Methods for Enhancing the Yield and Performance of Organic Solar Cells

by
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Abstract

Significant interest has been directed towards achieving high performance, large area roll-to-roll printed organic solar cells (OSCs). This thesis focuses on optimisation of the transparent electrode layer and application of a new dielectric material, SU-8, on top of the electron-transporting interlayer in inverted OSCs. The aim of this work is to achieve higher yields and efficiencies in OSCs and to elucidate the physical origins of the improved performance.

One of the main challenges for large area flexible devices has been the brittleness of indium tin oxide (ITO), the most popular transparent electrode and the scarcity of indium which leads to cost fluctuations. Of all the alternative electrodes so far developed, silver nanowires (AgNWs) are arguably the most promising, having been found to possess comparable sheet resistance and transmittance characteristics. When AgNWs are incorporated in devices, however, their high roughness often results in poor yield and performance. The first part of the thesis describes a series of optimisation steps performed on each layer in AgNW-based OSCs so as to develop a reliable fabrication protocol. When the protocol was employed, a significant improvement in performance and yield was achieved, such that the AgNW-based devices were then comparable to ITO-based devices.

In the next section, SU-8 was first applied to sol-gel-derived zinc oxide (ZnO) layer of inverted solar cells based on poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C₆ᵥ-butyric acid methyl ester (P3HT:PCBM), and a ~14% enhancement in device efficiency was found. The film and surface properties of SU-8-modified ZnO were analysed. The planarising effect of the SU-8 layer and the hydrophobic nature of the SU-8 surface were found to assist with the wetting of the organic blend layer, leading to improved interlayer-active layer contact. Carrier recombination inside the device was investigated through transient photovoltage measurements. These showed a longer carrier lifetime in SU-8-containing devices than in SU-8-free devices. Double injection measurements showed the ambipolar mobilities to be unaffected by the presence of SU-8. These findings indicate the device enhancement is due to slower recombination dynamics in the presence of SU-8. When tested in polycrystalline ZnO, similar enhancements in performance were found, suggesting the SU-8 could be employed with other electron-transporting layers for performance enhancement.

In the final section of the thesis, SU-8 was applied to bulk heterojunction (BHJ) devices based on another polymer polythieno[3,4-b]-thiophene-co-benzodithiophene (PTB7) and a
small molecule 7,7′-[4,4-Bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b′]dithiophene-2,6-diyl]bis[6-fluoro-4-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole] (p-DTS(FBTTh$_2$)$_2$). These devices showed similar enhancements in efficiency, although different reasons are suggested for the two cases. For PTB7 devices, there was likely better polymer orientation or phase separation, while in p-DTS(FBTTh$_2$)$_2$ devices, larger crystallite sizes, smaller d-spacing and reduced shunting was the likely cause of the enhanced device performance. These results suggest SU-8 may be beneficial for other BHJ OSCs.
Except where specific reference is made, the material presented in this thesis is the result of my own work. This thesis has not been submitted either wholly or in part to satisfy any degree requirement at this or any other university.

Ai Lin Christina, Pang

April 2015
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<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate</td>
</tr>
<tr>
<td>PTB7</td>
<td>Polyythieno[3,4-b]-thiophene-co-benzodithiophene</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Lifetime</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
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</tr>
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<td>$R$</td>
<td>Sheet resistance</td>
</tr>
<tr>
<td>$R_{\text{rms}}$</td>
<td>Root mean square roughness</td>
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<tr>
<td>$R_s$</td>
<td>Series resistance</td>
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<tr>
<td>$R_{sh}$</td>
<td>Shunt resistance</td>
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<tr>
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<td>Titanium dioxide</td>
</tr>
<tr>
<td>TPV</td>
<td>Transient photovoltage</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>$V_{\text{app}}$</td>
<td>Applied voltage</td>
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<tr>
<td>$V_{BI}$</td>
<td>Built-in voltage</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>X-ray diffraction</td>
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<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
</tr>
<tr>
<td>ZnO$_{\text{PC}}$</td>
<td>Polycrystalline zinc oxide</td>
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List of Publications


Chapter 1: Introduction

1.1 Solar energy and solar cell technology

With the global population expected to rise to 9 billion in the next 40 years,[1] a corresponding increase in energy demand is expected. Over 80% of present day energy supply is provided by fossil fuels such as oil, coal and natural gas[2] but this is unsustainable in the long run due to their finite supply. The use of fossil fuels also results in carbon emissions, the main contributor towards global warming.[3]

As a result, developing alternative renewable, sustainable and environmentally friendly energy sources has become a key challenge. Various sources of alternative renewable energy exist, e.g. wind energy, solar energy, geothermal energy and biomass. Of these, solar energy is the most abundant. The rate at which solar energy reaches the Earth is more than 5,000 times higher than the rate of global energy consumption.[4] Despite this, solar energy accounts for just 0.5% of the world’s current energy production,[5] since solar panels are expensive to manufacture and install (without government rebates or incentives), leading to a long payback time.[6]

A solar cell or photovoltaic cell converts light energy directly into electrical power. Since the first practical silicon solar cell was fabricated in 1954 at Bell Laboratories,[7] silicon solar cell technology has rapidly developed to reach high power conversion efficiencies of over 25%, as seen in Figure 1.1. It is now nearing the theoretical maximum (i.e. the Shockley-Queisser limit) of 30% for a single p-n junction silicon solar cell.[8] However, even though these first generation solar cells offer high efficiencies and stabilities, they remain expensive due to the need for high-purity silicon and energy-intensive fabrication processes.[9]

To reduce the cost per watt of energy generated, second generation cells comprising thin film photovoltaic materials such as amorphous silicon, copper/indium/gallium/selenide (CIGS) and cadmium telluride (CdTe) were developed.[10] Thin film solar cells use layers of semiconductor materials only a few micrometres thick, reducing material consumption and allowing flexible form factors to be realised. Overall efficiencies, however, have not yet exceeded those of first generation cells.
Figure 1.1: Best research-cell efficiencies. [This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO.]

Third generation photovoltaic cells include emerging technologies for example quantum dot cells, perovskite cells, dye-sensitised cells and organic solar cells. This thesis is concerned with the latter type of third generation device.

Due to the thin film nature of the technology, organic solar cells (OSCs) have the potential to be manufactured in high volumes and at low cost. They also provide the advantage of low temperature processing, solution-processability, and compatibility with flexible substrates and roll-to-roll printing.[11, 12]

In this chapter, we introduce organic semiconductors, review the operating principles of OSCs, summarise the aims of this work, and provide an outline of the thesis.

1.2 Organic semiconductor materials

Organic semiconductors, a class of conjugated carbon-based materials that possess semiconductor characteristics, have been widely studied due to their favourable properties, which include low cost, ease of processing and high absorption coefficients of $\sim 10^5 \text{ cm}^{-1}$ (cf. $\sim 10^4 \text{ cm}^{-1}$ for silicon). The latter property allows the use of thin films in devices yet still ensures
adequate photon absorption. The thin film nature of organic semiconductor devices ensures low material usage, leading to reduced cost and lightweight devices, which makes them well-suited for large area optoelectronic devices like solar cells. The two main categories of organic semiconductors used in OSCs are polymers and small molecules. Polymers are based on repeating units of conjugated monomers, with fluorene- and thiophene-based systems being amongst the most widely studied examples. Polymers typically have higher molecular weights with solubilising side-chains that allow them to be solution-processed to form amorphous or semi-crystalline films. Small molecules have low molecular weights, and have been mostly processed via high vacuum thermal evaporation, although solution-processing of suitably functionalised small molecules has been gaining interest recently.[13] Small molecule films generally give semi-crystalline to single-crystal films. Some well-known small molecule materials include phthalocyanine, pentacene and fullerene (C_{60}). Structures of the listed polymers and small molecules are shown in Figure 1.2.

![Figure 1.2: Molecular structures of some organic semiconductors.](image)

Polymer semiconductors can be processed in ambient conditions which reduces production costs and enables large area fabrication, while small molecules are processed mainly via vacuum thermal evaporation.[14] Solution-processing of small molecules has started to receive interest since they offer advantages like ease of purification, definite molecular weight and well-defined molecular structures ensuring reproducibility.[15] In general, they have better stability, higher $V_{oc}$ and mobility than polymeric materials.[16] On the other hand, poor film quality and unwanted crystallisation are areas of concern.[17]
Organic semiconductors have a conjugated π-electron system, consisting of alternating single and double bonds between carbon atoms. The electronic configuration of a ground-state carbon atom is 1s^22s^22p^2. In the sp^2 form of bonding seen in typical organic semiconductors, mixing of the 2s orbital and two of the three 2p orbitals gives rise to three sp^2 hybridised orbitals in a trigonal planar geometry on the molecular plane that form strong covalent σ-bonds, leaving a non-hybridised p_z orbital on each carbon atom perpendicular to the plane, which will overlap to form weaker π-bonds. Delocalisation of the π-electrons occurs over the entire conjugation length, with movement of the π-electrons being responsible for the conductivity in the material.

The interaction between p_z orbitals results in energy splitting, forming π- and π*-orbitals. In the ground state, the valence electrons from the initially half-filled p_z orbitals will occupy the lower energy bonding π-orbital (to form the highest occupied molecular level (HOMO)) while the higher energy anti-bonding π*-orbital (lowest unoccupied molecular level (LUMO)) will remain vacant. When these p_z orbitals interact with other p_z orbitals further along the conjugated chain, the energy splitting into π- and π*-orbitals is smaller. Overall, quasi-continuous bands are formed and separated by a band gap. This band gap represents the minimum photon energy required to excite an electron from the HOMO to the LUMO. Typical band gaps of conjugated materials are in the range 1.5 to 3.0 eV, corresponding mostly to the visible part of the electromagnetic spectrum.[18]

1.3 Device architectures of organic solar cells

1.3.1 Single layer cells

The earliest OSCs were composed of a pure organic material sandwiched between two conductive electrodes with different work functions.[19] Owing to the difference in work functions, an electric field is present in the organic layer which, after light absorption and exciton generation, assists with exciton diffusion, dissociation and charge collection. However, there are several drawbacks of this structure: i) The organic layer thickness is much greater than the singlet exciton diffusion length (on the order of 10 nm), causing most excitons to recombine before arriving at an electrode where dissociation could take place; ii) The built-in electric field strength is typically too weak to dissociate the strongly bound excitons; iii) Transporting both types of charges in a single layer increases the probability of charge recombination. In consequence, poor efficiencies of < 1% are typical for single layer devices.
1.3.2 Bilayer cells

The introduction of a bilayer heterojunction solar cell in 1986 by C.W. Tang marked a major breakthrough in organic photovoltaics. Two conjugated small molecule layers with different electron affinities (an electron donor and an electron acceptor) were used, leading to a device efficiency of ~1%.[20] A typical device configuration is shown in Figure 1.3(a). Since there are no minority free carriers in the undoped donor and acceptor phases, recombination during charge transport to the electrode is greatly reduced. There is also more effective exciton dissociation compared to single layer devices due to the energy offset at the interface. A limitation of the bilayer structure, however, is that while the donor layer has to be ~100 nm for sufficient absorption, free charges can only be generated from excitons close to the interface due to the short exciton diffusion length. Photon absorption in only a small region of the bilayer therefore contributes to the charge generation.

![Figure 1.3: Device configuration for (a) a bilayer device and (b) a bulk heterojunction device.](image)

1.3.3 Bulk heterojunction cells

To address the inadequacies of the bilayer structure, the bulk heterojunction (BHJ) architecture was developed in the 1990s.[21] A typical BHJ cell, consisting of an intimate blend of electron donor and acceptor materials sandwiched between two electrodes, is shown in Figure 1.3(b). Fullerene derivatives are commonly used as electron acceptors, while conjugated polymers or small molecules are typically used as the electron donors. The donor and acceptor
materials form an interpenetrating network of donor and acceptor domains with phase separation on the 10 to 20 nm length-scale, comparable to typical exciton diffusion lengths. Thus, the excitons generated in the donor material are generally able to diffuse to an interface within their lifetime, which increases the exciton dissociation efficiency. The main advantages of the BHJ structure are the increased interfacial area for exciton dissociation and the possibility of employing a thicker active layer for increased absorption due to the nanoscale phase separation.

As well as ensuring the domain size is comparable to the exciton diffusion length, it is also important to ensure sufficient percolation pathways in each phase for transport of the electrons and holes. Optimisation of the nanomorphology in the BHJ active layer is therefore much more complex than the bilayer structure. BHJ device efficiencies have been optimised by control of conditions such as the blend ratio composition,[22] choice of solvent,[23] drying time,[24] thermal[25] and solvent annealing[26] and addition of additives.[27]

Poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM), polymer-fullerene blend, has been the most studied and well-optimised materials system. [28-30] On account of its repeatability and consistency, P3HT:PCBM is employed in the ITO-free devices of Chapter 3 and in the SU-8 interlayer devices of Chapter 4. A high performance polymer and small molecule are used as the donor material in the BHJ in devices in Chapter 5 to study the effect of SU-8 interlayer addition in other BHJ systems.

1.4 Basic operating principles of organic solar cells

A solar cell converts solar radiation into an electrical current. The process is illustrated for a heterojunction cell in Figure 1.4, and can be broken down into six main steps:

1) Photon absorption and exciton generation

2) Exciton diffusion to the donor-acceptor interface

3) Charge transfer

4) Polaron pair dissociation

5) Charge transport

6) Charge extraction
Figure 1.4: Schematic diagram of the main steps involved in the operation of an OSC (a) photon absorption and exciton generation (b) exciton diffusion to the donor-acceptor interface (c) charge transfer and polaron pair dissociation (d) charge transport and charge extraction.

