Improving Organic Photovoltaic Device Efficiency through Nanoimprinting

Joseph B. Emah

Submitted for the Degree of Doctor of Philosophy from the University of Surrey

Advanced Technology Institute
Faculty of Engineering and Physical Sciences
University of Surrey
Guildford, Surrey, GU2 7XH, UK

September 2010

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Originality
I want to place it on note that, unlike all other results described in this thesis, the experimental part of the section on the XPS and UPS measurements were carried out by Dr Christina Giusca and Dr Hide Shiozawa as staff in charge of the safe operation of the equipment. The success of this project was possible as a result of an excellent discussions and comments by the supervisors particularly Dr Richard Curry. With the exception of the XPS and UPS measurements, more than 95% of the actual experimental work and the writing were performed by the author.

However, the term “we” is used throughout the text to emphasise the fact that every single result of the author’s work presented in this thesis was possible through provision of equipment, materials and scientific input from others. This is in consistency with the fact that modern research relies on collaboration and teamwork.

Joseph Emah
Dedicated to my dear wife, Edibon
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Abstract
Harnessing electrical energy from solar radiation using photovoltaic (PV) technology promises to be an essential component of future global energy production. For PV devices to become a sustainable energy source that can supply our daily energy needs, it must be made economically competitive with fossil fuels and other emerging renewable energy technologies. Semiconducting polymers and small molecule organic materials offer an alternative means of fabricating low cost organic solar cells. But these photoactive organic materials are characterised by large optical band gaps (1.5 eV–3.0 eV), low photo absorption and low charge carrier mobility (μ). These imply low radiation to electrical power conversion efficiencies (η) in such devices.

It is well known that using poly (3,4-ethylenedioxythiophene) poly (styrene sulfonate) (PEDOT:PSS) with higher work function (5.1 eV) as a buffer layer facilitates hole extraction and converts blocking contacts into ohmic by modifying the surface of ITO (4.7 eV).

In this thesis, we present and discuss the enhancement of the power conversion efficiency of organic solar cells through nano-imprinting of geometrical patterns into the PEDOT:PSS layer. Poly (3-hexylthiophene-2,5-diy) (P3HT)/[6,6]-phenyl-C61-butyric acid ester (PCBM) based solar cells were fabricated and the PEDOT:PSS buffer layers between the photoactive material and the ITO anode were modified through patterning by soft lithography. Poly (dimethylsiloxane) (PDMS) was used to make the stamps for the imprinting and two approaches of soft lithography; the “Lift-up” and “put-down” processes were used. Several bulk heterojunction organic solar cells were fabricated at different stamping temperatures to investigate the influence of temperature on the stamped features as it affects the device performance.

One of the device parameters that significantly limit the efficiency of polymer/fullerene-based solar cells is the open-circuit voltage ($V_{oc}$), which does not obey the metal-insulator-metal principle due to its complicated characteristics. The results show that modifying the
PEDOT:PSS anode buffer layer enhances the short circuit current density, the open circuit voltage and the fill factor of the device. The efficiency of polymer PVs have been improved by reducing the device series resistance and increasing its shunt resistance through patterning. This modification can be helpful when optimizing devices. Further studies on the optical and chemical modifications of the device interfaces provided insights to additional effects due to patterning and helped to further explain the hypothesis made from these experiments. Application of these findings may eventually lead to fabrication of large area, flexible and cheap organic solar cells.
Acknowledgement
Pursuing a PhD in a multidisciplinary research centre such as the Advanced Technology Institute gave me an opportunity to work with people of various background and experience. I drew from their experience through discussions, collaborative research activities, meetings and training on new equipment to build my own research experience. I therefore express my sincere gratitude to colleagues, collaborators and friends who have contributed in diverse ways towards the completion of this thesis.

Principally, I express my profound gratitude to Prof. Ravi Silva and Dr Richard Curry for their supervisory role and assistance throughout this research. I appreciate every help from Dr Ross Hatton, Dr Nanditha Dissanayake, Dr Damitha Adikaari, Dr Christina Giusca and Dr Hide Shiozawa through invaluable discussions. I also extend my appreciation to all the technical staff in the ATI for providing assistance and good and safe working environment.

I am grateful to the Akwa Ibom State University of Technology, Nigeria for sponsoring this PhD programme and Elf Petroleum Nigeria Limited for their financial assistance when it was most needed.

I am indebted to my wife, Edibon and my children, Etimbuk, Etieno, UfanAbasi and Daramfon for the demand my absence placed on them during the four years of research. I thank the Almighty God for this rare opportunity to undertake a PhD at the University of Surrey.
Publications

List of Conferences
1. The 6th International Conference on Organic Electronics, University of Liverpool, Uk.
2. First International Conference on Materials for Energy, Karlsruhe, Germany.

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Motivation

1.1.1 The Energy Crisis

Over the past century, technology has depended heavily on finite sources of fuel for its advancements. These include crude oil, coal and gas. Before the economic meltdown of 2008 through 2009, crude oil price went as high as $147 per barrel. With global concern that the world crude reserve is dwindling due to increased demand for oil, there is need to seek alternative but renewable source of energy.

Another big concern is the long-term effects of excess carbon dioxide and other environmentally damaging greenhouse gases (GHGs) stemming from the burning of fossil fuel. Greenhouse gases such as carbon dioxide, methane, nitrous oxide, ozone and water vapour behave like a blanket around Earth. Among all these, water vapour has a relatively short residence time in the atmosphere (around 10 days). These gases allow the Sun's rays to reach Earth's surface but impede the heat they create from escaping back into space. Any increase in the levels of greenhouse gases in the atmosphere mean that more heat is trapped and global temperature increases - an effect known as 'global warming'. Thus, temperature provide the clearest evidence that the climate is changing and globally, the average temperature has risen by more than 0.7 °C over the last 100 years. In just 200 years, the amount of carbon dioxide in the atmosphere has increased by around 35 per cent.

Supporting literature from the Intergovernmental Panel on Climate Change is given in this paragraph and the next. GHG emissions over the last three decades have increased by an
average of 1.6% per year with carbon dioxide (CO₂) emissions from the use of fossil fuels growing at a rate of 1.9% per year. It is projected that global energy demand and associated supply patterns based on fossil fuels – the main drivers of GHG emissions – will continue to grow.

Since pre-industrial times, increasing emissions of GHGs due to human activities have led to a marked increase in atmospheric concentrations of the long-lived GHG gases; carbon dioxide (CO₂), CH₄, and nitrous oxide (N₂O), perfluorocarbons PFCs, hydrofluorocarbons (HFCs) and sulphur hexafluoride (SF₆) and ozone-depleting substances (ODS; chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons). The human-induced radiative forcing (the change in net irradiance, i.e. the difference between the incoming and the outgoing radiation energy in a given climate system measured in Watts per square meter) at the atmospheric boundary between the troposphere and the stratosphere) of the Earth’s climate is largely due to the increases in these concentrations. The predominant sources of the increase in GHGs are from the combustion of fossil fuels. Atmospheric CO₂ concentrations have increased by almost 100ppm in comparison to its preindustrial levels, reaching 379ppm in 2005, with mean annual growth rates in the 2000–2005 periods that were higher than those in the 1990s. The direct effect of all the long-lived GHGs is substantial, with the total CO₂ equivalent (CO₂-eq) concentration of these gases currently being estimated to be around 455 ppm CO₂-eq (range: 433–477 ppm CO₂-eq). The effects of aerosol and land use changes reduce radiative forcing so that the net forcing of human activities is in the range of 311 to 435 ppm CO₂-eq, with a central estimate of about 375 ppm CO₂-eq.⁴

Global temperatures are predicted to rise by between 1.1°C and 6.4°C over the next century and since 1990, it has risen by 0.2°C. The ten warmest years on record have all been since 1990. Six of the ten warmest years on record in the UK were between 1995 and 2004.⁵
It is considered that the consequence of this temperature change have already increased the frequency of natural disasters and are likely to have more effects that are devastating for humans and other life forms in all parts of the Earth in the near future. These have necessitated increased research into finding alternative energy sources that are eco-friendly at competitive cost to existing conventional energy sources.

1.1.2 Renewable Energy Sources
The use of more natural and renewable energy sources is needed to take the burden off our current dependency on fossil fuels. The sources include solar, water (hydroelectric), wind, geothermal and biomass. These resources when used for energy generation will neither run out nor have any significant effects on our environment. There are more advantages than disadvantages of these renewable energy sources, some of which are listed below.

Advantages

- The sun, wind, and geothermal activity are all renewable and free to use.

- After the initial cost of solar panels, wind turbines, and geothermal energy equipment, the only cost to the consumer relates to any required maintenance.

- Use as much or as little of the renewable electricity one generates, without feeling guilty for any wastage.

- Oil, gas and coal supplies will most likely run out someday; if we have the infrastructure in place to generate energy from natural sources, this will not be a problem.

Disadvantages

- The initial cost of renewable energy technologies may be expensive.
The amount of power they can supply over a longer period often depends on geographical and weather conditions.

The above outlines the need to develop low cost technologies for renewable energy sources to save both the environment as well as meeting the future global energy demands. Statistics provided by the Intergovernmental Panel on Climate Change 2007: Mitigation of Climate Change; shows that renewable energy accounted for over 15% of world primary energy supply in 2004, including traditional biomass (7–8%), large hydro-electricity (5.3%, being 16% of electricity generated), and other ‘new’ renewables (2.5%). It added that renewable-energy systems can contribute to the security of energy supply and protection of the environment. These and other benefits of renewable energy systems were defined in a declaration by 154 nations at the Renewables 2004 conference held in Bonn (Renewables, 2004).

Broadly, renewable-energy technologies can be classified into four categories:

1) Technologically mature with established markets in at least several countries:— large and small hydro, woody biomass combustion, geothermal, landfill gas, crystalline silicon PV, solar water heating, onshore wind, bio ethanol from sugars and starch (mainly Brazil and US);

2) Technologically mature but with relatively new and immature markets in a small number of countries:— municipal solid waste-to-energy, anaerobic digestion, biodiesel, co-firing of biomass, concentrating solar dishes and troughs, solar-assisted air conditioning, mini- and micro-hydro and offshore wind;

3) Under technological development with demonstrations or small-scale commercial application, but approaching wider market introduction:— thin-film PV, concentrating PV, tidal range and currents, wave power, biomass gasification and pyrolysis, bio ethanol from ligno-cellulose and solar thermal towers; and
4) Still in technology research stages: organic and inorganic nanotechnology solar cells, artificial photosynthesis, biological hydrogen production involving biomass, algae and bacteria, bio-refineries, ocean thermal and saline gradients, and ocean currents. Focus of this thesis will be on one of the technologies in the last category (4), organic nanotechnology solar cells and is briefly introduced in the following sections along with the inorganic counterpart.

1.2 Solar Energy
Among the renewable energy sources, the most abundant and freely available, but not yet utilized, is solar energy. Our planet receives $\sim 1.2 \times 10^{17}$ W of solar power as opposed to the rate of worldwide energy consumption which is estimated to be $\sim 10,000$ times smaller at $\sim 1.3 \times 10^{13}$ W. By implication the Earth receives more solar energy in an hour than the total energy consumed in an entire year. Annual surface insulation varies with latitude, ranging between averages of $1000$ W/m$^2$ in temperate regions and $1200$ W/m$^2$ in low-latitude dry desert areas. Interestingly, many other forms of renewable energy sources originate from solar energy, except ocean tides and geothermal energy. And the land requirement for solar cells is minimal, requiring only $0.16\%$ of the Earth’s surface covered with $10\%$ efficient cells to provide $\sim 2 \times 10^{13}$ W of electricity, which is more than the current total energy demand of the planet. Electrical energy can be harnessed directly from sunlight using photovoltaic (PV) technology which has already been widely used in spacecraft power supply systems, and is increasingly extending into terrestrial applications such as incorporation into portable devices and houses. Electricity generated directly by utilizing solar photons to create free electrons in a PV cell is estimated to have a technical potential of at least 450,000 TWh/yr. However, realizing this potential will be severely limited by land, energy-storage and
investment constraints. A brief summary of the history of photovoltaic cells is presented in the proceeding section.

1.2.1 Inorganic Solar Cells
The photovoltaic effect was first reported by Edmund Bequerel in 1839, and photocurrent generation by W. Adams and R. Day in 1876 when they discovered that the action of light on selenium produced current spontaneously. This culminated in what was probably the first large area solar cell in 1894 demonstrated by Charles Fritts. These early cells were thin film “Schottky barrier” devices, where a semi-transparent layer of metal deposited on top of the semiconductor provided the asymmetric electronic junction, which is necessary for photovoltaic action and access to the junction for the incident light. In the 1950s, the development of silicon electronics followed the discovery of a method to manufacture p-n junctions in silicon. The first silicon solar cell was reported by Chaplin et al in 1954 with a power conversion efficiency of 6%. Later, other materials such as cadmium sulphide, gallium arsenide, indium phosphide, and cadmium telluride were used, but silicon remains the front-runner photovoltaic material owing to the significant advances in silicon technology. Further research led to a non-silicon thin film solar cell in 1979 (besides GaAs) which utilized Cu$_2$S/CdS material structures with efficiency of 10%. Currently, conventional crystalline solar cells can harvest up to 25% of the incoming solar energy which is already close to the theoretically predicted upper limit of 30%. According to the US Climate Change Technology Program, 2005, most commercially available solar PV modules are based on crystalline silicon cells with mono-crystalline at 18% efficiency having 33.2% of the market share. Polycrystalline cells at up to 15% efficiency are cheaper per Wp (peak Watt) and have 56.3% market share. Modules costing 3–4 US$/Wp can be installed for around 6–7 US$/Wp from which electricity can be generated for around 250 US$/MWh in high sunshine regions.
Sadly, fabrication of inorganic semiconductor based solar cells demand expensive technologies at present which result in very expensive photovoltaic devices (PVDs) and makes it difficult to compete with other conventional energy sources. A possible reason is associated with current industrial process of production from quartz to Si wafers which requires temperatures up to 1900°C.\textsuperscript{11,20}

1.2.2 Organic Solar Cells

If photovoltaic devices are to be considered to provide a major future global energy source, large-scale manufacturing at reasonably low cost is desired. This calls upon an entirely new type of material, namely, the organic semiconductors.\textsuperscript{21} The organic semiconductor comprise of “small molecules”\textsuperscript{22} and conjugated polymers\textsuperscript{23} and have major advantages when compared to their inorganic counterparts in particular with respect to costs, flexibility, and processability. Their light weight, mechanical flexibility, and semi transparency offer new opportunities for photovoltaic cell designs. Additionally, conjugated polymers possess a processing advantage:\textsuperscript{24} they are soluble in common organic solvents\textsuperscript{25} and thus can be deposited by solution processing and by using printing technologies.

Historically, anthracene was the first organic compound in which photoconductivity was observed by Pochettino\textsuperscript{26} in 1906 and Volmer\textsuperscript{27} in 1913. The first effort to fabricate organic photovoltaic devices using small molecules was made in 1975 with 0.001% power conversion efficiency.\textsuperscript{28} Further work by Tang \textit{et al.}\textsuperscript{29} in 1986 sparked the current interest in the field when they reported power conversion efficiency of 1%.

The discovery in 1977 by the groups of Heeger, Shirakawa and MacDiarmid that doped polyacetylene could achieve metallic conductivity initiated intense research on conjugated polymers.\textsuperscript{30} These materials, particularly $\pi$-conjugated polymers, have formed a new class of semiconductors which finds application in various optoelectronic devices. Such applications
includes PV devices\textsuperscript{31-32}, integrated electronic circuits based on field effect transistors\textsuperscript{33-34} and flat displays based on light emitting diodes.\textsuperscript{35} In certain cases these materials exhibit charge carrier mobilities between $0.1-1 \text{cm}^2\text{v.s}$ (hole mobility),\textsuperscript{36-37} and $1 \text{cm}^2\text{v.s}$ (electron mobility).\textsuperscript{38}

The simplest structure of an organic polymer solar cell is the superposition of a donor and acceptor material on top of each other, providing an interface where a photo-generated exciton (a quasiparticle, i.e. a quantum of energy that has position and momentum, consisting of a bound state of an electron and an imaginary particle called an electron hole in insulators and semiconductors) in the donor or acceptor can diffuse to. At this interface, the excitons are dissociated, releasing electrons, which are transferred to acceptors, and holes to drift within the donor layer to their respective electrodes.\textsuperscript{39} Due to short exciton diffusion lengths (10-20 nm),\textsuperscript{40,50-55} only those excitons generated within this distance from the donor-acceptor interface will contribute to the photocurrent, which limits drastically the generated current and hence, the overall efficiency of the bilayer solar cell.

The best performing polymer solar cells rely on bulk heterojunction (BHJ) networks of polymer/molecule blends, usually sandwiched between two metals with different work functions acting as the anode and cathode. The discovery of [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM),\textsuperscript{41} a soluble and processable derivative of fullerene C\textsubscript{60}, allowed for the fabrication of the first bulk heterojunction solar cell by blending it with poly(2-methoxy-5-(2-ethyl-hexoxy)-1,4-phenylene-vinylene) (MEH-PPV)\textsuperscript{42} with a power conversion efficiency of about 2.9%. These bulk heterojunctions can be deposited either by co-sublimation of small molecules or by spin-coating mixtures of polymers.

The BHJ structure suffers a major drawback in that a percolating pathway for the hole and electron transporting phase to the electrodes is needed for separated charge carriers to reach their corresponding electrodes. This implies that, if the phase separated domains are larger
than the exciton diffusion length, then most excitons will recombine and will not contribute
to the photocurrent. However, excitons generated in close proximity to an interface may be
separated into free charge carriers, which can diffuse or drift to the corresponding
electrodes.43

The advent of PCBM led to an increased research activity in organic solar cells. To obtain
higher efficiencies, regioregular poly (3-hexylthiophene-2,5-diyl) (P3HT) became the
material of choice as the electron donor, as it absorbs photons at longer wavelengths
compared to PPV (poly(p-phenylene vinylene) derivatives43. Several groups21,44-46 undertook
research with a record high power conversion efficiency of 5% reached in 2005.31 Recently,
efficiency reaching 7% have been reported47, the highest achieved so far. Refer to Blom et
al48 for an excellent summary of the device physics of PCBM:polymer solar cells.

A number of factors limit the efficiency of PV devices which is a trade-off between optical
absorption and the diffusion of excitons in polymers, prior to their dissociation at the donor-
acceptor junction, which dictates the device performance.29,49-50 This is mainly due to the fact
that the typical exciton diffusion length, \( L_D \), in conjugated organic compounds is of the order
of 10-20 nm,51-56 whilst the typical optical absorption length at suitable energies for
harvesting are an order of magnitude greater.57 As a result, only excitons generated close to a
dissociation site can separate into charge carriers and contribute to the photovoltaic process.

In a bid to optimize the optical aspects of the device, recent studies have focussed on
increasing the interaction of light within the photoactive layers by means of periodic
patterning on the optical wavelength scale of the solar cell surface.58-59 The studies reveal that
the incident wave momentum is modified such that the incident light remains trapped within
the solar cell layers by total internal reflections at the surface, which allows for a significant
increase in light absorption.
1.3 Outline of the Thesis
Chapter Two of this thesis introduces the general physics of the solar device and then, the electronic properties of organic semiconductors as the model for electrical conductivity in conducting polymers. These are only summarized briefly, whereas many excellent text books and other references offer more general properties of the organic semiconductors. More fundamental properties of the interlayer between the photoactive organic materials and the positive electrode of the devices is given for better understanding, as this is the layer upon which most of the engineering of the device fabrication is done.

The focus of Chapter Three is on providing a comprehensive insight into the parameters which characterise the solar cell and the relationship between these parameters. Thus, a compilation and summary of the relevant organic solar cell principles that is consistent with the experience and understanding of the author is contained in this chapter.

It suffices to say that, although a complete theoretical understanding of organic solar cells is still lacking, we have drawn analogies from the understanding of inorganic cells through the equivalent circuit diagram and the usual interpretation of the current voltage characteristics.

The principle used in the engineering of the device to make improvements in the device parameters, which defines the intention of the author, is also presented in this chapter.

Details of sample preparation, device fabrication and measurements, description of the equipment and methods for patterning the interlayer between the photoactive layer and the anode can be found in Chapter Four.

In Chapter Five the results of the preliminary experiments carried out to test the workability of the method used to improve the efficiency of the device and other device parameters is presented.

Further experiments to elucidate the improvements obtained in the preliminary results are given in Chapter Six which involves optical and material characterisation. Attempts to
explain the changes in the light path, the interface effects on the material and how they affect the device parameters are drawn from these results.

Chapter Seven concerns device optimizations based on the knowledge gained from the results of Chapter Six. Better improvements in the device characteristics including the open circuit voltage, which was compromised in the preliminary results of Chapter Five, justify the method of engineering applied to the devices within this thesis.

Chapter Eight concludes with a summary and discussion of the various results obtained for the adopted device architecture, patterning, optical, material characterization and some suggestions for future investigations.

1.4 Abbreviations

A  Electron acceptor
BHJ  Bulk heterojunction
CB  Conduction band
CdS  Cadmium sulphide
Cu$_2$S/CdS  Copper sulphide/Cadmium sulphide
D  Electron Donor
EQE  External Quantum Efficiency
eV  Electron volt
FF  Fill factor
FTIR  Fourier Transform Infrared Spectroscopy
GaAs  Gallium Arsenide
$h$  Planck's constant
HOMO  Highest occupied molecular orbital
$I_{dark}$  Dark current
\( I_{\text{max}} \)  
Current at maximum power point

InP  
Indium phushpide

\( I_{\text{ph}} \)  
Photocurrent

\( I_s \)  
Reverse saturation current

\( I_{\text{sc}} \)  
Short circuit current

ITO  
Indium tin oxide

\( J_{\text{sc}} \)  
Short circuit current density

\( k_B \)  
Boltzmann constant

\( L_D \)  
Exciton diffusion length

LED  
Light emitting devices

LUMO  
Lowest unoccupied molecular orbital

MEH-PPV  
Poly(2-methoxy-5-(2-ethyl-hexoxy)-1,4-phenylene-vinylene)

meV  
Milli-electron volt

\( \eta \)  
Power conversion efficiency (PCE)

OLED  
Organic light emitting devices

OPV  
Organic photovoltaic

P3HT  
Poly (3-hexylthiophene-2,5-diyl)

PCBM  
\([6,6]\)-Phenyl-C\(_{61}\)-butyric acid ester

PDMS  
Poly-dimethylsiloxane

PEDOT:PSS  
Poly (3, 4- ethylene dioxythiophene)-poly (styrene sulfonate)

PL  
Photoluminescence

\( P_{\text{max}} \)  
Maximum power point

PPV  
Poly(p-phenylene vinylene)

PVDs  
Photovoltaic devices

\( Q \)  
Electronic charge
\( R_{\text{series}} \) Series resistance

\( R_{\text{shunt}} \) Shunt resistance

Si Silicon

UPS Ultraviolet Photoelectron Spectroscopy

VB Valence band

\( V_{\text{max}} \) Voltage at maximum power point

\( V_{\text{oc}} \) Open circuit voltage

Wp Watt peak

XPS X-ray photoelectron spectroscopy

\( \Phi_M \) Work function of metal

References


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49. N.S. Sariciftci; *Primary photoexcitations in conjugated polymers: Molecularexciton versus semiconductor band model* (World scientific, Singapore, 1997).
Chapter 2

Semiconducting organic materials and their properties
Over the years, new material research for solar cell applications has been dominated by the inorganic semiconductor materials, silicon (Si) and gallium arsenide (GaAs). They have been influenced to a lesser extent by cadmium sulphide (CdS). These materials yield highly efficient photovoltaic devices but are expensive to produce. For instance, doped single-crystal Si devices have attained power conversion efficiencies as high as 24.7%,\(^1\) while more recent refinements of GaAs solar cells have produced efficiencies up to 22%\(^2\). In the case of Si and GaAs cells, the stringent purity requirements and the complicated device fabrication techniques demand a high device cost which stands today at about $4/Wp (the solar energy industry typically uses price per Watt peak (Wp) as its primary unit of measurement-\(\text{www.solarbuzz.com/StatsCosts.htm}\) ) and cannot be produced over large areas due to restrictions in the manufacture of crystalline materials.

