavat merkittävästi aurinkokennojen toiminnallisuuteen. Erityisesti rake nteelliset epähomogeenisuudet aktiivi- ja puskurikerroksissa heikentävät kennon hyötysuhdet. Kennojen stabilisuutta tarkasteltaessa myös mekaanisella rasitukseella, pitkittyneellä lämpöaltistuksella ja materiaalien reagoimilla keskenään kerrosten välillä, on selkeä negatiivinen vaikutus kennojen stabilisuuteen. Orgaaninen aurinkokennoteknologian kaupallisamisen rajoitteina ovat kennojen heikko hyötysuhdet ja stabiilisuus, joten menetelmät jotka tarjoavat ratkaisuja edellä mainituin ongelmiin, ovat erittäin tärkeitä teknologiaa kaupallistavalle teollisuudelle.


Tutkimuksen keskeisin tulos on, että esitelty keinot aurinkokkennojen hyötysuhteen ja stabilisuuden parantamiseen ovat edullisia, tehokkaita ja helppoja hyödyntää. Tulokset voivat merkitävästi edistää organisten aurinkokkennojen teknistä kehitystä ja kiihdyttää niiden tuloa kaupallisiksi tuotteiksi.

Asiasanat: aktiivinen kerros, aukkoja kuljettava kerros, halkeama, hyötysuhdet, liiallinen kiteytyminen, lisäaine, lämpökäsittely, läpinäkyvä metallioksidijohdin, pitketetty lämpöaltistus, välikerros
Dedicated to my lovely parents, elder brother, niece and sister in law
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Oulu, January 2016
Bobins Augustine
# List of terms, symbols and abbreviations

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force microscopy</td>
</tr>
<tr>
<td>AM-1.5G</td>
<td>Air Mass 1.5 Global, reference solar spectrum</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AgOx</td>
<td>Silver Oxide</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CAE</td>
<td>Constant Analyser Energy</td>
</tr>
<tr>
<td>DCB</td>
<td>1,2-Dichlorobenzene</td>
</tr>
<tr>
<td>DIO</td>
<td>1,8-Diiodooctane</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron transport layer</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>e</td>
<td>Elementary charge</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transport layer</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ISOS</td>
<td>International Summit on Organic photovoltaic stability</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>In 3d</td>
<td>3d orbital of the indium atom</td>
</tr>
<tr>
<td>I₀</td>
<td>the intensity of light entering the sample at a particular wavelength</td>
</tr>
<tr>
<td>I</td>
<td>the intensity of light exiting the sample at a particular wavelength</td>
</tr>
<tr>
<td>J</td>
<td>Current density</td>
</tr>
<tr>
<td>J₀</td>
<td>Current density through diode</td>
</tr>
<tr>
<td>Jₚ₀</td>
<td>Reverse saturation current density through diode</td>
</tr>
<tr>
<td>Jₚₗ</td>
<td>Current density generated during illumination</td>
</tr>
<tr>
<td>Jₛₖₗ</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>Jₘₘₓ</td>
<td>Maximum current density</td>
</tr>
<tr>
<td>Kₐ</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>Kα</td>
<td>Emission line resulting from electron transition from innermost K shell (principal quantum number 1) to L shell (with principal quantum number 2)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>$V_{max}$</td>
<td>Maximum voltage</td>
</tr>
<tr>
<td>vol%</td>
<td>Percentage amount of additive present in total volume of the active layer blend</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>$\Omega/\square$</td>
<td>Ohm per square, Unit of sheet resistance</td>
</tr>
<tr>
<td>$\mu m$</td>
<td>Micrometre</td>
</tr>
<tr>
<td>$$/W$</td>
<td>Dollar/Watt</td>
</tr>
<tr>
<td>mm</td>
<td>Millimetre</td>
</tr>
<tr>
<td>mA/cm$^2$</td>
<td>Milliampere per square centimetre</td>
</tr>
<tr>
<td>mW/cm$^2$</td>
<td>Milliwatt per square centimetre</td>
</tr>
<tr>
<td>mg/ml</td>
<td>Milligram per millilitre</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Mean free path of electrons</td>
</tr>
<tr>
<td>mN/m</td>
<td>Millinewton per metre</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle Theta</td>
</tr>
<tr>
<td>$\gamma_{SV}$</td>
<td>Interfacial tension between the solid and the vapour</td>
</tr>
<tr>
<td>$\gamma_{SL}$</td>
<td>Interfacial tension between the solid and the liquid</td>
</tr>
<tr>
<td>$\gamma_{LV}$</td>
<td>Interfacial tension between the liquid and the vapour</td>
</tr>
</tbody>
</table>
List of original articles

The thesis is based on the following articles (I-V). Copyrights for publications are obtained from the respective journals.


Author's contributions

I The author defined the research plan, carried out the experiments, fabricated the devices and measured them. The AFM studies were done by Jarkko Puustinen. The author did the literature review, analysed the results and wrote the manuscript.

II The author defined the research plan and conducted the experiments. The XPS analysis of the PEDOT:PSS layers were done by Santtu Heinilehto. The author did the literature review, analysed the results and wrote the final manuscript.

III The author defined the research plan, fabricated the device and did the photovoltaic measurements. The contact angle measurement was done by Rafal Sliz. The XPS study of Indium diffusion was conducted by Kimmo Lahtonen and Mika Valden. The author did the literature review, analysed the results and wrote the final manuscript.

IV The author contributed in the article as the second author. The author’s independent contribution was in the fabrication and measurement of OSC
devices made on top of mechanically treated ITO PET substrate produced by the first author. Thus this thesis focuses only on the work which author of this thesis has contributed.

V The author defined the research plan, fabricated the OSC devices and conducted the experiment. The author did the literature survey, analysed the results obtained from the experiments and wrote the final manuscript.
# Contents

Abstract  
Tiivistelmä  
Acknowledgements  
List of terms, symbols and abbreviations  
List of original articles  
Contents  

## 1 Introduction  
1.1 Solar cell classifications  
1.2 Organic solar cells (OSC) and working principle  
1.3 Main junction types  
1.3.1 Planar heterojunction  
1.3.2 Bulk heterojunction (BHJ)  
1.4 Solar cell characteristics  
1.5 Life time  
1.6 OSC - current status, challenges and prospect  

## 2 Aim and structure of study  

## 3 Materials and methods  
3.1 OSC device fabrication and experimental methods for (I – V) articles  
3.2 Characterisation methods  
3.2.1 Optical microscopy (OM)  
3.2.2 Atomic force microscopy measurements (AFM)  
3.2.3 X-ray photoelectron spectroscopy measurements (XPS)  
3.2.4 Contact angle measurement  
3.2.5 Transmittance measurement  
3.2.6 Photovoltaic characteristics measurement  

## 4 Results  
4.1 Efficiency studies  
4.1.1 Performance of P3HT:PC_{60}BM devices  
4.1.2 Effect of annealing on P3HT:PC_{60}BM  
4.1.3 Effect of glycerol additive  
4.1.4 Controlling component ratio of conducting polymer blend by annealing  
4.2 Stability studies  

17
4.2.1 Effect of acidic nature of PEDOT:PSS on ITO anode and performance of OSC device ........................................................................ 57
4.2.2 Method to counter ITO degradation by PEDOT:PSS .............. 58
4.2.3 Effect of cracked ITO anode on the device performance ........ 60
4.2.4 Effect of prolonged thermal exposure over 1,8-diiodooctane (DIO) doped PTB7:PC70BM based organic solar cells.................................................. 61

5 Discussion 63
5.1 An inexpensive route for performance improvements ............... 63
5.2 Stability enhancement and experimental analysis .................... 65
5.3 Future outlook .............................................................................. 68

6 Summary 71
References 73
Original articles 85
1 Introduction

Early humans started to harness energy in the form of fire for their various needs such as light, heat, cooking and safety at least 1.9 million years ago [1]. The current world of the 21st century depends on fossil fuels on a large scale for meeting its various energy demands. Since electricity is a flexible and convenient form of energy in modern society, a portion of energy obtained from fossil fuels is also converted to it. The use of non-renewable sources of energy such as petroleum, coal and wood would emit considerable levels of pollutants into the atmosphere [2]. The greenhouse gas like CO₂ and many other industrial pollutants are causing global warming, environmental and ecological problems. The CO₂ concentration in the atmosphere has risen from 280 ppm since the industrial revolution and surpassed 400 ppm level in March 2015 [3]. It is expected that the levels will be further elevated and reach around 570 ppm at the culmination of this century [4]. Thus there is a huge demand for finding clean and renewable energy sources. The renewable energy sources include hydroelectricity, wind energy, biomass, geothermal and solar radiation. Among the renewable energy sources, solar energy is the most abundantly available form of energy on earth. It has been estimated [5] that the solar radiation received by the earth’s surface in 90 minutes is enough to feed the global energy requirement for an entire year, and this signifies the huge potential of solar energy. The use of photovoltaic devices or solar cells is the easiest way to convert solar radiation directly into electricity and that is why remarkable efforts have been invested in the development of photovoltaic technology during past decades. The field of photovoltaics is currently dominated by inorganic and silicon based solar cells owing to its appreciable efficiency and stability.

Although solar cells have significant potential in providing clean energy, the biggest challenge is that traditional solar cells are still not competitive enough with fossil fuel based energy technologies in terms of cost per power generated. Renewable energy sources such as wind and solar are currently more expensive than non-renewables because they need intensive capital and costlier storage grids. Photovoltaic technologies need improvements for achieving higher efficiency, low cost, larger scale production and better storage of energy produced to realise the technology as a real solution for the world’s clean energy demand. In a recent report [6], UK climate advisors estimate that wind and solar energy prices would likely match fossil fuel based energy in 2020, if carbon prices are imposed. Although the price of oil is now down due to uncertainty in the global economy, the costs of non-renewable sources of energy are expected to rise further in the future owing to its
limited reserves on the earth, thus making the clean technology like photovoltaics more competitive in terms of cost. If we consider the scenario in 1977, the price of energy production from crystalline silicon solar panels was around 76 US $/W, and the price has plummeted over the years and reached around 0.3 US $/W in 2015 [7]. The photovoltaic technology which can ensure cheaper, efficient and more mobile energy production has significant potential to impact positively on the commercial market as well as the environment.

1.1 Solar cell classifications

Nowadays, there are many solar cell technologies existing with different degrees of development. The first photovoltaic effect was observed by Alexandre-Edmond Becquerel in an electrolyte solution in the year 1839 [8], and the initial development of modern day solid-state solar cells was initiated by the research at Bell Labs in 1954 [9]. Present solar cell technologies can be classified as first, second and third generation cells.

The first generation of solar cells include the predominant silicon solar cells. These types of solar cells include monocrystalline and polycrystalline silicon solar cells [10]. These devices can deliver efficiencies of up to 20% and last more than 20 years. The technology is very mature because of its development during the past 50 years. However, the cost is relatively high, owing to the need for high purity silicon and rigid structures.