(1) Photon absorption and exciton generation

Photon absorption occurs everywhere in the active area, whether in the donor or acceptor material, but in this work the focus is on photon absorption in the donor since we are generally concerned with fullerene acceptors that are only weakly absorbing.

When photons of incident energy at least as high as the band gap are absorbed, electrons undergo excitation from the HOMO to the LUMO (Figure 1.4(a)) to form a Coulombically bound electron-hole pair or “exciton”. The binding energies of excitons in conjugated polymers are typically on the order of 0.5 eV,[31] considerably higher than the thermal energy at room temperature (~26 meV) resulting in long-lived paired species that do not spontaneously dissociate into free carriers. In contrast, excitons in inorganic semiconductors like silicon have much lower binding energies that are lower than the thermal energy (on the order of 10 meV) and at room temperature photoexcitations typically result in the direct formation of free charge carriers.
Due to the high absorption coefficients of conjugated materials, the thicknesses of the active layer in OSCs can be as low as 100 nm, while providing close to full absorption of incident visible light. However, the relatively large band gaps of these polymers limit the absorption to wavelengths less than 800 nm, resulting in ~40% of the maximum achievable photocurrent for air mass (AM) 1.5 solar irradiation.

Air mass refers to the optical path length of the solar irradiation through the Earth’s atmosphere relative to the shortest path length from the zenith to the ground. As such, AM 1.5 corresponds to a path length 1.5 times as long as this shortest distance, which is at an angle of 48.2° to the zenith and of an irradiance of 1000 W/m². To ensure OSC device characteristics can be compared amongst different institutions, measurements are standardised and performed with a solar simulator under AM 1.5 or AM 1.5 G conditions (G represents Global which includes direct and diffuse radiation).[32]

Figure 1.5 shows the situation for the widely studied polymer P3HT, which has an absorption onset of 650 nm. In this case, approximately 25% of the maximum possible photocurrent can be achieved. In comparison, a silicon cell (band gap = 1.1 eV) absorbs at 1100 nm, leading to around 60% of total possible photocurrent. As such, there is a need to develop polymers with lower band gaps (and hence broader absorption ranges) to enable more efficient harvesting of light up to the near-infrared region.

![Figure 1.5: Comparison between the AM 1.5 solar spectrum and the absorption of P3HT. The response for a silicon cell and the cumulative photocurrent are also shown. Adapted and modified from [33] IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.](image-url)
(2) Exciton diffusion to the donor-acceptor interface

To enable their successful dissociation into free carriers, excitons need to first diffuse to the donor-acceptor interface (Figure 1.4(b)). Excitons typically have a lifetime of <1 ns before undergoing radiative recombination.[34] The singlet exciton diffusion length is typically in the range of 5 to 20 nm for conjugated polymers.[35] Hence, the thickness of the donor layer should be on the same length-scale as the exciton diffusion length to prevent recombination before reaching the interface.

(3) Charge transfer

Upon arriving at a donor-acceptor interface, an exciton can undergo charge transfer (CT) which results in the electron being transferred from the donor to the more electronegative acceptor (Figure 1.4(c)) via a charge-transfer state located on the acceptor. When in the charge-transfer state, the electron residing on the acceptor molecule and the hole on the donor molecule are still Coulombically bound to each other, and are collectively known as a geminate or polaron pair. The CT process occurs when the transition is energetically favourable.[36] This highly efficient photoinduced electron transfer process can happen within tens of femtoseconds,[37, 38] as compared to competing processes like luminescence (the radiative decay of excitons) which typically occur on the nanosecond time-scale.

(4) Polaron pair dissociation

Polaron pairs form the intermediate state between bound excitons and free polarons and can either recombine or dissociate into free polarons. The Onsager-Braun model depicted in Figure 1.6 is often used to describe the process of polaron pair formation and dissociation.[39-41]

In the Onsager-Braun model, a polaron pair can either recombine to the ground state with rate $k_f$ or overcome its binding energy to dissociate into free polarons with rate $k_{diss}(F)$, where $F$ is the electric field. A reverse process (with rate $k_r$) in which a polaron pair is regenerated from free carriers is also possible. In the Onsager-Braun model, the free carriers cannot decay directly to the ground state, but must instead form polaron pairs first, meaning that there is a
finite possibility of them undergoing dissociation again. The polaron pair dissociation probability $P(F)$ is given by Equation 1.1:

$$P(F) = \frac{k_{diss}(F)}{k_{diss}(F)+k_f}$$  \hspace{1cm} (1.1)

where rate $k_{diss}(F)$ is also dependent on the electron and hole mobilities, the initial polaron pair radius, the Coulombic binding energy and the temperature.

![Figure 1.6: Onsager-Braun model describing the dissociation of a polaron pair into free carriers, the loss of a polaron pair by relaxation to the ground state, and the formation of a polaron pair from free carriers. D and A denote the donor and acceptor regions, respectively.](image)

(5) Charge transport

After polaron pair dissociation, the free polarons need to be transported to their respective electrodes (holes in the donor towards the anode and electrons in the acceptor towards the cathode, see Figure 1.4(d)). Charge transport occurs via site-to-site hopping through percolating pathways. The driving force for this movement is provided by the built-in electric field (drift) or carrier concentration gradient (diffusion). In general, the hole-collecting electrode has a high work function and the electron-collecting electrode has a low work function. The built-in electric field is generated by the asymmetry of the electrode work functions which causes electrons to transfer from the cathode to the anode when the device is first fabricated. Upon exciton dissociation, there will be a high concentration of electrons and holes around the interface, setting up a carrier concentration gradient to drive the charge carriers away from the interface to their respective electrodes via diffusion.

At high electric fields, the drift current dominates and the drift distance $L_{drift}$, or the distance that photo-generated charge carriers can travel before recombination, can be expressed as:

$$L_{drift} = \mu \cdot \tau \cdot E$$  \hspace{1cm} (1.2)

where $\mu$ is the carrier mobility, $\tau$ is the carrier lifetime and $E$ is the electric field.
The diffusion current dominates at low internal fields (i.e. at high photovoltages) and the average diffusion length can be defined by Equation 1.3:

\[ L_{\text{diffusion}} = \sqrt{D \tau} = \sqrt{\frac{\mu \tau k T}{e}} \]  

(1.3)

where \( D \) is the diffusion coefficient, \( k \) is the Boltzmann constant, \( T \) is the temperature, and \( e \) is the electron charge.

From the expressions for \( L_{\text{drift}} \) and \( L_{\text{diffusion}} \), it is clear that for both drift or diffusion, the mobility-lifetime (\( \mu \tau \)) product determines the average distance a charge carrier travels before recombination, and therefore governs the overall device performance.

(6) Charge extraction

A current is generated when electrons and holes get extracted (into the external circuit) from the anode and cathode, respectively. An energy barrier at the electrode due e.g. to the formation of a high band-gap oxide layer will inhibit charge extraction, resulting in significant charge accumulation, and greater recombination losses.

With Ohmic contacts, the open-circuit voltage (\( V_{oc} \)) of the device will be governed by the difference in the LUMO energy level of the acceptor and HOMO energy level of the donor. For a device with non-Ohmic contacts, the \( V_{oc} \) is determined by the difference between the work function of the electrodes.[42] The energy barrier at the electrodes can be reduced by inserting interfacial layers, for example molybdenum trioxide (MoO\(_3\)),[43] zinc oxide (ZnO)[44] and titania (TiO\(_x\)).[45] In this work, the electron-transporting layer employed was sol-gel-processed ZnO. Sol-gel-derived ZnO films have been found to be rougher than other ZnO films, leading to an increased risk of shunting. The hole transporting layers used in this work are poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) and MoO\(_3\). PEDOT:PSS can be processed in ambient conditions and via spin coating and is therefore more scalable than thermally evaporated MoO\(_3\). However, the film formation of the aqueous PEDOT:PSS on the hydrophobic active layer in an inverted cell can be very poor compared to evaporated MoO\(_3\).

The most commonly used electrode for OSCs is indium tin oxide (ITO). ITO provides excellent conductivity and transparency but it is brittle and the scarcity of indium has raised
concerns about its sustainability. This led to a need for alternative transparent electrodes, such as carbon nanotubes,[46] metal films,[47] metal nanowires[48] and conducting polymers.[49]

For transparent electrodes, there is typically a trade-off between the transparency and conductivity, with thicker films being more conductive (possessing lower sheet resistances) but having lower transmittances. The transmittance $T$ versus sheet resistance $\mathcal{R}$ trade-off characteristics in transparent conductive films can be analysed using Tinkham’s formula:[50]

$$T = \left[1 + \frac{Z_0 \sigma_{op}}{2\mathcal{R} \sigma_{dc}}\right]^2$$

(1.4)

where $Z_0$ is the impedance of free space (377 $\Omega$) and $\sigma_{op}$ and $\sigma_{dc}$ are the optical and d.c. conductivities of the film, respectively.

The ratio $\frac{\sigma_{dc}}{\sigma_{op}}$ is a dimensionless figure of merit used to evaluate thin films. A higher $\frac{\sigma_{dc}}{\sigma_{op}}$ value implies a high transmittance for a given sheet resistance, and is more desirable in a transparent electrode. The minimum industry standard for the use of transparent electrodes in practical applications is $\mathcal{R} = 100$ $\Omega$/sq. and $T = 90\%$, which corresponds to $\frac{\sigma_{dc}}{\sigma_{op}} > 35$.[51]

1.5 Recombination processes in the bulk

As mentioned in the previous section, the magnitude of the extracted current is reduced by the occurrence of electron-hole recombination within the bulk. The main recombination mechanisms described here are: monomolecular (geminate and Shockley-Read-Hall), bimolecular (non-geminate) and space-charge recombination.

1.5.1 Monomolecular recombination

Monomolecular recombination is a first-order process which typically refers to geminate recombination[52] or Shockley-Read-Hall recombination.[53, 54]

Geminate recombination refers to two processes (i) the loss of bound excitons that relax to the ground state before reaching a donor-acceptor interface and (ii) geminate polaron pairs that recombine at the interface. The process is driven mainly by the Coulombic attraction between the electron and hole.
Shockley-Read-Hall (SRH) recombination, also referred to as trap-assisted recombination, describes recombination that occurs via trap states or recombination centres within the bandgap of the semiconductor, and is typically caused by impurities and structural defects. The process is considered monomolecular as there is only one carrier involved at any time – after the rapid capture of the first charge, the second charge (from a reservoir of mobile oppositely charged carriers) finds its way to the same trap. The four steps considered in the SRH model are illustrated in Figure 1.7: (a) an electron from the conduction band can be captured in the trap state (b) a trapped electron can be emitted to the conduction band (c) a trapped electron moves to the valence band and neutralises a hole (this step is equivalent to the hole being captured by the occupied trap) and (d) an electron from the valence band is trapped, leaving a hole in the valence band (this step is equivalent to the hole being emitted from the empty trap to the valence band). Recombination occurs when step (a) is followed by step (c), leading to the annihilation of an electron and hole. It is possible that the emission of a trapped electron to the conduction band (step (b)) may occur before recombination happens. Repeated trapping and de-trapping of charge carriers leads to slow charge transport since trapped carriers are immobile and cannot participate in conduction until they are released, reducing the time-averaged density of mobile charges.[55]

![Figure 1.7: The four steps in trap-assisted SRH model: (a) electron capture, (b) electron emission, (c) hole capture and (d) hole emission. (The arrows denote the movement of electrons.)](image)

### 1.5.2 Bimolecular recombination

Second-order recombination processes involving the annihilation of a pair of free (non-geminate) electrons and holes during transport toward their respective electrodes is referred to as bimolecular recombination. Bimolecular recombination in OSCs is limited by the rate at which the electrons and holes meet each other, which in turn is dependent on the carrier mobilities. For low mobility semiconductors, recombination occurs via a Langevin process, in
which an electron and hole will recombine if their Coulombic attraction exceeds the thermal energy $k_B T$. The recombination rate in the Langevin model is given by the following expression:

$$ R = \gamma (np - n_i^2) \approx \gamma np $$

where $n$ and $p$ are the photogenerated electron and hole densities, respectively, and $n_i$ is the intrinsic charge carrier density which can be taken to be negligible for a large band gap semiconductor. The Langevin recombination prefactor $\gamma$ is given by:

$$ \gamma = \frac{e}{\varepsilon_r \varepsilon_0} (\mu_n + \mu_p) $$

where $\varepsilon_r \varepsilon_0$ represents the dielectric permittivity and $\mu_n$ and $\mu_p$ are the mobilities of the electrons and holes, respectively.

While the Langevin recombination model has been widely employed for organic semiconductors systems, some studies have suggested that it may overestimate the recombination rate for polymer:fullerene BHJs by up to several orders of magnitude.[57, 58] This has led to the introduction of a Langevin reduction factor $\xi$, which for most BHJ systems is between $10^{-2}$ to 1[59, 60] and as low as $10^{-3}$.[61]

### 1.5.3 Space-charge recombination

The extraction of photogenerated carriers is determined by the mean carrier drift length $L_{drift}$, which is the distance a carrier travels during its lifetime. In a situation where the mean drift lengths $L_{drift,n}$ and $L_{drift,p}$ of electrons and holes respectively, are equal to or larger than the active layer thickness, charges are readily extracted and the internal field in the device is unaffected by the presence of photogenerated charges. On the other hand, if the mobility of one carrier is much higher than the other, the drift lengths will be very imbalanced. This will lead to accumulation of the carrier with the shorter drift length close to its parent contact and the accumulation of the opposite charge carrier close to the other contact. When space charge accumulates, the recombination of free carriers becomes significant, which lowers the FF and the device efficiency. If holes have the lower drift length, a large field strength will be created in the positive space charge region around the anode to improve the extraction of the slow holes, so as to ensure the external hole and electron currents are equal. The space-charge-limited photocurrent is given by the relation: [62]
\[ J_{ph} = e^{\left( \frac{\epsilon_F - \epsilon_D}{\epsilon_0} \right) \frac{1}{4} \frac{G^4 V^3}{\mu} } \]  \hspace{1cm} (1.7)

where \( \mu \) is the mobility of the slowest carrier (in this case, holes), \( G \) is the generation rate of charge carriers and \( V \) is the voltage drop across the active layer.