An alternative popular approach to solar cell material research has been the study of organic photoconductive compounds in the photovoltaic mode. These materials are potentially inexpensive and readily available, and device fabrication can be comparatively simple. But the overwhelming barrier to the successful application of such organic devices has been their low power conversion efficiencies which stood at 5%,\(^3\) but in most cases in the region of 2-4%, even under the best laboratory conditions. But recently, there has been a significant push towards efficiency enhancement which has resulted in ~7% power conversion efficiency.\(^4\)

Organic materials presently used in solar cells includes conducting polymers, dyes, pigments, and liquid crystals; thus, organic semiconductors are divided into the above four categories.
Further, organic molecules are distinguished between those that have only a few (oligomers) or no (monomers) repeat units and molecules which have more than about 10 repeat units (polymers). Oligomers and monomers that absorb visible light are often called chromophores, and are referred to as dyes if they are clearly soluble or pigments if they are not. Liquid crystalline materials exhibit a phase at certain temperatures where the molecules move like in a liquid but are still able to retain a certain structural order among the molecules as in crystalline materials. More details on the properties of the conjugated polymers will follow.

2.1 Conjugated polymers
Polymers are long chains of repeating chemical units, or monomers. They are macromolecules with a molecular weight exceeding \( \approx 10,000 \text{ gm/mol} \). Their chemical skeletal structures can be linear, cyclic or branched. Polymerization of one type of monomer gives a homopolymer, while polymerization of more than one type of monomer results into a copolymer. The distribution of monomers in the polymerization of the copolymers can be statistical, random or alternating. Some polymers have semiconducting properties due to their unique structural behaviour such as formation of alternating single and double bonds between the adjacent back-bone carbon atoms. These conducting polymers are known as \( \pi \)-conjugated polymers.

2.1.1 Semiconducting behaviour of conjugated polymers
Conjugated polymers are interesting materials as they possess both the electronic properties of metals and semiconductors with the processing advantages and mechanical properties of polymers. Following their discovery in 1977 by Heeger and co-workers, metallic conducting polymers have been demonstrated with electrical conductivity approaching that of...
Control of the electronic properties of conjugated polymers have been achieved through the modification of their fundamental molecular features, which allows for tailoring their optical properties (absorption and emission), based on specific needs. The semiconducting property of conjugated polymers originates from the overlap of the atomic orbitals formed by the valence electrons of chemically bonded C-atoms. The six electrons on a neutral carbon atom occupy the 1s, 2s and 2p orbitals with a ground state configuration as $1s^2 2s^2 2p^2 [1s(\uparrow\downarrow) 2s(\uparrow\downarrow) 2p(\uparrow\uparrow)]$. When a carbon atom forms a bond with another carbon atom, a 2s-electron is promoted to the vacant 2p-orbital resulting in an outer valence shell configuration as shown in Figure 2.1.

![Figure 2.1: The hybridization of the valence shell electrons of a carbon atom. The upper and lower panels show sp³ and sp² hybridization, respectively.](image)

These electronic orbitals hybridize by linear combination to produce a set of orbitals oriented towards the corner of a regular tetrahedron. The hybrid orbitals consisting of one $s$ orbital and three $p$ orbitals ($2s 2p_x 2p_y 2p_z$) are known as sp³ hybrid orbitals, which allow a strong degree of overlap in bond formation with another atom and produce high bond strength and stability in molecules. This arrangement gives rise to the tetrahedral structure that is found in the lattice of diamond in which available electrons are tied up in strong covalent bonds, known as copper.
σ-bonds. Carbon compounds containing σ-bonds formed from sp$^3$ hybrid orbitals are called saturated molecules, hence, their high band gaps which qualifies them as insulators.$^{16}$ In organic-conjugated polymers, the backbones consist of sp$^2$ hybridized carbons. This electron configuration results in three σ-bonding electrons, the 2s, 2p$_x$ and 2p$_y$ electrons, and a remaining 2p$_z$ electron. Two adjacent 2p$_z$ orbitals can overlap, forming a π-bond (Figure 2.2). In a conjugated polymer, the 2p$_z$ electron orbitals overlap along the backbone, giving rise to the delocalization of the π-electron system.$^8$ The π-bonds are thus considered as the basic medium of electron transport in the conjugated systems.$^{16,17}$

![Diagram of sigma and pi bonds](image)

Figure 2.2: Formation of carbon-carbon double bond

In light of the energy band description, the σ-bonds form completely filled bands, while π-bonds would correspond to a half-filled energy band. The molecular orbitals of a polymer form a continuous energy band that lies within a certain energy range. The anti-bonding orbitals located higher in energy ($\pi^*$) form a conduction band, whereas, the lower energy lying (π) bonding orbitals form the valence band, separated from the former by an energy gap known as the band gap ($E_g$) (Figure 2.3).
Figure 2.3: Energy level splitting orbitals in a conjugated polymer according to molecular orbital theory.

The two separate bands are characterized by two energy levels, namely, electron affinity and ionization potential. The electron affinity of a semiconducting polymer corresponds to the lowest state of the conduction band (π* state) or the lowest unoccupied molecular orbital (LUMO). On the other hand, the ionization potential corresponds to the upper state of the valence band (π state) and corresponds to the highest occupied molecular orbital (HOMO). The band gap of conjugated polymers is within the semiconducting range of 1 to 4eV.¹⁶
2.1.2 Comparing organic and inorganic semiconductors
As outlined by Nelson,\(^1\) organic photovoltaic materials differ from inorganic semiconductors in the following important aspects.

For organic materials:

- Photogenerated excitations ('excitons') are strongly bound by Coulombic interactions and do not dissociate spontaneously into charge pairs. (Dissociation requires \(~100\text{meV}\) compared to a few \(\text{meV}\) for a crystalline semiconductor.) This implies that absorption of light does not necessarily lead to carrier generation.

- Charge transport proceeds by hopping (some kind of transfer) between localised states, rather than transport within a band, thus, the mobilities are low.

\(^1\) Nelson, 18
• The spectral range of optical absorption is relatively narrow compared to the solar spectrum.

• Absorption coefficients are high (~10^7 cm\(^{-1}\)) so that high optical densities can be achieved at peak wavelengths with films less than 100nm thick.

• Many organic materials are susceptible to degradation in the presence of oxygen or water.

• As one-dimensional semiconductors, their electronic and optical properties can be highly anisotropic. This is potentially useful for device design.\(^1\)

The first two features are due to the fact that the intermolecular van der Waal forces in organic solids are weak, compared to bonds in inorganic crystals and much weaker than the intra-molecular bonds. Consequently, all electronic states are localised on single molecules and do not form bands. Low mobility is worsened by the high degree of disorder present in many organic solids. The optical excitations accessible to visible photons are usually \(\pi \to \pi^*\) transitions. Most conjugated solids absorb in the blue or green, thus, absorption in the red or infrared is harder to achieve.

These properties therefore impose some constraints on the design of organic photovoltaic devices;\(^1\)

• A strong driving force such as an electric field needs to be present to break up the photogenerated excitons.

• Low charge carrier mobilities limit the useful thickness of devices.

• Limited light absorption across the solar spectrum limits the photocurrent.

• Very thin devices mean interference effects can be important.

• Photocurrent is sensitive to temperature through hopping transport.
2.1.3 **PEDOT:PSS [Poly (3,4- ethylene dioxythiophene)-poly(styrene sulfonate)]**

One of the best known π-conjugated polymers is poly (3,4- ethylene dioxythiophene) (PEDOT) because of its excellent electrical conductivity and electro optical properties. Besides its high electrical conductivity (highly doped-550 S/cm\textsuperscript{19,20}) and metallic behaviour,\textsuperscript{19,21-26} PEDOT maintains moderate transparency and high stability in thin oxidized films,\textsuperscript{27-31} although it is insoluble. It became soluble when ‘doped’ with poly (4-styrene sulfonate) or PSS to form poly (3, 4- ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS), Figure 2.5. The PEDOT:PSS exhibits good film-forming properties, high electrical properties (10 S/cm), high transmission of visible light, and excellent stability.\textsuperscript{20,32-34}

PEDOT:PSS finds application in various fields, one of which is organic-based optoelectronics. It has been used as a buffer layer, sandwiched between indium tin oxide (ITO) and an active organic layer, in organic light-emitting devices (OLEDs)\textsuperscript{35-42} and photovoltaic cells.\textsuperscript{43-46}

![Figure 2.5: Chemical structure of poly (3, 4- ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS).](image)

Peumans et al\textsuperscript{47} found that the introduction of PEDOT:PSS improves the fabrication yield of OPVs to nearly 100% and if plasma treated, leads to further improvement in the device
parameters which will be discussed the proceeding chapter. However, it was reported elsewhere\textsuperscript{48} that PEDOT:PSS causes an increase in the series resistance of the solar cell, which results in a poor performance in one of the key device parameters. As speculated by Sun et al.,\textsuperscript{49} the contradictions between different research on the influence of PEDOT:PSS on the solar cell performance may be due to the fact that the device performance is dependent on the PEDOT:PSS thickness,\textsuperscript{50} and that PEDOT:PSS properties are dependent on the thermal treatments.\textsuperscript{51} These stem from the fact that very thin layers of PEDOT:PSS yield more pin holes, while thicker layers causing larger increase in the series resistance, with the conductivity and roughness of PEDOT:PSS films dependent on the annealing temperature and atmosphere\textsuperscript{51}. This work also aims to look at the effects of patterning a thin layer of PEDOT:PSS on its surface chemistry and electrical conductivity as it affects the general performance of organic solar cell when used as an interfacial layer between ITO and the active layer.

\subsection*{2.1.4 Models for electrical conductivity in conducting polymers}

In conducting polymers, carriers are spatially localized and cannot participate in transport except through hopping which is possibly due to nanoscale disorder in its structure.\textsuperscript{8,52-54} This demands for a model applicable to systems with strong disorder such that the disorder energy is much greater than its bandwidth. An appropriate model for conductivity, $\sigma$ is the Mott variable range hopping (VRH) model which has a general form described as

$$
\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^\frac{1}{(d+1)} \right]
$$

(2.1)

Where $T_0$ is defined as

$$
T_0 = \frac{c}{(k_B N (E_F))^L} \quad \text{(2.2)}
$$
The parameters in equation (2.1) and equation (2.2) are defined as follows: d is the dimensionality of the system, c is a proportionality constant, $k_B$ is the Boltzmann constant, L is the one dimensional localization length, T is the temperature, $\sigma_0$ is a weakly-temperature dependent prefactor and $N(E_F)$ is the density of states at the Fermi level.

Using $d=1$ in equation (2.1) corresponds to the behaviour of quasi-one-dimensional variable range hopping (Q1D-VRH), where the charge carriers primarily hop along a ‘one dimensional’ chain and occasionally hop to a nearest-neighbour chain to avoid energetically large barriers such that;

$$\sigma^{1D} = \sigma_0^{1D} \exp \left[ - \left( \frac{T_0^{1D}}{T} \right)^{\frac{1}{2}} \right] \quad \text{..........................(2.3)}$$

And

$$T_0^{1D} = \frac{16}{(k_B N(E_F) L_Z)} \quad \text{..........................(2.4)}$$

Here, L is the one-dimensional localization length and $Z$, the number of nearest neighbour chains. Other parameters are as defined above. If the one-dimensional chain is isolated, then equation (2.1) does not apply, and the temperature dependence of the conductivity is thermally activated reflecting the energy $\Delta E_B$ for excitation over the largest barrier encountered during charge transport along the chain,

$$\sigma^{1D} = \sigma_0^{1D} \exp \left[ - \frac{\Delta E_B}{T} \right] \quad \text{..........................(2.5)}$$
2.2 Photo-physics of Conducting Polymers

Conducting polymers are basically quasi-one-dimensional semiconductors with gaps typically such that in undoped material, the absorption edge is in the visible or near infrared.

Upon illumination of a polymer sample with light at higher energy than the absorption edge, excitation of a variety of entities or "particles" can result, without a clear distinction on which entity is a primary or secondary excitation. Some of these possibilities are described below.

2.2.1 Excited States of a Molecule

The energy states of molecules correspond to electronic, vibrational, rotational, and translational degrees of freedom. The dominant energy transitions are electronic with energy spacing of a few eV (designated by bold $S_n$ or $T_n$ in the Jablonski diagram in Figure 2.7).

![Jablonski diagram showing the radiative and non-radiative decay of an excited organic molecule. The straight-line arrows represent radiative processes, and wavy-line arrows non-radiative processes. The orientations of the electron spins are shown in the boxes next to each state.](jablonski_diagram.png)

Each electronic level corresponds to a vibrational manifold with typical sub-level spacing on the order of $\sim 0.1$ eV, and each vibrational sub-level corresponds to a manifold of rotational
and translational molecular energies with $\sim 0.01$ eV inter-level spacing. The Jablonski diagram indicates vibrational sub-levels by light horizontal lines. Each electronic state corresponds to a bonding or anti-bonding molecular orbitals. The orbital associated with a carbon-carbon bond can be either $\sigma$ or $\pi$ type, where in a $\sigma$-bond electrons are localized between the carbon atoms, while the $\pi$-bond establishes delocalized electron density above and below the atomic plane. Corresponding anti-bonding orbitals are $\sigma^*$ and $\pi^*$ and are of higher energy. There also exist molecular orbitals designated as $\pi$, whose valence-shell electrons do not participate in the formation of molecular bonds.

Absorption of a photon can promote an electron from its $\sigma$, $\pi$, or $\pi$ ground state to an $\sigma^*$ or $\pi^*$ excited state. Such electronically excited states of a molecule contain two unpaired electrons in different orbitals, giving rise to singlet ($S_0$) states (because the electron and hole are created with opposite spin) or triplet ($T_0$) states (where the spins of the two electrons are parallel, as such, a transition to the ground state, with the emission of a photon, involves a change of spin), respectively.

According to Farchioni et al., the ground state of all organic molecules is a singlet, because the lowest energy state molecular orbitals are almost always filled with paired electrons. By considering the spatial distribution of the lowest energy electron orbital $\Phi_0$ and the excited state orbital $\Phi_1$, the orbital overlap must be non-negligible in order to promote an electron from $\Phi_0$ to $\Phi_1$. The exclusion principle demands that two electrons with parallel spins cannot occupy the same eigen-state. Since there are no such restrictions on electrons with antiparallel spins, these can be found on average closer together. Thus, the average Coulombic repulsive energy is larger in the singlet than in the triplet state, so the triplet state is typically at a lower energy than the corresponding singlet state.
2.2.2 Electronic Transitions between Energy States of a Singlet Molecule
An electron can be promoted to an excited state by absorbing photons, by electrostatic interactions between neighbouring molecules, or by electrical injection (which may place the electron in an anti-bonding state). The electron in the excited state tends towards the ground state by losing energy via both radiative and non-radiative processes. Figure 2.7 shows various dissipative pathways which compete for the energy of the excited state where individual contributions are determined by the relative magnitudes of their rate constants.8

2.2.2.1 Radiative Transitions
The two radiative processes are fluorescence and phosphorescence. Fluorescence is a rapid radiative process (with a typical rate constant of $K_f \sim 10^6$ to $10^9$ S$^{-1}$) in which the spin multiplicities of the initial and the final states are the same. Typically in organic molecules, this corresponds to $S_i \rightarrow S_0$, and occasionally $T_n \rightarrow T_m$ transitions (where $n > m \geq 1$).

Phosphorescence is a result of radiative transition between states of different multiplicity, typically $T_i \rightarrow S_0$. According to Barltrop et al.55 this process is spin forbidden and has a much smaller rate constant ($K_p \sim 10^{-2}$ to $10^6$ S$^{-1}$) than that of fluorescence. In reality, $S \rightarrow T$ and $T \rightarrow S$ transitions may often occur due to spin-orbit coupling (i.e. any interaction of a particle’s spin with its motion. This causes a shift in an electron’s atomic energy level). Even so, the $S_0 \rightarrow T_i$ transitions are, in general, not observed in absorption.8

2.2.2.2 Non-radiative Transitions
An electron can transfer from one state to the other without changing the total energy of the system with no photon emission if vibrational manifolds of two different electronic states on the same molecule overlap in energy. Isoenergetic levels having the same spin multiplicities
give rise to the process known as internal conversion, while electron transfer between states of different multiplicities is called intersystem crossing (Figure 2.7).

An excited molecule can also transfer its energy non-radiatively to a neighbouring molecule via dipole-dipole interactions or electron exchange, known as Förster and Dexter transfer, respectively.

2.2.2.3 Franck-Condon Shift

Absorption of a photon of energy $E_A$ can promote an electron from $S_0$ to $S_I$. The excited molecule is confined between classical turning points $a^*_2$ and $c^*_2$, and may emit phonons to relax to sublevel $a^*_0 - c^*_0$ (Figure 2.8). Electron transfers exothermically from $S_I$ back to $S_0$, releasing a photon of energy $E_B$. Finally, the molecule can relax to its lowest sublevel $a^*_0 - c^*_0$ by further emission of phonons. The rate of non-radiative phonon emission is much larger than the radiative transition rate. Thus, radiative transitions are most likely to occur from the lowest vibrational level of an electronic state. This principle is known as Kasha's rule.

The energy of the emitted photon $E_B$ is lower than the energy of the absorbed photon $E_A$. The energy difference resulting from an energetic red-shift or “Stokes shift” (due to the nuclear displacement $\Delta r$) is called the Frank-Condon energy. Virtually all molecular organic compounds exhibit a Frank-Condon shift, which in some cases is as large as 0.5 eV.
2.2.3 Excitons

When a polymer absorbs a photon, an electron gets excited from the HOMO level to the LUMO level with a resultant positive charged hole left behind. This electron-hole pair which remains on the same chain bound to each other by their electrostatic attraction and to a lesser extent, by the (relatively small) chain deformation or relaxation they cause, is called an exciton. In solids with strong intermolecular interactions an exciton can be delocalized over a number of molecules and can be identified depending on the degree of delocalization as Frenkel, charge-transfer, or Wannier-Mott.8,56

2.2.3.1 Frenkel excitons

The Frenkel exciton (Figure 2.9 a) corresponds to a correlated electron-hole pair localized on a single molecule with a radius comparable to the size of the molecule (typically < 0.5 nm) or is smaller than the intermolecular distance, thus, having a strong Coulombic interaction. It is...
considered a neutral particle that can diffuse from site to site, perhaps moving hundreds of molecules away from its origin.\textsuperscript{8,57}

### 2.2.3.2 Wannier-Mott Excitons

Wannier-Mott (WM) excitons (Figure 2.9b) occur in uncorrelated, crystalline materials (e.g. Si, Ge, GaAs and InP), in which overlap between neighbouring lattice atoms reduces the Coulombic interaction between the electron and the hole of the exciton, resulting in a large exciton radius (40 ~ 100 Å), many times the size of the lattice constant. These excitons are not found in van-der-Waals bonded molecular organic solids.\textsuperscript{8}

![Figure 2.8: Schematic of a (a) Frenkel exciton showing the energy level diagram of discrete molecular states and (b) Wannier-Mott exciton with the corresponding semiconductor band diagram.\textsuperscript{8}]

(a) Frenkel Exciton

(b) Wannier Exciton
2.2A Electronic Energy Transfer

During energy transfer between molecules, an excited donor molecule, D*, transfers its energy to an acceptor, A, thereby promoting it to an excited state:

\[ D^* + A \rightarrow D + A^* \]  \hspace{1cm} (2.6)

If the donor and acceptor are the same species, the transfer is referred to as energy migration.

The energy transfer can be due to electrostatic (Coulombic or Förster) or electron-exchange (or Dexter) interactions.\(^8\)

2.2.4.1 Förster Energy Transfer

Förster energy transfer is a dipole-dipole interaction between the donor and acceptor molecules. The rate of energy transfer depends on the distance \( R \) between the donor and the acceptor molecules, given by:\(^55-56,58\)

\[
K_{ET}(R) = \left( \frac{1}{\tau} \right) \left( \frac{R_0}{R} \right)^6 
\]  \hspace{1cm} (2.7)

Where \( R_0 \), the Förster radius is defined by the integral over all energies \( h\nu \),

\[
R_0^6 = 1.25 \times 10^{-17} \frac{\phi_E}{n^4} \int F_D(\nu) \alpha_A(\nu) \frac{d\nu}{\nu^4} 
\]  \hspace{1cm} (2.8)

Here, \( \tau \) is the average donor exciton lifetime for recombination in the absence of energy transfer, corresponding to the rate

\[
K_D = \frac{1}{\tau} 
\]  \hspace{1cm} (2.9)

(when \( R=R_0 \) then \( K_{ET}=K_D \), and the probability that an exciton will recombine at the donor is equal to its transfer probability), \( \hbar \) is Planck’s constant, \( \nu \) is the photon frequency, \( \phi_E \) is the quantum efficiency of donor emission, \( n \) is the refractive index of the host, \( F_D \) is the normalized emission spectrum of the donor, and \( \alpha_A \) is the molar extinction coefficient (absorption spectrum) of the acceptor.
The Förster distance can be up to 10 nm due to phonon broadened emission and absorption spectra typical of organic molecular species.

The spin of both D and A is conserved in Förster energy transfer so that the allowed transitions are

\[ 1D^* + 1A \rightarrow 1D + 1A^* \] \hspace{1cm} (2.10 a)

and

\[ 1D^* + 3A(T_n) \rightarrow 1D + 3A^* (T_m) \] \hspace{1cm} (2.10 b)

Where \( 1D^* \) is donor excited singlet state, \( 1D \) is donor ground singlet state, \( 1A^* \) is the acceptor excited singlet state, \( 1A \) is acceptor ground singlet state and \( 3A^* \) is acceptor excited triplet state. The triplet-singlet transition

\[ 3D^* + 1A \rightarrow 1D + 1A^* \] \hspace{1cm} (2.10 c)

is forbidden since D and A do not have spin conservation.\(^5,55\)

2.2.4.2 Dexter Energy Transfer

Dexter energy transfer is a short-range triplet-to-triplet transfer mechanism between organic molecules. The Dexter process does not require allowed transitions on both donor and acceptor molecules, but, given sufficient molecular overlap, an exciton could diffusively hop from one molecule to the next with no change in spin.\(^8,59\)

The transfer probability from the donor to the acceptor may be expressed as a function of energy as:\(^58\)

\[ P_{da} = \frac{2\pi}{\hbar} Z^2 \int f_d(E) F_a(E) dE \] \hspace{1cm} (2.11)

Where, \( f_d \) is the normalized emission spectrum of the donor and \( F_a \) is the normalized absorption spectrum of the acceptor. \( Z \) is determined by the molecular overlap expressed as

\[ Z^2 \propto \exp \left( -\frac{2R}{L} \right) \] \hspace{1cm} (2.12)
Where $R$ is the intermolecular spacing between $D^*$ and $A$, and $L$ is the effective average Bohr radius. From equations (2.11) and (2.12), $Z^2$ and $P_{da}$ are rapidly decreasing functions of intermolecular separation, thus, Dexter transport occurs only over a short distance of $\sim 1$ nm, and is effectively restricted to neighbouring molecules.