The Second generation solar cells are also called thin film solar cells, because these are made from layers of semiconductor materials, only a few micrometres thick. This class of solar cells includes copper indium gallium selenide (CIGS) [11-14], cadmium telluride (CdTe) [15-22], amorphous silicon [23-26] and gallium arsenide (GaAs) [27-31] based solar cells. Second generation solar cells have lower associated costs compared to first generation solar cells. However, some of the materials used in the second generation devices such as cadmium are toxic, and the technology predominantly depends on scarce elements causing some limitations. The devices are flexible to some degree, which is an advantage but production costs are still high due to the need for vacuum processing and very high temperature curing.

Third generation solar cells are referred to as emerging solar cell technology, since it does not yet have a realised, large scale commercial application. This includes quantum dots [32-35], dye sensitised solar cells (DSSC) [36], perovskite solar cells [37-47], organic solar cells (OSC) [48-62] and hybrid solar cells [63-74].
In third generation solar cells, higher efficiencies can also be achieved through multi-junction architecture, which is the stacking of thin layers of material with varying bandgaps on top of each other. It was reported recently that a multi-junction solar cell based on GaAs achieved efficiency beyond 44% [75]. The perovskite devices recently achieved efficiencies of around 21%, which is closer to silicon solar cells [76]. The flexibility, ease of transport, freedom in material design and fabrication makes OSC devices attractive to the electronic market [77-80]. This thesis focuses on issues relating to organic solar cells, specifically organic bulk heterojunction OSC devices.

1.2 Organic solar cells (OSC) and working principle

The term “organic solar cells” refers to the device in which an organic layer based on conjugated polymers or small molecules is an essential part of the photovoltaic process for generating electricity. The OSCs may also be referred as the organic photovoltaic devices (OPV) or polymer solar cells. The typical active layer of the OSC device consists of two components, one which donates electron (donor) and one which accepts electron (acceptor). These are then brought in to intimate contact to form a donor-acceptor heterostructure. In OSC devices, a combined electron-hole pair called an exciton which is bound by coulombic force is created in the donor material when the incident photons are absorbed by the active layer.

The energy state diagram of the heterojunction OSC device is depicted in Fig. 1(a). The basic charge generation and its transfer process during illumination in OSC are depicted in Fig. 1(b).
Fig. 1. a) Energy state diagram in heterojunction OSC; $W_A$ - work function of the anode, $W_C$ - work function of the cathode, $\Delta E_A$ - difference in electron affinity between donor and acceptor, $\Delta I_p$ - difference in ionization potential of donor and acceptor. b) Charge transfer process during illumination.

The electron affinity ($E_A$) and the ionization potential ($I_p$) are the most important factors while choosing the donor and acceptor materials. The ionization potential and electron affinity of the donor or acceptor can be approximated as their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level energy respectively. The ionization potential of the donor should be lower than that of the acceptor, because the donor is the species that most easily gives away an electron. Conversely, the electron affinity of the acceptor should be larger than the electron affinity of the donor. When the photons are incident on the photoactive layer, they are absorbed and a photovoltaic effect is built in a sequence of processes as in Fig.1 (b): (1) excitation of the donor upon absorption of light and formation of exciton, (2) Diffusion of the generated exciton to the donor/acceptor interface, (3) If the off-sets of the energy levels of the donor of the acceptor materials are higher than the exciton binding energy, photo generated excitons in the donor side will dissociate by transferring electrons to the LUMO levels of the acceptor, while those created at the donor side will transfer the holes to the HOMO of the donor, (4) The separated electrons and holes are collected at the cathode and anode electrodes respectively. These steps constitute the basic working principle of the device.
1.3 Main junction types

The donor and acceptor materials can be deposited as two distinct layers (planar heterojunction) or blended in a homogeneous mixture throughout an interpenetrating network known as bulk heterojunction (BHJ) which presents a larger interfacial area. With the aim of covering the solar spectrum more effectively, another useful approach consists of stacking multiple photoactive layers with complementary absorption spectra in series to reach a tandem device. This thesis focuses mainly on the conventional BHJ-OSC device architecture.

1.3.1 Planar heterojunction

The first reported organic solar cell was based on a single layer of poly(acetylene), which demonstrated very low device efficiency [81]. Later, the modern solid-state solar cell based on organic materials with bi-active layer was developed by C. W. Tang [82]. In his work, the device was made by stacking the donor and acceptor. This type structure is referred to as planar heterojunction or bi-layer. The device studied by Tang had (3,4,9,10)-perylenetetracarboxylic-bis-benzimidazole (PTCBI) as the donor material and copper phthalocyanine (CuPc) as the acceptor material. The structure is depicted in Fig. 2.

![Fig. 2. Planar Heterojunction.](image)

Later, fullerene was introduced as the acceptor, which further increased efficiencies [83, 84]. Although a thick layer of the organic photoactive materials may be providing for higher absorption, in the planar heterojunction, the excitons will be
recombined excessively because of the short exciton diffusion length. The exciton diffusion length is the average distance that an exciton travels before it recombines. Thus it restricts the thickness of the active layers and should be thin enough within the exciton diffusion length for efficient charge transfer.

1.3.2 Bulk heterojunction (BHJ)

The major limitation of the planar heterojunction OSC due to the short exciton diffusion length can be solved by blending donor and acceptor materials together and thus minimising the travelling distance to donor-acceptor interface. Since the heterojunction is dispersed in the bulk of the layer by blending donor and acceptor materials, it is called bulk heterojunction. Bulk heterojunctions solar cells (BHJ) may consist of a large variety of materials. Generally, the mixtures of conjugated donor polymer with a fullerene derivative have been used as the active layer [85-101]. The first bulk-heterojunction structure was demonstrated by Friend [102] and Heeger [103] almost simultaneously in 1995 and the devices were showing superior performance than earlier planar heterojunction architectures. The typical conventional bulk heterojunction OSC is depicted in Fig. 3.

![Conventional BHJ-OSC](image)

In the conventional structure, the bottom anode must be a transparent conducting electrode which is generally indium tin oxide (ITO). The substrate can be either glass, polyethylene terephthalate (PET) or even transparent paper based on cellulose fibers. Normally, ITO is coated with a hole transporting layer (HTL) layer of poly(3,4-thylenedioxythiophene)-poly(styrenesulfonate) for effective transfer of
holes to the anode. A low work function electrode like Aluminum is deposited as cathode. A thin layer of lithium fluoride (LiF) is used as intermediate layer between the active layer and cathode to improve device performance by functioning as an electron transport layer (ETL). The BHJ architecture is widely opted for in OSC devices, since the advantage of having larger interface between the donor and acceptor materials and hence enhancing the amount of exciton dissociation at the interface and the collection of charges at their respective electrodes. The exciton diffusion lengths of various conjugated polymers in OSC are around 10 nm. The non-radiative recombination occurring when the photo generated excitons are unable to reach the donor-acceptor interface will significantly reduce the device efficiency [104,105].

The performance of BHJ OSC devices significantly depends on the morphology of the active layer, since it facilitates efficient percolation pathways for the generated holes and electrons to be transported through the active layer to their respective electrodes. As a result of the intimate mixing, the interface increases enormously where the charge transfer can occur. The exciton, created after the absorption of light, has to diffuse towards this charge-transfer interface for charge generation to occur. For efficient charge generation after absorption of light, each exciton has to find a donor acceptor interface within a few nanometres, otherwise it will be lost without the charge generation. An intimate bicontinuous network of donor-acceptor materials in the nanometres range should suppress exciton loss prior to charge generation. Control of morphology is essential for not only the creation of large charge generating interfaces, but also in the creation of efficient percolation pathways for the transfer of electrons and holes. The holes travel to the higher work function electrode and the electrons travel to the lower work function electrode. Annealing can enhance the performance in some polymer-fullerene active layers with the improvement in crystallinity, phase segregation and donor-acceptor network etc., which also helps in the efficient transport of charge carriers [106]. The BHJ structure also facilitates the solution processing of the organic layers. This is helpful especially in large-scale, high-speed roll to roll manufacturing process. The solution processing of both acceptor and donor layers for a planar heterojunction is challenging because the deposition of the second layer should not dissolve and remove the first layers beneath. Utilisation of bulk heterojunctions device structure simplifies solution processing because only single layer of donor and acceptor blend is needed to deposit as the active layer. The main challenge would be the proper percolation pathway creation for the holes and electrons. The solution processability of OSC is a great advantage in industrial
point of view, as these devices can be fabricated by a number of high throughput printing methods [107-111]. Process condition optimisation of each layer in the OSC is very essential since it affects crucially to the final performance of the device.

1.4 Solar cell characteristics

The electrical characterisation such as the current density vs voltage (J-V) characteristics of the inorganic and organic solar cells under dark condition resembles exponential response of the diode in forward bias. The illumination of the device generates the current in the cell in addition to the diode behaviour. Therefore, the solar cell can be considered as a current generator in parallel with a diode, as shown in Fig. 4. The $J_{ph}$ is the current density generated during illumination.

![Solar cell equivalent circuit.](image)

The contributions from the series resistance ($R_S$) and shunt resistances ($R_{SH}$) in the devices are also taken in to account in the model. The current density through the diode is given by the Shockley equation (1),

$$J_D = J_0 \left[ \exp\left(\frac{eV_D}{n k_B T}\right) - 1 \right]$$  

(1)

Where $J_D$ is the current density through the diode, $V_D$ is the voltage across the diode, $J_0$ is the reverse saturation current density of the diode, $e$ is the elementary charge, $n$ is the ideality factor, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The output current density ($J$) from the solar cell under illumination as a function of the voltage applied ($V$) is described in equation (2),
The performance of the solar cell is analysed from the measured J-V characteristic curve. The Fig. 5 depicts the J-V plot for an idealised solar cell under illumination. The most important performance parameters that can be obtained from the J-V curve measured for the device under illumination are open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$), fill factor (FF), and power conversion efficiency (PCE).

$$J = J_0 \cdot \exp \left( \left( \frac{e(V-J R_S)}{n k_B T} \right) - 1 \right) + \frac{V-J R_S}{R_{SH}} - J_{Ph}$$  \hspace{1cm} (2)

The performance of the solar cell is analysed from the measured J-V characteristic curve. The Fig. 5 depicts the J-V plot for an idealised solar cell under illumination. The most important performance parameters that can be obtained from the J-V curve measured for the device under illumination are open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$), fill factor (FF), and power conversion efficiency (PCE).