A large imbalance in electron and hole mobilities (greater than a factor of \( 10^2 \)) results in increased recombination and space-charge-limited current.\cite{63} Therefore for efficient carrier transport, balanced carrier mobilities are needed.

1.6 Normal and inverted structures

In a “normal” OSC, a PEDOT:PSS hole-transporting layer is typically coated on ITO to enhance hole collection at the anode and a low work-function metal, for example aluminium, is typically selected as the cathode, as shown in Figure 1.3. However, while this structure can yield good initial device efficiencies, the acidic PEDOT:PSS etches the ITO and the low work-function metal oxidises rapidly in air, leading to rapid device degradation and poor lifetimes.\cite{64}

![Figure 1.8: Device configuration for an inverted OSC.](image)

To improve the stability of OSCs, inverted architecture devices (Figure 1.8) have been developed in which the anode and cathode are in effect reversed by using an n-type electron-transporting buffer layer in contact with the ITO and a high work-function metal such as silver or gold as the anode. Often, a high work function hole transport layer is also inserted for better
energy level alignment and hole selectivity. Such a structure offers better environmental stability compared to the normal structure,[44] and has made possible the printing of the anode in air using conductive polymers or inks to achieve fully solution-processable devices [65] and enable roll-to-roll production. [66] For the specific case of P3HT:PCBM, an inverted structure is favourable because vertical phase separation occurs during annealing (attributed to differences in the surface energy of the two components), and results in the formation of a PCBM-rich layer on the side of the cathode, which improves electron extraction. [67] The same process in non-inverted devices can cause extraction barriers.

In the work reported here, all devices were fabricated with the inverted architecture, with ITO or silver nanowires as the cathode.

1.7 Device characteristics

Due to the low intrinsic carrier concentrations in organic semiconductors, the current-voltage ($I-V$) characteristics of a simple single junction device can be described using the metal-insulator-metal (MIM) model shown in Figure 1.9, treating the blend layer as an intrinsic semiconductor material between ITO and aluminium (Al) electrodes. Figure 1.10 shows the corresponding $I-V$ characteristics of the device.

![Figure 1.9: Metal-insulator-metal (MIM) model depicting the energy diagrams under different biasing conditions in the dark: (a) reverse bias, (b) short-circuit (c) flat band condition, $V_{app} = V_{BI}$ (d) forward bias, $V_{app} > V_{BI}$.]
In dark conditions, the solar cell behaves like a diode with rectifying behaviour. For applied negative biases ($V_{app} < 0$) (Figure 1.9(a), the injection barriers at the electrodes are too high for significant injection, leading to small negative currents. At $V_{app} = 0$ (Figure 1.9(b)), the device is shorted and there is no net current flow. At $V_{app} = V_{BI}$ (Figure 1.9(c)), where $V_{BI}$ is the difference in the energy levels of the electrodes, the internal electric field and thus drift current is zero. The dark current under this condition is entirely caused by the diffusion of carriers after injection from their respective electrodes. When $V_{app} > V_{BI}$ (Figure 1.9(d)), the dark current increases sharply due to charge injection from the electrodes, varying approximately exponentially with voltage.

![Graph](image)

**Figure 1.10:** Current-Voltage ($I$-$V$) characteristics of an OSC in the dark (black line) and under illumination (red line). Adapted from [33] IOP Publishing. Reproduced by permission of IOP Publishing. All rights reserved.

Figure 1.10 also shows typical $I$-$V$ characteristics of an OSC under illumination. At point (a), we consider the situation in which the excitons formed in the active layer spontaneously dissociate into free carriers as a result of the BHJ architecture. Under steady state conditions, photogenerated carriers diffuse towards both electrodes equally, which effectively results in no net diffusion current. (The negligible role that diffusion plays towards the total photocurrent is also applicable at all other applied voltages.) At this point, the applied reverse bias acts in the same direction as the built-in field, resulting from the difference in electrode work functions, which leads to a strong internal electric field that enhances the transport of photogenerated carriers.

35
carriers to their respective electrodes (electrons to Al and holes to ITO), giving a negative photocurrent. Under short-circuit conditions at point (b), there is no applied bias and only the built-in field is present to drive exciton dissociation and charge transport. As the applied bias is further increased, it opposes the built-in field, leading to a reduced internal field and decreased current. Eventually, point (c) is reached where there is a flat band condition ($V_{app} = V_{BI}$). Here the applied bias and built-in field are balanced such that there is no drift current. Carrier migration to electrodes is only via diffusion, which occurs at an equal rate towards both electrodes thus results in no net photocurrent. At this condition, electron-hole recombination is also possible. As the applied voltage is further increased to point (d) ($V_{app} > V_{BI}$), the internal field is now reversed, leading to electrons being driven to the ITO and holes to the Al, resulting in a field-dependent positive current. At sufficiently high electric field strengths, however, the photocurrent is no longer dependent on the field, instead is limited by the rate of photogeneration, which results in photocurrent saturation.

![Diagram](image)

**Figure 1.11:** A solar cell under illumination and connected in series with a load (a) of zero resistance (at short-circuit conditions) (b) infinite load (at open-circuit conditions) and (c) at a finite resistance.

Consider a solar cell under illumination and connected in series with a load resistance. At short-circuit condition when the resistance of the load is zero (Figure 1.11(a)), the resulting current ($I_{sc}$) represents the maximum photocurrent produced by the device at that particular illumination intensity. With an infinite load (Figure 1.11(b), there is no current flow and a photovoltage is developed across the electrodes due to photogenerated electrons accumulating at the cathode and holes at the anode. The voltage here ($V_{oc}$) is the largest possible voltage generated by the device at that light intensity. In both of these situations, the solar cell does not produce any useful power since the product of the voltage and current is zero. Instead, power generation only occurs when the load has a finite resistance (Figure 1.11(c)) and the cell
develops a voltage between 0 and $V_{oc}$ which allows current to flow through. The effect of the photovoltage is to reduce the internal field and therefore the driving force for photocurrent extraction. Hence the photocurrent drops continuously with increasing photovoltage.

From the analysis of the fourth quadrant of the $I-V$ curve where power is generated and delivered to the load, important devices parameters can be determined. The point where the product of the current and voltage is a maximum is the maximum power point (MPP). Dividing the maximum power by the optical input power $P_{in}$ gives the power conversion efficiency, $\eta$ (Equation 1.8):

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{MPP} \cdot V_{MPP}}{P_{in}}$$

(1.8)

where $I_{MPP}$ denotes the current at the MPP and $V_{MPP}$ the voltage at the MPP.

The FF measures the “squareness” of the $I-V$ curve and indicates how quickly the photocurrent decreases with increasing photovoltage. A perfect solar cell has a FF of 1 while an $I-V$ curve that resembles a straight line through $J_{sc}$ and $V_{oc}$ gives a FF of 0.25. The FF is given by:

$$FF = \frac{I_{MPP} \cdot V_{MPP}}{I_{sc} \cdot V_{oc}}$$

(1.9)

Equation 1.8 may therefore be rewritten as

$$\eta = \frac{P_{max}}{P_{in}} = \frac{FF \cdot I_{sc} \cdot V_{oc}}{P_{in}}$$

(1.10)

An important parameter in determining the device performance is the external quantum efficiency (EQE) at a given wavelength, defined as the ratio of the electron flux density $\Phi_e$ delivered to the external circuit to the incident photon flux density $\Phi_{ph}$ (Equation 1.11).

$$EQE(\lambda) = \frac{\Phi_e}{\Phi_{ph}} = \frac{J(\lambda) / e}{P_0(\lambda) / E_{ph}} = \frac{J(\lambda) h c}{e P_0(\lambda) \lambda}$$

(1.11)

where $J(\lambda)$ is the current density (in A/m$^2$), $P_0(\lambda)$ is the incident power density (in W/m$^2$), $E_{ph} = \frac{hc}{\lambda}$ is the energy of an incident photon, $h$ is Planck’s constant, $c$ is the speed of light and $\lambda$ is the wavelength of the light.

The theoretical short-circuit current density $J_{sc}$ may be obtained by integrating the EQE over all wavelengths at short-circuit conditions:

$$J_{sc} = \frac{e}{hc} \int \lambda E_{QE}(\lambda) P_0(\lambda) d(\lambda)$$

(1.12)
1.8 Equivalent circuit diagram

The electrical properties of a solar cell may be rationalised in terms of an equivalent circuit diagram. An ideal OSC can be modelled as a current source in parallel with a diode whose $I-V$ characteristics are governed by the Shockley diode equation (Equation 1.13):

$$I = I_0(e^{\frac{eV}{nkT}} - 1)$$

where $I$ and $I_0$ are the current and the dark saturation current respectively, $V$ is the voltage across the cell terminals, $n$ is the ideality factor for the diode (for an ideal diode, where there is infinite conductivity in one direction and infinite resistivity in the opposite direction, $n = 1$).

Non-ideality in real OSCs is accounted for by using ideality factors other than unity and including shunt resistance ($R_{sh}$) and series resistance ($R_s$) components in the circuit as shown in Figure 1.12. $R_{sh}$ is attributed to current leakages in the device, while $R_s$ accounts for the resistances of all cell components.

The equation for a solar cell taking into account $R_{sh}$ and $R_s$ can be written as:

$$I = -I_{ph} + I_0\left(e^{\frac{e(V-IR_s)}{nkBT}} - 1\right) + \frac{V-IR_s}{R_{sh}}$$

where $I_{ph}$ is the current generated in the device under illumination.

![Figure 1.12: An equivalent circuit diagram for a non-ideal solar cell.](image)

To maximise the power generated by the device, $R_s$ should be small and $R_{sh}$ should be very large. The effect of having a large $R_s$ or a small $R_{sh}$ is depicted in Figure 1.13. $R_s$ may be determined from the inverse of the slope at large forward bias (in this work, the slope is taken around 1 V). $R_{sh}$ may be determined from the inverse of the slope at zero bias. It is evident from the plots that an increase in $R_s$ or a decrease in $R_{sh}$ reduces the FF and $P_{max}$ of the device, both of which are undesirable.
1.9 Motivation and outline of thesis

**Chapter 1** briefly outlined the history and development of OSCs, their working principles, device architectures and characteristics.

In **Chapter 2**, the thin films and device characterisation techniques employed in this work are reviewed.

**Chapter 3** discusses a detailed study carried out on replacing ITO with an alternative transparent conducting electrode, solution-processed silver nanowires (AgNWs). Due to the brittleness of ITO and the scarcity of indium, considerable interest has been focused on developing alternative transparent electrode materials suitable for flexible devices and roll-to-roll printing.[68, 69] One potentially viable substitute for ITO is solution-processed AgNWs. These nanowires can form highly conductive and transparent films and possess good bending stability.[70, 71] One key drawback, however, is that they are much rougher than ITO.[72] Hence their incorporation into devices often leads to shorting or poor yield.[48] It is therefore important to alleviate the impact of AgNW roughness by developing fabrication protocols that give a reasonable yield and performance, at least comparable to that of ITO. This chapter describes how each layer in the OSC has been optimised to allow the use of AgNWs and to ensure optimal yield, providing comparable performance to standard ITO devices.

In order to attain commercially viable PCEs of 10%, much effort has been put towards materials development, morphology control and device engineering. The PCEs of state-of-the-art single-junction BHJ OSCs have improved substantially over the last few years,[73-76] with the highest reported PCE currently being ~11.1%.[77]
Chapter 4 and 5 relate to the development of interfacial layers which have played a crucial role in the advancement of OSCs.[78, 79] Apart from providing an Ohmic contact between the active layer and electrode, they also assist in charge selectivity, modification of the surface energy or act as an optical spacer. The use of sol-gel-processed ZnO as an electron-transporting layer,[80] while providing good charge selectivity by blocking the transport of holes, results in much rougher films than ZnO prepared via other routes,[81] leading to an increased risk of shunting. The surface traps known to be present on ZnO[82, 83] can also increase recombination, adversely affecting device performance. In view of this, we set out to investigate the effect on device performance and stability of coating an insulating polymer on ZnO.

In Chapter 4, the effect of depositing an SU-8 interlayer on top of ZnO is described for inverted P3HT-based devices. Carrier recombination and ambipolar mobilities were investigated through transient photovoltage and double injection experiments, respectively, to elucidate the device performance enhancement. Part of this chapter has been published as: Pang, C., Chellappan, V., Yim, J. H., Tan, M. J., Goh, T. W. G., Lee, S., Zhang, J., and de Mello, J. Enhanced Performance Using an SU-8 Dielectric Interlayer in a Bulk Heterojunction Organic Solar Cell. *ACS Applied Materials & Interfaces* 2015, 7 (9), 5219-5225.

In Chapter 5, the effect of the SU-8 interlayer on high performance polymer and small molecule solar cells, using polythieno[3,4-b]-thiophene-co-benzodithiophene (PTB7-) and 7,7’-[4,4-Bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b’]dithiophene-2,6-diyl]bis[6-fluoro-4-(5’-hexyl-2,2’-bithiophen]-5-yl]benzo[c][1,2,5]thiadiazole (p-DTS(FBTTh2)-based BHJ systems, is described, and a similar enhancement in efficiency is reported.