Another model depicts Dexter transport as a simultaneous transfer of an electron and a hole between $D^*$ and $A$, in which case, the mobility of a triplet exciton is expressed as

$$K_{ET} \propto K_e K_h$$

(2.13)

Where $K_e$ and $K_h$ are the electron and hole transfer rates from the donor to the acceptor.

In the Dexter transfer process, only the total spin of the $D^*A$ system is conserved, such that, the forbidden triplet-triplet energy transfer in Förster approximation, is allowed:

$$3D^* + 1A \rightarrow 1D + 3A^*$$

(2.14)

References


Chapter 3

Physics of photovoltaic devices
The radiation emitted by the sun spans wavelengths covering the ultraviolet, visible and the infrared sections of the electromagnetic spectrum. The energy of the sun corresponds to the radiation emitted by a black body at 5760K with a power density of 62MWM⁻², but the solar power density adjacent to the Earth’s atmosphere is reduced to 1353WM⁻² on account of the reduced angular range of the sun. To quantify the atmospheric attenuation, the quantity ‘Air Mass’ factor, \( \eta_{\text{Air Mass}} \) is used and is defined as:

\[
\eta_{\text{Air mass}} = \frac{\text{Optical path length to the sun}}{\text{Optical path length if the sun is directly overhead}} \tag{3.1}
\]

\[
\eta_{\text{Air mass}} = \text{Cosec} \gamma_s \tag{3.2}
\]

where \( \gamma_s \) is the angle of elevation of the sun. The sun’s radiation corresponds to a solar spectrum emitted outside the atmosphere, defined as AM 0 spectrum, which is relevant for satellite and space applications. The AM 1 spectrum, represents the sunlight at the Earth’s surface when the sun is overhead. The actual power reaching the surface of the Earth is approximately 1000 Wm⁻² due to attenuation by the atmosphere¹ (Figure 3.1 shows the spectral irradiance at sea level on a sunny day). This atmospheric attenuation is attributed on one part to the scattering by the molecules (Rayleigh scattering), and by the aerosols and dust particles, and on the other part by the absorption of radiation due to CO₂, H₂O and ozone O₃ (ultraviolet absorption) found in the atmosphere.

However, for convenience of device characterisation, the standard terrestrial solar spectrum is defined as the Air Mass 1.5 (or AM 1.5) spectrum normalized so that the integrated
irradiance is 1000 W/m². This was standardized by both the International Organization of
Standardization (ISO 9845-1:1992) and the American Society for Testing and Materials

Figure 3.1: Extra-terrestrial (Air Mass 0) solar spectrum compared with Standard terrestrial
(Air Mass 1.5) spectrum at sea level on a sunny day.

An important requirement for a solar cell to achieve high photoconversion efficiency is that
the absorption spectrum of the photoactive material must match the solar emission spectrum.
The absorption peaks and the spectral range of the organic materials used in this work will be
shown in Section 3.3.

3.1 Working Principle
When light is incident on polymer solar cells, photons having energy \( E = h \nu \) excites an
electron from the valence band (HOMO) of either the donor or the acceptor creating mobile
excitons (an electron-hole pair). Due to low exciton diffusion lengths (5 to 20 nm) of most
conjugated polymers\(^\text{2,3}\), most of the excitons recombine within the active layer. To extract
current from the OPVs, excitons need to dissociate into free charge carriers through the
electric field, bulk trap sites or interface of materials with different electron affinities. The electric field in a solar cell in its working range is quite low and does not lead to effective exciton dissociation. Several approaches have been adopted to achieve effective exciton dissociation\(^4^{-7}\) of which the bulk heterojunction (BHJ) consisting of blends of electron donor polymer and electron acceptor molecules offer one of the best options.

![Diagram of a BHJ based solar cell](image)

**Figure 3.2:** (a) Device structure of a BHJ based solar cell and (b) Energy diagram.

The polymer BHJ comprises of two materials with \(\Delta E\) off-set between the constituent valence and conduction bands. In molecular terms, this is the energy difference between the HOMO or LUMO levels of the two components\(^8\) (Figure 3.2b). If \(\Delta E\) is large compared to the exciton binding energy \(\varepsilon_B\) (for typical organic polymers, \(\varepsilon_B \approx 0.5\text{eV}\)), the photoexcited state decays to an interfacial charge-separation state.\(^9^{-11}\) This situation is desirable for photovoltaic systems where \(\Delta E\) provides the driving force for charge separation upon photoexcitation.\(^8\)

Specifically, when an exciton approaches the interface between two conjugated polymers, either energy or charge transfer can take place. And the difference in band-gap energy \(\Delta E\) between the two materials is a critical parameter governing charge versus energy transfer at the interface. As reported by Hall et al.,\(^12\) a large difference favours energy transfer towards the low band-gap partner, while a small band-gap difference opens the way for charge
transfer. It was further emphasized that the simple approach of relative positions of the HOMO and LUMO levels of the two partners is inappropriate to determine which type of transfer process can occur. It is worth mentioning that there are other competitive processes which may occur simultaneously with the charge carrier transfer. Such processes may be radiative (photoluminescence) or non-radiative (intersystem crossing) recombination. However, the charge transfer time from donor to acceptor is found to be around 50 fs\textsuperscript{13}, implying a quick process compared to other recombination processes which occur in microseconds\textsuperscript{14} time interval, and is considered to be close to 100% efficient.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.3.png}
\caption{The simplified four basic steps of photocurrent generation in BHJ based solar cells.}
\end{figure}

The photogenerated free carriers then migrate to and are collected at the electrodes consisting of a high work function metal anode (which collects holes) and a low work function metal cathode (which collects electrons). Thus, the photovoltaic process involves four basic steps,
viz: exciton creation, exciton migration, exciton dissociation and free charge transfer to the electrodes (Figure 3.3).

3.2 Photovoltaic Characterisation

3.2.1 Equivalent Circuit Diagram
The operating principle of inorganic solar cells may be represented by the equivalent circuit in Figure 3.4. Although the physical processes in the organic solar cells are different from the inorganic counterpart, the loss mechanisms are similar.

In electrical terms, the solar cell is equivalent to a constant current source in parallel with an asymmetric, non-linear resistive element (i.e. a diode) as shown in Figure 3.4. Under illumination, the ideal cell produces a photocurrent proportional to the light intensity, and is divided between the variable resistance of the diode and the load.

The photocurrent ($I_{ph}$) going through the load sets up a voltage across the diode, and generates a reverse current through it, known as the “dark current” ($I_{dk}$).

![Figure 3.4: Equivalent circuit of an ideal solar cell. ($I_{ph}$ is the photogenerated current, $I_{dk}$ is the current going through the diode, $V$ is the voltage across the load and $I$ is the load current).](image)

For an ideal diode, the dark current follows the Shockley relation as

$$I_{dk} = I_s(e^{\frac{qV}{kT}} - 1) \quad \text{.................................................. (3.1)}$$
where $I_s$ is the reverse saturation current of the diode, $k_B$ is Boltzmann’s constant and $T$ is temperature in degrees Kelvin. The photocurrent is taken as positive as a sign convention\(^1\).

The *current-voltage characteristic*, i.e., the overall current voltage response of the cell, is approximated as the sum of the short circuit photocurrent and the dark current. Thus,

$$I = I_{dk} - I_{ph} \quad \text{................................. (3.2)}$$

$$I = I_s \left( e^{\frac{qV}{k_B T}} - 1 \right) - I_{ph} \quad \text{................................. (3.3)}$$

For $I=0$, whereby the contacts are isolated giving the potential difference its maximum value, i.e., the open-circuit condition,

$$V_{oc} = \frac{k_B T}{q} \ln \left( \frac{I_{ph}}{I_s} + 1 \right) \quad \text{................................. (3.4)}$$

This is equivalent to a condition when the dark current and short circuit photocurrent exactly cancel out.

And for $V=0$, the short-circuit condition is,

$$I_{sc} = -I_{ph} \quad \text{................................. (3.5)}$$

In practice, no solar cell is ideal due to parasitic effects of shunt and series resistances on the device characterisation (Figure 3.4).

The shunt resistance $R_{sh}$ arises from the recombination processes near the dissociation sites and at the interface with the metal electrodes. The circuit of Figure 3.4 includes an additional parallel resistance to simulate the shorts due to pinholes. At small voltages the ideal diode does not conduct, thus, from Kirchoff’s law, the outer current controlled by the sum of the series and parallel resistances.

$$R_s + R_{sh} = \frac{V}{I_{I=0}} \quad \text{................................. (3.6)}$$

The series resistance comprises the resistance of the bulk material and resistance from the interface of organic material/metallic electrode. The conductivity of the charge carriers is
influenced by the thickness of the organic layer, and by the trap density. Thus, at high
voltages the conduction is determined to a large extent by the series resistance.

\[ R_s = \frac{V}{I|_{I \to \infty}} \]  \hspace{2cm} (3.7)

Optimum device performance requires a low \( R_{\text{series}} \) and a large \( R_{\text{shunt}} \). Taking into account
these parasitic resistances, the overall current of the cell is given as;

\[ I = I_s \left( e^{\frac{q(V-1R_s)}{k_BT}} - 1 \right) + I_{sh} - I_{ph} \]  \hspace{2cm} (3.8)

\[ I = I_s \left( e^{\frac{q(V-1R_s)}{k_BT}} - 1 \right) + \left( \frac{V-1R_s}{R_{sh}} \right) - I_{ph} \]  \hspace{2cm} (3.9)

Organic solar cells are more sensitive to the influence of these resistances and distortions of
the \( I-V \) curve are more pronounced when \( R_s \) and \( R_{sh} \) values are comparable.
The fill factor of the device is dependent on the shape of the \( J-V \) characteristic curve which is
defined by the \( R_s \) and \( R_{sh} \) parameters. The fill factor increases with decreasing series
resistance and increasing shunt resistance. Thus, for an efficient cell one would want the \( R_s \) to
be as small and \( R_{sh} \) to be as large as possible.

### 3.2.2 Current-Voltage Characteristics

Generally, polymer/acceptor bulk heterojunction solar cells are characterized by the short-
circuit current density \( (J_{sc}) \), the open-circuit voltage \( (V_{oc}) \), the fill factor \( (FF) \), and overall
power conversion efficiency \( (\eta) \). A typical current-voltage characteristic measured in the
dark and under white light illumination conditions are depicted in Figure 3.5 and each of the
characterisation parameters is briefly described below. The Metal-Insulator-Metal (MIM)
model is useful in understanding the rectifying behaviour of most organic devices.\(^{15}\) For
convenience the organic device is assumed to be a tunnel diode in which the depletion region
extends throughout the organic layer. The insets in Figure 3.5 illustrate the field distributions
in a tunnel diode under various bias conditions (illustrated for a single organic layer device).
The HOMO and LUMO lines indicate the top of the valence band and bottom of the conduction band respectively. The metals are represented by their Fermi levels. Inset $a$ illustrates the diode in short-circuit condition where there is no voltage applied, hence, there is no net current flowing in the dark, and the built-in electric field results from the difference in the work functions. Under illumination, separated charge carriers can drift in the electric field to the respective contacts: electrons to the lower (aluminium) and holes to the higher (ITO) work function metal. Thus, the device works as a solar cell.

![Figure 3.5: Current-Voltage response of a typical photovoltaic device under illumination.](image)

By applying a reverse bias (with the ITO contact held negative relative to the Al; inset $b$) the internal field increases in magnitude and in many cases this enhances the quantum efficiency of photoconductivity, allowing the cell to be used as an effective photodiode. With a high impedance load the flow of electrons and holes to opposite contacts allows a potential difference to develop across the cell, approaching the work function difference as the light intensity increases.
intensity increases. This describes the open-circuit voltage under which condition the bands are approximately flat: shown in inset c. Finally, if a forward-bias larger than the open-circuit voltage is applied (inset d), the contacts can effectively inject charges into the polymer layer. If these can recombine radiatively, the device works as a light-emitting diode (LED).\textsuperscript{16,17}

In Figure 3.5, under dark condition, no current flows until the contacts start to inject heavily at forward-bias at voltages larger than the open-circuit voltage. Under illumination, the current flows in the opposite direction to the injected currents. $J_{sc}$ indicates that the generated photocurrent flows under short-circuit conditions; $V_{oc}$ indicates that the photogenerated current is balanced to zero (flat band condition). In the fourth quadrant, the device generates power. At some point ($V_{max}$,$J_{max}$), denoted as the maximum power point, the product between current and voltage and hence the power output is largest. This power is compared with the incident light intensity to determine the efficiency of a solar cell.\textsuperscript{17}

Classical p/n junctions require doped semiconductors with free charge carriers to form the electric field in the depleted region, but a bilayer heterojunction (shown in Figure 3.6, neglecting all kinds of possible band bending due to energy level alignments) formed between undoped donor and acceptor materials is due to the differences in the ionization potential or electron affinity of the adjacent materials.

\textbf{Figure 3.6: Schematic of a bilayer heterojunction device.}

In one polarity of the device the hole injection to the HOMO of the donor layer from a high work function electrode and the electron injection into the LUMO level of the acceptor from

\[\text{ITO} \quad \text{D} \quad \text{Al} \quad \quad \quad \quad \text{A} \quad \text{ITO}\]
the low work function electrode are both easily possible and the device carries a large injection currents (forward-bias). In the opposite polarity of the device, the electron injection to the donor LUMO level from a high work function electrode and the hole injection to the acceptor HOMO level from a low work function electrode are energetically heavily unfavoured and strong barriers hinder the charge injection in both materials. Thus, the device is in reverse bias.\(^ {17}\)

**The short-circuit current density \( (J_{sc}) \)**

This is the photogenerated current per unit area of a solar cell under zero bias (i.e. at zero applied voltage), and is directly related to optical and electrical properties of the material. Thus, exciton dissociation and charge transport is driven by the so-called built-in potential. Figure 3.5 depicts that, for an applied voltage less than \( V_{oc} \), the \( J-V \) characteristics under illumination condition is by a photogenerated current. It is worth mentioning that the real \( J-V \) curve of an organic solar cell is far from being an ideal Shockley type and is characterized by three operating regimes. At higher positive voltages, a space charge region is formed and the \( J-V \) characteristics undergo a transition from a Shockley type diode behaviour to a dependence proportional to the second power of the voltage. (Mott & Guerney's law):

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \Theta \mu \frac{V^2}{d^2} \]

where \( \Theta \) is the trap density, \( \mu \) represents the mobility, \( \varepsilon_r \) represents the relative permittivity of the organic material, \( d \) is the thickness of the active layer.

**The open-circuit voltage \( (V_{oc}) \)**

The open-circuit voltage of a solar cell under illumination is the voltage at which the net current in the cell is equal to zero (see equation 3.4). For an ideal device, the current measured in the dark and under illumination conditions coincide for applied voltages, exceeding the \( V_{oc} \). This describes a flat band condition where the applied voltage often approaches the difference in the work functions of the electrodes.\(^ {18}\) This is in contrast to
many inorganic cells, in which the presence of dangling bonds and other surface defects causes pinning of the bands at the interface, reducing the open-circuit voltage.

**The fill factor (FF)**
The fill factor is a measure of the power that can be extracted from the cell and is defined as the ratio

\[ FF = \frac{J_{\text{max}} V_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}} \]  

(3.11)

and it describes the 'squareness' of the J-V curve. The quantity \( J_{\text{max}} V_{\text{max}} \) represents the maximum power that can be extracted from the cell (defined by the area of the filled rectangle in Figure 3.5. The fill factor is limited by the carrier drift length,\(^ {19} \) defined as (carrier mobility)x(carrier recombination lifetime)x(electric field). Thus, increasing the \( FF \) means increase in carrier mobility of the active layer for fixed thickness.

**The power conversion efficiency (\( \eta \))**
This is the ultimate measure of the device efficiency in converting photons to electrons and is mathematically defined as the ratio of the output power to the incident power, \( P_{\text{in}} \)

\[ \eta = \frac{J_{\text{max}} V_{\text{max}}}{P_{\text{in}}} \]  

(3.12)

Substituting equation 3.11 into equation 3.12 and taking the incident optical power as 100mWcm\(^2\), then \( \eta \) becomes

\[ \eta = \left( \frac{J_{\text{max}} V_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}} \right) \frac{J_{\text{sc}} V_{\text{oc}}}{P_{\text{in}}} \]  

(3.13)

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

(3.14)

Another important way to characterize organic photovoltaics and optimize their performance is by its spectral response. The short-circuit current generated at every wavelength defines the spectral response \( S_i \) of the solar cell, given as

\[ S_i = \frac{J_{\text{sc}i}}{P_{\text{in},i}} \]  

(3.15)
where $J_{sc,i}$ is the photogenerated short-circuit current at a specific excitation wavelength $\lambda_i$ and $P_{in,i}$ is the incident monochromatic photon flux. Relating $S_i$ to the external quantum efficiency (defined as the number of electrons generated per incident photon), we have:

$$EQE = \frac{n_e}{n_{ph}}$$ .................................................. (3.16)

$$EQE = \frac{J_{sc,i}}{P_{in,i}} \times \frac{hc}{\lambda e}$$ .................................................. (3.17)

Where $h$ is Planck's constant, $c$ is speed of light, $e$ is the elementary charge, $n_e$ is the number of electrons, and $n_{ph}$ is the number of photons. EQE is also referred to as incident photon conversion efficiency (IPCE).

### 3.3 Light Trapping in Patterned Devices

The optical absorption of the organic materials (P3HT and PCBM) used in this project cover only the visible spectrum, less than 700 nm, whereas, substantial solar energy is located in the red and infrared region of the normalized solar spectrum (Figure 3.8)
Although conjugated polymers have strong optical absorption, even at maximum absorption, the penetration depth of light into these materials is in the range of 10-100 nm\textsuperscript{20}, coupled with short exciton diffusion length, typically in the range of 5-20 nm\textsuperscript{2,3,18,21-24}. The efficiency is limited in this case by the small absorbance of the two components in the range of the solar spectrum combined with the necessity of small film thickness of the absorbing layer (<200 nm) which is determined by the restricted mobility of the charge carriers. Thus, a significant part of the light cannot be absorbed.

To circumvent the above limitations on the efficiency while keeping the geometrical length (i.e. the cell thickness) minimal, it becomes necessary to resort to “light trapping” schemes by diffraction into guided modes in the thin polymer films. Such techniques would allow for an increase in surface area, interfacial absorption as well as effectively increasing the optical path length through multiple internal reflections at the top and bottom of the cell. This approach has already been used to enhance light trapping and absorption in silicon solar cells\textsuperscript{25}, particularly in the energy range where optical absorption in silicon is low, thus
increasing the power conversion efficiency. Similar approaches are being used in this project to trap light into the thin polymer films.

Enhancing the absorption by an appropriate light-trapping scheme such as regular patterns would result in an increased short circuit current density $J_{SC}$. This implies that the cells could be made with a thinner photoactive layer and would still provide the same $J_{SC}$. In such a configuration, the advantage is a lower bulk recombination that will lead to a higher open circuit voltage $V_{OC}$. Any increase in either $J_{SC}$ or $V_{OC}$ will ultimately enhance the power conversion efficiency $\eta$ of the solar cell.

The term "light-trapping" is used to refer to the redistribution of the incoming light into new directions within the solar cell. Ideally, total internal reflection will then prevent this redirected light from escaping from the solar cell. One of such schemes achieved for inorganic solar cell is the so called Lambertian light distribution coupled with a perfect back reflector. The Lambertian light distribution is achieved by incorporating an appropriately structured surface, whose nature can be either statistical (rough surfaces) or deterministic (periodic arrangements). Light-trapping is usually measured in terms of the path length enhancement $k$. The combination of the back side reflector and the Lambertian light distribution has led to an effective path length enhancement of

$$k = 4n^2$$ ..................................................... (3.18)

Where $n$ is the refractive index of the solar cell material. For a standard semiconductor solar cell ($n=3.5$) $k \approx 50$ may be achieved. An absorption enhancement can also be obtained by applying other photonic concepts, such as periodically structured back reflectors, which are optimized to increase the optical path length for wavelengths around the band gap of the absorbing layer.

In this research, instead of using a special material as the Lambertian scatterer, the surface of the PEDOT:PSS interlayer between the active material and the ITO anode will be modified to
achieve the same scattering effect through geometrical schemes. The idea is that light, incident normally to the glass substrate, will enter the photoactive layer obliquely at the PEDOT:PSS/active layer interface (Figure 3.9).

![Figure 3.9: Schematics showing light-trapping using patterned PEDOT:PSS as geometrical light scheme.](image)

Borrowing from the literature presented by Campbell et al\textsuperscript{33} the aim in a geometrical light scheme is to redistribute the direction of light internally within the photoactive layer. This can be achieved using the periodic patterns and smaller features on the regular patterns as the Lambertian scatterer to redistribute light in all directions within the device as shown in Figure 3.9. Thus, light of wavelength less than the dimensions of the features will be scattered by Raleigh scattering in different directions and those features comparable to the wavelength of the incoming light will be scattered by Mie scattering. Some of the redistributed light gets reflected back into the device at the Al back electrode by total internal reflection and thus travel longer within the photoactive layer. For the organic materials used, i.e. P3HT:PCBM with refractive index ($n \approx 1.85$)\textsuperscript{34}, the effective path length enhancement $k$ using equation 3.18 should be approximately 14.

Although the size of the features may be small, there is bound to be refraction effect at the interface between the PEDOT:PSS and the photoactive layer where the incident light meets the interface at angle other than normal. This should naturally occur due to the different refractive indices of P3HT:PCBM and PEDOT:PSS estimated at $\approx 1.55$ and 1.85 respectively.\textsuperscript{34,35}
In patterning semiconducting polymers such as PEDOT:PSS, methods suitable for polymers and which do not add to the manufacturing cost of device fabrication is preferable if more widespread use of photovoltaics is to become a reality. Soft lithography is an attractive option as it creates new opportunities for forming microstructures of polymers, ceramics, and metals. Few of the different methods that are regarded as soft lithography methods includes:

- Lift-up
- µCP (Micro Contact Printing)
- µTM (Micro Transfer Molding)
- MIMIC (Micro Molding In Capillaries)
- Put-down
- REM (Replica Molding)
- SAMIM (Solvent-Assisted Micro Molding)
- SE (Soft Embossing)

Two of these methods (lift-up and put-down) have been applied to imprint the surface of PEDOT:PSS in this research and will be discussed in subsequent Chapter.

The stamp is a critical component in soft lithography, as it is used to generate the features required and must therefore be compatible (e.g. non-reactive) with the materials being patterned. The material of the stamp and its preparation are outlined in the next chapter.
Reference

Chapter 4

Experimental Techniques
In this chapter, the experimental methods used in the patterning, fabrication and
characterisation of the organic photovoltaic devices are discussed. This chapter will also
cover the equipment used for device characterisation, surface analysis and material
characterisation. Some literature on the working principles of some of the equipment will be
given in order to understand better the measurements and results obtained from them, as well
as their limitations.