![Fig. 5. Typical J-V curve of solar cell under illumination.](image)

The $V_{OC}$ is the voltage across the solar cell when $J = 0$ or when the device being open-circuited. The open-circuit voltage can be considered as the point at which the photocurrent generation and dark current process compensate each other. The short-circuit current density $J_{SC}$ is the current density when $V = 0$, or when the electrodes are short circuited. The $V_{OC}$ and $J_{SC}$ mark the boundaries of power production in a solar cell, the maximum power density $P_{max}$ occurs at the voltage $V_{max}$ and current density $J_{max}$ where the product of $J$ and $V$ is at the maximum. Due to the factors such as diode behaviour, additional resistance and recombination losses, the values of $J_{max}$ and $V_{max}$ in practice are always less than $J_{SC}$ and $V_{OC}$. The Fill Factor (FF) is the parameter that determines maximum power output from the device and is defined as in equation (3),
Graphically FF can also be described as the degree of squareness of the J-V curve.

The power conversion efficiency (PCE) is defined as the percentage of incident irradiance light power per unit area \((P_{in})\) that is converted to output power.

The PCE is represented as in equation (4),

\[
PCE = \frac{P_{max} \times V_{max}}{P_{in}} = \frac{(FF \times I_{sc} \times V_{oc})}{(P_{in})}
\]  

(4)

The PCE determines how effectively the active area of the solar cell is utilised in producing electricity. PCE is very dependent on the power and spectrum of the light source, since all the solar cells do not convert all the incident radiation which has different wavelengths.

Solar panels do not generally operate under exactly one atmosphere's thickness since the sun is at an angle to the Earth's surface and thus the solar irradiation is influenced by the varied effective thickness. An Air Mass (AM) number is representing the spectrum at mid-latitudes. AM 1.5 G corresponds to a solar zenith angle of \(z = 48.2^\circ\) and it is used as the standard spectrum which matches the spectrum of solar irradiation on earth’s surface.

The quantity that defines the quality of energy conversion in the device is called quantum efficiency (QE). It is basically the number of charge carriers collected at the electrode per number of incident photons on the area of the solar cell at a given wavelength. It can be defined in two ways, as external and internal quantum efficiencies.

The external quantum efficiency (EQE) is the fraction of incident photons converted into current by the device. It can be defined as the ratio of the number of electrons generated by the device to the incident number of photons at the given wavelength.

The internal quantum efficiency (IQE) is the ratio between the number of charge carriers collected and the number of all photons absorbed by the active layer at a given wavelength. It does not take into account the photons that transmit through or reflect from the cell or absorbed by other layers since it does not take part in the process of photo conversion.

1.5 Life time

The stability of OSC is an important factor which must be controlled to some extent in order to make OSC technology commercially successful. The quality of a device
or material to retain a major portion of its original state of performance over a prolonged time period is referred to as stability. Currently, the OSC stability is relatively low, lasting only few years whereas the inorganic silicon solar cells have a lifetime exceeding 20 years [112].

In order to improve lifetime, it is necessary to investigate the factors that are causing the degradation OSC devices. Life time tests carried out by various research groups [113-115] confirm the fact that the degradation in OSC does not take place as the result of a single cause. There might be many parallel degrading mechanisms taking place and the dominance of each degrading factor may differ according to the device structure, used materials and surrounding conditions. Among the component layers in OSC, some layers and layer interfaces are more prone to degradation than the other. In case of common OSC device structures, the interface between the PEDOT:PSS and ITO is problematic due to the acidic nature of PEDOT:PSS which etches the ITO anode. The PEDOT:PSS and active layers are sensitive to heat, light, oxygen and moisture. To understand the trend of decay in performance in OSC devices, the best way is to plot the variation of its photovoltaic parameters such as $V_{OC}$, FF, $J_{SC}$ and PCE with aging time. The crucial parameters in lifetime measurement are $J_{SC}$ and PCE, since it directly reflects the ability of the device to convert the incident light to the electricity. Degeneration of the devices occurs even in dark conditions, but it decays faster when the device is illuminated. The speed of degradation even varies with the intensity of the light. It is clear that the lifetime of OSC can be improved with suitable shielding. For instance, the LiF layer in OSC structure acts as such a shielding layer preventing the diffusion of cathode electrode into the polymer layer [116].

The main degradation of OSCs can be divided into intrinsic as well as extrinsic degradations. The intrinsic factors include the degradation occurring inside the device such as the degradation of the active layer, instability between component layers etc. The donor polymer and the acceptor material present inside the active layer can also degrade upon prolonged illumination [113,115,117-120]. The extrinsic factors include instances such as the degradation of the metal cathode, due to delamination, oxygen and moisture ingress. The electrode–organic interface is the spot where the major degradation dominantly occur [121].

In simple lifetime measurement, the parameters $J_{SC}$, $V_{OC}$, FF and PCE are measured as the function of time. The $J_{SC}$ is the crucial factor that gets degrades over the period of time and its rate of degradation depends on the type of solar cell. The $V_{OC}$ also degrades with time, but it is slower in most cases. The FF is also a measure of the internal losses influencing on the charges generated in the active
layer. The sensitivity to degradation may vary according to the active material and the structure of the device. The typical reasons for degradations in OSC devices are due to mechanical stress, temperature, oxygen, moisture and UV radiation. The performance variation of the OSC devices varies according to the testing conditions. In order to make traceable lifetime testing, ISOS standards have been published since 2008 [121]. The standards are defined for basic, intermediate and advanced levels. The specifications also include if the devices are encapsulated, measured outdoor or indoor and surrounding conditions. The standards for stability studies are defined as ISOS D, ISOS L and ISOS T. ISOS D corresponds to the shelf life time study in the ambient conditions. ISOS L corresponds to the life time testing under laboratory weathering. ISOS T corresponds to the thermal cycling testing for life time. In the advanced level of thermal cycling test, the samples are stored in a thermal chamber and cycles of temperature ranging from – 40 °C to +85 °C are applied whereas for lower levels of ISOS T, the range is between room temperature and 65/85 °C. Those laboratories which are not able to fulfil these standards are recommended to report the measuring conditions together with the life time data. The ISOS protocols can be adopted for evaluating the effect of air, moisture, light and temperature on OSC device performance.

The typically observed decay pattern for OSC is a “burn in” period characterised by an exponential loss in efficiency followed by a linear decay period. The decay pattern followed by most of the OSC devices as mentioned by ISOS [121] is depicted in Fig. 6.
Fig. 6. Typical decay curve of OSC device.

The parameters in Fig. 6 correspond as follows,

- $E_0$: Initial PCE, $T_0$: Time when $t = 0$,
- $E_{80}$: PCE after $E_0$ has decayed by 20%,
- $T_{80}$: Time when the PCE has decayed 20% of $E_0$,
- $E_S$: PCE at the point when there is change in the slope of the curve,
- $T_S$: Time at $E_S$,
- $E_{S80}$: PCE after $E_S$ has decayed 20%, $T_{S80}$: Time at $E_{S80}$

In the case of extensive analysis of the decay mechanism, ISOS recommends measuring these above mentioned parameters. However, there is no straightforward method for choosing $T_S$ and $E_S$ points and thus often marked arbitrarily. It can be difficult in some cases to identify these points since the decay curve can vary depending on the type of measurement and the type of degradation under study. The device undergoing complete degradation will give significant information regarding the behaviour of the materials as well as the stability.
An overview of the degradation pattern can be analysed by allowing the device to age in the specific condition over a considerable span of time and comparing the trend of change in the photovoltaic parameters over the course till the final measurement. The internal degradation can occur simultaneously inside the device in parallel with other degradations occurring due to the influence of light, temperature, air and moisture etc., [113, 114]. By excluding some of the agents of degradation, certain other degradation factors can be specifically studied.

The internal degradation process like chemical reaction between the ITO and PEDOT:PSS starts already during the so called ‘burn in period’, so in our study the initial PCE to the final PCE value over the appreciable amount of time was important. The ITO is sensitive to acidic materials, releasing indium atoms causing its diffusion in to subsequent layers [122]. The most widely used hole transporting layer PEDOT:PSS has hygroscopic and acidic nature [123] and thus it can etch the bottom ITO anode. Thus analysing the degradation pattern over a broad time period accounting the initial and final device values helps to explain better the stability state of the device.

There are still quite few stability studies conducted in the field of OSC when compared with efficiency enhancement research carried out in the same technology. Thus more research efforts on enhancing the device stability are needed to make the OSC technology more competitive among other renewable technologies.

### 1.6 OSC - current status, challenges and prospect

OSC was hailed since a decade owing to its various merits [124]. The OSC technology has a major strength due to the fact that the photoactive materials of the device can be synthesised and tailored in number of ways to match the performance needs. The organic photovoltaic devices have also the advantage of having wide range of colours which is increasing its aesthetic values in products. OSC devices can be made even semi-transparent or even close to fully transparent. The time line of progress in OSC technology among various PV technologies according to NREL is depicted in Fig. 7.
The highest reported efficiency by NREL for OSC devices recently was 11.5%, achieved by researchers in Hong Kong UST [126]. Although not confirmed by NREL, the Heliatek reported 12% efficiency for OSC devices couple of years ago. Thus the state of art OSC devices has the capability to deliver efficiencies in the range of 10 to 12%. The successful preliminary stage implementations of OSC devices are achieved by leading PV companies like BELECTRIC, Nano Flex and Heliatek. However, the price of silicon and other thin film based photovoltaics had plummeted currently which makes them more competitive with OSC technology. Although such situations arise at the moment, the OSC devices still has a place in the market and a role to play in building integrated photovoltaics and flexible electronics. The OSC technology is currently facing some major challenges for its large-scale adoption and these issues are discussed as below.
1. **Manufacturing costs:** The major cost contributor in traditional OSC is the use of ITO and its patterning on the substrate. The maximum percentage price contribution for this can account to almost 51.2% of total material cost for the OSC module, having an area of 1 m² [127]. The economical alternative for ITO can cause significant reduction in the manufacturing cost. Fullerene based acceptor materials are widely used till date despite their relatively high costs. An inexpensive alternative for fullerene would greatly reduce the overall cost of the photovoltaic devices as well. The primary advantage of OSC technology over inorganic counterparts is its ability to facilitate high throughput production techniques which helps in cost reduction. The substrate and electrode reuse can also account to cost reduction. The other cost is related to the expense regarding the encapsulation of the OSC devices. In some cases, there might be better encapsulation which is expensive, but the incorporation of such barrier layers would raise production costs. Thus, techniques are necessary to develop inexpensive and effective protective barriers for organic PV technology.