A summary of the work is given in Chapter 6 with some recommendations for possible directions for future work.

### 1.10 References


Chapter 2: Characterisation Techniques

2.1 Film characterisation

2.1.1 UV-Vis transmittance and absorbance spectroscopy

The transmittance and absorbance of films were measured using UV-Vis spectroscopy. Light from a continuous source was passed through a monochromator, splitting the beam into individual wavelengths. Subsequently the monochromatic light passed through a beam splitter, giving two optical paths, one through the reference and the other through the sample. Transmittance $T(\lambda)$ spectra were recorded as:

$$T(\lambda) = \frac{l}{I_0}$$  \hspace{1cm} (2.1)

where $I$ is the intensity of the transmitted light and $I_0$ is the intensity of the reference beam.

The absorbance as a function of wavelength $A(\lambda)$ was determined from:

$$A(\lambda) = \log_{10} \frac{I}{I_0}$$  \hspace{1cm} (2.2)

At Imperial College, the UV-Vis transmittance spectra of films were measured using a Perkin-Elmer Lamda-25 spectrometer. At IMRE, transmittance and absorbance spectra were measured using a Shimadzu UV-3101 Spectrophotometer.

All samples were measured at room temperature. Unless otherwise specified, the spectra shown were not corrected for absorbance of the glass substrate.

2.1.2 Atomic force microscopy (AFM)

The surface topography of films was characterised using AFM, a high resolution form of scanning probe microscopy. In a typical AFM measurement, a micromachined cantilever probe with a sharp tip near the end, usually made of silicon or silicon nitride, is used to scan over the sample surface in a raster manner. The interaction of the tip with nearby surfaces causes the cantilever to be deflected. These deflections are measured and quantified by the reflection of a laser spot off the back of the cantilever onto position-sensitive photodiodes. The data obtained is then used to map an image of the sample.
In this work, AFM was carried out in ambient conditions using Bruker’s Dimension Icon Atomic Force Microscope (AFM) system with scan settings of 512 × 512 pixels at 1 Hz. Tapping mode was employed to analyse the surface topography and roughness of films. This mode, as compared to contact mode, results in minimal damage to the sample surface and tip while maintaining high resolution. The cantilever is oscillated at or around its resonance frequency and brought into close proximity with the sample surface, during which the tip intermittently contacts the surface. The amplitude of the oscillations is reduced as the tip-sample distance decreases, due to repulsive forces. A feedback loop is employed to maintain the height between the tip and sample to ensure a constant oscillation amplitude. The height adjustments are recorded to provide information on the topography.

2.1.3 Contact angle measurement

Contact angle measurements were used in this work to analyse the wetting properties of the surfaces of films, in particular before and after surface modifications to determine their efficacy. Young’s equation (Equation 2.3) is used to describe the relationship between the respective interfacial energies and the contact angle[1] and is depicted in Figure 2.1.

\[ \gamma^{sg} = \gamma^{lg} \cos \theta + \gamma^{ls} \]  \hspace{1cm} (2.3)

where \( \theta \) is the contact angle, \( \gamma^{sg} \) is the solid-gas interfacial energy, \( \gamma^{lg} \) is the liquid-gas interfacial energy and \( \gamma^{ls} \) is the liquid-solid interfacial energy.

The static contact angle of water and solutions on films were measured using a Ramé-Hart 100-00 contact angle goniometer. A 10 µL droplet of water from a water dispensing system, controlled by the DROPimage Advanced software, was first dispensed on the sample. (A micropipette was used for dispensing other solutions.) Next, a picture of the droplet was taken and the contact angle measurement was performed using the same software. Five measurements were taken over the sample and the average obtained.

![Figure 2.1: Young’s model showing the interfacial energies and contact angle of a liquid droplet wetting a surface.](image)
2.1.4 X-ray diffraction (XRD)

XRD is a non-destructive technique commonly used to identify compounds, determine their crystal phase and structure and investigate material stress and strain. In this work, films were characterised by two-dimensional XRD using a “Bruker D8 Discover” general area detector diffraction system using Cu Kα ($\lambda = 1.541838$ Å) radiation. Bragg’s law (Equation 2.4) describes the diffraction of X-rays by the crystalline phases within the sample:

$$n\lambda = 2dsin\theta$$  \hspace{1cm} (2.4)

where $n$ is the order of diffraction, $\lambda$ is the wavelength of the X-ray, $d$ is the spacing between adjacent atomic planes in the crystalline phase and $\theta$ is the angle between the incident ray and the crystal plane.

Diffraction occurs only when the X-ray beams scattered by the atomic planes undergo constructive interference. The spatial distribution and intensity of the scattered X-ray vary with different materials and are dependent on their structure, orientation and extent of crystallinity.

2.1.5 X-ray photoelectron spectroscopy (XPS)

XPS, also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a highly sensitive technique based on the photoelectric effect, describing the emission of electrons from a material surface after absorption of photons from incident electromagnetic radiation above a threshold frequency, in this case soft X-rays. XPS is widely used to evaluate the chemical state and elemental composition of material surfaces. In XPS, the sample is irradiated with a beam of low-energy monochromatic X-rays in ultra-high vacuum conditions to remove adsorbed contaminants and minimise inelastic collisions of photoelectrons with gas molecules. Only core-level electrons within ~10 nm of the surface can escape with sufficient energy to be detected. The kinetic energy, $E_k$, of emitted photoelectrons is measured by an electron energy analyser and is given by the following equation:

$$E_k = h\nu - E_b - \Phi_{spec}$$ \hspace{1cm} (2.5)

where $h\nu$ is the photon energy, $E_b$ is the electron binding energy and $\Phi_{spec}$ is the work function of the spectrometer.
An electron multiplier tube or a multichannel detector is used to detect the photoelectrons. By obtaining the electron binding energy and intensity of photoelectron peaks, the chemical state and quantity of each element present on the material surface can be determined.

In this work, the XPS experiments were performed in a high vacuum chamber (< 10\(^{-10}\) mbar) using the VG ESCALAB-220i XL. The instrument was first calibrated with pure gold, silver and copper standard samples by setting the Au 4f\(_{7/2}\), Ag 3d\(_{5/2}\) and Cu 2p\(_{3/2}\) peaks at binding energies of 83.98 ± 0.02 eV, 368.26 ± 0.02 eV and 932.67 ± 0.02 eV, respectively. A monochromatic Al K\(\alpha\) (1486.6 eV) was used as the radiation source.

### 2.1.6 Ultraviolet photoelectron spectroscopy (UPS)

Also based on the photoelectric effect, UPS employs ultraviolet (UV) light as a photoexcitation source and is also a surface sensitive technique. However, in contrast to XPS, UPS is not a quantitative technique and it measures the valence electrons due to the low photon energy of the UV source.

In this work, UPS was performed also on the VG ESCALAB 220i XL system, with He I (21.2 eV) as the excitation source. The samples were biased at -5.0 V to observe the low kinetic energy secondary cutoff. The work function of metals and conducting materials like ITO is given by:

\[
\Phi = h\nu - W = h\nu - (E_{SEC} - E_F)
\]  

(2.6)

where \(W\) is the spectral width given by the difference between the secondary electron cutoff \(E_{SEC}\) and the Fermi level \(E_F\) of the sample, which is referenced at 0 eV.

The ionisation potential (IP) of semiconducting materials such as ZnO, which is the energy difference between the vacuum level and valence band edge, is given by:

\[
\text{IP} = h\nu - (E_{SEC} - E_{VBE})
\]  

(2.7)

where \(E_{VBE}\) is the energy level of the valence band edge.
2.2 Device characterisation

2.2.1 Current-voltage measurement

At Imperial College, $J–V$ characteristics were acquired with a xenon lamp ScienceTech SS150W solar simulator, equipped with a solar spectral filter, and using a Keithley 2400 source meter. The device was placed in a testing chamber while under nitrogen atmosphere and exposed to AM 1.5 spectral conditions under an irradiation intensity of 100 mW cm$^{-2}$. Calibration was performed with a silicon photodiode detector (Newport UV-818).

At IMRE, $J–V$ characteristics were measured in N$_2$ under 100 mW cm$^{-2}$ AM 1.5 G conditions with a XES-151 S SanEi solar simulator and recorded by a Keithley 2400 source meter. Calibration was performed with a crystalline silicon reference solar cell.

2.2.2 External quantum efficiency (EQE)

The EQE was obtained by comparing the current produced by a calibrated photodiode to the current of the solar cell at the same incoming light intensity. Measurements were performed in N$_2$ under illumination with monochromatic light from a xenon lamp (Figure 2.2). The incident beam was first dispersed by an optical chopper at a chopping frequency of 280 Hz. Subsequently, the chopped beam was passed through a monochromator and the monochromated output beam was guided through an optical fiber to the device. The measured photocurrent versus wavelength was calibrated against a silicon photodiode. Both photocurrents were measured using a lock-in amplifier (Stanford Research System, SR510). The illumination wavelength was varied in the range of 300 nm to 800 nm in steps of 2 nm.

![Figure 2.2: A schematic diagram of the EQE measurement setup.](image-url)
2.2.3 Transient photovoltage (TPV)

For TPV measurements (Figure 2.3), devices were connected to a high input (1 MΩ) impedance oscilloscope (Agilent Infiniium 1 GHz). The photovoltage ($V_{oc}$) was controlled by varying the level of illumination using a white light lamp. At each $V_{oc}$, steady state conditions were allowed to establish, where the rates of charge generation and recombination are balanced, leading to a time invariant charge distribution in the device. A small perturbation on $V_{oc}$ ($\Delta V_{oc} < 20$ mV) was generated using a Nd:YAG pulsed laser operating in the third harmonic (wavelength 532 nm, pulse intensity 60 mJ, pulse width < 5 ns, frequency 1 Hz). The laser intensity was attenuated with neutral density filters, where necessary. Under open-circuit conditions, the voltage decay is proportional to the photogenerated excess carrier relaxation ($dV_{oc}/dt \propto d\Delta n/dt \approx \Delta n/t$), allowing direct measurement of the carrier lifetime.[2, 3]

![Figure 2.3](image)

**Figure 2.3:** A schematic diagram of the TPV measurement setup.

2.2.4 Double injection (DoI)

In DoI, a square voltage pulse of amplitude $U$ is applied to the device in forward bias to inject carriers through both electrodes (electrons through the cathode and holes through the anode), and the dark current transient is recorded on an oscilloscope across a low impedance load of 50 Ω.[4] A schematic diagram of the setup is shown in Figure 2.4.

Figure 2.5 shows the current transient and time-derivative of the transient. An RC decay occurs immediately upon application of the voltage pulse, after which the current increases until it reaches the saturation value $j_s$ as a result of carrier recombination.
For DoI current into high conductivity semiconductors, the saturated current-voltage relation may be described by the following expression:[5]

\[ j_s = \frac{8e}{9} \sqrt{\beta \mu_n \mu_p (n_0 - p_0)} \frac{U^{3/2}}{d^2} = \frac{8U}{9d} \varepsilon_r \varepsilon_0 \sqrt{\frac{1}{\beta \tau_{\sigma} \alpha}} \quad \text{when } \tau_{\sigma} \ll \tau_{\alpha} \quad (2.8) \]

where \( \mu_n (\mu_p) \) is the electron (hole) mobility, \( n_0 (p_0) \) is the electron (hole) concentration, \( \beta \) is the bimolecular recombination coefficient, \( d \) is the sample thickness, \( \tau_{\sigma} \) is the dielectric relaxation time, \( \tau_{\alpha} \) is the ambipolar charge carrier transit time and \( \beta_L \) is the Langevin recombination coefficient.
The current transient can be written as:

\[
j(t) = \begin{cases} 
\sigma E \left(1 - \frac{2}{3} t \right)^{-\frac{1}{2}}, & t < \frac{5}{6} t_a \\
\frac{3}{2} \sigma E + (j_s - \frac{3}{2} \sigma E) \tanh \left( \beta \Delta n_s \left(t - \frac{5}{6} t_a \right) \right) , & t > \frac{5}{6} t_a 
\end{cases}
\] (2.9)

where \(\sigma\) is the conductivity of the sample, \(E\) is the applied external field, \(\Delta n_s\) is the saturated concentration of injected charge carriers.

The ambipolar carrier mobility \(\mu_a\) may be estimated by using the ambipolar carrier transit time:

\[
\mu_a = \frac{d^2}{t_a U} = \frac{5d^2}{6t_m U}
\] (2.10)

where \(t_m = \frac{5}{6} t_a\) is the maximum position of the current derivative \(dj/dt\).

\(\mu_a\) may alternatively be expressed as:

\[
\mu_a = \frac{\mu_n \mu_p (n_0 - p_0)}{n_0 \mu_n + p_0 \mu_p}
\] (2.11)

In our DoI experiments, devices were fabricated with an active area of 2 or 3 mm\(^2\) in order to lower the RC time constant. Employing Equation 2.10, \(t_m\) obtained from the current derivative will be used to estimate the ambipolar carrier mobility.