4.1 Device Fabrication
The organic photovoltaic devices researched in this project were synthesised on 1 mm thick
glass substrates coated with 100 nm indium tin oxide (ITO) (5-15 Ω/□). PEDOT:PSS (from
Sigma Aldrich) was used throughout as a polymer electrode between the ITO and the
photoactive layer comprising of poly (3-hexylthiophene), P3HT (Ricke Metals) and[6,6]-
phenyl-C61-butyric acid methyl ester, PCBM (Nano-C) blended together in the ratio 1:1 (i.e.
8 mg P3HT: 8 mg PCBM) in 1 ml dichlorobenzene (DCB) as solvent in the devices presented
in Chapter Five, and 10 mg P3HT:10 mg PCBM in 1 ml DCB in some of the devices in
Chapter Seven. The devices in Chapter five were deposited by spin coating (Chemat
technology spin-coater KW-4A, 600-8000 rpm) at variable spin speeds to give the desired
layer thicknesses. A different spinner (Laurell Technologies Corporation, S/N 07348) was
used for the deposition of the component materials in the devices fabricated for the results in Chapter Seven.

Patterned or imprinted devices will be used to refer to devices that the PEDOT:PSS layer was imprinted upon with a PDMS stamp to produce the desired features. The top aluminium contact was deposited by vacuum evaporation through a shadow mask. Figure 4.1 shows the schematics of a substrate and the shadow mask used for the device fabrication. The average device area fabricated was 10 mm².

4.1.1 Sample preparation

Rectangular ITO glass substrates were cut to 25 x 20 mm² and etched using a dilute solution of HCL with Zinc as a catalyst, leaving about 8 mm of the conductive oxide layer. The etched substrates were subjected to five stage cleaning procedure.

The five stage cleaning procedure is described in Table 4.1. The steps involving ultrasonication in the table were performed by placing the ITO substrates in staining glass containers, immersed in analytical grade solvents, in an Ultra-wave ultrasonicator. The cleaned and dried substrates were plasma treated using a Plasmatic systems plasma etcher. Plasma etching removes any remaining hydrocarbon residue from the ITO slides and makes
the surface ultra-clean and hydrophilic. Oxygen was used as process gas for the plasma etching as it modifies the ITO anode characteristics by increasing its work function $\phi_{\text{ITO}}$, a major advantage over argon, which would reduce the work function of ITO.\(^1\)

**Table 4.1: Five stage substrate cleaning process.**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Chemical</th>
<th>Cleaning process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>Sonicated for 30 minutes to remove all aromatic substances from the substrates after etching</td>
</tr>
<tr>
<td>2</td>
<td>Acetone</td>
<td>Washed in acetone to remove the toluene from the substrates.</td>
</tr>
<tr>
<td>3</td>
<td>Decon 90(^\circ) in deionised water</td>
<td>Sonicated for 30 minutes to remove all water soluble substances from the substrates.</td>
</tr>
<tr>
<td>4</td>
<td>Deionised water</td>
<td>Washed in deionised water to remove the excess Decon 90(^\circ) from the substrates.</td>
</tr>
<tr>
<td>5</td>
<td>Acetone</td>
<td>Sonicated for 30 minutes to remove all remaining aromatic aliphatic organic materials and the remaining water from the substrates. The substrates were suspended in a vapour of refluxing acetone and blown with dry $N_2$ flow.</td>
</tr>
</tbody>
</table>

**4.1.2 Preparation of PDMS Stamp**

An elastomeric stamp is the key element of soft lithography. It is made of polydimethylsiloxane (PDMS) or Sylgard 184 (Dow Corning), consisting of a pre-polymer and a curing agent (Figure 4.2). The PDMS was prepared by weighing 10 parts (by weight, ~20 g) of sylgard 184 pre-polymer and 1 part (~2 g) of the curing agent into a plastic cup and stirred
until they were completely mixed. The mixture was then degassed in a vacuum desiccator until it became clear.

![Poly dimethyl siloxane (PDMS)](image)

**Figure 4.2: Poly dimethyl siloxane (PDMS)**

A DVD disc (TDK DVD+R) was used as the master stamp by physically removing the protective polymer layer to expose the relief features. Also used was a Blu-ray disc (Verbatim BD-R) from which the hard coating was removed by etching in concentrated HNO₃ overnight and then washed in water thereby exposing the features. The PDMS mixture was dispensed at the centre of the master, taking care to avoid trapping air between surfaces. Once an even spread of the PDMS was achieved, it was heat cured at 70°C for 1 hour in an oven, then allowed to cool to the ambient. The PDMS was then cut at the edge of the master and peeled off while maintaining an angle of about 30°C between the stamp and the master to avoid deformation of the features. The PDMS stamp was then cut to the same size of the device substrate and treated in oxygen plasma for 15 seconds at 75 W to make the surface of the PDMS stamp hydrophilic by incorporating oxygen atoms in the PDMS surface forming SiOH.

PDMS stamps were also prepared using other master stamps viz: a sample stamp supplied with a 2.5 inch Nano Imprinting Lithography (NIL) system (Obducat AB, Sweden), and an excimer laser annealed a-Si stamp.
**4.1.3 Spin Coater**

Spin coating is used for many applications where relatively flat substrates are coated with thin layers of material. Soluble organic and inorganic nano-crystal materials are deposited by the process of spin coating. The various steps involved are illustrated in Figure 4.3.

![Diagram of spin coating process](image)

Figure 4.3: Schematic diagram showing steps involve in spin-coating.

A quantity of a polymer solution is first placed on the substrate, which is then rotated at a fixed speed of several thousand revolutions per minute (or the solution can be applied while the substrate is slowly rotating). The solution flows radially outwards, reducing the fluid layer thickness. Evaporation of the solvent results in a film of uniform thickness.\(^2\) A simple theory predicts the following relationship between the thickness of the spun film, \(d\), the viscosity coefficient of the solution, \(\eta\), its density, \(\rho\), the angular velocity of the spinning, \(\omega\), and the spinning time, \(t\).\(^2,3\)

\[
d = \left(\frac{\eta}{4\pi\rho\omega^2}\right)^{\frac{1}{2}} t^{-\frac{1}{2}} \quad \text{.................................................. (4.1)}
\]

Thus, an increase in angular velocity decreases the film thickness.

In the first part of the experiment (results of Chapter five), a Chemat Technology spin coater KW-4A, 600-8000rpm was used for the deposition of PEDOT:PSS and the photoactive layer on the substrates which were held in place by vacuum for a maximum duration of 60 seconds.
An excess quantity of a solution was dropped on the substrate, which was then rotated at high speed (3000 rpm for PEDOT:PSS and 600 rpm for P3HT:PCBM blend) in order to spread the fluid evenly by centrifugal force across the slide leaving a thin film. Later in the research, a spinner (Laurell Technologies Corporation, S/N 07348), which replaces the old one, was used and the spinning speed for the PEDOT:PSS was also changed to 2500 rpm for 40 seconds to achieve thicker films and better imprinted features. Generally, the thickness of the final film depends on the concentration of the solution, spinning speed and spinning time.

4.1.4 Stamping Procedure
The PEDOT:PSS layer was imprinted with features using the PDMS stamp. The procedures adopted for stamping is known as the “lift-up process” and/or the “put down process”. The lift-up process is illustrated in Figure 4.4, while the put-down process is described in the last section of Chapter Five, the major difference being that the solution is spin cast on the stamp in the case of the put-down process. The steps for the lift-up stamping procedure are outlined below.

Step 1: The PDMS stamp is treated in O₂ or Ar⁺ plasma for 15 seconds at 75 W during which its surface is made hydrophilic. It is worth noting that, if the hydrophilic stamp is left in ambient for 15 minutes, the hydrophobicity returns.

Step 2: PEDOT:PSS is spin cast on the oxygen plasma treated cleaned glass substrate (section 4.1.3). The hydrophilic stamp is then placed on the PEDOT:PSS immediately starting from one side and ensuring that no air is trapped between the stamp and the PEDOT:PSS surface. The weight of the stamp provides the only pressure for the imprinting. A slight pressure from the thumb may be applied to remove any trapped air.

Step 3: The setup is now cured in the oven for 30 minutes at 150°C and allowed to cool completely to the ambient temperature.
Step 4: The stamp is carefully removed from the PEDOT:PSS surface, leaving it with a replica of the features of the stamp. For the purpose of characterising the features formed on the PEDOT:PSS surface and obtaining an optimum temperature for stamping, the temperature was varied from 140°C to 180°C.

![Diagram](image)

Figure 4.4: A schematic representation of the stamping procedures.

4.1.5 Multi-crucible Evaporator

The top contact of aluminium was deposited by vacuum sublimation. In the deposition of the top contact at an atomic level the rate of arrival of the species from the gas phase should be low and fairly constant over the duration of the deposition to obtain the required thickness. A reasonable criterion would be that no more than a few per cent of an atomic layer of atoms should attach themselves to the surface from the gas phase per unit time. Evaluating this
requirement from simple kinetic theory of gases, the rate of arrival of atoms or molecules from a gas is given by \(^4\)

\[
r = P \left( \frac{1}{2\pi k_B T m} \right)^{\frac{1}{2}} \tag{4.2}
\]

Where \(P\) is the pressure expressed in Torr (i.e. mm of Hg) \(T\) is absolute temperature in K, \(m\) is the particle’s mass and \(k_B\) is the Boltzmann’s constant. A convenient form of this expression in which \(m\) is substituted by the molecular weight \(M\) multiplied by the atomic mass unit gives

\[
r = \frac{3.51 \times 10^{22} P}{(TM)^{\frac{1}{2}}} \tag{4.3}
\]

Figure 4.5 represents a schematic of the multi-crucible thermal evaporator (Edward 306) used for the deposition process. The aluminium wire was rolled into a small ball and placed in the tungsten boat which served as the heater. The nominal vacuum required for sublimation is between \(8.0 \times 10^{-6}\) Torr to \(5.0 \times 10^{-5}\) Torr which was achieved by an oil diffusion pump.

![Figure 4.5: Multi crucible thermal evaporator.](image-url)
The tungsten boat was heated electrically until the critical temperature (melting point of Al is 660°C) where the aluminium evaporates. The rate of evaporation and thickness was measured by a thickness monitor (Intellemetrics IL 150) connected to the evaporator. The thickness monitor operates by measuring the change in the oscillating frequency of a quartz crystal. This frequency is a function of the mass of the evaporated material deposited on the crystal. Thus, the deposited thickness is directly calculated by the equipment using the density and the acoustic impedance of the evaporated material.

4.2 Device Characterisation
The current-voltage characteristics of the fabricated organic solar cells was measured using an Oriel 81160 class B solar simulator with ≤ 5% spectral irradiance mismatch with the solar light.

![Diagram of Oriel 81160 solar simulator cross sectional diagram.](image-url)

Figure 4.6: Oriel 81160 solar simulator cross sectional diagram.
The simulated AM 1.5 light was incident on the fabricated devices to generate a photocurrent. Figure 4.6 shows the optics of the Oriel simulator. The optical power of the lamp can be calibrated by changing the electrical power (up to 15%) and by changing the position of the lamp (80%). Initial calibration was done at AM 1.5G (1000 Wm\(^{-2}\) according to CEI/IEC 904-3 standard) with a Molectron PS19 thermopile detector and a Molectron PM500AD laser power meter. The Molectron PS19 detector has a spectral bandwidth of 0.3\(\mu\)m – 11 \(\mu\)m. The current-voltage was measured by a Keithley2400 digital source-meter controlled by labview software connected by IEEE 488 bus.

**Figure 4.6:** AM 1.5 simulated solar radiation

![Diagram of AM 1.5 simulated solar radiation](image)

**Figure 4.7:** Current-voltage characterisation output with photovoltaic device.

The Keithley 2400 has 10pA and 1\(\mu\)V current and voltage resolution respectively, which is ideal for measuring solar devices in light and dark conditions. Figure 4.7 represents the schematic of the output characteristics. The electrical measurements are done by sweeping the bias voltage and registering the current through the device and voltage drop at the device terminals. The Keithley 2400 is designed to measure fourth quadrant operations for photovoltaic characterisation.
4.3 Material Characterisation

4.3.1 Ultraviolet, Visible and Near Infrared Absorption Spectroscope

A UV-VIS-NIR spectrophotometer measures the amount of electromagnetic radiation absorbed by a solution or a thin film per wavelength. As absorption takes place, the intensity of light passing through a solution attenuates exponentially according to Beer-Lambert's law given as;

\[ I = I_0 e^{-\alpha bc} \] ............................................ (4.4)

where \( \alpha \) is the absorption coefficient (absorptivity) of the solution with units Lmol\(^{-1}\)cm\(^{-1}\) and Lg\(^{-1}\)cm\(^{-1}\) and \( c \) is its concentration. \( I_0 \) is the intensity of the light source, \( I \) is the intensity of the light after passing through the sample, and \( b \) is the width of the absorbing medium.

Absorptivity is also given in units of cm\(^{-1}\) for solids. Figure 4.8 shows a beam of monochromatic radiation of intensity \( I_0 \) directed at a sample solution.

\[ A = \log\left(\frac{I_0}{I}\right) \] .................................................. (4.5)

Substituting equation 4.4 into 4.5 yields
Another measurable parameter from the UV-VIS-NIR spectrometer is the transmittance $T$, which is the fraction of incident light at a specified wavelength that passes through a sample.

$$ T = \frac{l}{l_0} \qquad \text{(4.7)} $$

The transmittance of a sample is usually given as a percentage, defined as

$$ T\% = \frac{l}{l_0} \times 100 \qquad \text{(4.8)} $$

And it is related to absorbance $A$ as

$$ A = -\log_{10} T = -\log_{10} \frac{l}{l_0} \qquad \text{(4.9)} $$

$$ A = 2 - \log T\% \qquad \text{(4.10)} $$

where $T\%$ is the per cent transmittance and $T$ is “per one” transmittance.

In this project, a Varian Cary 5000 UV-VIS-NIR (175-3300 nm) spectrophotometer was used for all absorbance measurements. Figure 4.9 shows a schematic of the spectrophotometer.

A mercury lamp provides UV radiation and a tungsten lamp provides visible to near infrared radiation. The monochromator has two collimating mirrors and a grating for wavelength selection. Spectral light is chopped at 30Hz through the sample and a reference cell by an optical chopper. The difference of the transmitted light from the two paths is collected by an assembly of optics and focused onto a PbS detector. The double Littrow monochromator in the Varian Cary 5000 is designed to reduce the photometric noise and give the spectrophotometer a high resolution.
4.3.2 Atomic Force Microscope

Atomic force microscope (AFM) is a very high resolution microscope with demonstrated resolution of fractions of a nanometre, more than 1000 times better than the optical diffraction limit. It is used to obtain topographical surface images in nanometre resolution.

The AFM consists of a micro scale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. Piezoelectric elements are used to control the height of the imaging tip. Images are taken by measuring the deflections of the cantilever as a function of the lateral position. There are two main modes of operation: contact mode and non-contact mode (distances greater than 1 nm from the sample surface).

In contact mode, the tip deflections are caused by ionic repulsion forces whereas Van der Waals, electrostatic, magnetic or capillary forces are responsible for deflections in non-contact mode. In the non-contact mode of operation, a vibrating tip is used for scanning. The
natural frequency of the tip is reduced by the interaction of the Van der Waals forces when the tip is close to the surface. If an excitation frequency of the tip of $\omega_m > \omega_0$ ($\omega_0$ is the resonance frequency) is selected and kept constant, the amplitude of the vibration decreases as the tip approaches the sample, since interaction becomes increasingly stronger. Figure 4.10 shows resonance curves of the tip without and with interaction with a van der Waals potential. The interaction leads to a shift $\Delta \omega$ of the resonance frequency with the consequence that the tip excited with the frequency $\omega_m$ has vibration amplitude $a(\omega)$ attenuated by $\Delta a$. Thus, the vibration amplitude also becomes a measure for the distance of the tip from the sample surface. A schematic of the optical lever system used in AFM is represented in Figure 4.11. The tip deflection is measured by detecting the reflection of a laser beam on to a photo diode array. A digital Instruments Dimension 3100 AFM was used for all the AFM imaging in this project.

Figure 4.10: AFM resonance curves.
Photoluminescence (PL) spectroscope

Photoluminescence (PL) spectroscopy is a contactless, non-destructive method to probe the electronic structure of materials. Variation of the PL intensity with external parameters like temperature and applied voltage can be used to characterize further the underlying electronic states and bands.

Because PL often originates near the surface of a material, PL analysis is an important tool in the characterization of surfaces. The utility of PL for this purpose is derived from its unique sensitivity to discrete electronic states, many of which lie near surfaces and interfaces. The energy distribution and density of interface states can be ascertained by studying the excitation intensity dependence of the PL spectrum.

PL is simple, versatile, and non-destructive. The instrumentation that is required for ordinary PL work is modest: an optical source and an optical power meter or spectrophotometer. A typical PL set-up is shown in Figure 4.12. Because the measurement does not rely on electrical excitation or detection, sample preparation is minimal.
The fact that PL can be used to study virtually any surface in any environment means it can be used to monitor changes induced by surface modification in real time. For example, unlike most surface characterization techniques, PL is generally not sensitive to the pressure in the sample chamber. A Varian Cary Eclipse fluorescence spectrophotometer fitted with an intense Xenon lamp, coupled with optimized grating blaze angles and coatings to ensure sensitivity across the whole wavelength range, was used to measure the PL of the patterned and imprinted devices. The samples were excited at 350 nm wavelength at PMT (photomultiplier tube) voltage of 700 V. The emission wavelength range was selected to 360-800 nm.

4.3.4 Fourier Transform Infrared Spectroscopy
Infrared spectroscopy is a non-destructive, highly sensitive technique that provides information about impurities, chemical environment, and free-carrier properties. Performing Fourier transform infrared (FTIR) spectroscopy on a sample gives a picture of its bonding structure. The technique benefits from high FT sensitivity and can be used with database searches of extensive libraries of FTIR to chemically identify samples and sample components. Measurement of the reflectance and transmittance of infrared radiation reveals...
signature spectroscopic peaks allowing identification of elemental and molecular constituents within organic and inorganic compounds. The basic optical component of Fourier transform spectrometers is the Michelson interferometer shown in Figure 4.13.

Light from an infrared source is collimated and directed onto a beam splitter, creating two separate optical paths by reflecting 50% of the incident light and transmitting the remaining 50%. In one path the beam is reflected back to the beam splitter by a fixed-position mirror, where it is partially transmitted to the source and partially reflected to the detector. The beam from the movable mirror is also returned to the beam splitter where it is partially reflected back to the source and partially transmitted to the detector. Although the light from the source is incoherent, the split components are coherent and will produce interference phenomena when combined.5

![Figure 4.13: Fourier transform infrared spectroscope schematics.](image)

What is measured in FTIR is the interferogram \( I(x) \) (a series of maxima and minima), containing not only the spectral information of the source, but also the transmittance
characteristics of the sample. Of interest is the spectral response, calculated from the interferogram using the Fourier transformation,\(^5\)

\[
B(f) = \int_{\omega_0}^{\omega_1} I(x) \cos(2\pi f x)dx
\]

\(B(f)\) contains the spectral content of the source, the sample, and the ambient in the path of the measurement. Usually atmospheric \(\text{H}_2\text{O}\) and \(\text{CO}_2\) absorption lines are reduced by purging the apparatus with dry nitrogen. The effect of the source is eliminated by making one measurement without the sample, i.e., background measurement, and one with the sample. The ratio of the two eliminates the background. The ATR-FTIR measurement was done using a Nicolet Protégé 460 (E.S.P) spectrometer fitted with 1 mW HeNe laser (633 nm).

### 4.3.5 Micro Raman Spectroscope

Raman spectroscopy is a form of vibrational spectroscopic technique, much like infrared (IR) spectroscopy. However, whereas IR bands arise from a change in the dipole moment of a molecule, Raman bands arise from a change in the polarizability. In many cases, transitions that are allowed in Raman are forbidden in IR, so these techniques are often complementary. When a beam of light impinges upon a sample, photons are absorbed by the material and scattered. The scattered light from the surface of the sample is found to contain mainly wavelengths that were incident on the sample (Raleigh scattering). But a tiny portion of the scattered radiation (approximately 1 in \(10^8\) parts)\(^5\) is shifted to different wavelengths and at very low intensities. These wavelength-shifted photons are called Raman scatter. This "Raman shift" is an intrinsic property of the sample and is only practical when an intense monochromatic light source like a laser is used.

Raman spectroscopy is based on the Raman Effect first reported by Raman in 1928.\(^5\) If the incident photon imparts energy to the lattice in the form of a phonon (phonon emission) it emerges as a lower-energy photon. This down-converted frequency shift is known as Stokes-
shifted scattering. In Anti-Stokes-shifted scattering the photon absorbs a phonon and emerges with high energy. The anti-Stokes mode is much weaker than the Stokes mode and it is the Stokes mode that is usually monitored.\(^5\)

During Raman spectroscopy measurements a laser pump beam is incident on the sample (in this project a 514 nm laser line was used) (Figure 4.14). The weak scattered signal is passed through a double monochromator or to reject the Raleigh scattered light and the Raman-shifted wavelengths are detected by a photodetector. In the Raman microprobe, a laser illuminates the sample through a commercial microscope. Laser power is usually held below 5 mW to reduce sample heating and decomposition. The technique is non-destructive and requires no contact with the sample. The wavelengths of the scattered light are analysed and matched to known wavelengths for identification.

![Figure 4.14: Typical Continuous Wave Raman layouts.](image)

### 4.3.6 Ellipsometer

Ellipsometry is a contactless, non-invasive technique measuring changes in the polarization state of light reflected from a surface.\(^5,7\) The experimental data are usually expressed as two parameters \(\Psi\) and \(\Delta\) that are related to the Fresnel reflection coefficients \(R_p\) and \(R_s\) which contain information related to material optical properties and physical dimensions. The polarization state of the light incident upon the sample may be decomposed into an \(s\) and a \(p\) state.
component (the s-component is oscillating parallel to the sample surface, and the p-component is oscillating parallel to the plane of incidence). The intensity of the s and p component, after reflection, is denoted by $R_s$ and $R_p$. The fundamental equation of ellipsometry is then written:

$$\rho = \frac{R_p}{R_s} = \tan(\Psi) e^{i\Delta} \quad \text{......................................................... (4.12)}$$

Where $j = (-1)^{1/2}$, $\Psi(0^\circ \leq \Psi \leq 90^\circ)$ and $\Delta(0^\circ \leq \Delta \leq 360^\circ)$ and are defined as

$$\Psi = \tan^{-1} |\rho|, \quad \text{......................................................... (4.13)}$$

$$\Delta = \text{differential phase change} = \Delta_p - \Delta_s \quad \text{......... (4.14)}$$

Since $\rho$ is the ratio of reflection coefficients, i.e., the ratio of the intensities and the relative phase difference. It is not necessary to make absolute intensity and phase measurements. In other words, ellipsometry is used predominantly to determine the thickness of thin dielectric films on absorbing substrates, line width, and optical constants of films or substrates. It does not measure the film directly, but optical properties from which thickness and other sample parameters are derived. Figure 4.15 illustrates the schematics of a typical ellipsometer. The ellipsometer used in the measurement of the thicknesses in this research was the Plasmos SD 2000 ellipsometer fitted with a He-Ne 632.8 nm laser.
4.3.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy, otherwise known as electron spectroscopy for chemical analysis (ESCA), is a vacuum based analytical technique used for identifying chemical species at the sample surface, allowing all elements except hydrogen and helium to be detected. Irradiation of a substrate with X-ray photons results in the ejection of photoelectrons from any orbital with energies exceeding the binding energy. The measured energy of the ejected electron at the spectrometer $E_{sp}$ is related to the binding energy $E_b$, referenced to the Fermi energy $E_F$, by

$$E_b = h\nu - E_{sp} - q\phi_{sp} \quad \text{............... (4.15)}$$

Where $h\nu$ is the energy of the primary X-rays and $\phi_{sp}$, the work function of the spectrometer (3 to 4 eV). Since $E_b$ depends on the X-ray energy, then the incident X-ray source must be monochromatic. The electron binding energy is influenced by its chemical surroundings.
making $E_b$ suitable for determining chemical states, thus allowing chemical and elemental identification. XPS is surface sensitive because the emitted photoelectrons originate from the upper 0.5 – 5 nm of the sample.\textsuperscript{5,9} The depth is governed by the electron escape depth or the related electron mean free path. Those electrons excited deeper within the sample are unable to exit the surface. Since the electronic structure, the core levels and valence region, is unique for all atomic and molecular species, XPS can thus be used as a “fingerprint” method in analysing the sample’s chemical composition in the surface region.\textsuperscript{10}

Figure 4.16: Schematics of XPS/UPS measurements.