2. **Initial PCE/ Efficiency:** The current efficiency ranges are not competitive in the commercial market. The OSC devices that are manufactured in high throughput techniques still holds lower performances. The efficiency of these devices can be increased to a certain extent by sandwiching active layers of complementary absorption ranges in the device forming a tandem device. The morphology of the active layer is a critical factor to be optimised for enhancing the BHJ device performance [128-132]. For instance, large domains in the phase-separated structure will prevent efficient charge separation, whereas small domains will result in a poorly percolated domain structure and thereby increase the possibility of charge carrier recombination [132]. Recently, the Israeli research group led by Prof. Nir Tessler reported [133] that they have developed a patented technique for improving the efficiency of converting solar energy into electric current inside the cell from 10% to 15%, and adding 0.2 volts to the cell's voltage. The development is based on increasing the energy gap between the electrodes by changing their fixed position in the system. By doing so, the researchers were able to increase the voltage, leading to an increase in system power. There are also some design rules for active layer identified in view of enhancing the efficiency. It was understood based on previous research [134] that the gap between HOMO of the electron donating polymer and the LUMO of the electron acceptor should be maximised.
in order to increase the $V_{OC}$, at the same time the band gap of the polymer should be minimised to increase photon absorption and thus short circuit current. The LUMO of the donor polymer should be positioned above the LUMO of the acceptor fullerene derivative at least 0.2 to 0.3 eV, to ensure efficient electron transfer [134].

3. **Life time/ stability:** The organic materials used in the devices are prone to degradation from moisture, air, light and heat, and degradation from the organic and metallic layer interfaces inside the device. Polymer materials have dynamic character, and are prone to degrade by a range of factors. When the organic active layer is illuminated, the materials react through photolytic and photochemical processes [135-138]. The materials are also not heat stable and can suffer from heat and solar radiation-induced morphology changes or interfacial degradation over their lifetime. The bulk heterojunction with a specific morphology of interconnected domains do not necessarily represent the most thermodynamically stable configuration and the alteration in optimal morphology under prolonged thermal exposure has been observed [139-142]. Polymer solar cells can also sustain damage to the top electrode, often made from a low work-function metal that is reactive and easily oxidised in ambient air [143, 144]. The device operation could be prolonged to few years with suitable encapsulation [145]. Other predominant degradation happens at the organic- metallic interface of the devices and the electrodes. The presence of hot spots and considerable increase in overall temperature of the device under prolonged illumination is a common problem in solar cells. OSC devices are sensitive towards the temperature changes due to the fact that organic materials can degrade and even change morphology under prolonged thermal exposure and illumination. Energy of UV photons is in the order of bonding energies of some organic materials present in the active layer of OSC devices and result in accelerated degradation [138]. Thus, it is necessary to have modified encapsulation techniques which provide protection in addition to oxygen and moisture, also from thermal exposure and unfavourable wavelengths that account to photodegradation.

**Prospects of OSC technology:** The OSC devices hold currently a small portion in the market and its applications are predominantly in mobile/disposable electronics. Unless the OSC technology surpasses the previously mentioned challenges, the
introduction of the devices to the commercial market would be prolonged. The photovoltaic technologies in general are becoming cheaper and their efficiencies are getting higher. Most probably, the difference between the solar cell technologies will be decreased in terms of cost per power generated. In such cases, the next edge on which different PV technologies will compete would be based on factors such as stability, low weight, form factors, aesthetic appeal, transparency, recyclability and eco-friendliness. OSC devices already have the advantage of aesthetic appeal, form factors, transparency and low weight per device etc. If the OSC technology evolves by intensive research in coming years to highly efficient and stable devices, it has the great potential of ruling the flexible and portable electronics market. Significant improvements in the efficiency can be achieved in future by forming hybrid with inorganic structures such as perovskites. That may provide key advantages to these devices like cost efficiency, material abundance, ease of preparation, near perfect crystallinity at low temperatures and large carrier diffusion length. According to Swanson’s law [146], the price of solar cells will drop 20% for every doubling of the industrial capacity. But the interesting aspect is that the Swanson’s law is applicable to all kinds of PV technology exist today. Thus the large industrial scale ups for various PV technologies can be expected in the future. The price reduction is the prime motive for major share of various PV technologies. The OSC technology although was very promising in the initial years of the launch, the large scale market realisation as product has not yet realised owing to the fact that many of the initial challenges are not yet tackled. At last, the race in various PV technologies is about harnessing solar energy in the most efficient, cheap and eco-friendly way.
2 Aim and structure of study

The aim of this doctoral thesis was to develop methods to analyse and reduce various problems affecting the efficiency as well as the stability of the OSC devices. The studies can be divided into two main categories: Efficiency studies and Stability studies. The work conducted in articles I & II comprises the efficiency studies. Methods to enhance efficiency of the polymer-fullerene BHJ-OSC devices were developed with the emphasis on the OSC active layer morphology enhancement with an additive and optimising the component ratio in PEDOT:PSS hole transporting layer (HTL). The articles III-V comprise the stability studies addressing various internal and external degradation issues such as instability at the ITO/PEDOT:PSS interface, the effect on OSC performance due to ITO breakage during bending and the effect of prolonged thermal exposure on the active layer of low band gap polymer-fullerene based OSC device. In these studies, solutions are developed for the interface instability problems and the extents and influence of these degradation phenomena are analysed. The structure of the study is depicted in Fig. 8.

![Diagram of study structure](image_url)

Fig. 8. Structure of the study.
3 Materials and methods

This section describes the materials and methods used to fabricate and characterise the OSC devices during the studies. The materials and fabrication parameters used in the articles within the scope of this thesis are depicted in the following Table 1.

Table 1. Materials used in the work.

<table>
<thead>
<tr>
<th>Articles</th>
<th>Substrates</th>
<th>Dimension / Specifications</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>I,II,III,V</td>
<td>Glass with patterned ITO</td>
<td>6.25cm² square glass substrate with 1.3 cm wide ITO stripe in the middle, 20 Ω/□ sheet resistance, ITO thickness -150 nm</td>
<td>Thin Film Devices Inc.</td>
</tr>
<tr>
<td>IV</td>
<td>PET with patterned ITO</td>
<td>Dimension of substrate for OSC device was same as above, Nominal resistance were 40-60 Ω/□, ITO thickness -125 nm</td>
<td>Dupont</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Articles</th>
<th>HTL (PEDOT:PSS)</th>
<th>Spin coating parameter</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>PH500</td>
<td>6700 RPM / 1 minute</td>
<td>H.C STARCK</td>
</tr>
<tr>
<td>II,V</td>
<td>PH500</td>
<td>6700 RPM / 1 minute</td>
<td>Heraeus</td>
</tr>
<tr>
<td>III,IV</td>
<td>PVP AI4083 PEDOT-PSS</td>
<td>(III) 5200 RPM/1minute &amp; (IV) 6200 RPM/1minute</td>
<td>H.C STARCK</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Articles</th>
<th>Donor</th>
<th>Acceptor</th>
<th>solvent</th>
<th>Active layer blend ratio</th>
<th>Annealing Temp.(ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I,II</td>
<td>P3HT</td>
<td>PC60BM</td>
<td>DCB</td>
<td>1:0.8 (30 mg/ml)</td>
<td>150 ºC / 30 minute</td>
</tr>
<tr>
<td>III,IV</td>
<td>P3HT</td>
<td>PC70BM</td>
<td>DCB</td>
<td>1:0.8 (30 mg/ml)</td>
<td>(III) 160 ºC/ 30 minute &amp; (IV) 150 ºC/ 15 minute</td>
</tr>
<tr>
<td>V</td>
<td>PTB7</td>
<td>PC70BM</td>
<td>DCB + 3 vol% DIO</td>
<td>1:1.5 (25 mg/ml)</td>
<td>no annealing</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Articles</th>
<th>Donor Producer</th>
<th>Acceptor Producer</th>
<th>Cathode for devices in (I-V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-IV</td>
<td>Sigma-Aldrich</td>
<td>Nano C</td>
<td>LiF and Al</td>
</tr>
<tr>
<td>V</td>
<td>1-Material Inc.</td>
<td>Nano C</td>
<td></td>
</tr>
</tbody>
</table>

3.1 OSC device fabrication and experimental methods for (I – V) articles

The fabrication of organic solar cell consists of sequential deposition process. The basic structure of the conventional bulk heterojunction organic solar cell is illustrated in Fig. 3 and this structure was employed for the OSC devices in this work. It consists of a transparent anode which is usually a glass substrate coated with ITO. Since each organic layer in the device is deposited by spin coating, it
necessary that the surface of the substrate is devoid of any contaminants. To ensure this, the substrates are first cleaned by washing with acetone, isopropyl alcohol (IPA) and methanol respectively. Then it is plasma treated for one to five minutes inside a Plasma PREEN II-862 asher, which helps in enhancing the surface energy of the substrate so that the hole transporting layer has superior wettability over the surface. Then a hole transporting layer (HTL), usually PEDOT:PSS is used. After the deposition of the HTL, it is then subjected to 1 hour annealing (at 120 °C inside the vacuum for articles I-III & V and at 110 °C in article IV), to ensure the removal of the moisture content. The active layer blends in article I-IV were stirred at 55 °C and at 70 °C for article V. Then the active layer material which was stirred overnight is deposited by spin coating. Subsequently, it is dried at room temperature for 1 hour inside the glovebox and then annealed at optimum temperature. Finally, the electrodes are deposited. A 0.6 nm thick LiF and 120 nm thick aluminum respectively are deposited on the sample as cathode by thermal evaporation technique. The materials are used inside the nitrogen filled glovebox which ensured inert atmosphere. The photovoltaic polymers used are very sensitive to moisture and oxygen. Thus every processing was handled inside the glovebox, except for the spin coating of the HTL.

In the article I, the experiment performed was to identify the inhomogeneities in the morphology of the active layer based on the P3HT:PC60BM blend during the annealing process. The active layer was spin coated at 450 RPM for 2 minutes. As a method to reduce the non-uniformity in the morphology, the effect of glycerol addition in varying concentration to the active layer is analysed.

In article II, the effect hole transporting layer PH500 annealed in different atmospheres was studied. The cleaned and plasma treated substrate was spin coated with PH500 in three batches. Then it is annealed in air, nitrogen and vacuum for 1 hour. The temperature ranged from 70 °C to 270 °C with 50 °C interval variation for each annealing step. After the annealing the active layer of P3HT:PC60BM was spin coated at 450 RPM as before annealed at 150 °C for 30 minutes.

In article III, the study was focused on understanding the degradation caused by the chemical reactions between the hole transporting layer and the ITO anode layer of the device and also develop solutions to reduce such degradation. The hole transport layer (HTL) used in the device was PVP AI4083 PEDOT:PSS, which is poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate). The active layer was spin coated at 450 RPM for 2 minutes. After drying the sample inside the glove box for 1 hour in room temperature, it was annealed at 160 °C for 30 minutes. For studying the effect of the presence of the plasma treated Ag interlayer on reducing
chemical instability caused by PEDOT:PSS on ITO, a different set of devices were made in which the Ag layers were deposited by thermal evaporation on top of ITO patterned substrates before the deposition of PEDOT:PSS. The two thicknesses that tried for Ag interlayers in OSC in the study were 1 nm and 5 nm. After the Ag layer deposition, plasma treatment was done for 5 minutes to enhance the wettability of subsequent deposition of PEDOT:PSS. By conducting contact angle measurement, it was found that the plasma treatment of the sample with thin Ag layer increased its surface energy significantly from 36.6 mN/m to 75.2 mN/m.