2.3 References

Chapter 3: Silver Nanowires Electrodes for Solar Cells – Optimisation of Processes for Improved Yield and Performance

3.1 Introduction

ITO, the most widely used transparent electrode material in optoelectronics and for OSCs, provides excellent electrical conductivity (< 20 Ω/sq.) and high transparency (> 80% transmittance) in the visible region. However, the processing of ITO requires high temperatures and vacuum-based sputtering, which limit the throughput and result in high production costs.[1] ITO is also brittle and thus poorly suited for use on flexible substrates. Furthermore, indium is increasingly scarce, leading to concerns about its sustainability, and suffers from significant price fluctuations.[2]

As we move towards flexible substrates and commercial applications, it is imperative to identify alternative electrode materials which are inexpensive, solution-processable and suitable for roll-to-roll processing. To be a viable replacement for ITO, a material should possess low sheet resistance (1 – 100 Ω/sq. depending on application) and excellent transparency (at least 90% transmittance at 550 nm).[3] Alternative transparent electrode materials that have been studied include conductive polymers (e.g. PEDOT:PSS), carbon nanotubes and graphene, metals (e.g. metal nanogrids, metal nanowires, ultrathin metal films) and metal oxides.[2, 4] Often, these are also employed as composites for improved performance.

Silver nanowires (AgNWs) have been attracting much attention due to their high electrical and thermal conductivity, and their high transparency across the visible spectrum.[5, 6] They are one of the most promising candidates to replace ITO[7, 8] in terms of their transparency versus sheet resistance trade-off characteristics.

Solution-processed AgNWs of aspect ratio > 10³ form sparse continuous networks when deposited in thin films, allowing them to form robust, highly conductive and transparent films (25 Ω/sq. at 95% transmittance). Costs are potentially low due to the thin film nature of the electrodes and their high void content.[8] Random networks of silver nanowires have also been found to increase photocurrent generation in photovoltaic devices as a result of significant
scattering of the incident light which causes multiple passes through the active layer.[9] The same property however has restricted their application in displays due to unwanted haze.[10]

Compared to ITO-based devices, fabrication of AgNW devices is a considerable challenge. This is mainly due to the rough nature of the nanowire films, especially where the nanowires overlap. This may lead to large dark currents and increase the likelihood of inter-electrode shorting, resulting in low yield and poor repeatability.[7, 11] An \( R_{\text{rms}} \) of less than 3 nm is desirable for reliable device performance.[12, 13]

Various research groups have attempted to alleviate the surface roughness of silver nanowire films. Gaynor et al. subjected the silver nanowire film to mechanical pressure, by first flattening it and then laminating it as a transparent top electrode.[14] The AgNWs however had to be pulsed at 10 V to “burn out” localised shunts to enable device operation. AgNW-polymer composite electrodes have also been fabricated, for example by laminating AgNWs on PEDOT:PSS,[7] by having a mesh of AgNWs backed by a layer of polyvinyl alcohol[15] and by embedding a mixture of short and long AgNWs in a methacrylate film[16]. None of these methods are ideal as all of them involve multiple processing steps which increases manufacturing costs. Noh,[17] Madaria[18] and Choi[19] demonstrated spray coating of AgNW-PEDOT:PSS meshes either through a single step or double step process. However, such films when incorporated in conventional OSCs[17, 19] yielded much lower efficiencies than equivalent ITO devices and left the AgNW film directly exposed to the acidic PEDOT:PSS, risking device degradation as a result of acidic corrosion of the AgNWs.[19, 20] When AgNWs are employed as the cathode in a bottom-illuminated inverted device, the thickness of the overlying electron-transporting layer can be increased to planarise the rough electrode layer, as was done by Leem et. al.[8] using an optically transparent titania layer. They reported high efficiencies comparable to ITO-based reference devices. ZnO has also been employed as a buffer layer in inverted OSCs and device performance was enhanced when ITO was replaced by AgNWs due to higher transparency of AgNWs which resulted in higher photocurrent.[21]

In the case of bottom contact AgNW devices, the performance and yield can be affected greatly by the high roughness of the underlying AgNW electrode. It is therefore important to optimise all layers to ameliorate or compensate for the high roughness. In this chapter, a recipe is developed and optimised for fabricating AgNW-based devices for high yield and performance comparable to ITO control devices, while working towards achieving a fully
solution-processable device. Spin coating was used to deposit the AgNWs but the findings here may transfer to other solution-based deposition methods.

3.2 Experimental

3.2.1 Device fabrication

12 × 12 mm alumina silicate glass substrates with a pre-patterned 8 mm ITO strip of sheet resistance 15 Ω/sq. (PsioTec Limited) were used to fabricate ITO-based control devices, see Figure 3.1(a). Bare alumina silicate glass substrates (without ITO) were used to fabricate AgNW-based devices.

Prior to spin coating, the substrates were cleaned thoroughly. The ITO-coated glass substrates were supplied with a protective resist layer that was first removed by physically rubbing with acetone. All substrates were cleaned by sequentially sonicitating in a 10% (v/v) mixture of Teepol detergent (Shell Chemical Co.) in de-ionised (DI) water, followed by DI water, acetone and isopropanol (IPA). The substrates were stored in IPA until use, at which point they were dried by a nitrogen gun. ITO-glass substrates were used directly, while bare glass substrates were treated with oxygen plasma for 7 min at 100 W prior to deposition of the ClearOhm AgNW ink (provided by Cambrios Technologies Corporation) for improved wetting and adhesion. Once coated, the AgNWs were patterned using a razor blade.

![Figure 3.1: (a) Electrode design and (b) device structure of the inverted OSCs.](image-url)
To avoid the use of air-sensitive top electrodes and prevent contact of the acidic PEDOT:PSS with the cathode, an inverted device structure was chosen, using the architecture shown in Figure 3.1(b). An approximate energy level diagram is shown in Figure 3.2. (UPS was employed to determine the approximate energy levels for ITO and ZnO as shown in Appendix 1.)

A ZnO sol-gel precursor was synthesised according to the procedure of Sun. [22] Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, Sigma Aldrich, 99%) was dissolved in a mixture of ethanolamine (NH$_2$CH$_2$CH$_2$OH, Aldrich, 99.5%) and 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, Aldrich, 99.3%). The molar ratio of zinc acetate dihydrate to ethanolamine was kept at 1:1, with a Zn concentration of 0.5 M (except where stated otherwise). The solution was stirred vigorously overnight in air (to allow the hydrolysis reaction to reach completion) and then passed through a 0.2 µm PTFE filter. This precursor solution was found to be stable for a few months when stored in a fridge at 4 °C.

The precursor solution was spin coated using a Laurell spin coater (WS650S-6NPP LITE) at 5000 rpm for 40 s onto the patterned ITO or AgNW films, then annealed at 150 °C for 1 h in air. A 1:0.8 blend by weight of poly(3-hexylthiophene-2,5-diyl) (P3HT, Merck) and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM, Nano-C) was prepared in 1,2-dichlorobenzene (50 mg/mL), passed through a 0.45 µm PTFE filter, and spin coated at 1000 rpm for 120 s. The coated substrates were annealed in an N$_2$ environment at 140 °C for 10 min.
Next, PEDOT:PSS (Clevios P VP Al4083) which had been stirred vigorously with 1 vol% of Zonyl fluorosurfactant FS-300 (Fluka), was filtered through a 0.45 µm PVDF filter. The solution was deposited on top of the active layer by spin coating at 5000 rpm for 1 min and then annealed at 140 °C in N₂ atmosphere for 20 mins, to form a ~50 nm hole-transporting layer. Finally, an 80 nm silver anode was thermally evaporated under a vacuum of $5 \times 10^{-6}$ mbar through a shadow mask.

The active area of each pixel was 4.5 mm². $J-V$ characteristics were measured using a Keithley 236 source measure unit. For testing, each device was placed in a chamber under nitrogen atmosphere and exposed to an AM 1.5 G xenon lamp solar simulator under an irradiation intensity of 100 mW cm⁻².

### 3.2.2 Deposition of AgNWs

To study the properties of the AgNW films, as-received AgNW ink was spin coated at spin speeds between 500 and 5000 rpm for 120 s. The films were then dried at 50 °C for 90 s and baked at 140 °C for 5 min, as recommended by Cambrios. Figure 3.3(a) shows the UV-Vis transmittance spectra of the AgNWs deposited on glass (using glass as the reference during measurements), with higher spin speeds resulting in films of reduced surface coverage and thus higher transparency. For spin speeds of 1000 rpm and above, high transmittances of greater than 85% were recorded between 500 and 800 nm.

**Figure 3.3:** (a) Transmittance of spin coated AgNWs on glass using spin speeds between 500 and 5000 rpm (b) Transmittance versus sheet resistance of spin coated AgNW films; the result for a 17 Ω/sq. sample of device-grade ITO is also shown for comparison.
Figure 3.3(b) shows the 550 nm trade-off characteristics for AgNW spin coated at different speeds (with glass as the reference during measurements). With higher spin rates, a thinner AgNW film is formed which leads to increased sheet resistance and is in accordance with expectation. Also shown for reference are results for device-grade ITO with a sheet resistance of $17 \ \Omega$/sq. and a transmittance of 97%. The closest AgNW film in terms of sheet resistance has a sheet resistance of $15.2 \ \Omega$/sq. at transmittance of 92.5%.

To determine the figure of merit (FoM) $\frac{\sigma_{dc}}{\sigma_{op}}$ for the AgNW film, we rewrite the Tinkham formula in Equation (1.4) as:

$$T^{-\frac{1}{2}} - 1 = \frac{188.5 \sigma_{op}}{\sigma_{dc} R}$$

and plot $T^{-\frac{1}{2}} - 1$ versus $\frac{1}{R}$ for varying sheet resistances at $T > 80\%$. (Figure 3.4)

![Figure 3.4](image)

**Figure 3.4:** Transmittance versus sheet resistance plot for extraction of the figure of merit. The data has been linearised according to Tinkham’s formula and the best fit line is shown.

The value of $\frac{\sigma_{dc}}{\sigma_{op}}$ determined from the best fit line is $297 \pm 10$. This value is comparable to similar AgNW films,[23, 24] and much higher than other transparent electrodes like carbon nanotubes (FoM ~25)[25] and graphene (FoM < 70),[26] although it is still inferior to ITO whose FoM value is ~500.
AgNW films spin coated from the as-received ink showed some aggregates when viewed under a dark field microscope (Figure 3.5(a)). The presence of these aggregates did not have a significant influence on the sheet resistance which was consistently less than 16 Ω/sq. for a T ≈ 92% film. However, to achieve the smoothest possible films and so minimise the possibility the aggregates would adversely affect subsequent device performance, the ink was filtered with an 11 µm pore size Nylon filter membrane (Millipore NY1102500) before use. Most of the larger aggregates were removed after filtering as seen in Figure 3.5(b).

![Figure 3.5: (a) Dark field microscope image of the as-received AgNW ink after spin coating, and (b) when filtered ink was used (scale bars represent 100 µm).](image)

Figure 3.6(a) shows the SEM image of a typical ~15 Ω/sq. Cambrios AgNW film. The nanowires have typical diameters of a few tens of nanometers and lengths a few tens of micrometers. Consequently, at junctions where multiple wires overlap, the feature height can be up to 100 nm. A 20 × 20 µm AFM image is shown in Figure 3.6(b) and the 3-D image in Figure 3.6(c), with the Rrms being 12.0 nm. While this is a fairly low number, the Rrms under-represents the rough morphology of the AgNW films (because a large fraction of the area is the smooth exposed substrate) and the average peak-to-trough height (taken at ten random points on the film) was much higher at ~39 nm.
3.3 Performance and yield of preliminary devices

Figure 3.7 shows current density-voltage ($J-V$) curves of ITO- and AgNW-based devices made according to the fabrication steps described in the previous section. The efficiency, consistency and yield of ITO and AgNW devices are compared in Figure 3.8. The average efficiency of the ITO-based devices was 3.1% compared to 2.5% for the AgNW-based devices, and the best efficiencies were 3.2% and 2.7%, respectively. Using ITO as a transparent electrode, all six of the pixels by contrast, were found to be operational, each having approximately the same efficiency. Using AgNWs as the transparent electrode, only two of the six pixels generated a reasonable photocurrent (and even then with very different efficiencies of 2.7% and 2.2%). The rest of the devices were either shorted or had efficiencies less than 25% of the best performing device (and were thus not included in the calculation of yield or average
efficiency). The differences in performance and yield between the ITO and the AgNW devices can be attributed to the roughness of the bottom AgNW layer, which leads to the formation of shunts between the electrodes and therefore increases the leakage current and the likelihood of shorting. In the following sections, I describe how the individual layers in the AgNW devices were optimised to achieve improved performance and yield.

![Figure 3.7: J-V curves of (a) ITO- and (b) AgNW-based devices.](image)

![Figure 3.8: Comparison of efficiency, consistency and yield of preliminary ITO and AgNW devices.](image)

3.4 Optimisation of device fabrication protocol

3.4.1 Patterning of AgNW films

Prior to device fabrication, the AgNW film must first be patterned to define the active area where the cathode and anode will overlap after fabrication. Several methods of patterning AgNWs have been reported in the literatures, e.g. employing photolithography[27], etching with a razor blade[28] or removal of undesired areas with water.[21]
The first method of patterning employed was photolithography (assisted by Dr. Jong Hyuk Yim), which provided the most well-defined edges. The photolithography steps (schematic diagram shown in Figure 3.9) included spin coating AZ 1512, a positive photoresist, on the AgNW film, soft baking at 95 °C for 120 s, selective exposure of the photoresist to UV irradiation (180 mJ), development of the exposed photoresist by immersion in AZ developer, hard baking at 120 °C for 120 s, immersion in aluminium etchant type A solution (50 °C for 120 s) and removal of the photoresist on the AgNWs by acetone. After lithography, the AgNW films were found to suffer an increase in sheet resistance from 15 Ω/sq. to 50 Ω/sq., which may be attributed to the removal of some poorly adhered nanowires during the resist removal step or the chemical incompatibility with the resist developer or etchant solutions. It is therefore decided that photolithography should not be used to pattern the nanowires.

Figure 3.9: Schematic diagram of lithography steps to pattern AgNWs.