XPS instruments are usually equipped with a hemispherical electron energy analyzer (spectrometer), a high vacuum and the X-ray source, usually light element like Al ($E_{ka} = 1.4866$ KeV) or Mg ($E_{ka} = 1.2566$ KeV) with full width at half maxima (FWHM) of about
~1.2 eV and ~0.8 eV respectively (Figure 4.16). The XPS electrons are detected by one of several types of detectors.

In this work, an Omicron Multi probe Ultra-high vacuum system equipped with an Omicron EA125 hemispherical analyzer was used for the XPS measurement. Spectra were acquired with a pass energy of 50 eV and 20 eV for survey and higher resolution respectively, using Al Kα radiation (hv = 1.4866 KeV) from a VG XR3E2 twin anode source. Binding energies were normalized with respect to the position of Au substrate 4f 7/2 line at 84 eV. Apart from the sample preparation, the XPS and UPS measurements were taken with the assistance of Dr Hide Shiozawa and Dr Christina Giusca who were in charge of the equipment.

4.3.8 Ultraviolet Photoelectron Spectroscopy (UPS)

Ultraviolet photoelectron spectroscopy (UPS) is a powerful technique for studying the valence electronic structure and uses lower photon energies than that used for XPS. The low photon energy in UPS means that deep core electron levels cannot be excited and only photoelectrons emitted from the valence band or shallow core levels are accessible. UPS can also be used to identify molecular species on surfaces by identifying characteristic electron energies associated with the bonds of the molecules.4

The most common ultraviolet photon source is the He resonance lamp, providing photons of 21.1 eV (HeI) and 40.8 eV (HeII) in energy, with a line width (FWHM) of about ~30 meV, much narrower than that of the X-ray photon sources.10 UPS is surface sensitive, but not necessarily as surface specific as some other surface analytical techniques. Photoelectron spectroscopy of solid samples is carried out with the binding energy given relative to the Fermi level, EF, but when interpreting the photoelectron spectra, changes in the work function of the sample that occur upon doping or other modifications to the sample is taken into account.10
By measuring the position of the zero kinetic energy cut-off of the secondary electron
distribution, $E_{co}$, the work function of a sample may be obtained. This enables the adjustment
of the binding energies so that the vacuum level is taken as the reference. The work function
of the sample, $\phi$, can be derived from the following equation
\[
\phi = h\nu - (E_{co} - E_F) \tag{4.16}
\]
To measure the work function of the samples in this project using the UPS technique, an
Omicron Multi probe Ultra-high vacuum system equipped with an Omicron EA125
hemispherical analyzer was used (schematically shown in Figure 4.16). HeI (21.22 eV) from
an Omicron HIS13 windowless He lamp constituted the UV source. The pass energy was set
to 5 eV for a 6 mm diameter analysis area defined by the entrance slit to the analyzer.

Reference
   Press, 1994).
10. R. Farchioni and G. Grosso (Eds), "*Organic Electronic Materials: Conjugated Polymers and Low
CHAPTER 5

5.1 P3HT:PCBM Based Solar Cells
Of the many organic solar cell structures currently being studied, the donor/acceptor bulk heterojunction polymer solar cell is considered as the most promising approach, where efficient light-induced charge separation is enabled by a large-area donor-acceptor interface.\textsuperscript{1-3} Poly(3-hexylthiophene) (P3HT) is typically one of the most extensively investigated p-type polymer (donor) materials in polymer solar cells blended with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as an electron acceptor.\textsuperscript{4} This is due to the unique properties of P3HT over other polymers, such as its high degree of crystallinity, high hole mobility in the regioregular state (10\textsuperscript{-4} to 10\textsuperscript{-1} cm\textsuperscript{2}/Vs),\textsuperscript{5,6} extended absorption edge up to 650 nm,\textsuperscript{7} stability and solution processability. High efficiencies have been achieved using this material combination,\textsuperscript{8-12} yet performance depends critically on material properties and processing conditions.\textsuperscript{1} Intense research has already focussed on nanoscale morphology,\textsuperscript{7} stability,\textsuperscript{13-14} concentration ratio\textsuperscript{15} and thermal annealing\textsuperscript{10,16-18} towards improvement in the device performance. This chapter covers the preliminary work carried out in the early part of this research which involved the fabrication of reference devices as well as the nanoimprinting method used to enhance the device parameters.

5.1.1 Absorption Properties of P3HT and PCBM
In Figure 5.1, the molecular structures of the materials used to form the active layer in the fabrication of the devices in this thesis are shown. The absorption coefficients of films of
these materials on glass are shown in Figure 5.2, in comparison with the air mass (AM) 1.5 standard solar spectrum displaying the fraction of the sunlight which can contribute to the energy conversion.

![Molecular structure of Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM).](image)

Figure 5.1: Molecular structure of Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM).

![Absorption spectra of films of P3HT, PCBM and P3HT:PCBM are depicted in comparison with the standard AM 1.5 terrestrial solar spectrum.](image)

Figure 5.2: Absorption spectra of films of P3HT, PCBM and P3HT:PCBM are depicted in comparison with the standard AM 1.5 terrestrial solar spectrum.

It is found that the absorption spectrum of the composite structure becomes broader with addition of PCBM, due to the absorption of PCBM at shorter wavelength, a property which is highly desirable for a photovoltaic device. It also indicates that the absorption edge of the composite material is at 650 nm in consonance with what is widely reported. Borrowing from the conclusion of the work by Rait et al, the composition ratio of the P3HT:PCBM...
was chosen as 1:1 throughout this research work on account that only the 1:1 wt/wt ratio film gives a balanced, non-dispersive electron and hole transport.\textsuperscript{12}

Regrettably, the efficiency of devices using this material composition is limited by the small absorbance of the two components in the range of the solar spectrum coupled with the small film thickness of the absorbing layer determined by the restricted charge carrier mobility.\textsuperscript{19}

According to Svetlana \textit{et al.},\textsuperscript{20} ~300 nm can absorb most of the light, but the best performance of P3HT/PCBM devices is often observed for thicknesses of active layers which are (up to 2 times) lower than those required for maximum light absorption.\textsuperscript{21-23} However, the exact value of this optimum thickness for highest efficiency depends on many other parameters, such as chemical architecture of the components (which include molecular weight distribution and regio-regularity of P3HT), impurities in P3HT and/or PCBM (which may deteriorate electronic properties but may also promote crystal growth by serving as nucleation centres for crystallization), and optimum processing condition, type of the organic solvent used, presence of crystalline aggregates of P3HT or PCBM in solution/dispersion prior to film deposition, type of a film deposition technique used (spin-coating, doctor blading, inkjet printing), exact conditions of film formation (such as spin speed), etc.\textsuperscript{24}

\textbf{5.1.2 Device Structure}

The reference devices fabricated in the early part of this research were based on the structure ITO(150nm)/PEDOT:PSS(40nm)/P3HT:PCBM(150nm)/LiF(1nm)/Al(50nm) as depicted in Figure 5.3 along with the energy level diagram showing the LUMO and HOMO of the composite material forming a bulk heterojunction. The photoactive layer consists of the interpenetrating network of P3HT and PCBM with a mixing ratio of 1:1 by weight (8mg:8mg) dissolved in 1ml dichlorobenzene. The bottom electrode comprised of indium tin oxide (ITO) upon which poly[3,4-(ethylenedioxy) thiophene]: poly(styrene sulfonate)
(PEDOT:PSS) was coated. A deposition of a thin layer of LiF and Al in a vacuum evaporator through a shadow mask formed the top electrode. The mask allowed for three set of devices to be fabricated on one substrate at the same time. These devices were fabricated in ambient conditions. The full device fabrication procedure is as explained in Chapter 4.

![Schematic diagram showing the device structure (left) and the energy level diagram of the bulk heterojunction device (right).](image)

**Figure 5.3:** Schematic diagram showing the device structure (left) and the energy level diagram of the bulk heterojunction device (right).

![Current density-Voltage (J-V) curves of a P3HT:PCBM reference device performance under AM 1.5 illumination.](image)

**Figure 5.4:** Current density-Voltage (J-V) curves of a P3HT:PCBM reference device performance under AM 1.5 illumination.

The device demonstrated a 2.63 mA/cm² short-circuit current density, 640 mV open-circuit voltage, 55% fill factor and a 0.93 % power conversion efficiency, Figure 5.4.
The device has a series resistance of 25.7 $\Omega \text{cm}^2$ calculated by fitting a gradient to the first quadrant of the J-V curve. A shunt resistance of 1045.6 $\Omega \text{cm}^2$ was similarly derived from the third quadrant of the J-V characteristics. Other reference devices made are given in Table 5.1.

Table 5.1: Characteristics of reference devices.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Jsc(mA/cm$^2$)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ ($\Omega \text{cm}^2$)</th>
<th>$R_{sh}$ ($\Omega \text{cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.8872</td>
<td>0.3835</td>
<td>0.4939</td>
<td>0.93</td>
<td>20.43</td>
<td>463.58</td>
</tr>
<tr>
<td>2</td>
<td>4.5768</td>
<td>0.375</td>
<td>0.4856</td>
<td>0.83</td>
<td>22.19</td>
<td>396.75</td>
</tr>
<tr>
<td>3</td>
<td>3.5744</td>
<td>0.3509</td>
<td>0.4764</td>
<td>0.6</td>
<td>25.07</td>
<td>503.92</td>
</tr>
<tr>
<td>4</td>
<td>2.539</td>
<td>0.5763</td>
<td>0.3684</td>
<td>0.54</td>
<td>58</td>
<td>269.67</td>
</tr>
<tr>
<td>5</td>
<td>2.8192</td>
<td>0.6407</td>
<td>0.5633</td>
<td>1.02</td>
<td>26.02</td>
<td>1008.22</td>
</tr>
<tr>
<td>6</td>
<td>2.4497</td>
<td>0.6379</td>
<td>0.5425</td>
<td>0.85</td>
<td>31.4</td>
<td>993.14</td>
</tr>
<tr>
<td>7</td>
<td>2.9002</td>
<td>0.6388</td>
<td>0.5726</td>
<td>1.06</td>
<td>23.7</td>
<td>979.39</td>
</tr>
</tbody>
</table>

The reference devices in Table 5.1 show large variations in the $J_{sc}$ and $V_{oc}$ implying non-reproducibility. It was later discovered that the fabrication procedure had an inherent error in all the devices and did not affect the device equally. During spin coating, the active material spreads outward and some of the solution gets underneath the substrate, covering some or all of the active area. When light is incident on the device through that side of the substrate, the performance of the device got affected in two ways; (i) the light gets absorbed first by the unwanted layer before going into the device thereby reducing the absorption depth. Thus, less excitons are created which explains the poor values of the $J_{sc}$. And due to the irregular thickness of the unwanted layer, the values also vary largely. (ii) The unwanted layer also reduces the intensity of light going into the device which directly has a negative effect on the $V_{oc}$ of the devices. This error was corrected in the results presented in Chapter Seven of this thesis but the same procedure was used in obtaining the rest of the results discussed in this Chapter.
5.1.3 Effect of LiF on Device Performance

Insertion of thin layer of lithium fluoride (LiF) between the organic active layer and the aluminium has been shown to increase both the open circuit voltage and the fill factor of devices, yielding an increased power conversion efficiency.\textsuperscript{25} Mechanisms suggested so far for the improved efficiency due to LiF includes the following:

(i) lowering of the effective work function of the aluminium

(ii) dissociation of the LiF and subsequent chemical reaction (doping) of the organic layer

(iii) formation of a dipole layer leading to a vacuum level offset between the organic layer and the aluminium; and

(iv) protection of the organic layer from the hot Al atoms during thermal deposition.

Two devices were fabricated sequentially, one with LiF and the other without LiF inserted between the active layer and the Al electrode. Their $J-V$ characteristics obtained are as shown in Figure 5.5. The device with LiF ($J_{sc} = 2.63\text{mA/cm}^2$, $V_{oc} = 640\text{mV}$, FF = 55%, $\eta = 0.93\%$) shows improvements in the power conversion efficiency and the fill factor over the device without LiF ($J_{sc} = 2.44\text{mA/cm}^2$, $V_{oc} = 627\text{mV}$, FF = 41%, $\eta = 0.62\%$). Quantitatively, this is about 25% and 33% increase in the fill factor and power conversion efficiency respectively. Also, insertion of LiF helped reduce the series resistance by more than half ($R_{\text{series}} = 25.7 \\Omega\text{cm}^2$, $R_{\text{shunt}} = 1045.6 \\Omega\text{cm}^2$) and increased the shunt resistance significantly when compared with the device without LiF ($R_{\text{series}} = 69.7 \\Omega\text{cm}^2$, $R_{\text{shunt}} = 555.5 \\Omega\text{cm}^2$).
To understand the improved performance due to the insertion of LiF between the Al and the active matrix, Brabec et al.\textsuperscript{25} proposed the following combined mechanisms, some of which were drawn from existing references: (i) due to the strong dipole moment of LiF (6.3D),\textsuperscript{26} even a monomolecular layer of LiF can cause a significant vacuum level offset,\textsuperscript{27} which is a well-established fact in the field of surface science for the deposition and adsorption of molecules on metal surfaces;\textsuperscript{27,29} (ii) change in the work function (or surface potential) of the metal, as verified for LiF/Al electrodes by ultraviolet photoelectron spectroscopy (UPS).\textsuperscript{30} This was explained (i.e. lowering of the metal work function or shifting of the molecules levels towards higher energies) by an alignment of LiF resulting from the Li\textsuperscript{+} adhering preferentially to the organic surface and the F\textsuperscript{-} pointing towards the metal surface. Brabec et al.\textsuperscript{25} further suggested that dissociation of LiF and subsequent doping of the underlying organic layer due to the formation of metallic Li\textsuperscript{+} was not required to explain the enhancement seen in their study for solar cells, and that the dissociation of LiF by way of chemical reactions that lead to charge transfer across the interface can produce an interface dipole much the same as intact LiF molecules.
Owing to significant effects of small amounts of LiF on the $FF$ and $J_{SC}$, coupled with the need to equalise the fabrication conditions for both the reference and the patterned devices prepared at the same time, LiF were not included in devices fabricated for the study in the following sections and chapter thus, eliminating the effect of varying thicknesses of LiF on the two devices due to their separation in the vacuum evaporator.

5.2 PEDOT:PSS Surface Modification

Solar cell performance is influenced by many factors one of which is the work function of the electrodes. The $V_{OC}$ of solar cells with non-Ohmic contacts has been shown to be determined by the work function difference of the electrodes. For Ohmic contacts the $V_{OC}$ is governed by the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the acceptor and donor, respectively, which pin the Fermi level of the cathode and anode. Band bending, created by the accumulated charges at both interfaces due to Ohmic contacts, can contribute towards a considerable reduction in $V_{OC}$. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS), has been used extensively in photovoltaic devices and light emitting diodes as a hole-collecting or hole-injecting anode due to its high work function and electron blocking characteristics. In another study, the use of PEDOT:PSS has also been shown to increase the lifetime of optoelectronic devices, and as opposed to some inorganic oxide electrodes, the work function of the PEDOT:PSS is relatively stable, allowing for more reproducible device characteristics. Usually, it is used as a bi-layer configuration with indium-tin-oxide (ITO) contact due to its relatively low charge mobility when compared to its inorganic counterparts. Efforts have been made to improve device performance through PEDOT:PSS modification via addition of glycerol to a PEDOT:PSS solution prior to spin coating which reduces the sheet resistivity of the dried films by three orders of magnitude. In the following section,
the results of surface modification of PEDOT:PSS to be used to further enhance the device parameters are presented. This is followed by the results of devices fabricated (hereby referred to as “patterned” or “imprinted” devices) on the surface modified PEDOT:PSS which clearly show significant improvements in the short-circuit current density and in most cases, the fill factor.

5.2.1. Patterned PEDOT:PSS Surfaces through Soft Lithography (Lift-Up Process)
The PEDOT:PSS layer was patterned using the PDMS stamp prepared as outlined in Chapter 4. Figure 5.6 shows the AFM image and the depth profile of the PDMS stamp. The stamp contains regular radial ridge-like features obtained from the DVD master with depth of ~27 nm and a period of 700 nm.

Figure 5.6: AFM image and depth profile of PDMS stamp made from a DVD disk master.

These features were replicated in the PEDOT:PSS film by placing the plasma treated PDMS stamp over the polymer without any pressure other than the weight of the stamp, and annealed at 150°C. The period of the imprinted features remained the same at 700 nm, subsequent to annealing, with a reduced depth of ~10 nm as shown in Figure 5.7. This
demonstrates that the simple procedure described may be used to pattern the polymer film with nanometre scale features.

Figure 5.7: AFM image and depth profile of imprinted PEDOT:PSS surface made from a DVD PDMS stamp (baked at 150 °C for 30 min, ~10 nm depth and 700 nm period).

Another look at the depth profile of the stamped PEDOT:PSS in Figure 5.7 shows smaller features on the crest of each regular pattern which will bring about significant scattering as their periodicity (which is variable, ranging from 230 to 400 nm) will be much less than the wavelength of the incoming light resulting in Raleigh scattering.

Features of PDMS stamp made from the master stamp supplied with a 2.5 inch Nano Imprinting Lithography (NIL) system is shown in Figure 5.8 along with its depth profile.

Figure 5.8: AFM image and depth profile of a regular 3D PDMS stamp made from an industrial master stamp.
The stamp contains grooves of varying sizes and depths but aligned in one direction. It has an average period of 800 nm and 100 nm depth. The replicated features of the stamp on PEDOT:PSS is shown in Figure 5.9. The troughs of the PEDOT:PSS profile shows a good resemblance of the crests of the PDMS stamp profile. The profile shows an average period and depth of 700 nm and 18 nm respectively.

Figure 5.9: AFM image and depth profile of PEDOT:PSS replicated from a regular 3D PDMS stamp made from an industrial master stamp.

Another PDMS stamp made from an excimer laser annealed a-Si master is shown in Figure 5.10 with its profile. The stamp has irregular features of varying depths and widths. Some of the features have a depth up to 300 nm.

Figure 5.10: AFM image and depth profile of an irregular 3D PDMS stamp made from an Excimer laser annealed a-Si master.
Additionally, the time for curing during the imprinting was varied from 10 minutes to 30 minutes at each temperature to determine the time for obtaining best quality features on PEDOT:PSS after stamping.

Figure 5.11 shows AFM images of PEDOT:PSS after stamping at 180°C with a 30 minutes curing duration. The corresponding profiles of the AFM images indicate that best features are obtained by increasing the time for curing. The profile of the PEDOT:PSS baked for 25 min and 30 min duration has average depth of ~ 10 nm whereas those baked for 10-20 min are between 5 and 8 nm.

Comparing the feature quality and depth profiles of the patterned PEDOT:PSS baked at 150°C - 180°C, it is observed that more pronounced features are obtained at 150°C and its profile is smoother, although the average depth is still ~10 nm.
Figure 5.11: AFM images and corresponding profiles of PEDOT:PSS baked at 180°C during stamping for (a) 10 min, (b) 15 min, (c) 20 min, (d) 25 min, and (e) 30 min.
**5.2.2 Devices with Patterned PEDOT:PSS Layers**

Two sets of devices (reference and patterned-using 2D stamps) were fabricated at the same time under atmospheric conditions. The PEDOT:PSS layer of the reference and patterned devices were annealed at 150°C for 30 min to allow for direct comparison of the effect of patterning on the device performance, thereby removing any changes in device property due to temperature effects. Figure 5.12 shows the $J-V$ characteristics of the reference and patterned devices. The patterned device shows increases in device parameters ($J_{SC} = 3.029$ mA/cm$^2$, $V_{OC} = 623$ mV, $FF = 42.7\%$, $\eta = 0.81\%$) over the reference device ($J_{SC} = 2.435$ mA/cm$^2$, $V_{OC} = 627$ mV, $FF = 40.6\%$, $\eta = 0.62\%$).

![Figure 5.12: J-V characteristics comparing the reference and patterned devices at 150°C PEDOT:PSS baking temperature.](image)

It is evident that patterning the PEDOT:PSS layer has allowed for a 24% increase in $J_{SC}$ and approximately 30% increase in device power conversion efficiency.

It is suggested that the direct patterning of the surface of PEDOT:PSS layer has increased its surface area by $\sim 0.04\%$ (assuming an imprint peak height of 10 nm every 700 nm). This directly increases the number of charge carriers being extracted from the photoactive layer. However, looking at the percentage increase in the surface area, it is significantly less than...
the increase in $J_{sc}$. The huge difference implies that there is an additional effect present other than only the increase in surface area. Suggestions for such effects include: (i) improved charge extraction through reduction in PEDOT:PSS thickness; (ii) improved charge extraction through modification of the band alignment at the PEDOT:PSS/P3HT:PCBM interface; and (iii) increased optical absorption due to light trapping by the imprinted pattern through scattering and little contribution from refraction at the interface between PEDOT:PSS and P3HT:PCBM. Besides an increase in $J_{sc}$, the fill factor of the device also increased upon patterning which implies that there is a decrease in the series resistance of the cell as a result of patterning.

The suggestions above may be explained from Figure 5.7. A reduction in film thickness of ~10 nm could be present at the ‘bottom’ of the imprinted pattern which corresponds to a reduction of ~20% in PEDOT:PSS film thickness at this point and ~10% overall assuming that the width of the troughs and crests are similar. Modification of the band alignment may occur due to the deposition of small quantities of PDMS on the PEDOT:PSS layer during patterning as reported elsewhere.$^{39}$

Presented in Figure 5.13 are $J-V$ characteristics of reference and patterned devices whose PEDOT:PSS layers were annealed at temperatures ranging from 140°C to 180°C. Each of the values given is the average from measurements on three identical devices fabricated on a single substrate. The effect of imprinting can clearly be seen to increase the $J_{sc}$ in all devices regardless of annealing temperature. The electronic parameters that characterise the devices are given in Table 5.2. There is an increase in the $FF$ of all devices as a result of patterning with only a small reduction in $V_{oc}$ which may be due to modifications of the PEDOT:PSS surface as explained above. It is also noted that there is some variability in the increase in efficiency as the temperature is changed. This may be related to variations in imprint quality or changes to the PEDOT:PSS conductivity as previously reported.$^{40}$ Alternatively, variations
in the definition of the features imprinted could change the strength of any optical confinement of photons within the device thus changing absorption properties.