The article IV was a collaborative work. The contribution of the author was the experiment conducted to understand the effect of the bending of ITO substrate on the performance of the OSC of smaller area. This thesis focuses only on the author’s independent contribution. The substrates were made from PET-ITO sheets. The brittle nature of ITO and the bending stress motivates the substrate to undergo certain defects such as cracks. The analysis of ITO surface defects on OSC device performance was carried out by fabricating OSC device on top of the cracked ITO by bending stress. The bending procedures were carried out by placing the substrate strip on the surface of cylinder 10 mm in diameter and hanging a weight of 1 kg. The diameter of the cylinder was chosen as mentioned to ensure definite cracking of the PET ITO substrate. The samples were initially UV treated for 1 minute to enhance the wetting properties. Later the successive component organic layers and electrodes are deposited over it.

In article V, the motivation of the experiment was to understand the effect of varying ranges of thermal exposure on the performance of the low band gap polymer: fullerene active layer blend. The blend of PTB7:PC70BM with a 3 vol% of 1,8 diiodooctane (DIO) additive, was utilised as the active layer. It was reported that the presence of additives like DIO in the active layer enhances the initial device efficiency [147]. Firstly the optimised spin coating speed of active layer is determined by analysing the parameter providing highest PCE value for the device. The active layer was spin coated at the optimised spin speed of 700 RPM. To understand specifically the thermal degradation happening to the active layer, the thermal exposure was done solely to the active layer coated substrates before the deposition of the electrode. The varying temperature profile was selected for pre-annealing to mimic the outdoor exposure of such solar cells in intense thermal conditions. The temperature was varied starting from room temperature by increasing 20 °C every 3 hours till it reached 107 °C and then decreased by the same amount for every other 3 hours under dark condition till it reached the initial temperature of the experiment.
In our specific degradation studies in Article III and Article V, we have studied unencapsulated devices inside the inert glovebox which eliminated the influence of moisture and air. In article III, the initial and final efficiencies were very important, since it makes possible the complete analysis of the performance changes due to the presence of the interlayers. The unencapsulated OSC device when exposed to light and air, there can be various degrading phenomena occurring at the same time such as oxygen and moisture ingress, reaction of oxygen and water with electrodes and active layer. To study specifically certain degrading factors, the procedure adopted was to isolate the circumstances causing the degradation other than the interested phenomena. However, the ISOS related standards were not strictly followed in our experiments. Analysing the degradation pattern over a broad time period accounting the initial and final PCE values help in understanding better the stability state of the device. Shelf lifetime provides significant information regarding the inherent capability of the organic materials to retain its initial efficiency over a period of time. The shelf life time measurements are conducted inside an inert atmosphere like the nitrogen filled glovebox. The devices are stored in the dark and photovoltaic performance was monitored at specific intervals of time by illuminating the device with solar simulator.

### 3.2 Characterisation methods

This section mentions all the characterisation techniques employed in this work for understanding topographical and photovoltaics properties of the samples and devices. Although these surface characterisation methods are well known and commonly used in this type of research, the principles behind some of these are explained briefly.

#### 3.2.1 Optical microscopy (OM)

The excessive crystallisation of the acceptor components in the active layer of the OSC devices in the experiments of article I were identified using a Nikon universal design optical microscope (UDM) ECLIPSE LV 100DA-U. For this measurement, the samples with Pristine PC$_{61}$BM and PC$_{61}$BM with glycerol additive, pristine P3HT, P3HT with glycerol additive were initially analysed for annealed and not annealed samples. The glycerol additive concentration used was 30 vol% and annealing conditions applied in the investigation were the same as during the fabrication process. The split analysis was also conducted where a section of the
sample was coated with pristine PC₆₀BM and another section coated with PC₆₀BM with glycerol additive to understand clearly the distinction in phase segregation due to the excessive crystallisation of the fullerenes. The effect in real active layer blend of P3HT:PC₆₀BM with and without the glycerol additive on the ITO\PH500\active layer structure is analysed finally with annealed and unannealed conditions.

3.2.2 Atomic force microscopy measurements (AFM)

The changes in surface roughness due to the presence of additive in active layer of OSC devices in the experiments of article I were studied using the AFM measurement technique. The AFM employed in our experiment was AFM Veeco Dimension 3100. The projected image area was 25µm². The device set up utilised in the work is depicted in Fig. 9.

**Fig. 9. AFM Veeco Dimension 3100 tapping mode set up.**

In AFM measurement system, the information regarding the surface of the sample is obtained by scanning a small probe across the sample. The AFM can be used as a tool to understand the physical topography as well as material properties of the sample such as its magnetic properties, stiffness, surface chemistry etc., [148-151]. The three dimensional images of solid surfaces including non-conducting samples such as polymers and ceramics could be generated by AFM at a very high resolution. However, in case of topographical investigation on soft samples such as polymers,
the lateral forces exerted by the tip of the probe can lead to image artefacts due to rupture of the surface. The tapping mode is typically used to solve this problem. In tapping mode, a cantilever oscillating at or near its resonant frequency with high amplitude is employed. The oscillating tip is then scanned at a height where it barely touches or taps the sample surface. Thus, the shear forces under which the tip and the sample interact are greatly reduced by this method. The vibration is set such that the tip contacts the sample surface once in every vibration period. Because of the tip-induced damage, the AFM measurement, the studies done on the sample surfaces in this work were therefore taken in the tapping mode.

3.2.3 X-ray photoelectron spectroscopy measurements (XPS)

The information regarding the composition and the chemical state of the material surfaces could be obtained using the analysis technique called X-ray Photoelectron Spectroscopy (XPS) \[152,153\] and was utilised for articles II & III. The XPS is also known as Electron Spectroscopy for chemical Analysis (ESCA). In this measurement system, the specimens are placed in an ultra-high vacuum (UHV) to prevent contamination of the surfaces and then exposed to x-ray source. The ejection of core-level electrons from the sample atoms occurs when x-rays are incident. The emitted electrons, which have mean free path lengths of the order of 1 nm, are detected over the energy range 0 to 1000 eV. The mean free path \( \gamma \) is determined by the thickness of matter through which 63% of the traversing electrons will lose energy. As a consequence of this energy loss, only electrons out of the first ten nanometers may leave the surface and be detected as photoelectrons. By knowing the binding energy of a particular shell of an atom, the element can be identified. The photoelectron peaks are associated with a particular core level of an element. All elements, except hydrogen and helium can be detected. The concentrations of the elements are determined by integrating the area under a characteristic peak for each element taking sensitivity factors into account.

In article II, component variation of PEDOT and PSS in the hole transporting layer PH500 under different annealing condition was analysed by using X-ray photoelectron spectroscopy (XPS). The XPS experiments were performed by the system Thermo Fisher Scientific ESCALAB- 250Xi. Avantage software was used for the analysis of the data and background subtraction. Monochromatic Al Ka X-rays (1486.68 eV) were utilised for excitation and detection area was set to 900 \( \mu \)m in diameter. The detector mode was in Constant Analyser Energy (CAE). Survey scan pass energy was 150 eV with step size 1 eV. The chemical states of compounds
were identified and quantified by analysing the photoelectron transitions of S 2p. In article III, the XPS technique was utilised for analysing the indium diffusion and etching issue in the OSC device. The XPS experiments were performed in a UHV system equipped with VG Microtech Multilab ESCA 3000 electron spectrometer. Non-monochromatised Mg Kα X-rays (1253.6 eV) were utilised for the excitation, and the detection area was set to 600 µm in diameter. The chemical states of compounds were identified and relative atomic concentrations of indium were quantified by analysing the photoelectron transition of In 3d.

### 3.2.4 Contact angle measurement

The changes in the wettability due to plasma treatment of the thin Ag coated ITO layer (article III) were identified with the contact angle measurement. Contact angle measurement is a surface analytical method for investigating the wetting and surface energy properties. The surface energy of a solid material can be understood from the known surface tension values of the probing liquids and the contact angle θ, made by them with the surface of the solid material. The contact angle can be measured by the angle between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid substrate, at any point along their line of contact. The contact angle formed between a liquid and a solid in equilibrium with vapour phase, and the surface energy difference between these were determined by Young [154]. The inferences made by Young are graphically depicted in Fig. 10 and its simplified mathematical form is represented in equation (5).

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cdot \cos \theta \]  

(5)

![Fig. 10. Force balance according to Young.](image-url)
Where $\theta$ is the contact angle, $\gamma_{SV}$ is the interfacial tension between the solid and the vapour, $\gamma_{SL}$ is the interfacial tension between the solid and the liquid and $\gamma_{LV}$ is the interfacial tension between the liquid and the vapour. The Owens-Wendt-Rabel-Kaelble [155] method is used to calculate the surface energy. In this method, the surface energy of a solid consists of two components, a dispersive and a polar component. In our experiment, the static sessile drop contact angle measurement method was applied by using Kruss DSA100 system to measure the surface energy. In order to calculate the surface energy, two fluids such as deionised water and ethylene glycol were used. For each fluid, five contact angle measurements were performed and the results were averaged. Importantly, the measurement was done separately for plasma – treated and untreated samples.

### 3.2.5 Transmittance measurement

The normal transmittance measurement of the samples in article III were done to understand the effectivity of photons to pass through the substrate with the presence of additional interlayer. The samples undergone the specified measurement were the ITO coated glass substrate and the substrate modified with plasma treated Ag layers (1 nm and 5 nm thick layers). For the normal transmittance measurement, the spectrophotometer system (Optoelectronics Laboratory, USA) in the range 300 nm – 900 nm was unutilised. The samples were placed in the line of the illumination from the spectrophotometer and the automated system detected the percentage transmittance for each sample in the specified wavelength range. The transmittance is defined mathematically in equation (6).

$$\text{Transmittance} = \frac{I_0}{I_t} \quad (6)$$

The transmittance is the ratio of the intensity of light entering the sample ($I_0$) to that exiting sample ($I_t$) at a particular wavelength.

### 3.2.6 Photovoltaic characteristics measurement

The photovoltaic measurement for all the devices fabricated in the experiments were evaluated under AM 1.5G, class AAA solar simulator (Oriel Inc.), as the light source. A solar simulator (also artificial sun) is a device that provides illumination approximating natural sunlight. An ideal spectral match for a solar simulator is based on the percentage of the integrated light intensity in the six spectral ranges.
having 100 nm interval ranges from 400 nm to 1100 nm. The class AAA solar simulator meets the class A requirement for all the three performance criteria such as spectral performance, uniformity of irradiance and temporal stability. The purpose of the solar simulator is to provide a controllable indoor test facility under laboratory conditions, used for the testing of solar cells, sun screen, plastics, and other materials and devices. The light intensity was calibrated to be 100 mW/cm² by using NREL calibrated crystalline silicon reference cell. The parameters such as $V_{OC}$, $J_{SC}$, FF and PCE are measured from corresponding J-V curve obtained from the device under illumination. The information of the photovoltaic characteristics of the device is derived by Botest LIV organic electronics tester system connected to it.