The second patterning method attempted was with a razor blade. After spin coating and baking of the AgNW films, the substrate was affixed to a stencil printed on paper with the desired electrode pattern. The razor blade was used to scrape away unwanted AgNWs in the areas outside of the 8 mm electrode pattern. The typical height profile of an edge of a razor blade patterned film is shown in Figure 3.10(a). There is a very large spike in the height profile, of more than 500 nm, which is likely to result in shorting when this film is employed in devices.
In the third method of patterning, the same stencil was employed except that water-moistened cotton buds were used instead of the razor blade and wiped over areas outside of the electrode area. The height profile of the resulting AgNW strip is shown in Figure 3.10(b). There is a ~100 nm difference between the highest point at the edge and the substrate, compared to 500 nm using a razor blade. The patterning method of choice for the rest of the work was to use wet cotton buds to remove the excess AgNW on the edges of the substrate to form the electrode strip in the middle of the substrate, as done by Ajuria.[21] It is noted that this method of patterning will only be feasible for electrodes that are in strip form and not for complex electrode patterns.

![Razor blade patterning and Water patterning](image)

**Figure 3.10:** Height profile at the edge of (a) a razor blade patterned film and (b) a film patterned with water.

### 3.4.2 Improving the adhesion of AgNWs and wetting characteristics of ZnO precursor

A tape test was done on the as-deposited AgNW films on glass. Regular finger pressure was exerted to stick a piece of 3M Magic Tape on the AgNW film. The tape was then peeled off the substrate while the area under the tape was examined. The AgNWs were visibly delaminated from the substrate during tape removal implying poor adhesion to the glass substrate. A second concern with the as-deposited AgNW films was that the static contact angle of the ZnO sol-gel precursor solution on the AgNWs was relatively high at $29.6^\circ \pm 0.5^\circ$, implying poor wetting. (Figure 3.11(b)) This compared to a contact angle of $12.5^\circ \pm 0.2^\circ$ for the same solution on ITO (Figure 3.11(a)).
To improve the adhesion of the AgNWs to the glass substrate, Cambrios suggested that the (undisclosed) binders present in the AgNW film (proprietary information to Cambrios) could be removed by manually agitating the AgNW film in DI water for 90 s. The substrate was then dried with N\textsubscript{2} gas and heated on a hotplate at 80 °C for 20 mins to remove residual water. Although this treatment made the AgNWs much more resistant to delamination during the tape test, subsequent wetting of the ZnO sol-gel precursor solution remained poor with a similar contact angle of 31.0° ± 0.3° (Figure 3.12(a)).

In order to improve wetting, a layer of Tyzor BTP, a polymeric butyl titanate from DuPont (prepared 0.1 wt% in ethanol), was spin coated at 5000 rpm on top of the AgNWs and annealed at 120 °C for 40 mins to form a thin (< 5 nm) layer of TiO\textsubscript{2}.[24] The wetting of the ZnO sol-gel precursor on the AgNWs before and after coating the TiO\textsubscript{2} layer was tested by measuring the contact angle. The contact angle reduced from 31.0° before deposition of the TiO\textsubscript{2} layer (Figure 3.12(b)) to 19.6° ± 0.1° afterwards, a value that is much closer to the contact angle of the ZnO sol-gel precursor on ITO and is sufficiently low for reliable device fabrication.
3.4.3 Deposition of ZnO sol-gel precursor

After deposition of TiO$_2$ and ZnO sol-gel precursor over the AgNW film, AFM and 3-D images of the film were recorded, see Figure 3.13. The $R_{\text{rms}}$ value was found to be 9.6 nm compared to 12.0 nm for the pristine AgNW films while the average peak-to-trough height was reduced from 39 nm to 26 nm.

**Figure 3.13:** (a) AFM image of film after deposition of TiO$_2$ and ZnO (scale bar represents 5 µm); (b) corresponding 3-D image.

**Figure 3.14:** ZnO films on glass at increasing concentrations of precursor (the right edge of each substrate was covered with tape during spin coating and removed afterwards to distinguish the AgNW film from the substrate).

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>0.1</th>
<th>0.25</th>
<th>0.5</th>
<th>0.8</th>
<th>1.2</th>
</tr>
</thead>
</table>
Figure 3.14 shows an image of ZnO films made from varying concentrations of precursor in the range 0.1 to 1.2 M. Figure 3.15 shows the transmittance spectra of the same films, using glass as the reference. Between 400 nm to 800 nm, the films made with concentrations up to 0.8 M were highly transparent, showing an average transmittance of at least 98.8%. At 1.2 M, however, the film transmittance was reduced significantly to an average of 92.4% over the same range, likely due to substantial optical scattering.

Figure 3.15: Transmittance spectra of ZnO at varying concentrations.

![Figure 3.15: Transmittance spectra of ZnO at varying concentrations.](image1)

To optimise the electron-transporting layer, AgNW devices were fabricated using different concentrations of ZnO in the precursor. All other layers were fixed at the values used for the best ITO device. Figure 3.16 shows the $J$-$V$ characteristics in the light and dark for the best

Figure 3.16: $J$-$V$ characteristics of the best performing AgNW-based devices with varying Zn concentration in the precursor (a) under illumination and (b) in the dark.

![Figure 3.16: $J$-$V$ characteristics of the best performing AgNW-based devices with varying Zn concentration in the precursor (a) under illumination and (b) in the dark.](image2)
performing devices obtained using the different concentrations of the sol-gel precursor. Average and best device characteristics are summarised in Table 3.1.

**Table 3.1:** Device characteristics of P3HT:PCBM OSCs with varying concentrations of Zn in the sol-gel precursor.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Thickness of ZnO (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Shunt resistance $R_s$ (Ω cm$^2$)</th>
<th>Series resistance $R_s$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>7</td>
<td>0.52 ± 0.02</td>
<td>9.4 ± 0.5</td>
<td>2.14 ± 0.22</td>
<td>393 ± 9</td>
<td>3.0 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.54)</td>
<td>(9.2)</td>
<td>(2.40)</td>
<td>(392)</td>
<td>(3.1)</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>15</td>
<td>0.54 ± 0.01</td>
<td>9.5 ± 0.1</td>
<td>2.64 ± 0.11</td>
<td>506 ± 67</td>
<td>2.2 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.54)</td>
<td>(9.4)</td>
<td>(2.71)</td>
<td>(444)</td>
<td>(2.4)</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>35</td>
<td>0.55</td>
<td>9.6 ± 0.2</td>
<td>3.17 ± 0.08</td>
<td>590 ± 27</td>
<td>2.2 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.55)</td>
<td>(9.9)</td>
<td>(3.29)</td>
<td>(573)</td>
<td>(2.1)</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>60</td>
<td>0.55</td>
<td>9.2 ± 0.2</td>
<td>1.89 ± 0.07</td>
<td>265 ± 62</td>
<td>23.7 ± 3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.55)</td>
<td>(9.4)</td>
<td>(1.95)</td>
<td>(336)</td>
<td>(22.5)</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>100</td>
<td>0.55 ± 0.01</td>
<td>7.1 ± 0.2</td>
<td>1.07 ± 0.09</td>
<td>133 ± 18</td>
<td>46.5 ± 9.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.55)</td>
<td>(7.3)</td>
<td>(1.17)</td>
<td>(153)</td>
<td>(39.4)</td>
<td></td>
</tr>
</tbody>
</table>

Note: The average PCE and standard deviations were obtained from devices on a single substrate, and the values in parentheses correspond to the best performing devices.

Short-circuit currents for devices in which the zinc concentrations in the precursor was less than 0.8 M were similar, but there was a significant drop at 1.2 M attributable to the reduced transmittance of the ZnO film as well as increased series resistance (Table 3.1). The FF saw an improvement of about 25% from 0.1 M to 0.5 M, as a likely consequence of improved coverage of ZnO and better planarisation of the rough AgNW layer, along with better contact between the zinc oxide and the active layer. [29] Above 0.5 M there was a drastic drop in FF due to the large increase in series resistance which may have resulted from the film being thicker than necessary, with larger grain size and greater roughness, as reported previously.[30, 31] The $V_{oc}$ increased from 0.1 to 0.5 M and maintained a relatively constant value above that concentration. Overall, the PCE was found to be maximum at a concentration of 0.5 M.

Figure 3.16(b) shows $J-V$ curves for the devices in the dark. The 0.1 M devices showed high leakage and poor rectification. The rectification increased with increasing Zn content up to 0.5 M, above which it was reduced as a result of the increased series resistance (leading to reduced saturation current) and shunting (greater leakage).

In this optimisation step, only the concentration of the precursor had been varied (with the spin rate kept constant), but it is acknowledged that different thicknesses, roughness and grain
sizes etc. of the ZnO layer could result in different electronic characteristics and thus impact the overall device performance. However, on the basis of the findings reported here, the Zn concentration in the precursor was fixed at 0.5 M for subsequent work.

### 3.4.4 Deposition of P3HT:PCBM blend

The thickness of the active layer is a crucial factor in determining the device performance. If the layer is too thin there will be insufficient absorption of light and an increased risk of inter-electrode shunting, while if the layer is too thick significant electron-hole recombination will occur before charges can be collected at the electrodes.

P3HT:PCBM films of varying thickness were deposited onto the ZnO-coated AgNW films, using the optimised conditions discussed in sections 3.4.1 to 3.4.3. The active layer thickness was optimised by varying the spin speed of the blend solution from 600 rpm to 2000 rpm, while keeping all other conditions constant. Figure 3.17 shows a photograph of the resulting films at the different spin rates. After deposition and annealing, the film thicknesses were determined using a surface profiler. Thickness measurements were made at the four corners and in the middle of the active area and the average was calculated. Table 3.2 summarises the average values and the thicknesses obtained in the middle of the substrate.

![Figure 3.17: Image of films of P3HT:PCBM on glass/ITO/ZnO, after spin coating at varying spin rates.](image)

As the spin speed was reduced from 2000 rpm to 600 rpm, the average thickness increased from 143 nm to 371 nm and the standard deviation increased significantly from 3 nm to 124 nm. The larger standard deviation in film thickness at lower spin rates is attributable to the corner beads of blend solution remaining wet even after extended duration of spin coating. (See photograph in Figure 3.17)
Table 3.2: Average film thickness over the whole substrate and thickness in the middle of the substrate, corresponding to each spin rate.

<table>
<thead>
<tr>
<th>Spin rate (rpm)</th>
<th>Average film thickness (nm)</th>
<th>Film thickness in the middle of substrate (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>143 ± 3</td>
<td>140</td>
</tr>
<tr>
<td>1500</td>
<td>166 ± 5</td>
<td>160</td>
</tr>
<tr>
<td>1000</td>
<td>199 ± 5</td>
<td>190</td>
</tr>
<tr>
<td>800</td>
<td>238 ± 14</td>
<td>220</td>
</tr>
<tr>
<td>600</td>
<td>371 ± 124</td>
<td>250</td>
</tr>
</tbody>
</table>

As seen in Figure 3.18(a) and Table 3.3, the short-circuit current obtained from the device with active layer spun at 2000 rpm was significantly lower than at higher spin speeds, and this can be attributed to the thinner absorption layer which leads to lower current generation. The fill factor reached a maximum at a thickness of 199 nm (spin speed of 1000 rpm) and is reduced above that, due to the increased recombination in the active layer. The shunt resistance was found to reach a maximum at 1000 rpm. Series resistances remained fairly constant over all thicknesses of the active layer, due to the similar interfaces in all devices, but is increased for 600 rpm due to the additional resistance from the much thicker active layer. From Figure 3.18(b), the dark current rectification ratio at ±1 V increased from $5.6 \times 10^2$ at 2000 rpm to $4.4 \times 10^3$ at 1000 rpm, below which it remained relatively constant. The low rectification ratio with the thinnest active layer at 2000 rpm was likely due to increased shunting.

Figure 3.18: J-V characteristics of AgNW-based devices with varying active layer thicknesses (a) under illumination and (b) in the dark.
On the basis of the above results, the optimum spin speed for the active layer was determined to be 1000 rpm, giving a thickness of $199 \pm 5$ nm. This spin speed was accordingly used for all subsequent work.

Table 3.3: Photovoltaic characteristics of P3HT:PCBM OSCs with varying spin rates of the active layer blend.

<table>
<thead>
<tr>
<th>Spin rate (rpm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Shunt resistance $R_{sh}$ (Ω cm$^2$)</th>
<th>Series resistance $R_s$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>0.54 ± 0.01 (0.55)</td>
<td>8.2 ± 0.1 (8.3)</td>
<td>49.3 ± 8.8 (57.8)</td>
<td>2.18 ± 0.49 (2.68)</td>
<td>410 ± 240 (515)</td>
<td>2.5 ± 0.2 (2.3)</td>
</tr>
<tr>
<td>1500</td>
<td>0.55 (0.55)</td>
<td>8.9 ± 0.5 (9.2)</td>
<td>58.2 ± 3.2 (58.4)</td>
<td>2.83 ± 0.13 (2.97)</td>
<td>505 ± 135 (479)</td>
<td>2.3 ± 0.3 (2.5)</td>
</tr>
<tr>
<td>1000</td>
<td>0.55 (0.55)</td>
<td>9.7 ± 0.2 (9.8)</td>
<td>59.0 ± 0.1 (59.6)</td>
<td>3.18 ± 0.06 (3.23)</td>
<td>603 ± 140 (633)</td>
<td>2.5 ± 0.5 (2.5)</td>
</tr>
<tr>
<td>800</td>
<td>0.55 (0.55)</td>
<td>8.9 ± 0.2 (9.1)</td>
<td>56.4 ± 2.4 (58.0)</td>
<td>2.72 ± 0.16 (2.88)</td>
<td>529 ± 32 (513)</td>
<td>2.9 ± 0.6 (2.3)</td>
</tr>
<tr>
<td>600</td>
<td>0.54 ± 0.01 (0.55)</td>
<td>8.9 ± 0.8 (9.9)</td>
<td>53.0 ± 2.3 (56.3)</td>
<td>2.52 ± 0.33 (2.99)</td>
<td>425 ± 61 (502)</td>
<td>3.6 ± 0.1 (3.5)</td>
</tr>
</tbody>
</table>

Note: The average PCE and standard deviations were obtained from devices on a single substrate, and the values in parentheses correspond to the best performing devices.