Figure 5.13: J-V characteristics of device performance under AM1.5 illumination (a) Reference devices at temperatures 140°C, 150°C, 160°C, 170°C and 180°C (b) Patterned devices at same temperatures. Device parameters are shown in Table 5.2.
Table 5.2: Characteristics of Patterned and Reference Devices.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>% Increment in $J_{SC}$</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>% Increment in FF</th>
<th>PCE (%)</th>
<th>% Increment in PCE</th>
</tr>
</thead>
<tbody>
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<td>140</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Patterned</td>
<td>1.58</td>
<td>4.0</td>
<td>0.55</td>
<td>0.47</td>
<td>62.1</td>
<td>0.41±0.01</td>
<td>51.9</td>
</tr>
<tr>
<td>Reference</td>
<td>1.52</td>
<td></td>
<td>0.61</td>
<td>0.47</td>
<td></td>
<td>0.27±0.01</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Patterned</td>
<td>3.03</td>
<td>24.2</td>
<td>0.62</td>
<td>0.43</td>
<td>4.9</td>
<td>0.81±0.01</td>
<td>28.6</td>
</tr>
<tr>
<td>Reference</td>
<td>2.44</td>
<td></td>
<td>0.63</td>
<td>0.43</td>
<td></td>
<td>0.63±0.01</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Patterned</td>
<td>1.72</td>
<td>18.6</td>
<td>0.59</td>
<td>0.31</td>
<td>6.9</td>
<td>0.31±0.01</td>
<td>19.2</td>
</tr>
<tr>
<td>Reference</td>
<td>1.45</td>
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<td>0.61</td>
<td>0.29</td>
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<td>0.26±0.01</td>
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<td>170</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Patterned</td>
<td>2.01</td>
<td>67.8</td>
<td>0.56</td>
<td>0.41</td>
<td>41.3</td>
<td>0.46±0.01</td>
<td>109.1</td>
</tr>
<tr>
<td>Reference</td>
<td>1.20</td>
<td></td>
<td>0.63</td>
<td>0.29</td>
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<td>0.22±0.01</td>
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<td>180</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Patterned</td>
<td>2.00</td>
<td>69.5</td>
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<td>0.36</td>
<td>24.1</td>
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</tr>
<tr>
<td>Reference</td>
<td>1.18</td>
<td></td>
<td>0.62</td>
<td>0.29</td>
<td></td>
<td>0.21±0.01</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.14: Change of device power conversion efficiencies due to patterning and annealing of PEDOT:PSS.

Also shown in Figure 5.14 is the change in PCE for each set of devices, and are tabulated in Table 5.1 along with the percentage increments in $J_{SC}$, FF and PCE between the patterned
and reference devices. As would be expected when the increase in $J_{SC}$ and $FF$ is taken into account, along with the negligible reduction in $V_{OC}$, we observe that the PCE increases following patterning with a general trend indicating that higher annealing temperatures are beneficial. It is noted that whilst the highest PCE (and highest $J_{SC}$, $V_{OC}$ and $FF$) is observed for the device annealed at 150 °C, the increase in PCE is similar as observed for the devices annealed at 170 and 180 °C. Critically, $J_{SC}$ is increased more at the higher temperatures compared to 150 °C. Thus, in devices in which all processing can be carried out under controlled conditions, these should result in the highest PCEs.

So far, the optical characterisation of these devices have not been performed and will be conducted in Chapter six following the improvement in the stamping procedure to obtain an increased stamping depth in PEDOT:PSS.

5.2.3 Alternative Stamping Method – (Put-Down Process)

As mentioned in the preceding section, the direct patterning of the surface of PEDOT:PSS layer has increased its surface area by -0.04% (assuming an imprint peak height of 10 nm every 700 nm). A reduction in film thickness of -10 nm could be present at the ‘bottom’ of the imprinted pattern which corresponds to a reduction of ~20% in PEDOT:PSS film thickness at this point and ~10% overall assuming that the width of the troughs and crests are similar. The implication of this result is a prolonged absorption path in the absorption region compared to the flat interfaces (the absorption of reference and patterned devices is given in Chapter six). To improve on the above mentioned gains, an alternative stamping procedure was chosen in order to increase the imprint peak height beyond the 10 nm already achieved through the lift-up process. The alternative method, the put-down process is described schematically in Figure 5.15. The main difference in this procedure is that the PEDOT:PSS was spin-cast directly on the PDMS stamp instead of the substrate. To increase the imprint
depth, the spinner was set to 2500 rpm for 40 seconds as opposed to 3000 rpm (60 seconds) used in previous experiments.

Figure 5.15: Schematics of the device fabrication showing the put-down process.

The set up was cured on a hot plate at 80°C for 10 min and allowed to cool to room temperature before the PDMS stamp was lift-off leaving well-defined features on PEDOT:PSS. Thereafter, the resulting ITO/PEDOT:PSS structure was further annealed at 150°C for 20 min to remove remaining water from the sample. The results of the devices fabricated using this new adopted method will be presented and discussed in Chapter Seven. Figure 5.16 shows the AFM image of PEDOT:PSS and its depth profile using the put-down procedure. The depth profile indicates that the imprint peak height was increased to ~42 nm with a period of ~727 nm. This represents a significant improvement in the quality of these structures using this low-cost approach of nanoscale patterning over what was previously...
reported. It should be noted that there is less sub-features on the patterns as compared to observed in the stamped PEDOT:PSS using the lift-up process.

Figure 5.16: AFM image (a) and profile (b) of DVD-patterned PEDOT:PSS. The increase in the surface area due to DVD patterning is ~0.7% which is capable of pushing device performance a bit further besides other considerations.

The same procedure described here was also applied to patterned PEDOT:PSS using PDMS stamps made from Blu-ray master stamp.

Figure 5.17: AFM image (a) and profile (b) of Blu-ray-patterned PEDOT:PSS. AFM analysis of the Blu-ray-stamped PEDOT:PSS (Figure 5.17 a and b) reveals an imprinted profile depth and period of ~10 nm and ~340 nm respectively. This represents an increase in the surface area of ~0.2%.
In the proceeding chapter, all the optical characterisation was done using stamped samples prepared by the put-down process described above.

**Summary**

In this chapter we have found that:

- Simple and commercially available DVD discs can be used as a master stamp to fabricate PDMS stamps with replica features of the DVD.

- PEDOT:PSS layer can successfully be imprinted by applying a low-cost technique using PDMS stamp with feature depth down to ~10 nm and ~700 nm period.

- Nanoimprinted features can be used to optimize the device leading to ~24% increase in $J_{SC}$ of the device.

- General trend of increase in the fill factor of the devices fabricated resulting from the reduction of the series resistance of the device and increase in the shunt resistance.

- Positive effects on the device parameters, except the $V_{OC}$, due to patterning ultimately led to ~30% increase in the device power conversion efficiency.

- Inconsistency in the improvement of the device parameters was attributed to an unwanted layer deposited beneath the glass substrate, thus absorbing part of the incident light leading to decreased absorption and lower light intensity passing into the device which manifested in the slight decreases in the $V_{OC}$.

- Deposition of the PEDOT:PSS on the stamp (put-down method) before stamping on the substrate and reducing the spin coating speed resulted in an increase in the imprint peak height from ~10 nm to ~42 nm, with slight increase in the period from ~700 nm to ~727 nm.
References


Chapter 6

Optical Characterisation of Devices
The results presented in the preceding chapter which show improvements in the measurable device parameters demands further experiments to understand the underlying effects which brought about such improvements. Optical study of the imprinted samples along with its reference counterparts can provide clues to the observed changes. In this chapter the research focussed on the behaviour of light through the imprinted PEDOT:PSS layer and its non-imprinted counterpart, as well as its behaviour through the active layer as it is affected by the imprint features. All samples used in this chapter followed the same procedure as described in Chapter Four but with precautions to avoid the error of having the solution underneath the back of the devices as previously presented in Chapter Five.

6.1 Transmittance of Surface Modified PEDOT:PSS
Two approaches were followed to obtain the optical transmission properties of the surfaces of PEDOT:PSS studied in this research. Firstly, a set-up passing light through a monochromator and optical alignments (Iris and collimator lens) was used to focus light on the samples and were then collected by a Si detector connected to a Newport meter linked to a computer. The full description is already given in Chapter Four. Also, transmittance was measured with a UV-VIS-NIR spectrometer to compare with that of the set-up and the results are presented in Figure 6.1a and 6.1b.
The results indicate that the reference sample transmits light more than the imprinted samples especially within the wavelength range of 400 to 650 nm. This is assumed to be due to the scattering of light by the imprinted features on the PEDOT:PSS out of the aperture of the detectors in both experiments. This is desirable because the scattered light will have to go through a different and elongated path in the active layer deposited on the PEDOT:PSS. This should naturally culminate into an increased absorption within the photoactive layer which is presented in the following section. The difference in the spectra from the two methods is because the transmittance through the substrate was corrected for in the UV-VIS-NIR spectrometer, but the same correction was not made for the measurement using the set-up with the monochromator. Thus, the distortion between the 240 and 380 nm range is due to the absorption by the glass substrate.

![Figure 6.1: Transmission spectra of PEDOT:PSS and imprinted PEDOT:PSS measured using (a) Monochromator/Newport power meter, and (b) UV-VIS-NIR spectrometer.](image)

As is proposed in the next chapter, there is a mono layer residue of PDMS left on the samples after stamping. UV-Visible light transmission was measured on different thicknesses of the PDMS materials to investigate any possible absorption due to it. The thickness ranged from 0.39 mm to 2.40 mm and the results is as shown in Figure 6.2. The results indicate a fairly constant transmittance of about 90%, regardless of the thickness between the 400 nm and 650
nm spectral range of interest, and do not follow any particular trend. In the ultraviolet region where it absorbs, the transmittance is seen to decrease with increase in thickness to below 60%. This is indicative of the fact that a monolayer of PDMS would not have caused the decrease in the transmittance of the imprinted PEDOT:PSS observed in Figure 6.1 and thus, is entirely attributed to scattering by the features.

Figure 6.2: Transmission spectra of different thicknesses of PDMS measured by UV-VIS-NIR spectrometer (The transmission axis is presented in logarithmic scale for clarity).

6.2 Transmittance and Absorption of P3HT:PCBM on Imprinted PEDOT:PSS

To investigate the effects of the scattered light due to the imprinted features on the photoactive layer, the composition materials as well as the blended P3HT:PCBM were deposited on the samples. Transmission and absorption measurements were carried out using a UV-VIS-NIR spectrometer. Figure 6.3 presents the transmission through a DVD-patterned device with device structure stamped-PEDOT:PSS/P3HT:PCBM along with its reference device with no features. The absorption coefficient was calculated thus:

\[ \text{Abs} = \log\left(\frac{1}{T}\right), \quad \text{.................................(6.1)} \]
where \( T = \frac{I}{I_0} \) is the percentage transmittance, and

\[
I = I_0 e^{-(\alpha d)}
\] ...........................(6.2)

Where \( I_0 \) = Intensity of the incident light source

\( I \) = Intensity of light after passing through the film

\( d \) = Thickness of the film

Thus,

\[
\alpha = -\frac{\ln(I_0/I)}{d}
\] ............................... (6.3)

Converting the natural logarithm to base 10,

\[
\ln \left( \frac{I_0}{I} \right) = \ln(10) \log \left( \frac{I_0}{I} \right)
\] ................................. (6.4)

\[
\ln \left( \frac{I_0}{I} \right) = 2.303 \log \left( \frac{I_0}{I} \right)
\] ................................. (6.5)

Therefore,

\[
\alpha = -\frac{2.303 \times Abs}{d}
\] ............................... (6.6)

The thickness of the film was measured from an ellipsometer as \( d = 200 \) nm.

The results show more light transmission through the reference device in the visible spectral region with increase in the separation between the two curves as compared to Figure 6.1. The effect of imprinting on the optical properties of films made from the composite materials, P3HT and PCBM, and films of the bulk heterojunction P3HT:PCBM devices is illustrated in Figure 6.4a and 6.4b, and Figure 6.5 respectively.

The absorption coefficient increases after patterning in the absorbing P3HT and the blend, particularly beyond the 340 nm up to the red shoulder at 600 nm. This suggests an increase in the optical path length within the photoactive layer originating from light scattering by the imprinted features as well as refraction at the PEDOT:PSS/P3HT:PCBM interface. There
may also be a contribution from differences in the thickness of the films due to the patterned PEDOT:PSS surface.

![Graph showing transmission spectra](image)

**Figure 6.3**: Transmission spectra of reference and patterned devices measured by UV-VIS-NIR spectrometer.

![Graph showing absorption coefficients](image)

**Figure 6.4**: Absorption coefficients of pristine and imprinted (a) PEDOT:PSS/P3HT, and (b) PEDOT:PSS/PCBM samples.

However, any contribution from the thickness at the trough of the pattern should be counterbalanced by less thickness at the crest considering the fact that the spot size of the incident light is much greater than the period of the features. Furthermore, a close look at the
samples by eye showed a lighter film colour on the patterned samples suggesting that the thickness of the stamped sample is less than that of the flat sample.

Figure 6.5: Absorption coefficients of reference and imprinted devices for device structure (a) PEDOT:PSS/P3HT:PCBM and (b) ITO/PEDOT:PSS/P3HT:PCBM.

6.3 Photoluminescence Measurements
Photoluminescence (PL) spectra of P3HT, P3HT:PCBM, DVD-imprinted and Blu-ray-imprinted samples fabricated on PEDOT:PSS are shown in Figure 6.6. The quenching of the PL for the samples with PCBM is obvious (Figure 6.6a) and is attributed to efficient electron transfer from the polymer donor (P3HT) to the PCBM acceptor.\textsuperscript{1} From the intensity of photoluminescence spectra of the blended devices in Figure 6.6b, it is clear that there is further quenching due to patterning of the interfacial PEDOT:PSS layer. The quenching due to the underlying patterns in this case can be attributed to scattering of the luminescence in different directions and as such, most of the scattered light could not be collected thereby reducing the external quantum efficiency as observed. This is also indicative of the fact that charge carrier recombination near the patterned interfacial PEDOT:PSS is reduced, which would translate into better device performance.
6.4 Raman Spectroscopy Measurements

To understand the effect of patterning on the surface of PEDOT:PSS on a molecular level, the films were studied by Raman spectroscopy. Raman spectroscopy is a powerful tool for studying conducting polymers. Advantages of Raman studies include direct experimental observables at the molecular level, and chemical information from peak position and bandwidth analysis.

Firstly, the Raman spectrum of PDMS is presented in Figure 6.7 with numbers showing the vibrational peaks as compared with ref [6]. This is to bear in mind that any chemical modification on the surface of PEDOT:PSS would only come from the PDMS stamp as it made a conformal contact with it during stamping. Table 6.1 shows the vibrational modes of each of the peaks identified using ref [6].
Figure 6.7: Raman spectrum of PDMS film under 514 nm laser excitation.

Table 6.1: Vibrational modes of PDMS from Raman spectroscopy.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Raman Shift (cm⁻¹)</th>
<th>Approximative Description of Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>487</td>
<td>Si-O-Si symmetric stretching</td>
</tr>
<tr>
<td>2.</td>
<td>613</td>
<td>Si-CH₃ symmetric rocking</td>
</tr>
<tr>
<td>3.</td>
<td>701</td>
<td>Si-C symmetric stretching</td>
</tr>
<tr>
<td>4.</td>
<td>790</td>
<td>CH₃ asymmetric rocking + Si-C asymmetric stretching</td>
</tr>
<tr>
<td>5.</td>
<td>842</td>
<td>CH₃ symmetric rocking</td>
</tr>
<tr>
<td>6.</td>
<td>1254</td>
<td>CH₃ symmetric bending</td>
</tr>
<tr>
<td>7.</td>
<td>1407</td>
<td>CH₃ asymmetric bending</td>
</tr>
<tr>
<td>8.</td>
<td>2900</td>
<td>CH₃ symmetric stretching</td>
</tr>
<tr>
<td>9.</td>
<td>2960</td>
<td>CH₃ asymmetric stretching</td>
</tr>
</tbody>
</table>

The Raman spectra of the unpatterned and the patterned PEDOT:PSS films are shown in Figure 6.8 with strongest signal observed between 1400 and 1500 cm⁻¹, which corresponds to the stretching vibration of Cₓ=Cᵧ on the five-member ring of PEDOT.²⁻⁴
The patterned PEDOT:PSS exhibited a broader band at a higher position than the unpatterned PEDOT:PSS with a shoulder at 1456 cm$^{-1}$. Although the changes in the spectrum of the patterned PEDOT:PSS cannot directly be traced to the Raman spectrum of PMDS above, it is proposed that any residual monolayer of the PDMS stamp left on the surface of the PEDOT:PSS after imprinting could cause the slight broadening of its spectrum.

### 6.5 Fourier Transform Infrared Spectroscopy Measurements

To provide direct evidence of the presence of a PDMS residue on the patterned PEDOT:PSS film, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) measurements were performed. Figure 6.9 shows the ATR-FTIR spectrum of the imprinted PEDOT:PSS film and of the PDMS stamp. Though noisy this clearly indicates a PDMS residue on the PEDOT:PSS with characteristic features at $\sim$1259 cm$^{-1}$ (CH$_3$ symmetric mode) and a split peak $\sim$1015 cm$^{-1}$ and 989 cm$^{-1}$ (Si-O-Si asymmetric deformation mode). Further
peaks may be identified above the noise level at \( \sim 860 \text{ cm}^{-1} \) (Si-C) and \( 788 \text{ cm}^{-1} \) (Si-[CH\(_3\)]\(_2\)), further supporting the presence of PDMS.

![ATR-FTIR spectra of PDMS and patterned PEDOT:PSS](image)

*Figure 6.9: ATR-FTIR spectra of PDMS and patterned PEDOT:PSS carried out using a PDMS stamp.*

### 6.6 Ultraviolet Photoelectron Spectroscopy Measurements

To assess the impact of the residual PDMS film on the electronic properties of the interfacial layer, UPS measurements were undertaken on PEDOT:PSS surfaces before and following imprinting using the PDMS DVD stamp. The UPS cut-off spectra of PEDOT:PSS and stamped PEDOT:PSS films biased at -3V are shown in Figure 6.10 corrected for the applied bias and analyzer work function. The work function in the UPS spectra is given by the secondary electron cut-off, since the electrons responsible for the secondary edge have just sufficient energy to overcome the work function of the material. Details of how the values were extracted using equations as given by Bundgaard *et al.*⁸ are presented below.
\[
\Phi_{Au} = h\nu - BE_{max} \quad \cdots \quad (6.7)
\]
\[
E_{F}^{VB} = BE_{min} \quad \cdots \quad (6.8)
\]
\[
E_{F}^{VAC} = h\nu - BE_{max} \quad \cdots \quad (6.9)
\]
\[
IP = E_{F}^{VB} + E_{F}^{VAC} \quad \cdots \quad (6.10)
\]
\[
\Delta = E_{F}^{VAC} - \Phi_{Au} \quad \cdots \quad (6.11)
\]

where \(BE_{max}\) and \(BE_{min}\) are the cut-off at high binding energy and the onset at low binding energy, respectively. \(BE_{min}\) represents the injection barrier for holes from gold into the valence band of the polymer material \((E_{F}^{VB})\). The work function of the substrate \((\Phi_{Au})\) is obtained from Eq 6.7, where \(BE_{max}\) is obtained by measurements on a clean sample, where the Fermi level of gold is established. \(E_{F}^{VAC}\) is the distance from the Fermi level to the vacuum level and is obtained from Eq 6.9. IP, the ionization potential, is a material constant, and \(\Delta\) is the vacuum level shift, i.e., the effect of the dipole layer at the interface of vacuum and the polymer layer.\(^8\)

The work function of the samples was measured by applying a bias of -3V, -5V, -7V and -10 V, respectively and determined by the intersection of the low kinetic energy cut-off of the accelerated electrons with the base line of the spectra. After subtracting the bias voltage in each case, the same value for the work function was obtained for all applied voltages, which rules out any charging effects of the sample.
Figure 6.10: Secondary electron energy cut-off of unpatterned and patterned PEDOT:PSS films as measured by UPS.

UPS measurements of as deposited PEDOT:PSS reference films yielded a work function of ~5.1 ± 0.1 eV. In contrast to this, the measurement of patterned PEDOT:PSS films yielded a much lower work function of ~ 4.7 ± 0.1 eV. Previously reported values of the unmodified PEDOT:PSS work function range from 4.8 to 5.15 eV, hence the modified value is outside this range. Given the large difference between these values, series of measurements were undertaken varying experimental conditions (e.g. bias voltages, effective sample area measured, and calibration using an Au reference) all of which confirmed the shift in binding energy following patterning and excluded it being an experimental artefact. This decrease of ~0.4 eV to 4.7 eV is highly significant as the interfacial work function is now lower than the HOMO of P3HT (5 eV) and thus the barrier for hole transfer to the anode has been removed and the effect on the device parameter is discussed in Chapter Eight.
6.7 X-ray Photoelectron Spectroscopy (XPS) Measurements

To study any chemical modification of the PEDOT:PSS surface, X-ray photoelectron spectroscopy of the oxygen O(1s) and sulfur S(2p) core levels of the reference and patterned PEDOT:PSS were undertaken, Figure 6.11 (No Si X-ray photoelectron signal was observed from PDMS, presumably due to its small cross-section and lower concentration if the PDMS film is incomplete). A chemical shift of 0.5 eV was observed in the O(1s) spectrum of the imprinted sample following imprinting. Previous reports of acid treatment of PEDOT:PSS demonstrate a similar shift to higher energy upon conversion of PSS-\( \text{Na}^+ \) to PSSH.\(^\text{10}\)

Similarly, the S(2p) spectrum displays a broad peak 165 eV originating from previously described sulfur peaks within the PEDOT (not resolvable in our spectrum) at 164.5 and 165.6 eV. The higher energy peak 169 eV is assigned to sulfur within the PSS. No change in peak position is observed upon patterning though a slight broadening of the peak 165 eV is observed.

![Figure 6.11: O(1s) and S(2p) core-levels of unpatterned and patterned PEDOT:PSS films, as measured by XPS.](image)

These results therefore indicate that any modification occurring is limited to the surface PSS layer via the oxygen atom bound to the sulfonic acid group.
Summary
In this chapter we have found that:

- Planar PEDOT:PSS samples have slightly higher percentage transmittance than the imprinted sample, attributed to light scattering by the imprinted features out of the aperture of the detector. Hence, a photoactive layer deposited on such surface would result in increased interaction of light within the material.

- PDMS has fairly constant transmittance of about 90% regardless of the thickness which is indicative of the fact that, any residue left on PEDOT:PSS surface after stamping, does not affect the intensity of light entering the device within the spectral range of interest.

- More light transmission is observed in the devices with planar PEDOT:PSS layer with the photoactive material deposited on it. Enhanced absorption is observed in the patterned devices where the scattered light defines a longer absorption path.

- Light scattering by the imprinted features were also noticed by the lower photoluminescence of the patterned devices.

- A monolayer of residual PDMS was confirmed from the ATR-FTIR with characteristic features at ~1259 cm\(^{-1}\), 1015 cm\(^{-1}\) and 989 cm\(^{-1}\) representing different vibrational modes of the PDMS molecule.

- The work function of PEDOT:PSS was reduced from 5.1±0.1 eV to ~4.7±0.1 eV upon imprinting as measured by UPS and is shown to have a significant effect on the device performance in Chapter Seven.