Each and every solar cells fabricated during individual experiments in the study had an active cell area of 15 mm². For each experiment, the average performances were measured for at least 15 cells (5 individual cells per 3 solar cell modules). The O₂ and H₂O levels were normally 0.1 ppm each inside the nitrogen filled glovebox. For our stability studies, the unencapsulated devices were stored inside the glovebox in dark condition. The photovoltaic measurements were carried out under the solar simulator at specific intervals inside the glove box, thus reducing the parallel degrading mechanisms such as influence of oxygen and moisture.
4 Results

The results are divided into two major sections. The first section describes about the efficiency studies of bulk heterojunction solar cells. Various factors affecting the efficiency of the device are analysed in this section and methods are implemented to enhance the efficiency of the devices. The second section deals with the stability studies of the device. Some of the internal and external degradation factors causing reduction in stability of the device are investigated and techniques are developed to reduce those degrading factors.

4.1 Efficiency studies

The efficiency enhancement studies were carried out for the P3HT:PC$_{60}$BM bulk heterojunction solar cell. The component layers such as active layer and the hole transporting layer contribute significantly towards the performance of the device. The irregularities in these layers can influence the final device efficiency to a greater extent. In this section, some of such issues responsible for the lower efficiency of the device were identified and suitable methods to enhance the performance of these devices have been found out.

4.1.1 Performance of P3HT:PC$_{60}$BM devices

In bulk heterojunction solar cells based on P3HT:PC$_{60}$BM active layers, the annealing process helps to facilitate better interlinking of the donor and acceptor materials in the active layer. The P3HT acts as the donor and PC$_{60}$BM acts as the acceptor material respectively in the layer. During the annealing process, the extent of donor material crystallisation may affect the morphology crucially since it is necessary to have nanoscale bicontinuous network between acceptor and donor materials to have excellent route for charge transfer [156]. It is known that some of the unfavourable mechanisms taking place during the processing of active layer can reduce the efficiency of the device [157]. The good morphology of the active layer will result in higher efficiency for the device. The annealing of the active layer is essential for controlling the morphology, but since some unfavourable phase segregation can easily arise due to excessive crystallisation, the better understanding of the phenomena is needed.
4.1.2 Effect of annealing on P3HT:PC60BM

The optical microscope images in Fig. 11 reveals the excessive crystallisation of PC60BM components present inside the active layer after annealing. The excessive crystallisation issue was investigated using the optical microscope since the micrometer scale crystals are formed during annealing.

![Image of optical microscope images](image)

Fig. 11. (a) ITO/IP500/P3HT:PC60BM (pristine) unannealed (b) ITO/IP500/P3HT:PC60BM (pristine) after annealing, scale 100 µm. (Article I, published with the permission of © Hindawi Publishing Corporation 2015).

The morphology changed crucially with excessive crystallisation of the acceptor material. This happens due to the fact that the solvent present inside the layer evaporates suddenly with the thermal exposure leaving the components to crystallise under annealing. This type of morphology change causes unfavourable condition for the ease of charge transfer. The optimal condition is to have the morphology to be in nanoscale bi continuous network [156].

4.1.3 Effect of glycerol additive

The problem of fast evaporation of solvents from the layer can be reduced by adding some amount of additive solvents with higher boiling point. Thus a very inexpensive and common material, glycerol was added to the blend to investigate, if it can help to reduce the excessive crystallisation problem. The glycerol concentrations from 0 to 70 vol% have been investigated. Fig. 12 shows the PCE
variation of the device with active layer having glycerol doping in various concentrations.

![Graph](image)

**Fig. 12. Variation of PCE with glycerol additive in the P3HT:PC60BM active layer.** (Article I, published with the permission of © Hindawi Publishing Corporation 2015).

It can be seen from the plot that average efficiency of the device from 2% at 0 vol% concentration is increased almost near to 3% at 30 vol% glycerol concentration in the active layer. Further presence of higher concentration of glycerol was found to reduce the efficiency. The morphology changes by the annealing were investigated by the optical microscope, in Fig. 13.
As comparing with the morphology of the blend in Fig. 11 (b) and Fig. 13 (b), it can be clearly seen in the latter that the amount and extent of excessive crystallisation of PC60BM due to annealing is lesser with the presence of glycerol additive. This mechanism greatly contributes to the enhanced performance of the device as in OSC devices since the morphology acts as the significant factor in determining the efficiency of the device. It was reported that [156] when the contact surface area between donor and acceptor components in the active layer are higher, better would be the transport of charges at the interfaces and hence resulting in better working of the device.

Further, the AFM measurements revealed the fact that the active layer with glycerol additive was having a smoother surface. It was reported [130] that the smoother surface lead to better adhesion of the successive component layers and enhances device efficiency. On the contrary, there were other reports [158] which stated that the rough surface of blend film is a signature of higher efficiency. It was argued that the rougher surface increased charge collection by increasing the contact area between blend and metal cathode at the interface and also increased light absorption by improving internal reflection. However, it was explained by Dutta et.al [159] in his report that an increase in efficiency was not directly attributed to the changes in roughness, but to the improved ordering of P3HT chains and optimal donor-acceptor phase distribution in both lateral and vertical directions. Thus it can be...
expected that the efficiency improvement observed in this study may predominantly depend on the morphological improvement obtained in the active layer.

4.1.4 Controlling component ratio of conducting polymer blend by annealing

The electrical performance and also surface energy properties of conducting polymers used as hole transporting layer depends on its surface compositions. Appropriate annealing of the HTL polymer layer could enhance its morphology and hence the device performance. In this study, we investigated how the different atmospheres such as vacuum, N2 and air with various temperatures affect to the performance of PEDOT:PSS in OSC. The temperature was varied from 70 °C to 270 °C. The performance variation of PH500 in OSC with temperature and different atmosphere is represented in Fig. 14.

![Fig. 14. PCE variation with temperature and atmospheres. (Article II, published with the permission of © Hindawi Publishing Corporation 2015).](image)

At temperature 220 °C, it can be seen from Fig. 14 that the performance was higher for devices with PH500 annealed in each of the three atmospheres. Annealing in air was demonstrating lower PCE value and the efficiency values were higher for
the devices annealed in N$_2$ and vacuum. Annealing in N$_2$ has also found to cause an increase in $J_{SC}$ values than for devices annealed in vacuum. It was found that the optimum temperature was 220 °C in all three atmospheres. The Nitrogen atmosphere was demonstrating better condition for the PEDOT: PSS layer to achieve higher PCE in OSC devices. The average performances in the three atmospheres are depicted in Table 2.

Table 2. Average photovoltaic parameters at optimum annealing temperature. (Article II, published with the permission of © Hindawi Publishing Corporation 2015).

<table>
<thead>
<tr>
<th>Annealing atmosphere</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>0.625</td>
<td>61.85</td>
<td>6.70</td>
<td>2.58</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.635</td>
<td>56.57</td>
<td>7.43</td>
<td>2.67</td>
</tr>
<tr>
<td>Air</td>
<td>0.631</td>
<td>61.20</td>
<td>5.62</td>
<td>2.17</td>
</tr>
</tbody>
</table>

In order to understand better the efficiency variation caused by annealing, the behaviour of PEDOT and PSS component variation in PH500 was analysed by XPS spectroscopy. The sulfur atoms in both PEDOT and PSS can be easily distinguished because they have different binding energies. The sulfur peaks at S 2p having lower binding energy, 164.6 eV and 163.4 eV correspond to the PEDOT component and the higher binding energy 169 eV and 167.8 eV correspond to PSS [160]. The variation S2p peaks of PH500 annealed in different atmosphere at the optimum temperature are represented in Fig. 15.
In PEDOT:PSS, the excess PSS present in the blend acts slightly insulating and PEDOT is relatively more conductive \cite{161,162}. Analysing the component content of PEDOT and PSS in the Fig. 15, it was found that the PEDOT content in PH500 layer annealed in \(\text{N}_2\) and vacuum was higher and PSS content lower compared to the PH500 layer annealed in air. The PH500 layer annealed in \(\text{N}_2\) had comparatively the highest PEDOT content and lower PSS content. The reason for such kind of component variation might be due to the reported phenomena that at higher annealing temperature the PSS shell around the conducting PEDOT grain gets shrunk and thus exposing more conductive PEDOT to the surface \cite{163, 164}. At temperature greater than 220 \(^\circ\text{C}\), the performance of PH500 deteriorates and might be due to the fact that as larger component variation is taking place. The variation of ratio content of PSS/PEDOT with power conversion efficiency and current density is plotted in Fig. 16.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig15.png}
\caption{S 2p XPS peaks of PH500 samples annealed at optimum temperature in different atmospheres. (Article II, published with the permission of © Hindawi Publishing Corporation 2015).}
\end{figure}
The strong behavioural dependence of PSS/PEDOT ratio content with PCE and J_{SC} is evident in Fig. 16. It was found that when the component ratio of PSS/PEDOT is closer to 1.1 the efficiency and current density is the highest in any atmosphere of N₂, vacuum and air. The results achieved are very relevant due to the fact that it helps the manufacturer to understand how the specific component ratio formulation of the conducting polymer blend performs in the respective atmospheres. In our further experiments, we have also investigated the effect in various other types of PEDOT:PSS such as PVP A14083, neutralised PEDOT:PSS, HTL solar PEDOT:PSS and similar kind of behaviour was observed.

4.2 Stability studies

Organic solar cell (OSC) devices currently face many stability issues. Additional focus on studying degradation happening inside the device is needed. This is due
to the fact that a straightforward solution does not exist for addressing internal degradation issues as compared with external degrading factors where the choice of suitable encapsulation of the device can be adopted to restrict the degradation to a certain degree. We had invested our effort to study some of such factors causing internal degradation and explored a suitable modus operandi to tackle etching of ITO by PEDOT:PSS. Further the investigations were done for understanding the factors such as influence of ITO surface defects due to bending stress on the device performance and effect of extended thermal exposure on the active layer of high efficiency OSC devices.