3.4.5 Deposition of PEDOT:PSS layer

Uniform deposition of the PEDOT:PSS layer on top of the P3HT:PCBM active layer is important for ensuring high yield, as incomplete coverage of PEDOT:PSS in any pixel could potentially result in shunts.

Voigt et al. employed 1 vol% Zonyl fluorosurfactant in PEDOT:PSS to reduce its surface energy so as to improve the wetting and film formation on the hydrophobic active layer.[32] In the work here, the film formation of the PEDOT:PSS layer on the active layer was first tested with and without the addition of 1 vol% Zonyl, using both AgNWs and ITO as the underlying electrode. Photographs taken of a typical film under each condition are shown in Figure 3.19 without Zonyl and using an AgNW bottom electrode. The wetting of the PEDOT:PSS was very poor, leading to almost no coating on the active layer (Figure 3.19(a)). Slightly improved wetting was observed for PEDOT:PSS with 1 vol% Zonyl (see Figure 3.19(b)), although it was still largely inhomogeneous with significant dewetting on the edges of the substrate.
Figure 3.19: Image of PEDOT:PSS coating on the active layer when the solution (a) contained no Zonyl and the transparent electrode is AgNW, (b) contained 1 vol% Zonyl and the electrode is AgNW, (c) contained 1 vol% Zonyl and the electrode is ITO. PEDOT:PSS forms a dark orange coating on the pale yellow P3HT:PCBM active layer.

Using Zonyl and ITO as the bottom electrode, the PEDOT:PSS solution gave homogeneous films with mild dewetting on the edges (Figure 3.19(c)). Hence, it is evident that the underlying AgNW layer can influence the film formation of layers all the way up to the PEDOT:PSS.

Ravirajan et al.,[33] have previously shown that the wetting of PEDOT:PSS on the organic layer can be improved by heating the PEDOT:PSS solution at 90 °C for 15 mins. Here, the wetting of PEDOT:PSS was further investigated by heating the PEDOT:PSS (with 1 vol% Zonyl) in this way. A photograph of the resulting films is displayed in Figure 3.20, which shows greatly enhanced wetting compared to the films in Figure 3.19(b), although there are still slight inhomogeneities in the films.

Figure 3.20: Stacks of films coated with PEDOT:PSS (with 1 vol% Zonyl) where the PEDOT:PSS was deposited hot at 90 °C.
Figure 3.21: Inhomogeneity in the PEDOT:PSS layer caused by aggregates in the underlying unfiltered P3HT:PCBM blend film, compared to a more uniform PEDOT:PSS coated on a filtered P3HT:PCBM blend film (the approximate region where the 6 pixels would subsequently lie are marked out in red dashed boxes).

Next, the effect of active layer roughness on the PEDOT:PSS film formation was studied. Figure 3.21 shows two batches of otherwise identical thin-film stacks in which the top layer of PEDOT:PSS has been spin coated onto P3HT:PCBM active layers formed from unfiltered and filtered blends (the latter obtained using a 0.45 µm PTFE filter). There was significantly improved PEDOT:PSS coverage using filtered P3HT:PCBM solutions, and these were therefore used for all subsequent work.

To investigate if incomplete PEDOT:PSS coverage could be improved by repeated spin coating, we tried coating additional layers of PEDOT:PSS (up to 3 layers) to attempt to cover the uncoated areas. Films were prepared as before, except that after annealing of the first PEDOT:PSS layer (Figure 3.22(a)), another layer (or two layers) was coated and annealed. Although the coverage may be improved by an additional coating (Figure 3.22(b)), the final device yield was unaffected. In addition, even pixels which had a good coverage of multiple coats of PEDOT:PSS showed poorer performance as compared to those with only one good coat of PEDOT:PSS (Figure 3.23). This is likely due to the increase in resistance from a thicker than necessary PEDOT:PSS film (the thickness of every layer of PEDOT:PSS was approximately 55 nm), which led to a reduction in current and fill factor. Hence we conclude that it is most critical to obtain a good coverage at the first deposition of PEDOT:PSS. As reported above, this can be achieved by minimising the roughness of all the underlying layers and heating the PEDOT:PSS solution (with 1 vol% Zonyl) at 90 °C before spin coating for improved wetting.
Figure 3.22: (a) Single coat of PEDOT:PSS (b) Double coat of PEDOT:PSS. The blue areas correspond to a double thickness of PEDOT:PSS and the orange areas correspond to a single thickness.

Figure 3.23: J-V plots of devices with 1, 2 and 3 coats of PEDOT:PSS.

3.5 Final optimised AgNW-based devices and comparison with ITO-based devices

On the basis of the previous measurements, we settled on the following optimised protocol for device fabrication (Figure 3.24): AgNWs were deposited onto glass by spin coating, and then patterned with a wet cotton bud. 0.1% Tyzor solution was then deposited onto the AgNW film at 5000 rpm and annealed in air at 120 °C for 40 mins. This was followed by spin coating of 0.5 M ZnO sol-gel precursor at 5000 rpm and annealing at 150 °C in air for 1 h. Next, a 1:0.8 P3HT:PCBM blend by weight was filtered using a 0.45 µm PTFE filter and spin coated at 1000 rpm. The entire stack was then annealed in N₂ at 140 °C for 10 mins. PEDOT:PSS solution mixed with 1 vol% Zonyl surfactant was heated to 90 °C and spin coated on the active layer at 5000 rpm. The entire stack was then annealed in N₂ at 140 °C for 20 mins. 80 nm Ag was evaporated on PEDOT:PSS to complete the device.
ITO- and AgNW-based devices were made using the optimised protocol and the device performance was compared. The $J-V$ curves are shown in Figure 3.25 compared to the preliminary results in Figure 3.7. The performances of both devices are now more comparable and the standard deviation has reduced for the AgNW-based devices. The yield has greatly improved to 83.3% (Figure 3.26), in contrast to the 33.3% yield reported for the preliminary devices. The average efficiencies for both ITO-based devices and AgNW-based devices have improved after the optimisation to $3.31 \pm 0.12\%$ and $3.13 \pm 0.11\%$ respectively, with a much smaller difference between the two.

**Figure 3.24:** Flow diagram of optimised steps in AgNW device fabrication.
3.6 Conclusion

Preliminary inverted devices based on ITO and AgNW were fabricated and tested. It was found that while ITO-based devices gave efficiencies that averaged 3.1%, comparable to literature values, and had a yield of 100%, AgNW-based devices showed substantially lower efficiencies ~2.5% with a poor yield of 33.3%. The standard deviation for AgNW devices was also larger than for ITO devices. This significant difference in performance and yield stemmed from the rough AgNW layer which influenced the film formation of subsequent layers. An optimised fabrication protocol was therefore developed for each layer in the device.
After the deposition conditions had been optimised, the performance and yield of AgNW-based devices drastically improved, from a PCE of 2.5% to 3.1% and more than twice the initial yield was obtained, making them comparable to ITO-based devices.

This work forms the basis for a further study undertaken with collaborators in Ajou University, Korea, to develop fully solution-processed OSCs based on the optimised protocol described here. The work was published in reference [24]. By employing a transparent top electrode, a fully solution-processed semi-transparent AgNW device giving PCEs of 2.3% was obtained. This result was comparable to equivalent ITO cells using the same configuration.

3.7 References


4.1 Introduction

As discussed in Chapter 1, for efficient operation of an OSC, charge carriers formed in the active layer under illumination should be efficiently transported to their respective electrodes (holes to the anode and electrons to the cathode) for extraction to the external circuit. If significant extraction barriers exist between the active layer and the electrodes, significant charge accumulation and charge recombination occurs, which adversely affects device performance. It is therefore necessary to select interfacial layers that can block one carrier type, while still providing barrier-free access of the other carrier to the electrode. [1, 2] Interfacial layers can also serve other functions, e.g. acting as an optical spacer[3, 4] or creating a barrier to oxygen or water ingress into the active layer.[5, 6]

In this chapter, we focus on a new electron-transporting interfacial layer for inverted OSCs. Various wide band-gap metal-oxide materials have been used for the electron-transporting layer, including titanium oxide (TiO$_2$),[2, 7] zinc oxide (ZnO)[1, 8] and aluminium oxide (Al$_2$O$_3$).[9] Of these, ZnO has been most widely applied due to its high transparency, good environmental stability, low cost and good electron-transporting properties. In addition, ZnO can also block short wavelength UV-light, slowing down degradation of the active layer.[10]

ZnO deposition is most frequently carried out by sputtering,[11] evaporation,[12] atomic layer deposition,[13] spin coating of crystalline nanoparticle dispersions,[14] or sol-gel precursors.[1] Due to their compatibility with low cost roll-to-roll processing, solution deposition methods are particularly attractive.

Although ZnO nanoparticle dispersions can be processed at low temperatures,[15] the nanoparticles are challenging to synthesise,[16] moisture-sensitive, and tend to aggregate unless stabilised by ligands.[17] Sol-gel precursors are easier to prepare and have been found to be stable for months, yielding crystalline films under thermal annealing. Sol-gel-processed ZnO prepared in situ from zinc acetate is frequently used for this purpose, but requires high annealing temperatures of at least 250 ºC for the complete removal of organic reagents and to
induce crystallisation.[18] As a result, it is ill-suited to flexible substrates and tandem cells where the high processing temperatures would cause the underlying polymer to degrade. To address this issue, Sun et al.[19] and Chou et al.[20] incorporated sol-gel-derived ZnO films into OSCs using processing temperatures of 150 ºC and below, with the resultant film comprising a mixture of ZnO and residual zinc acetate.[20] The reduced processing temperature was found to give better diode characteristics with higher rectification ratios and reduced leakage currents.[20] However, ZnO prepared in this way is substantially rougher than that prepared by other routes,[21, 22] suggesting such an approach would benefit from the use of an additional planarising interlayer to reduce the risk of device shunting.[23]

Conjugated polyelectrolytes (CPEs) - conjugated polymers with ionic functionalities - have been reported as promising (electron-transporting) alternatives to metal oxides. When deposited on ITO they can planarise the surface, lower the effective work function, and increase the $V_{oc}$ of the final device, thereby leading to improved efficiencies.[24-26] However, the stability of devices employing CPEs has not been widely reported, and at least one published report has noted poorer stability compared to control devices without CPEs.[24]

Ultrathin insulating interlayers, for example poly(4-hydroxystyrene) (PHS)[27] and poly(vinylpyrrolidone) (PVP).[28] have previously been used as cathodic interlayers in conventional (non-inverted) OSCs. However, PHS, apart from offering the advantage of being solution-processable, did not show any significant improvement in performance compared to lithium fluoride and calcium when inserted between the active layer and the cathode. And PVP is a hydrophilic material that may promote the uptake of water into the device, leading to accelerated degradation. To our knowledge, ultra-thin insulating polymer layers have until now only been used as cathodic interlayers in conventional architecture devices, and they have not previously been applied to inverted architectures.

In this chapter, we investigate the effect of inserting insulating dielectric materials on sol-gel-derived ZnO. Materials of different dielectric constants $\kappa$ were selected to be tested, namely poly(methyl methacrylate) (PMMA) ($\kappa = 3.5$), SU-8 epoxy resin ($\kappa = 4.1$) and polyvinyl alcohol (PVA) ($\kappa = 10$) as these materials have previously been widely used as gate dielectric materials in thin film transistors, and have good film forming properties. While the inclusion of all three materials led to enhancements in device performance, SU-8 gave the most significant improvement. The origin of the enhanced performance was investigated, in terms of the interfacial properties of the SU-8 layer, and its effect on carrier recombination and
ambipolar mobilities. SU-8 was also applied to polycrystalline ZnO prepared from an ammine-hydroxo zinc complex solution to determine whether a similar enhancement might be observed with different surface composition and crystallinity of the underlying electron-transporting layer.

4.2 Experimental

Experiments in this and the next chapter were carried out in IMRE, Singapore. 25 × 25 mm glass substrates with pre-patterned ITO of sheet resistance 11 Ω/sq. (Xinyan Technology Ltd.) were used, as shown in Figure 4.1.

![Figure 4.1: ITO-glass substrate used for device fabrication.](image)

The basic device structure is depicted in Figure 4.2:

ITO/ZnO/(dielectric)/P3HT:PC_{61}BM/MoO_{3}/Ag

![Figure 4.2: Schematic diagram of OSC device structure at IMRE.](image)

The materials, substrate cleaning procedures and device fabrication steps were the same as those described in the previous chapter, with the following exceptions:

1. P3HT employed in IMRE was Sepioloid P200 from Rieke Metals, Inc. The active layer was spin cast in a N\textsubscript{2} environment due to increased humidity in the laboratories in Singapore.
2. 10 nm of thermally evaporated molybdenum trioxide (MoO\textsubscript{3}) was used as the hole transport layer in place of PEDOT:PSS for the purpose of controlled deposition.
3. The active area of each of the four pixels was 9 mm$^2$, unless otherwise stated. Devices used for charge-transport studies had areas of 2 mm$^2$ (2 mm $\times$ 1mm) or 3 mm$^2$ (3 mm $\times$ 1 mm) to lower the RC time constant and therefore enable faster charge transport processes to be studied.