- XPS measurements presented a chemical shift of about 0.5 eV in the O(1s) spectrum of the imprinted sample of the PEDOT:PSS confirming a chemical modification of the surface PSS by the PDMS monolayer.
References
Chapter 7

Enhancement of Open Circuit Voltage of Organic Devices

Among the essential parameters which determine the power conversion efficiency of thin film photovoltaic devices is the open-circuit voltage ($V_{OC}$). Of note is the fact that organic solar cells produce respectable open-circuit voltages. Following the metal-insulator-metal (MIM) model, it has been demonstrated that for a photodiode based on a single layer of conjugated polymer, the $V_{OC}$ scales with the work function difference between the electrodes.\textsuperscript{1,2} This is also true in bilayer devices comprising of electron- and hole-accepting polymers in which the $V_{OC}$ scales linearly with the work function difference, but with a further contribution depending on the light intensity.\textsuperscript{3} This contribution, according to Mihailetchi et al.,\textsuperscript{1} is due to the accumulation of charge carriers at the organic/organic interface, giving rise to a diffusion current which must be compensated for by a drift current at open circuit. There is a linear correlation of the $V_{OC}$ in bulk heterojunction solar cells with the reduction potential of the acceptor as reported by Brabec et al.\textsuperscript{4} This is expected with ohmic contacts, where the negative and positive electrodes match the lowest unoccupied molecular orbital (LUMO) level of the acceptor and the highest occupied molecular orbital (HOMO) level of the donor respectively, by pinning the Fermi levels of the cathode and anode.\textsuperscript{1}

It therefore means that the most effective way to enhance the $V_{OC}$ of BHJ solar cells is to shift the LUMO level of the acceptor material closer to the vacuum level,\textsuperscript{5} or lower the HOMO level of the donor material further from the vacuum level.\textsuperscript{6,7} Doing so isn’t without its
attendant compromise on desirable properties, such as the absorption limit, charge separation efficiency and charge mobility.\textsuperscript{8} Other than this, $V_{OC}$ has been enhanced by insertion of insulating LiF between the active layer and the cathode.\textsuperscript{9,10} Instead of LiF, Zhang \textit{et al}\textsuperscript{11} demonstrated that a thin film of poly(ethylene oxide) (PEO) spin-cast on the active layer before deposition of the aluminium (Al) cathode can substantially enhance the $V_{OC}$ of polymer solar cells. Furthermore, modification of the interfacial properties of ZnO/cathode contacts by incorporation of carboxylic acid-based self-assembled molecules of various dipole moments led to larger $V_{OC}$ values.\textsuperscript{12} Work by He \textit{et al}\textsuperscript{13} demonstrated up to 150 mV enhancement in $V_{OC}$ by using polyfluorene copolymers (PFCs) as cathode interlayers. In this chapter, an effort made to enhance the open-circuit voltage alongside other device parameters already achieved is presented. Instead of modifying the top electrode, the underlying PEDOT:PSS layer was modified \textit{via} nanoimprinting. With the results obtained, further experiments were pursued to establish the origin of the enhancement of the $V_{OC}$, some of which was already presented in the preceding Chapter under optical measurements.

\begin{flushleft}
\textbf{7.1 Reference Devices with cleaned glass surfaces}
\end{flushleft}

The results of the first batch of experiments presented in Chapter Five indicate an enhanced short circuit current density ($J_{SC}$) and the fill factor ($FF$) with slight reduction in the open-circuit voltage ($V_{OC}$). This was consistent throughout all experiments performed which led to a conclusion in ref \cite{14} that modifying the interfacial PEDOT:PSS will automatically lead to a reduced $V_{OC}$.

On a closer look at the devices fabricated, the glass surface which admits light into the device during measurements had the active material smeared over it and was not cleaned after the fabrication of the device. This would generally reduce light absorption as it passes through the smeared material and get absorbed, as well as reduce the light intensity. Drawing from the
work by Kumar et al., a reduced light intensity from 100 mW/cm² which was used for the measurements of the $J-V$ characteristics would affect both the $J_{SC}$ and $V_{OC}$. To investigate the effect of the spills of the active material on the glass surface of the devices, a set of three devices were fabricated using the usual procedure as the ones presented in Chapter Five (denoted as pristine) and measured. The glass surface of the devices was then cleaned using a clean-room wipe soaked with toluene and then re-measured. Figure 7.1 shows the J-V characteristics in the dark and under AM1.5 illumination.

![J-V characteristics of pristine device and same device cleaned with toluene. Devices structure was ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al.](image)

It is apparent from the $J-V$ characteristics that the performance of the devices presented in Chapter Five were affected negatively by the smear of the active material on the glass side of the device, thus the worse results were obtained. Cleaning the device has shown significant improvements in all device parameters including the $V_{OC}$ (see the table in Figure 7.1).
7.2 Reference Devices
Reference devices were fabricated following the procedure given in Chapter Four but with the spin speed of the PEDOT:PSS reduced to 2500 rpm for 40 seconds (instead of 3000 rpm for 60 seconds earlier used) in consonance with that used for stamping to allow for direct comparison. Kim et al. have shown that the device performance is not strongly sensitive to PEDOT:PSS thickness over the measurable range of 65 nm to 160 nm. Thus, reducing the spin speed and time which leads to thicker film does not change the overall performance of the new set of devices made. The best reference device fabricated with device structure ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al is shown in Figure 7.2a. The device exhibits 2.24% power conversion efficiency, 6.12 mA/cm² short-circuit current density, 66% fill factor, 551 mV open-circuit voltage, a series and shunt resistance of 8.15 Ω cm² and 597.66 Ω cm² respectively. Figure 7.2b shows the external quantum efficiency spectrum of the reference device when illuminated through the ITO contact which peaks at ~520 nm corresponding to 47%.

![Figure 7.2: (a) J-V characteristics of the best performing reference device made in this work, and (b) external quantum efficiency.](image)

Other reference devices with/without LiF and different composite material concentrations are presented in Table 7.1 below. Compared to earlier devices presented in Chapter Five, the
reference devices are well above the 1% benchmark in power conversion efficiency which
caracterised those results.

Table 7.1: J-V characteristics of reference devices.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>6.1104</td>
<td>0.5571</td>
<td>0.658</td>
<td>2.24</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>5.9599</td>
<td>0.5569</td>
<td>0.6508</td>
<td>2.16</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>6.0097</td>
<td>0.5552</td>
<td>0.6324</td>
<td>2.11</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>4.9122</td>
<td>0.5897</td>
<td>0.5899</td>
<td>1.71</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>4.7831</td>
<td>0.5899</td>
<td>0.5759</td>
<td>1.63</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>4.7097</td>
<td>0.5864</td>
<td>0.5884</td>
<td>1.63</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>4.7945</td>
<td>0.5687</td>
<td>0.5974</td>
<td>1.63</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>4.5909</td>
<td>0.5506</td>
<td>0.6477</td>
<td>1.61</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>4.6364</td>
<td>0.5695</td>
<td>0.5973</td>
<td>1.58</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>5.9215</td>
<td>0.5543</td>
<td>0.5996</td>
<td>1.97</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>5.2419</td>
<td>0.5739</td>
<td>0.602</td>
<td>1.81</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>5.2362</td>
<td>0.5602</td>
<td>0.5891</td>
<td>1.73</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>4.8224</td>
<td>0.4557</td>
<td>0.5415</td>
<td>1.19</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>3.9063</td>
<td>0.441</td>
<td>0.5805</td>
<td>1.00</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>3.7489</td>
<td>0.445</td>
<td>0.5455</td>
<td>0.91</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>5.0429</td>
<td>0.5815</td>
<td>0.5763</td>
<td>1.69</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>5.2162</td>
<td>0.5766</td>
<td>0.5686</td>
<td>1.71</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>5.0544</td>
<td>0.5798</td>
<td>0.5699</td>
<td>1.67</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al</td>
<td>4.6749</td>
<td>0.5719</td>
<td>0.5386</td>
<td>1.44</td>
</tr>
</tbody>
</table>

7.3 Nanoimprinted Devices
To further the effect of modifying the interfacial PEDOT:PSS between the ITO anode and the
photoactive layer beyond enhancements in $J_{sc}$ and $FF$, the alternative stamping procedure
(put-down process) described in section 5.2.3 was used to imprint the surface of
PEDOT:PSS. In this case, the PEDOT:PSS was spin-cast directly on the PDMS stamp and
then placed over the oxygen-plasma treated ITO substrate to make conformal contact and
cured on a hot plate at 80°C for 10 min, allowed to cool before removing the stamp. Thereafter, the resulting ITO/PEDOT:PSS structure was further annealed at 150°C for 20 min to remove remaining water from the sample. This method allows PEDOT:PSS to fill the grooves of the stamp directly instead of filling by capillary action. This also allows enough time for the PSS component which dominate the surface of PEDOT:PSS to make any chemical interaction with the PDMS. The best DVD-patterned device fabricated with device structure ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al is shown in Figure 7.3.

![J-V characteristics](image)

Figure 7.3: J-V characteristics of the best performing DVD-patterned device made in this work.

The device exhibits 3.36% power conversion efficiency, 10.02 mA/cm² short-circuit current density, 59% fill factor, 563.6 mV open-circuit voltage, a series and shunt resistance of 10.83 Ω.cm² and 335.87 Ω.cm² respectively. It is worth noting that the best devices were obtained when the concentration of the photoactive material was increased from 8 mg wt/wt 1:1 ratio in 1 ml dichlorobenzene to 10 mg. The external quantum efficiency of this device was not measured. Other imprinted devices with/without LiF and different composite material concentrations are presented in Table 7.2. The highest power conversion efficiency achieved in the course of this work is 3.36% with a short-circuit current of 10.02 mA/cm².
Table 7.2: J-V characteristics of imprinted devices.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVD</td>
<td>5.9707</td>
<td>0.5811</td>
<td>0.5189</td>
<td>1.80</td>
</tr>
<tr>
<td>8mg:8mg in</td>
<td>5.1298</td>
<td>0.5821</td>
<td>0.4789</td>
<td>1.43</td>
</tr>
<tr>
<td>1ml DCB</td>
<td>4.9506</td>
<td>0.5823</td>
<td>0.5099</td>
<td>1.47</td>
</tr>
<tr>
<td>Blu-ray</td>
<td>5.9904</td>
<td>0.5855</td>
<td>0.5504</td>
<td>1.93</td>
</tr>
<tr>
<td>8mg:8mg in</td>
<td>5.2443</td>
<td>0.5799</td>
<td>0.5403</td>
<td>1.64</td>
</tr>
<tr>
<td>1ml DCB</td>
<td>4.8239</td>
<td>0.5744</td>
<td>0.5151</td>
<td>1.43</td>
</tr>
<tr>
<td>DVD</td>
<td>10.0155</td>
<td>0.5636</td>
<td>0.5944</td>
<td>3.36</td>
</tr>
<tr>
<td>(10mg:10mg in</td>
<td>9.7994</td>
<td>0.5598</td>
<td>0.5721</td>
<td>3.14</td>
</tr>
<tr>
<td>1ml DCB)</td>
<td>9.872</td>
<td>0.5624</td>
<td>0.5491</td>
<td>3.05</td>
</tr>
<tr>
<td>DVD</td>
<td>12.6807</td>
<td>0.4302</td>
<td>0.4348</td>
<td>2.37</td>
</tr>
<tr>
<td>(10mg:10mg in</td>
<td>12.0484</td>
<td>0.4202</td>
<td>0.4375</td>
<td>2.22</td>
</tr>
<tr>
<td>1ml DCB)</td>
<td>11.8267</td>
<td>0.4303</td>
<td>0.3784</td>
<td>1.93</td>
</tr>
<tr>
<td>DVD</td>
<td>5.8051</td>
<td>0.5806</td>
<td>0.5156</td>
<td>1.74</td>
</tr>
<tr>
<td>(10mg:10mg in</td>
<td>5.9845</td>
<td>0.5888</td>
<td>0.4807</td>
<td>1.69</td>
</tr>
<tr>
<td>1ml DCB)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.4 Nanoimprinted and Reference Devices fabricated together

To allow for direct comparison, all imprinted devices made side by side with its reference counterparts were fabricated without LiF interlayer. As explained earlier in Section 5.1.3, even a monomolecular layer of LiF can cause a significant vacuum level offset which would introduce disparity in the devices placed side by side. Figure 7.4 (a) shows the J-V characteristics in the dark and under AM 1.5 illuminations of an imprinted and its reference device fabricated at the same time and (b) is the dark J-V characteristics showing the reduced dark current after imprinting.
Figure 7.4: (a) J-V characteristics in the dark and under AM 1.5 illuminations of a DVD-imprinted ($J_{SC}=6.4609 \text{ mA/cm}^2$, $V_{OC}=0.5061 \text{ V}$, $FF=0.5219$, $\eta=1.71\%$, $R_s=20.26 \Omega \text{ cm}^2$, $R_{sh}=465.7 \Omega \text{ cm}^2$) and its reference ($J_{SC}=5.3355 \text{ mA/cm}^2$, $V_{OC}=0.4655 \text{ V}$, $FF=0.5215$, $\eta=1.3\%$, $R_s=18.77 \Omega \text{ cm}^2$, $R_{sh}=448.14 \Omega \text{ cm}^2$) device fabricated at the same time and (b) the dark J-V characteristics. Device structure: ITO/PEDOT:PSS/P3HT:PCBM/Al.

Besides the obvious enhancement in both the $J_{SC}$ and $FF$, the $V_{OC}$ is optimized by 40.6 mV (~9% increase) resulting in an improved PCE up to 1.71% (~32% increase). Significantly, there is also ~4% increase in the shunt resistance of the imprinted device which is desirable. As revealed by the J-V characteristics of the devices in the dark (Figure 7.4b), which may contribute to the $V_{OC}$ enhancement in the imprinted device, it is also found that the dark current of the imprinted device is significantly suppressed. Other imprinted devices using a Blu-ray PDMS stamp with periodic patterns having period and imprinting depth of 340 nm and 10 nm respectively, and DVD PDMS stamp having period and imprinting depth of 727 nm and 42 nm respectively, are summarized in Table 7.3 with their respective reference devices made at the same time under the same conditions for comparison. All devices here have the same composite material concentration of 8mg:8mg P3HT:PCBM in 1 ml of dichlorobenzene. The seemingly poor performance in some of the results summarized is attributed to different batch of solution made for the fabrication.
Table 7.3: J-V characteristics of imprinted and its reference counterpart devices.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blu-ray ITO/PEDOT:</td>
<td>6.2504</td>
<td>0.4291</td>
<td>0.4586</td>
<td>1.23</td>
</tr>
<tr>
<td>PSS/P3HT:</td>
<td>5.8564</td>
<td>0.4295</td>
<td>0.4612</td>
<td>1.16</td>
</tr>
<tr>
<td>PCBM/A1</td>
<td>5.0841</td>
<td>0.3895</td>
<td>0.4648</td>
<td>0.92</td>
</tr>
<tr>
<td>Average</td>
<td>5.7303</td>
<td>0.4096</td>
<td>0.4670</td>
<td>1.10</td>
</tr>
<tr>
<td>SD</td>
<td>0.4844</td>
<td>0.0204</td>
<td>0.0037</td>
<td>0.13</td>
</tr>
<tr>
<td>Blu-ray ITO/PEDOT:</td>
<td>5.3300</td>
<td>0.4310</td>
<td>0.4850</td>
<td>1.02</td>
</tr>
<tr>
<td>PSS/P3HT:</td>
<td>5.9700</td>
<td>0.3850</td>
<td>0.4900</td>
<td>1.22</td>
</tr>
<tr>
<td>PCBM/A1</td>
<td>4.9700</td>
<td>0.3850</td>
<td>0.4900</td>
<td>0.25</td>
</tr>
<tr>
<td>Average</td>
<td>5.4233</td>
<td>0.4194</td>
<td>0.4900</td>
<td>1.10</td>
</tr>
<tr>
<td>SD</td>
<td>0.5065</td>
<td>0.0118</td>
<td>0.0052</td>
<td>0.14</td>
</tr>
<tr>
<td>Blu-ray ITO/PEDOT:</td>
<td>2.6529</td>
<td>0.4395</td>
<td>0.5570</td>
<td>0.65</td>
</tr>
<tr>
<td>PSS/P3HT:</td>
<td>2.9505</td>
<td>0.3994</td>
<td>0.6070</td>
<td>0.72</td>
</tr>
<tr>
<td>PCBM/A1</td>
<td>2.9496</td>
<td>0.4193</td>
<td>0.5850</td>
<td>0.72</td>
</tr>
<tr>
<td>Average</td>
<td>2.8510</td>
<td>0.4194</td>
<td>0.5830</td>
<td>0.70</td>
</tr>
<tr>
<td>SD</td>
<td>0.1716</td>
<td>0.0011</td>
<td>0.0025</td>
<td>0.10</td>
</tr>
<tr>
<td>DVD ITO/PEDOT:</td>
<td>3.3272</td>
<td>0.3908</td>
<td>0.5103</td>
<td>0.53</td>
</tr>
<tr>
<td>PSS/P3HT:</td>
<td>4.5518</td>
<td>0.3297</td>
<td>0.5331</td>
<td>0.80</td>
</tr>
<tr>
<td>PCBM/A1</td>
<td>4.6173</td>
<td>0.3498</td>
<td>0.5263</td>
<td>0.85</td>
</tr>
<tr>
<td>Average</td>
<td>4.1654</td>
<td>0.3298</td>
<td>0.5232</td>
<td>0.73</td>
</tr>
<tr>
<td>SD</td>
<td>0.2767</td>
<td>0.0005</td>
<td>0.0117</td>
<td>0.17</td>
</tr>
<tr>
<td>DVD ITO/PEDOT:</td>
<td>4.0833</td>
<td>0.4404</td>
<td>0.5394</td>
<td>0.97</td>
</tr>
<tr>
<td>PSS/P3HT:</td>
<td>4.6124</td>
<td>0.4203</td>
<td>0.5726</td>
<td>1.11</td>
</tr>
<tr>
<td>PCBM/A1</td>
<td>4.3333</td>
<td>0.4105</td>
<td>0.5790</td>
<td>1.03</td>
</tr>
<tr>
<td>Average</td>
<td>4.3323</td>
<td>0.4203</td>
<td>0.5657</td>
<td>1.03</td>
</tr>
<tr>
<td>SD</td>
<td>0.2647</td>
<td>0.0041</td>
<td>0.0213</td>
<td>0.07</td>
</tr>
<tr>
<td>DVD ITO/PEDOT:</td>
<td>3.2290</td>
<td>0.4757</td>
<td>0.5239</td>
<td>0.81</td>
</tr>
<tr>
<td>PSS/P3HT:</td>
<td>6.4360</td>
<td>0.4629</td>
<td>0.5200</td>
<td>1.55</td>
</tr>
<tr>
<td>PCBM/A1</td>
<td>6.3143</td>
<td>0.4638</td>
<td>0.5202</td>
<td>1.53</td>
</tr>
<tr>
<td>Average</td>
<td>5.3585</td>
<td>0.4655</td>
<td>0.5215</td>
<td>1.30</td>
</tr>
<tr>
<td>SD</td>
<td>1.8248</td>
<td>0.0044</td>
<td>0.0022</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Some batches were made from materials purchased at different times which explain the varying performance in the sets of devices presented. However, comparing the patterned devices with its own reference device fabricated at the same time replicates the same trend of enhancements in the device parameters. The Voc enhancements range from 2.4% to 14.5% while the Jsc optimizes up to 69% from 11%.

To further study this effect, single layer P3HT patterned OPV devices were fabricated and characterised, Figure 7.5. Analysis of the single layer P3HT devices shows that though the Jsc increased with patterning, the Voc was reduced leading to a reduced FF and only a small improvement in device efficiency was gained (1.3%). The presented result is an average of three single layer devices (Table 7.4) fabricated at the same time with device structure ITO/PEDOT:PSS/P3HT/AI.
Figure 7.5: J-V characteristics in the dark and under AM 1.5 illuminations of a DVD-imprinted and its reference single layer device fabricated at the same time.

Table 7.4: J-V characteristics of DVD-imprinted and its reference single layer devices.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>Jsc (mA/cm²)</th>
<th>Inc</th>
<th>Voc (V)</th>
<th>Inc</th>
<th>FF</th>
<th>Inc</th>
<th>Eff (%)</th>
<th>Inc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single ITO/PEDOT:</td>
<td>0.0151</td>
<td>0.0223</td>
<td>0.4306</td>
<td>0.2804</td>
<td>0.3753</td>
<td>0.2879</td>
<td>0.0024</td>
<td>0.0018</td>
</tr>
<tr>
<td>PSS/ P3HT/AI</td>
<td>0.0208</td>
<td>0.0431</td>
<td>0.3906</td>
<td>0.3706</td>
<td>0.3803</td>
<td>0.3688</td>
<td>0.0031</td>
<td>0.0059</td>
</tr>
<tr>
<td>** Average</td>
<td>0.0194</td>
<td>0.0298</td>
<td>0.5361</td>
<td>0.3205</td>
<td>-0.1994</td>
<td>0.3915</td>
<td>0.3225</td>
<td>-0.1762</td>
</tr>
<tr>
<td>SD</td>
<td>0.0039</td>
<td>0.0117</td>
<td>0.0288</td>
<td>0.0494</td>
<td>0.0173</td>
<td>0.0462</td>
<td>0.0006</td>
<td>0.0023</td>
</tr>
</tbody>
</table>

7.5 Flat PDMS stamped Device as Reference device
Devices with PDMS modified PEDOT:PSS surface without nanoimprinted features were fabricated alongside their reference counterpart as described earlier to further ascertain the effects that are due only to PDMS residue and those due to nano-patterns (Figure 7.6a). The values of Voc and FF in both devices were similar with only 9.5% improvement in Jsc in the flat PDMS stamped device. Figure 7.6b shows the EQE of the flat-stamped and the reference devices. The EQE spectra of both the flat-stamped and the reference devices show roughly the same features. That of the flat-stamped device increases slightly between the 320 and 620 nm wavelengths and is blue shifted by ~10 nm at the first peak (at 325 nm). The slight
increase in the current may be due to the chemical modification of the surface PSS of PEDOT:PSS originating from the interaction with the PDMS stamp as indicated by the XPS result presented in the previous Chapter. But the improvement is not much compared to that obtained from the nanoimprinted features.

Figure 7.6: (a) J-V characteristics of flat-stamped ($J_{SC}=5.0379$ mA/cm$^2$, $V_{OC}=0.4374$ V, $FF=0.5275$, $\eta=1.16\%$) and its reference ($J_{SC}=4.5987$ mA/cm$^2$, $V_{OC}=0.4332$ V, $FF=0.5672$, $\eta=1.13\%$) device fabricated at the same time, and (b) their external quantum efficiencies. Device structure: ITO/PEDOT:PSS/P3HT:PCBM/Al.

In contrast, the nanoimprinted device (Figure 7.7a) shows marked improvements in $V_{OC}$ and $J_{SC}$ from ~0.46V to ~0.50V and from ~3.50 mA/cm$^2$ to ~3.75 mA/cm$^2$ respectively, as well as an increase in $FF$ from 40% to 50% over the flat stamped device used as reference. This confirms that the observed improvements in the device parameters are due largely to the interfacial modification of PEDOT:PSS. The EQE spectra also indicate the improvement in the current density of the imprinted device with a blue shift at the 320 nm wavelength and a pronounced dip at the 360 nm wavelength than the flat-stamped device. The highest peak of
the imprinted device at 520 nm is also blue shifted although by a very small amount.

![Graph](image)

**Figure 7.7:** (a) J-V characteristics of DVD-patterned ($J_{SC}=3.7499$ mA/cm$^2$, $V_{OC}=0.4951$ V, $FF=0.4950$, $\eta=0.92\%$) and its flat-stamped ($J_{SC}=3.4979$ mA/cm$^2$, $V_{OC}=0.4573$ V, $FF=0.4015$, $\eta=0.65\%$) device fabricated at the same time, and (b) their external quantum efficiencies. Device structure: ITO/PEDOT:PSS/P3HT:PCBM/Al.