4.2.1 Effect of acidic nature of PEDOT:PSS on ITO anode and performance of OSC device

The poly(3,4-ethylenedioxythiophene) (PEDOT) normally does not dissolve in usual solvents and it has to be attached with PSS in order to make it more soluble. PEDOT:PSS has acidic pH value between 1 and 2 at 20 °C [165]. The PEDOT:PSS is hygroscopic and with the presence of moisture during PEDOT:PSS deposition, it can react with ITO layer beneath. The ITO is highly soluble in acidic medium. The interfacial degradation of ITO anode in the device takes place due to the etching effect of the acidic PEDOT:PSS and the indium and tin components will diffuse through PEDOT:PSS to the active layer. The degradation of the ITO anode due to etching and the migration of etched products through the subsequent organic layers will together contribute in reducing the performance of the device and the performance gets reduced as it ages.
From the Fig. 17, it can be seen that the efficiency falls rapidly within first five days and continues the degradation pattern and at the last day of measurement the degradation was about 66% from the initial efficiency of 2.65%. In order to understand the stability degradation of polymer solar cell predominantly due to ITO etching, the studies and measurement were conducted so that other parallel degrading factors such as photo bleaching, thermal exposure, oxidation and moisture were restricted to the minimum.

4.2.2 Method to counter ITO degradation by PEDOT:PSS

The presence of interlayer between the ITO and the conducting polymer layer might lessen the direct acidic influence of PEDOT:PSS. The interlayer cannot be too thick because it will affect to the transmittance and the performance of the layers. The properties of plasma treated silver as the interlayer was investigated. The interlayer thicknesses of 1 nm and 5 nm were used to demonstrate the influence.
Fig. 18. Influence of plasma treated Ag interlayers on stability of OSC (Article III, published with the permission of © Elsevier 2014).

From Fig. 18, it can be seen that the initial PCE value is changed to 2.32% with the insertion of 1 nm thick interlayer and to 2.21% with 5 nm thick plasma treated Ag layer. The thinner interlayer of 1 nm resulted in degradation up to 56% from its initial value, whereas with 5 nm thick plasma treated Ag layer contributed to enhancing the stability by restricting the degradation to only 30% from its initial PCE. Additional transmittance measurement showed that the influence of light transmission was reduced slightly with the presence of the interlayer which was reflected in the initial PCE values of devices with the interlayers.

The interfacial degradation mechanism with indium diffusion due to etching by PEDOT:PSS was later analysed with XPS measurements. It was found that the indium atoms etched out from ITO starting from the first day and at the end of 30 days, there was significant percentage of indium content diffused through PEDOT:PSS. It was found for the samples with 5 nm interfacial layer that the diffusion of indium was restricted by the presence of the plasma treated Ag layer. This was thus reflected in the enhanced stability with 5 nm thick interlayer. The use of interlayer of 1 nm was found to be not very effective due to the fact the layer
may be very thin or may have non uniform distribution on the surface to contribute shielding against acidic PEDOT:PSS.

4.2.3 Effect of cracked ITO anode on the device performance

The solution processability of the OSC technology enable large scale flexible devices to be made on PET substrates. Since ITO is brittle [166-170], large bending of the substrate can cause cracks on the ITO surface and it will reduce the conductivity of the surface which can reflect in the device performance. In this section, we tried to understand how the device would perform if the OSC is fabricated on the already cracked ITO substrates. The mechanism behind ITO breaking is studied and its effect on OSC is analysed. Table 3 depicts the average performance of the functioning devices.

Table 3. OSC- PCE for functional cells based on cracked ITO (Samples) and uncracked ITO (References). (Article IV, published with the permission of © Elsevier 2013).

<table>
<thead>
<tr>
<th></th>
<th>Total number of solar cells</th>
<th>Functioning cells</th>
<th>Average PCE (%)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>40</td>
<td>36</td>
<td>0.78</td>
<td>0.25</td>
</tr>
<tr>
<td>References</td>
<td>16</td>
<td>15</td>
<td>0.52</td>
<td>0.21</td>
</tr>
</tbody>
</table>

It was surprising that the statistical difference in the broken and reference samples are not very significant. During the initial stages of cracking, the decrease in conductivity may be compensated with increased effective surface. These results showed that even with samples cracked with 10 mm cylinder did not collapse the OSC device performance. Although the substrates were broken in a direction that expected to decrease the performance drastically, it was found that the direction of the crack does not have major influence on the performance of the OSC devices made on top of it. The efficiency of the device did not collapse although the ITO substrate was undergone bending stress under the critical 10 mm cylinder which created higher density of cracks. This might be insightful by revealing the fact that the thin film non uniformities in ITO is not very critical in smaller area. The sheet resistance of the ITO surface has greater influence when the surface area is higher [171], but the effect of cracked ITO requires more investigation to be understood better.
4.2.4 Effect of prolonged thermal exposure over 1,8-diiodooctane (DIO) doped PTB7:PC70BM based organic solar cells

The active layer is both prone to degradation due to continual illumination as well as continuous thermal exposure. In this study, other degrading factors are restricted and specifically studied how an extended and varying temperature profile would affect the performance of the low band gap polymer over an entire day. This study is very crucial in developing thermally stable and efficient OSC devices. The research on thermal stability of polymer solar cells is important since the devices are exposed to the sun for a prolonged time and the degradation of the polymer can take place due to prolonged heating effect associated with illumination [172, 173]. The prolonged thermal exposure affects adversely the efficiency of the low band gap active layer polymers in OSC devices. We have investigated the effect of varying temperature on the performance of DIO doped PTB7:PC70BM organic solar cells. The whole study was conducted inside the nitrogen filled glove box and hence the inert atmosphere restricted other parallel degrading mechanisms [115] and helped to study the effect specifically coming from thermal exposure of the active layer. The plot in the Fig. 19 represents the changes in power conversion efficiency (PCE) of the devices under varying thermal exposure over the whole day.

![Graph showing the changes in power conversion efficiency (PCE) of the devices under varying thermal exposure over the whole day.](image)

**Fig. 19.** Average variation of PCE with varying pre-annealing condition. (Article V, published with the permission of © EUPVSEC 2015).
From the measurement plots in Fig. 19, the initial average efficiency was found to be 7.15%. In the case of device under thermal exposure, the efficiency had steep degradation slope in the first 6 hours and the next six hours the efficiency was almost constant. The efficiency was slightly increased at 18th hour which characterised a short recovery period and sheer decline in efficiency thereafter. This may be associated with the critical changes in morphology due to prolonged temperature variation. The efficiency reached to 5.47% at the end of the day with heating. Almost 23% degradation took place from the initial value. The pristine device which had no thermal exposure had shown some degradation but was not significant as compared to the active layer under thermal exposure. The unheated devices degraded only about 2.15% from its initial value. Although the devices showed clear decrease in power conversion efficiencies from thermal exposure, it was observed that the $V_{OC}$ of the devices increased during the period whereas the $J_{SC}$ has fallen. The FF values were also found to drop with the thermal exposures after 6th hour. This might suggest that the morphology of the active layer has undergone a process of dynamic change where the generated excitons are limited somehow from dissociation and charge transfer. However, the accurate knowledge of the observed performance variations can be obtained only after further detailed morphological investigations.
5 Discussion

It is interesting to draw implications of the outcome generated from the different methods employed and experiments conducted in this work regarding the device performance and stability enhancement. These issues are discussed below.

5.1 An inexpensive route for performance improvements

Achieving the highest possible power conversion efficiency for OSC is a necessity for ensuring its competence among other thin film technologies. The cost effectiveness of the applied methods for achieving significant efficiency improvements was an important consideration during our research. Moreover, we have utilised a targeted approach for performance improvement, i.e. targeting and mitigating the anomalous characteristics of the constituent layer of the device or the components inside the layer. The morphology improvements of the bulk heterojunction active layer and the optimisation of conducting polymer HTL characteristics through regulated annealing conditions were found to be the straightforward methods to enhance the device efficiency in this work. The morphology enhancement achieved in this study was demonstrated by reduction in unfavourable phase segregation with addition of glycerol additive at optimised concentrations. The enhanced interfacial contact area between acceptor and donor phases due to reduction in excessive fullerene crystallisation [156] may have resulted in effective exciton dissociation. The probability of enhanced charge transport and reduction in series resistance is also suggested by the observation of significantly improved $J_{SC}$. In addition to reduction in interfacial contact area, it was reported that the irregularity occurring due to excessive crystallisation of fullerene components can also result in reducing light-harvesting capability of the active layer [156]. These factors reinforce the gravity of our achieved results regarding morphology improvement. The motivations for choosing glycerol as an additive in the active layer were based on the priorities such as low cost, eco-safe, hydrophilic nature and having higher boiling point. We expected that this type of additive could effectively target the PC60BM components in the active layer which was reported to have higher surface energy and hydrophilicity [174]. We also assumed that the rapid evolution of the solvent could also be prevented by elevating the boiling point with the introduction of suitable additive. The additive was found to be very effective in enhancing the performance of the device by 42% from its initial PCE. Apart from the BHJ lateral morphology, the vertical composition distribution is also an important issue, since
charges have to be vertically transported to their respective electrodes after they are generated at the donor-acceptor interface of the polymer-fullerene active layer. The other similar reported methods where additives were used to address the unfavourable phase segregation in the active layer include the use of 1,2,3,4-tetrahydronaphthalene (THN) [175] and bisadduct of PC60BM [156]. But our method outweighs these reported methods in terms of cost and rate of improvement from the initial PCE values.

Considering the scenario in large scale manufacturing process, a variety of annealing requirements are necessary for buffer layers constituting the device structure. For instance, annealing of the conducting polymer HTL such as PEDOT:PSS is essential for moisture removal. The cost effective methods for annealing in large scale processing is definitely not cleanroom and vacuum based conditions. We thus need to understand effect of other non-optimal processing and annealing conditions which are cost effective for making the technology profitable. Understanding the factors causing the improvement or deterioration in the layer during annealing in various atmospheres, would provide information enabling us to even design the specific conducting polymer buffer layer material to perform superior in non-optimal but cost effective atmosphere such as air. Thus it motivated us to investigate OSC performance with device structure consisting of water based and atmosphere susceptible conducting polymer such as PEDOT:PSS and annealing it under different pressures and atmospheres, for instance in vacuum, N2 filled glovebox and ambient air atmosphere. Previous studies had given very little focus on the effect of atmosphere conditions on the performance conducting polymer PEDOT:PSS layer during annealing. We have thus enhanced the efficiency of the OSC-BHJ device by obtaining optimised annealing condition for PEDOT:PSS, which was actually a distinct route employed to enhance device efficiency apart from morphological improvement of active layer. It was reported [176] that the contribution of electrical performance of the conducting polymer layer depends predominantly on the composition ratio between PSS and PEDOT in the layer. The interesting observation made from our experiments is the fact that the samples coated with the conducting polymer buffer layer at the same parameters, subjected to same annealing temperatures but distinct atmospheres, behaved rather differently. Moreover, the proportion content of PSS to PEDOT on the surface varied depending on the atmosphere and temperature in which the sample was annealed. There are other consequences with composition ratio differences and one of the major influences is on the subsequent wetting of the active layer. When the PSS content is getting reduced, the layer may become less hydrophilic and the

64
active layer consisting of non-polar solvent might have better wettability. Analysing only the conductivity changes in the sole layer would not guarantee its optimum functionality in the overall performance of the device. Thus the conducting polymer layer functionality on the whole device performance was important for us owing to the wettability variations after annealing. The conformational structure of PEDOT:PSS consists of random coil entanglement of PSS chains with attached PEDOT oligomers, and the components are distributed such that the PEDOT-rich core is covered by PSS-rich shell [177]. The shrinkage and expansion of these shells depends on the water content and evidently the annealing affect significantly on these variations, morphology of the layer and how it may expose more conductive PEDOT grains to the surface etc., which is directly reflected in enhanced $J_{SC}$ and PCE values. It was reported that the degradation of the conducting polymer initiates at higher temperatures above 260 °C [163]. This effect is consistent with our results where the devices exhibited the lowest performance at its maximum annealing peak in the experiment. The implication of the achieved results in the study is the fact that proper annealing condition can be used as a tool to control the composition of the HTL/PEDOT:PSS layer to obtain enhanced device performance. Moreover the optimal compositional ratios for PEDOT:PSS in various annealing conditions were also found out. This may help the industry to design the conducting buffer layers in future to deliver cost effective and superior performance irrespective of atmosphere annealing constraints.