![Graph](image)

**Figure 7.8:** (a) J-V characteristics of DVD-patterned ($J_{SC}=4.7747$ mA/cm$^2$, $V_{OC}=0.6031$ V, $FF=0.5031$, $\eta=1.45\%$) and its reference ($J_{SC}=4.3559$ mA/cm$^2$, $V_{OC}=0.5737$ V, $FF=0.4546$, $\eta=1.14\%$) device fabricated at the same time, and (b) their external quantum efficiencies. Device structure: ITO/PEDOT:PSS/P3HT:PCBM/Al.

A final repeat of the patterned and reference devices using the last batch of composite materials used in the fabrication of the last two presented devices is shown in Figure 7.8 with their external quantum efficiencies. The devices indicate the same trend observed for all other devices presented in this research.
Figure 7.9: (a) J-V characteristics in the dark and under AM 1.5 illuminations of DVD-imprinted and its reference devices fabricated at 600 rpm and 1000 rpm respectively, and (b) their external quantum efficiencies. Device structure: ITO/PEDOT:PSS/P3HT:PCBM/Al.

Additionally, patterned and reference devices were fabricated at different spin speeds of 600 rpm and 1000 rpm to investigate the response of the device to the photoactive layer thickness. Although the measurement of the layer thicknesses could not be presented here due to faulty ellipsometer used for the measurement, the films spun at 600 rpm are thicker than that spun at 1000 rpm. The J-V characteristics of these devices are shown in Figure 7.9a with their external quantum efficiencies (Figure 7.9b). The EQE of the thicker devices increase significantly while the EQE of the thinner devices decrease in the longer wavelength. The second peak (410 nm) of EQE spectra of the thicker devices are red shifted by about 40 nm but maintains approximately the same peak position at the maxima.

As summarized in Table 7.5, the thicker films absorb more in each patterned and reference device which translates to higher short-circuit current densities. This is also indicated by the red shift and higher EQEs of the 600 rpm devices.
Table 7.5: J-V data of the DVD-imprinted and reference devices fabricated at 600 rpm and 1000 rpm respectively.

<table>
<thead>
<tr>
<th>P3HT:PCBM spin speed</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference 600 rpm</td>
<td>4.0586</td>
<td>0.506</td>
<td>0.6043</td>
<td>1.241</td>
</tr>
<tr>
<td>Reference 1000 rpm</td>
<td>2.7479</td>
<td>0.4912</td>
<td>0.5579</td>
<td>0.753</td>
</tr>
<tr>
<td>Patterned 600 rpm</td>
<td>4.5297</td>
<td>0.5191</td>
<td>0.6226</td>
<td>1.464</td>
</tr>
<tr>
<td>Patterned 1000 rpm</td>
<td>3.2833</td>
<td>0.5086</td>
<td>0.5821</td>
<td>0.972</td>
</tr>
</tbody>
</table>

Summary

In this chapter we have found that:

- There was an error in the devices presented in chapter five originating from the fabrication procedure which affected the light intensity going into the devices resulting in poor device performance. Devices with additional precautionary measures to eliminate the error yielded various degrees of improvements in the device parameters including $J_{SC}$, $V_{OC}$ and the power conversion efficiency.

- A different approach to stamping which yielded better imprinting features led to further improvements in the device parameters including the $V_{OC}$. The depth and period of the features went up from 10 nm and 700 nm to 42 nm and 727 nm representing 320% and 3.9% increases respectively.

- Best performing reference device yielded up to 2.24% power conversion efficiency with a short-circuit current density of 6.11 mA/cm². Its external quantum efficiency at 520 nm peak was ~47%.

- Best performing imprinted device fabricated separately yielded up to 3.36% power conversion efficiency with a significant improvement in the $J_{SC}$ up to 10.02 mA/cm².
Reference and imprinted bulk heterojunction devices fabricated side-by-side show some improvements in the $V_{OC}$ of the imprinted devices ranging from 2.4 to 14.5% over the reference counterpart, while the increase in $J_{SC}$ ranged from 11 to 69% due to imprinting.

The dark $J-V$ characteristics of the imprinted devices are significantly suppressed supporting real enhancements in the $V_{OC}$ following imprinting.

Single layer P3HT devices show enhancements of $J_{SC}$ of the imprinted devices but with significant reduction in the $V_{OC}$.

Values of the $V_{OC}$ and $FF$ of the flat-stamped and reference devices are similar with only 9.5% improvement in the $J_{SC}$ of the flat-stamped device. The slight improvement of the $J_{SC}$ may be due to chemical modification of the PSS surface layer of the PEDOT:PSS and a change in the molecular dipole moment as earlier proposed from the results of the XPS measurements.

The EQE spectra of the flat-stamped and reference devices show roughly the same features except a blue shift of ~10 nm at 325 nm wavelength and a slight increase of the EQE spectrum of the flat-stamped device.

Nanoimprinted devices confirmed parameters enhancements including the $V_{OC}$ over the flat-stamped devices similar to those observed for the reference devices.

Thicker devices have higher $J_{SC}$ and EQE than thinner devices owing to increased absorption in the thicker devices.

EQE spectra of the thicker devices increased and skewed towards longer wavelength while the EQE spectra of the thinner devices decrease in the longer wavelength.

The repeated devices didn’t show up to 3% as earlier obtained because the solution was made from a different batch of active materials. This is also seen in the performance of their reference counterpart.
References

8.1 Final Analysis of the Results Summary

The results obtained by patterning the interfacial PEDOT:PSS layer and used for the fabrication of organic photovoltaic cells are summarized and discussed in relation to existing literature to obtain an overview on the mechanisms which led to the enhancements in the device parameters. Such enhancements as the increase in the short-circuit current density, the open-circuit voltage, the fill factor and ultimately, the power conversion efficiency are explained with clues from optical experiments including absorption, transmission, photoluminescence, Raman spectroscopy, Fourier transform infrared spectroscopy, ultraviolet photoelectron spectroscopy, X-ray photoelectron spectroscopy and external quantum efficiency measurements. The gains in each of these device parameters due directly to the interfacial modification of the PEDOT:PSS and other effects are discussed below.

8.1.1 Nanoimprinting by Soft Lithography

Soft lithography using PDMS was employed to make periodic patterns on PEDOT:PSS. DVD disks were successfully used as master stamps to transfer the patterned features onto PDMS. Two approaches were followed in transferring the features to PEDOT:PSS. The first approach using the 'lift-off' process yielded a period and imprinted depth of 700 nm and 10 nm respectively (Chapter Five). This pattern has proven successful in trapping light thereby boosting the optical absorption within the photoactive materials of the solar cells made while
maintaining the thickness at its minimum. This was first evident from the enhancement in the $J_{SC}$ of the device fabricated with patterned PEDOT:PSS layer allowing for a 24% increment leading to increase in power conversion efficiency of 30%. The second approach utilising the 'put-down' process, yielded a further boost in the imprinting depth up to 42 nm and a period of 727 nm. This marked a significant improvement of 320% and 3.9% in depth and period respectively over the lift-off process. While the 'lift-off' process increased the surface area of the patterned PEDOT:PSS surface by ~0.04%, the 'put-down' process increased it further to ~0.7%. This represents a significant improvement in the quality of the structures using this low-cost approach to nanoscale patterning. The increase in surface area from our analysis directly leads to increase in the number of charge carriers being extracted from the photoactive layer.

Using a Blu-ray based imprinting resulted in a reduced period of the imprinted features to ~340 nm. However, the reduction in the period is accompanied by a reduction in the profile depth to a little below 10 nm. The increase in surface area due to Blu-ray patterning is ~0.2% and thus the significant improvements in OPV performance must be attributed to interfacial effects other than this.

With the photoactive layer having different refractive index from the PEDOT:PSS, it is apparent that most of the incident photons will pass into the device through the periodic patterns at certain angles different from the normal (Figure 8.1 and 8.2).

![Figure 8.1: Schematics showing optical path within the photoactive layer.](image-url)
Figure 8.2: Schematics showing optical refraction at the PEDOT:PSS/P3HT:PCBM interface.

The angle $\theta$ is obtained as

$$\theta = \tan^{-1}\left(\frac{181.75}{21}\right) = 83.4^\circ$$

Thus, the incident angle is: $i = 90^\circ - 83.4^\circ = 6.6^\circ$. From Snell’s law, the incident angle relates to the refracted angle by the expression:

$$\frac{\sin i}{\sin r} = \frac{n_r}{n_i}$$

Where $n_r$ and $n_i$ are the refractive indices of P3HT:PCBM and PEDOT:PSS approximately given as 1.85 and 1.55 respectively. Substituting these values into equation 8.2 gives $\sim 1.2$.

Given that $\sin \theta \approx \theta$ for small angles, then

$$r = \frac{\sin i}{1.2} = \frac{6.6}{1.2} = 5.5^\circ$$

Using the angle $\phi$ that the incident ray makes with the refracted ray ($\phi = \theta - r = 1.1^\circ$), we calculate the refracted path $R$ by considering the fact that our device had a 200 nm thickness. At the point of maximum refraction (i.e. mid-way between the crest and the trough of any pattern is 21 nm), light would have traversed through $W = 179$ nm if there was no refraction.

From cosine rule, the refracted path $R$ is obtained as:

$$\frac{W}{R} = \cos \phi \Rightarrow R = \frac{W}{\cos \phi} = \frac{179}{\cos 1.1} = 179.03 \text{ nm}$$
Thus, light travels additional 0.03 nm before reaching the Al electrode which is about 0.017% enhancement in the optical path length. This implies that there is very little contribution to the enhancement of optical path length within the active layer as the light is refracted at the interface.

Another contribution to the increase in optical absorption is through the Lambertian light distribution by Raleigh/Mie scattering at the PEDOT:PSS/P3HT:PCBM interface for feature sizes less than or equal to the wavelengths of the incoming light. Both the redirected and the refracted light would undergo reflections and total internal reflections at the P3HT:PCBM/Al interface thus, reducing the chances of easy escape leading to increase absorption and subsequent exciton generation.

This is supported by the optical transmission spectra of the surface modified PEDOT:PSS obtained with its planar counterpart by both monochromator/Newport power meter and UV-VIS-NIR spectrometer(Figure 6.1). The results indicate that the reference sample transmits light more than the imprinted samples, especially within the wavelength range of 400 to 650 nm. This is assumed to be due to the scattering/refraction of light by the imprinted features on the PEDOT:PSS out of the aperture of the detectors in both experiments. This is desirable because the scattered light will have to go through different and elongated optical pathways in the active layer deposited on the PEDOT:PSS.

The above claim was further investigated by optical transmission of P3HT:PCBM as well as absorption of light through the thin films of P3HT, PCBM and P3HT:PCBM deposited on both the patterned and planar PEDOT:PSS (Figures 6.3, 6.4 and 6.5). It is obvious from the results that there is an increase in optical absorption due to direct patterning of the PEDOT:PSS. Photons entering the device through the nano-patterns are scattered/refracted within the active layer resulting in longer optical pathways and multiple reflections, thus,
scattered/refracted photons with energy greater than the band gap of the photoactive material will generate excitons.

Further to this, is the quenching of photoluminescence in the patterned devices (Figure 6.6). As stated in Section 6.3, the quenching due to the underlying patterns in this case can be attributed to scattering of the luminescence in different directions and as such, most of the scattered light could not be collected thereby reducing the external quantum efficiency as observed. This is also indicative of the fact that charge carrier recombination near the patterned interfacial PEDOT:PSS is reduced due to phase separation between P3HT and PCBM through 'pattern-directed spinodal decomposition'\textsuperscript{1,2} which would translate into better device performance.

8.1.2 Enhancements of Device Parameters
How this affects the device parameters can be seen in the $J-V$ data presented in Figure 7.4 and Table 7.3. The significant increase in $J_{SC}$ is directly attributed to (i) increased optical absorption due to light trapping by the imprinted pattern which have been explained in the preceding paragraphs, (ii) improved charge extraction through reduction in PEDOT:PSS thickness and increase in surface area. Of note is the increase in the fill factor of most of the devices which is a direct consequence of the increase in the shunt resistance of the devices. Besides, there were gains in the $V_{OC}$ of the patterned devices, although not in great quantities (up to 14.5\% in one of the Blu-ray devices and 14.2\% in one of the DVD-patterned devices). The success of increasing the $V_{OC}$ in addition to the $J_{SC}$ and $FF$ as a result of interfacial modification is an important finding which has the potential to significantly impact on OPV device efficiencies. This is significant in the sense that it is difficult to enhance the open-circuit voltage by engineering the LUMO level of the acceptor and the HOMO level of the donor material without compromising other desirable properties, such as the absorption limit, charge separation efficiency and charge mobility.\textsuperscript{3} Because this was consistent in almost all
the devices made using the put-down process for the patterning, it is therefore clear that the increase in $V_{OC}$ is a direct result of the interfacial modification undertaken.

To further study this effect, single layer P3HT patterned OPV devices were fabricated and characterised, Figure 7.5 and Table 7.4. Analysis of the single layer P3HT devices shows that though the $J_{SC}$ increased with patterning, the $V_{OC}$ was reduced leading to a reduced $FF$, and only a small improvement in device efficiency was gained (1.3 %). The $\sim54$ % increase in $J_{SC}$ is assigned to the extension of the optical path length within the photoactive layer due to scattering and refraction at the PEDOT:PSS interface with the blend and reflection at the P3HT/A1 interface followed by subsequent internal reflection. The reduction in $V_{OC}$ implies that there is direct loss in the internal electric field due to patterning at the anode interface. This could be explained by the presence of an interfacial film that has the effect of reducing the anode work function, since the $V_{OC}$ of single layer devices scales with the work function difference between the electrodes.\cite{4,5} One possibility of such an interfacial film could originate from the PDMS stamp leaving a residual mono-layer as confirmed by ATR-FTIR measurements (Figure 6.9) and would also account for the increase in $V_{OC}$ observed in the patterned P3HT:PCBM blend devices.

The reduction in the anode work function was confirmed by the UPS measurements in which the work function of the PEDOT:PSS was reduced from $\sim5.1\pm0.1$ eV in the reference to $\sim4.7\pm0.1$ eV in the imprinted PEDOT:PSS. This decrease of $\sim0.4$ eV is highly significant as the interfacial work function is now lower than the HOMO of P3HT (5 eV) and thus the barrier for hole transfer to the anode has been removed. In principle this should therefore increase charge extraction from the device as observed for both the single layer P3HT and the P3HT:PCBM blend devices. It will also decrease the $V_{OC}$ for the single layer devices as observed. Relating to what has been reported by He et al,\cite{6} there is a correlation between the dark $J-V$ characteristics and the $V_{OC}$ enhancement. In the metal/insulator...
(semiconductor)/metal framework, the dark \( J-V \) characteristics of BHJ polymer solar cells can be described by the thermionic emission theory, as

\[ J = J_s \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right], \quad (8.5) \]

Where \( J_s \) is the reverse dark saturation current density given by

\[ J_s = A^* T^2 \left[ \exp \left( \frac{-q\phi_B}{kT} \right) - 1 \right]/S, \quad (8.6) \]

Where \( A^* \) is the Richardson constant, defined as

\[ A^* = \frac{4\pi m^* k^2}{h^3}, \quad (8.7) \]

Where \( m^* \) is the effective mass of an electron, \( h \) is Planck’s constant; \( \phi_B \) is the semiconductor/metal contact barrier height and \( S \) is the effective area of the device.

From the UPS measurements, the effective work function of the PEDOT:PSS was reduced after imprinting due to a residue of PDMS interlayer; as a result, in reverse bias conditions, the contact barrier for hole injection is increased which implies a higher \( \phi_B \) at the interface, resulting in a significant reduction in the reverse dark saturation current density, and thus the dark current density (Figure 7.4b). For solar cells with very large shunt resistance, the \( V_{OC} \) can be expressed as,

\[ V_{OC} = \frac{nkt}{q} \left( \ln \frac{J_{ph}}{J_s} + 1 \right), \quad (8.8) \]

Where \( J_{ph} \) is the photocurrent, \( n \) is the ideality factor, \( k \) the Boltzmann constant, and \( q \) the elementary charge. Eq8.8 indicates that decreasing reverse dark saturation current density could help enhance \( V_{OC} \) in the devices which holds good for p-n junction-based solar cells. However, even though the donor/acceptor interface can be treated as a classical p-n junction, the active layer-metal electrode contact for bulk heterojunction polymer solar cells is a Schottky contact in nature, which then implies that their operational principles are fundamentally different, and as such there is no detailed model to describe the dark \( J-V \) characteristics of bulk heterojunction polymer.
It has been shown that UPS measurements are surface dependent with the majority of signal originating from the uppermost 1.5 nm.\textsuperscript{10} If we consider the interfacial layer to consist solely of PDMS then this reduction in work function might not initially be expected due to the HOMO of the PDMS being below that of PEDOT:PSS. However, it is known that substitution of the methyl group in poly(dimethylsilane) can have the effect of raising the highest occupied valence band (H O VB-MO) due to interaction of the side groups with delocalized $\sigma$-electrons of the Si-Si backbone.\textsuperscript{11,12} In PDMS, the electrons are still somewhat delocalised along the Si-O backbone and side groups may still interact and modify the HOMO.\textsuperscript{13} However, the relative chemical stability of PDMS may preclude such modification of the side group, for example via the sulfonic acid group of PSS which is known to phase segregate and form the surface layer of PEDOT:PSS,\textsuperscript{14} though this cannot be discounted. Furthermore, it is possible that the polymer backbone is itself directly modified which would have a greater effect on the HOMO. An alternative mechanism for lowering the work function of the interface is simply due to interfacial charge transfer driven by the large dipole moment of the PSS film. In either case the change observed via UPS indicates the PDMS deposited during the patterning must be of monolayer-like thickness.

In the flat-band energy level diagram in Figure 8.3 is inserted a PDMS layer to indicate the interfacial layer between the PEDOT:PSS and P3HT:PCBM blend. The measured PEDOT:PSS work function following patterning is indicated as the dotted line within the PDMS band gap. UPS measurements of thick PDMS films were undertaken in order to confirm the HOMO and LUMO values used. However, due to charging and significant out-gassing no reproducible data could be obtained for PDMS. The values given are therefore taken from the literature for the bulk PDMS ionisation energy\textsuperscript{13,15} and the optical band gap absorption onset energy.\textsuperscript{16}
However, it is noted that preparation of PDMS films may vary significantly and the properties of bulk PDMS may also vary significantly from that of very thin PDMS films. The large ionisation energy of PDMS (8.3 eV) clearly does not preclude the extraction of holes from the devices due to the measured patterned PEDOT:PSS work function (4.7 eV). This therefore suggests that the PDMS is sufficiently modified by the PSS, and if no interaction occurred one might expect the work function to increase rather than decrease as observed and supported by the device characteristics. Despite this, the alignments shown do allow the observed behaviour to be rationalised. As confirmed by the XPS measurements, this surface modification is limited to the surface PSS layer via the oxygen atom bound to the sulfonic
acid group, indicated by the chemical shift observed only in the O(1s) core-level spectrum of
the imprinted sample towards higher binding energy (Figure 6.11).

Furthermore, thin film of PDMS being an electrically inert material, could reduce the number
of charge recombination sites at the interface between the PEDOT:PSS and P3HT:PCBM
layer, reported by Yamakawa et al\textsuperscript{17} as interfacial passivation, resulting in improvement of
the device performance. This was confirmed by the performance of the devices presented in
Figure 7.6 where a flat PDMS was used in the same stamping procedure described for
patterning. The $V_{OC}$ clearly remained fairly similar in both the reference and the flat-stamped
device but there was a slight improvement in the $J_{SC}$ from 4.599 to 5.038 mA/cm\textsuperscript{2}, although
the efficiencies were not remarkably different.

It is also suggested here that the underlying patterns with the interfacial film could induce a
phase separation between the P3HT and PCBM through the ‘pattern-directed spinodal
decomposition’.\textsuperscript{(1,2)} The self-organised P3HT would thus improve hole transport to the
PEDOT:PSS. The phase separation will also result in the active layer being P3HT rich near
the PEDOT:PSS which explains the increase in $R_{sh}$ in P3HT:PCBM devices and the reverse
in pure P3HT device. Besides, the PDMS thin film on PEDOT:PSS can enhance the buffer
effect on the anode in a similar way as the insertion of buffer material between the cathode
and the active layer, which is known to increase $R_{sh}$\textsuperscript{18} by preventing diffusion of the cathode
material into the active layer. The P3HT:PCBM devices with increases in shunt resistance
indicates a significant reduction in the recombination currents and/or leakage currents which
translates directly to the increase in the fill factor of the devices.

To obtain further information on how the interfacial patterning affects the optical response of
the devices, the spectral dependence external quantum efficiency (EQE) was measured for
both reference and patterned devices (Figure 7.8b). The effect of patterning is seen to
increase the EQE at the wavelengths 400-620 nm due to increase in absorption resulting from
the increase in optical path. This is replicated in the devices made with different active layer thickness (Figure 7.9) with additional red shifting of the devices with thicker active layers.

8.2 Conclusions
The aim of this research has been the investigation of a low-cost patterning method to improve the power conversion efficiency of devices through the enhancement of the various device parameters. This work has therefore demonstrated that low-cost patterning of PEDOT:PSS interfacial layers inserted between ITO and P3HT:PCBM blends leads to an improvement in OPV device performance. Significantly, the research demonstrates improvements in all the device parameters including the $V_{oc}$ without compromising other device parameters. It can be observed that on average, devices with the nano-scale patterns on the interfacial PEDOT:PSS perform better than the planar reference devices. Comparatively, using a flat-stamped PEDOT:PSS layer to form the reference device still links most of the improvements to the PEDOT:PSS surface modification by nanoimprinting. Both the absorption and EQE spectra indicate increase in optical absorption resulting from the extension of the optical path length within the active layer. This culminated into better improvement of the $J_{sc}$ in the imprinted devices including the single layer P3HT devices. ATR-FTIR investigation of the interfacial PEDOT:PSS film following patterning indicates the presence of a PDMS residue which is supported by consideration of the effect on single layer P3HT and P3HT:PCBM blend device performance. UPS measurements demonstrated a reduction in the work function of the interfacial PEDOT:PSS layer by $\sim$0.4 eV following nanoimprinting which may originate from chemical modification by the PDMS residue or interfacial dipole formation. XPS spectrum of the imprinted PEDOT:PSS also shows a chemical shift in the O(1s) core-level towards higher binding energy signifying interaction of the PDMS stamp residue with the PSS dominated surface of PEDOT:PSS. This led to
significant improvement in the $V_{oc}$ and ultimately, the PCE. This improvement can be assigned to two effects resulting from a PDMS residue on the PEDOT:PSS surface: (i) the reduction of the anode work function which in turn decreases the hole extraction barrier, and (ii) the reduction of the number of charge recombination sites at the interface between the PEDOT:PSS and P3HT:PCBM layer. The enhancement of the $V_{oc}$ is further supported by the investigation of the dark $J-V$ characteristics which shows that the dark current density of the imprinted devices is significantly suppressed. Ultimately we have demonstrated up to a 39% improvement in OPV device performance via simple low-cost modification of the anode interfacial layer with little or no compromise between $J_{sc}$ and $V_{oc}$. Given the widespread use of PEDOT:PSS interfacial layers in OPVs, this method should enable significant improvement in reported device performances to be achieved.

8.3 Suggestions for Future Investigations
In the future, the investigation and exploitation of the effects of patterning the interfacial PEDOT:PSS by varying the period and imprinting depth of the patterns will most likely allow for further enhancements of device parameters which could lead to better efficiencies. This will depend on the ability to source master-stamps with features capable of reproducing the desired periods and depths. This will also afford the research into the upper limits of enhancements due to such nano-scale imprinting.

Also, research into coupling plasmonic structures with the imprint may lead to further improvements to the device performance by trapping more light within the device.
References