5.2 Stability enhancement and experimental analysis

Once the highest possible efficiency of the OSC-BHJ device is achieved, the next challenge is to sustain at least 80% of its initial efficiency as long as possible. This is a general problem for the devices in the field of organic electronics. In this section of work regarding the stability studies of the devices, we have utilised an empirical approach which identified and limited some of the stability degenerating aberrations occurring in various strata and component layer interfaces within the device structure. Precisely the reactions [122] occurring at ITO anode and PEDOT:PSS conducting polymer buffer layer interface contribute significantly towards the stability degeneration. In the conventional OSC-BHJ structure, the same interface occurs predominantly. Moreover, the previously mentioned etching reaction on ITO could result in decreasing the conductivity of the transparent conducting anode. This might in turn act responsible for decreasing the device efficiency in the process owing to increased series resistance. It can be assumed
that a suitable interlayer would reduce or screen the direct acidic effect of the conducting polymer buffer layer on the anode. It was reported by W.J.Yoon [178], that the plasma treated AgO$_x$ interlayer between the ITO and PEDOT:PSS enhanced the efficiency of the device by providing the interface energy step which was reflected by 2 mA/cm$^2$ increase in $J_{SC}$. Thus, it inspired us to conduct the study utilising plasma treated Ag as an interlayer in view of obtaining both increased efficiency and stability. From our experiment, the stability of the device was significantly improved with a thicker interlayer, although there was no significant increase in the efficiency. The situation is ideal if the interlayer could increase the efficiency of the device significantly and contribute to increase stability by reducing the internal degradation of the device. The other methods that can be employed in mitigating such interface degradation inside the device are the choice of ITO compatible HTL layers such as molybdenum trioxide, adoption of inverted architecture, use of neutralised conducting polymer buffer layer and use of ITO alternatives. However, all these methods are not perfect and have many shortcomings. For instance, the processability of the neutralised PEDOT:PSS is difficult due to its low oxidation potential [179,180] and presence of unfavourable additives. Our method is found to be very relevant and efficient among them, since we had addressed the problem directly at the interface and not avoided either of the mutually reactive component layers which were some of the previously existing solutions.

During the usage cycle of OSC-BHJ devices, there are two major stability degenerating stress issues occurring on the device. These are issues relating to bending stress and thermal exposure due to prolonged illumination. The devices undergo bending or flex stresses during fabrication (roll to roll production), deployment, transport and critical angular stress for portable devices in the hands of the end user etc. Especially when ITO is utilised as their transparent conducting anode, these bending stresses can seriously influence the device performance owing to the brittle nature of the anode. Thus, we have done experimental investigation to obtain an understanding of the influence of already cracked ITO on the device performance. But our experiments done on the substrates revealed that if the ITO is broken within certain limiting diameter of bending, the influence is not significant on smaller scale OSC. Previous reports [181] suggest that solar cell device efficiency should drop with the conductivity drop due to mechanical defects on ITO. There are many possible explanations for the results we obtained. One of the possible explanations why the performance of the device did not collapse with the presence of cracks in ITO may be due to the fact that the conductivity losses
due to cracks may be compensated with the infiltration of conducting polymer buffer layer. It might also have influenced on enhancing light scattering in to the active layer. In addition to these, the dimensions of the devices were rather small. It is possible therefore to expect that the mechanical defects on ITO might not yet decrease the efficiency of the device in such smaller areas. There is also a high probability that the performance depends on the extent of congruency in the surface defects on ITO. Further investigations are necessary to understand the real mechanism behind these observed effects and analysis on larger dimensions might provide better insights regarding the phenomenon.

In the case of outdoor application of OSC, these devices are exposed to prolonged solar radiation. The significant elevation in module temperature and hot spots of over hundred degrees are some of its ramifications. The investigations on these thermal variations generated and subsequent effect on the device performance in OSC devices was rarely focussed. The organic active layers of the OSC-BHJ devices which are known to be thermally sensitive [141] is a core area to concentrate in view of enhancing stability of the device. Unlike some of the semi-crystalline polymers like P3HT, the active layer based on low band gap polymer PTB7 and fullerene does not have any positive effect on thermal influence. Thus the experimental investigation analysing the impact of varied thermal exposure on the high efficiency DIO doped PTB7:PC_{70}BM active layer on device performance is interesting. Most of the previous studies were based on analysing the effect at constant temperature. But we explored the issue closer to real life situation where the temperature changes are dynamic. The efficiency of the device was found to drop with the prolonged thermal exposure. Degradations due to fullerene aggregation and its excessive crystallisation under prolonged thermal exposure can also contribute to the observed decline in PCE values. Although the additive DIO enhances the initial device efficiency in the PTB7:PC_{70}BM based active layers by enhancing fine scale morphological distribution [147], it is reported to have many deteriorating properties [182] in the long run, specifically under extended thermal influence. Moreover it was reported [183] that the presence of DIO makes the active layer more prone to photo degradation when exposed to sunlight, thus contributing adversely in the outdoor application of the device. The temperature variations undergone by the active layer are well below the boiling point of the additive, thus the presence residual additive might have continued its negative contributions towards stability throughout the process. The morphological changes of the active layer blend during prolonged thermal exposure can affect the charge mobility and the generation of charge transfer complex which is reflected in
reduced current density of the devices under prolonged thermal exposure. The probability of donor-acceptor phase segregation and changes in defect states which control the recombination is reflected in the $V_{OC}$ of the device which was found to rise during the heating process. The fill factors of the devices were also found to drop which suggest an increase in series resistance and limitation in the charge transport. The existence of some period of duration where the device recovered its performance to a certain extent was also observed. The morphological transformation of the active layer under study has undergone a fluctuated temperature conditions characterised by high and low values. Thus the real characteristic transformations and mechanisms behind this could be expected to be much more complex. The deeper analysis on the phenomenon could be gathered by analysing carefully the morphological transformations at each temperature and correlating it with the photovoltaic characteristics. Nevertheless, the strategies to enhance the thermal stability allow OSC technology to ensure the continuous, prolonged and efficient operation of the devices under extensive outdoor applications.

5.3 Future outlook

In our future work, the focus would be placed more on obtaining very high efficiency devices by conducting deeper investigations on low band gap polymer based active layers and also the organic-inorganic hybrid perovskite devices. Some of the methods developed in this study are equally applicable in inverted perovskite-organic photovoltaic devices. The effectiveness of the techniques developed during this study would be also explored in those devices as well.

Although the most efficient acceptor material till date is fullerene, it is one of the expensive parts in OSC. Thus a low-cost and superior alternative for fullerenes would be investigated in our further studies. There is also as added reason which motivates us for the search of fullerene alternatives and it is because of the fact that the fullerenes, especially [6,6]-Phenyl-C61-butyric acid methyl ester contributes towards the stiffness of the active layer which in turn reduces the mechanical freedom of the flexible OSC devices.

Another issue that will be handled in our future work is the reuse and recycling of the device substrate. The thorough focus on fully recyclable organic photovoltaics will give boost to the environmental friendliness of the technology. Strategies to reuse the substrate would greatly help to reduce the overall manufacturing cost which helps the industry to produce devices at higher profit
margin. The reduced manufacturing cost will also reflect in the final product price which makes the devices more affordable and attractive for the consumers in the commercial market. Especially the re-use of ITO patterned PET substrates can help in reducing the production cost due to limited indium supply and expenses related to patterning requirements. This will also enable the technology to attain full green label since the plastic flexible substrates also get recycled or reused in the process. The ITO is still is the leader in transparent electrode market owing to its excellent optical transparency and conductivity. There are a few alternative exists today although their performance is little less than ITO. Few of these include graphene layers, highly conductive poly (3,4-ethylenedioxythiophene)-poly(styrene sulfonate) and transparent conducting layer with silver nanowires embedded in it. However, most of these alternatives are still in its research phase and not widely available with a reasonable price.

Our future research will be taking in to account all the above mentioned aspects in a view of obtaining efficient, inexpensive, stable and eco-friendly organic photovoltaic devices.
6 Summary

OSC is currently facing a variety of challenges and the main bottleneck is its lower efficiency and stability when compared with other thin film solar cell technologies. The motivation of this thesis was based on the fact that simple and robust techniques are necessary to synergistically enhance the efficiency and stability of the device. This thesis identified various factors causing low efficiency and stability in BHJ-OSC, some of its mechanisms were understood and methods to reduce those degradations were also explored. Fig. 20 illustrates problems studied in the scope of this thesis.

Fig. 20. Issues analysed in the thesis.

The studies conducted and methods developed in this thesis were regarding mostly the materials commonly used among many other organic devices apart from OSCs. The organic photovoltaic materials are also useful in photodetector applications such as photoelectric transducers for optical communications or optical imaging systems. Thus the results of the study on component layers have broader scope of utility. Especially the results regarding ITO and PEDOT:PSS may find its applicability also among Organic light emitting diodes (OLEDs) and inverted perovskite-organic PV devices where some of the mentioned component layers are also used. The efficiency and stability issues described in the thesis occur usually in the device and the organic solar cell industry faces these problems very often. We recognise that our conducted studies addressing these issues might therefore impact the OSC technology by providing choices in problem mitigating techniques and pin pointing the core areas to focus.
References


Original articles


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581. Su, Xiang (2016) Lightweight data and knowledge exchange for pervasive environments
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583. Lanz, Brigitte (2016) Compact current pulse-pumped GaAs–AlGaAs laser diode structures for generating high peak-power (1–50 watt) picosecond-range single optical pulses
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587. Razzakainen, Miika (2016) Intelligent knowledge discovery on building energy and indoor climate data
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