The ammine-hydroxo zinc complex solution used in the last section of this chapter was provided by Dr. Tan Mein Jin. The synthesis procedure was adapted from reference [29]. Briefly, zinc nitrate hexahydrate (Zn(NO$_3$)$_2$$\cdot$6H$_2$O) was first dissolved in DI water under magnetic stirring at room temperature. Potassium hydroxide (KOH) was added dropwise into the solution and stirred for 2 hours, during which zinc hydroxide was formed. A hydroxide slurry was obtained after centrifugation and was redispersed in ammonia to give the complex solution. This solution gave a polycrystalline ZnO film of approximate thickness 30 nm when spin coated at 3000 rpm and annealed at 150 °C for 15 mins.

Preparation of dielectric solutions, spin coating and annealing conditions:

1. **Poly(methyl methacrylate) (PMMA)** from Micro Resist (mr-I PMMA, $M_w = 35k$), was diluted in anisole. The solution was spin coated in a two-step process at 500 rpm for 5 s and 1000 rpm for 45 s. PMMA films were annealed at 150 °C for 5 mins.

2. **Polyvinyl alcohol (PVA)** from Aldrich ($M_w = 31 - 50k$) was dissolved in water by gradual heating to 85 °C and stirring overnight. 25% IPA was added for improved wetting on ZnO. PVA solutions were spin coated in a two-step process at 500 rpm for 5 s and 3000 rpm for 1 min. PVA films were annealed at 100 °C for 5 mins.

3. **SU-8**: SU-8 2050 (Microchem) was diluted to 0.08% (w/w) using the SU-8 thinner cyclopentanone. The solution was spin coated onto ZnO in a two-step process at 500 rpm for 5 s and 1000 rpm for 45 s. The substrates were then soft-baked at 65 °C for 1 min and at 95 °C for 2 mins to evaporate the solvent and densify the film. To cross-link the SU-8 and render the layer insoluble during subsequent deposition of the active layer, the sample was exposed to 365 nm UV irradiation for 45 s, baked at 65 °C for 1 min, at 95 °C for 2 mins, and then hard baked at 150 °C for 5 mins.

For each of the three interlayer materials, uncoated layers of ZnO were subjected to equivalent processing steps (annealing, baking and UV irradiation).
Completed devices were encapsulated in a cover glass and sealed with an epoxy resin for further studies and stability tests.

4.3 Application of dielectric layer and effect on device performance and stability

4.3.1 Performance of devices fabricated with different dielectric materials

Devices with and without a dielectric layer were fabricated and their normalised device characteristics (with respect to dielectric-free devices) are shown in Figure 4.3. From this point on, a dielectric layer made from, for example, a 1% (w/w) SU-8 solution will be denoted as 1% SU-8. It should be noted that the concentration in wt% of dielectric added cannot be compared between different materials, and is not representative of their relative thickness (i.e. a 0.2% SU-8 film is not expected to have the same thickness as a 0.2% PVA film), since each starting material was in a different form (PVA was prepared from solid while SU-8 and PMMA were prepared from solution) and solutions were subjected to different processing conditions.

![Figure 4.3](image-url)

**Figure 4.3:** Normalised (a) $V_{oc}$ (b) $J_{sc}$ (c) FF and (d) PCE of devices with different dielectrics at varying concentrations.
From Figure 4.3(a) it is evident the $V_{oc}$ did not improve significantly after inclusion of the interlayers. In fact it was found to decrease with higher concentrations of PMMA and PVA. At higher concentrations of dielectric used, the devices suffered substantial losses in $J_{sc}$ due to the insulating nature of the dielectric (Figure 4.3(b)). The most significant enhancement was observed for the FF (Figure 4.3(c)), where the maximum increase was about 8 to 10% for each material. The overall PCE shown in Figure 4.3(d) showed promising results, and the improvement was most significant for SU-8 at 0.08% (for which a 14% enhancement in efficiency was observed compared to the SU-8-free device). To understand the origin of the observed behaviour, the effect of the SU-8 interlayer on the device carrier recombination and ambipolar mobilities was further investigated.

4.3.2 Introduction to SU-8 and performance of devices with SU-8 interlayer

Bisphenol-A novolac glycidyl ether, commonly known as SU-8, is a commercially available epoxy-based dielectric material (chemical structure shown in Figure 4.4). It is mechanically robust, possesses high thermal stability[30] and optical transparency at visible and near-infrared wavelengths.[31] It also has a high glass transition temperature of 200 °C, and a very high degradation temperature of 380 °C.[32] Cross-linked SU-8 is highly chemical resistant, which allows additional layers to be coated on top of it without damage. These favourable properties have led to its widespread use as an insulating dielectric material in conventional microelectronics, and make it an attractive candidate for use in organic devices.[33-36]

![Figure 4.4: Chemical structure of SU-8.](image)

Figure 4.5 shows the $J-V$ curves of the P3HT:PCBM BHJ solar cells with and without SU-8, under illumination and in dark conditions, with the typical photovoltaic characteristics summarised in Table 4.1.
Control devices without an SU-8 interlayer had an average $V_{oc}$ of $604 \pm 3$ mV, a FF of $57.6 \pm 0.3\%$ and a $J_{sc}$ of $8.6 \pm 0.1$ mA cm$^{-2}$. These values correspond to a PCE of $2.98 \pm 0.02\%$. Devices having a 0.08% SU-8 interlayer had a slightly higher average $V_{oc}$ of $614 \pm 2$ mV, an increased FF of $63.4 \pm 0.2\%$ and a similar $J_{sc}$ of $8.7 \pm 0.1$ mA cm$^{-2}$, leading to a higher overall PCE of $3.40 \pm 0.02\%$.

The increase in FF is an indication of more efficient charge collection and a reduced rate of recombination in the devices containing 0.08% SU-8. The higher shunt resistance and FF can be attributed to a reduction in surface roughness and voids at the interface.[23] Importantly, the series resistance was not significantly affected by the inclusion of the 0.08% SU-8 layer, indicating it allows charges to tunnel/flow through readily.

With 0.2% SU-8, the FF showed only a 3% increase relative to the SU-8-free device due to an increase in $R_s$, and the overall PCE remained largely unchanged. The device with 1% SU-8 showed an obvious S-shaped kink in its $J-V$ curve, which can be attributed to the 20-fold increase in $R_s$ from a much thicker SU-8 layer. Electron extraction at the electrode is likely to be hindered by the thick SU-8 layer leading to the observed reduction in $J_{sc}$ (6.1 mA cm$^{-2}$) and FF (22.3%) in the device, which has been previously observed in references [37, 38].

To understand the effect of the SU-8 layer on the electrical characteristics, we compared the dark $J-V$ curves and found that the leakage currents for all devices to be comparable. Therefore,
the improvement in FF cannot be attributed to significantly reduced leakage in the device. The dark current under forward bias was found to significantly decrease for the device with 1% SU-8, suggesting the SU-8 layer is impeding the transport of both electrons and holes.

Table 4.1: Device characteristics of P3HT:PCBM OSCs without and with varying concentrations of SU-8 interlayer.

<table>
<thead>
<tr>
<th>Interlayer</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>PCE (%)</th>
<th>Shunt Resistance $R_{sh}$ (k$\Omega$ cm$^2$)</th>
<th>Series Resistance $R_s$ (k$\Omega$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>604 ± 3 (606)</td>
<td>57.6 ± 0.3 (57.2)</td>
<td>8.6 ± 0.1 (8.7)</td>
<td>2.98 ± 0.02 (3.00)</td>
<td>0.96 ± 0.12 (1.01)</td>
<td>2.9 ± 0.1 (2.7)</td>
</tr>
<tr>
<td>ZnO + 0.08% SU-8</td>
<td>614 ± 2 (613)</td>
<td>63.4 ± 0.2 (63.6)</td>
<td>8.7 ± 0.1 (8.8)</td>
<td>3.40 ± 0.02 (3.43)</td>
<td>1.12 ± 0.17 (1.09)</td>
<td>2.9 ± 0.1 (2.7)</td>
</tr>
<tr>
<td>ZnO + 0.2% SU-8</td>
<td>613 ± 1 (613)</td>
<td>60.2 ± 0.9 (59.2)</td>
<td>8.5 ± 0.2 (8.7)</td>
<td>3.13 ± 0.03 (3.14)</td>
<td>0.99 ± 0.06 (0.95)</td>
<td>4.7 ± 0.4 (5.1)</td>
</tr>
<tr>
<td>ZnO + 1% SU-8</td>
<td>610 ± 4 (610)</td>
<td>21.9 ± 0.6 (22.3)</td>
<td>5.9 ± 0.2 (6.1)</td>
<td>0.79 ± 0.04 (0.83)</td>
<td>0.11 ± 0.01 (0.11)</td>
<td>60 ± 13 (54)</td>
</tr>
</tbody>
</table>

Note: The average PCE and standard deviations were obtained from 4 cells, and the values in parentheses correspond to the best performing devices.

The EQE spectra of devices, with and without 0.08% SU-8, are shown in Figure 4.6. The ratio of the measured $J_{sc}$ values agreed to within 3% with the ratio of the integrated EQE spectra. Both devices had a maximum EQE of 65% at a wavelength of 550 nm. The shape of the spectral response did not change appreciably in the presence of SU-8, implying the SU-8 does not significantly influence the optical field distribution in the device.

![EQE Spectra](image)

Figure 4.6: EQE of the devices with and without a 0.08% SU-8 interlayer.
4.3.3 Device stability with and without a 0.08% SU-8 interlayer

The stability in ambient conditions of encapsulated 0.08% SU-8 and SU-8-free devices was investigated (see Figure 4.7). After 33 weeks, the SU-8 device showed a 2% drop in $V_{oc}$ and a 6.5% increase in FF under AM 1.5 G conditions, while the control device suffered a 7% reduction in $V_{oc}$ and a 6% decrease in FF. The two devices saw a similar reduction in $J_{sc}$, to about 82% of the initial values. Overall, the SU-8 device retained 85% of its initial PCE after 33 weeks, while the control device retained only 72% of the initial PCE. The results suggest superior stability for devices with an SU-8 interlayer.

![Figure 4.7](image)

Figure 4.7: Normalised photovoltaic parameters of encapsulated devices with and without 0.08% SU-8 versus storage time in air: (a) $V_{oc}$; (b) $J_{sc}$; (c) FF; (d) PCE.

The reason for the improved stability requires further investigation but, upon application of a voltage or UV illumination (during testing), oxygen adsorbed on the ZnO is liable to be released into the adjacent layers.[39, 40] The insertion of SU-8 between the active layer and ZnO may reduce oxygen uptake by the active layer, and thereby slow down the overall rate of
degradation. Also, the presence of the SU-8 may reduce the interaction of surface-trapped charges on the ZnO with the active layer, and thereby inhibit any detrimental interactions with the active layer.[41]

4.4 Characterisation of SU-8-modified ZnO

Here we study the film and surface properties of SU-8-modified ZnO films by characterisation via UV-Vis transmittance, AFM, contact angle measurements, and XPS.

The UV-Vis transmittance spectra of glass/ITO/ZnO, and varying thicknesses of SU-8 (made from 0.08%, 0.2% and 1% SU-8 solutions) are shown in Figure 4.8. High transmittances of more than 80% across the visible range were measured in all cases. The addition of SU-8 caused a slight red-shift in the transmittance spectrum but no significant change in the average transmittance between 400 to 800 nm (86.0% without SU-8, 85.8% with 0.08% SU-8, 86.0% with 0.2% SU-8 and 86.6% with 1% SU-8). From this, we conclude the addition of SU-8 does not adversely affect the overall transmittance although it does weakly influence the optical field distribution.

Figure 4.8: UV-Vis transmittance spectra of glass/ITO/ZnO, with and without SU-8 films deposited from solutions of varying concentrations.
Figure 4.9 shows AFM topographic images of ITO, ITO/ZnO and ITO/ZnO/SU-8 on glass for various thicknesses of SU-8. An increase in root mean square roughness ($R_{rms}$) from 3.5 nm to 4.1 nm was evident after deposition of the ZnO layer on ITO-coated glass. However, after depositing 0.08% SU-8 on the ZnO, the $R_{rms}$ decreased to 2.6 nm and was further reduced to 1.2 nm with 0.2% SU-8 and to 0.5 nm with 1% SU-8. This indicates that SU-8 has a beneficial planarising effect which was found to be more significant as the thickness of SU-8 increased. This reduction in surface roughness may also account for the previously discussed increase in shunt resistance and FF in devices with up to 0.2% SU-8. The average thickness of SU-8 was estimated via ellipsometry to be approximately 2.5 nm for 0.08% SU-8, 5.5 nm for 0.2% SU-8, and 21 nm for 1% SU-8.

Static water contact angle measurements on the films from Figure 4.10 showed that ITO/ZnO/SU-8 was more hydrophobic than pristine ZnO ($29.5 \pm 1.7^\circ$). The contact angle increased with SU-8 concentration, from $54.2 \pm 0.8^\circ$ with 0.08% SU-8 to $69.1 \pm 0.6^\circ$ with 0.2% SU-8, and $75.8 \pm 0.7^\circ$ with 1% SU-8. A flat and pure SU-8 layer has a water contact angle of $80^\circ$,\[42\] which therefore shows that while the deposition of a more concentrated SU-8 solution on ZnO results in the surface displaying more SU-8 character, it appears the underlying ZnO still affects the surface roughness and the wetting. The smoother and more hydrophobic surface provided by SU-8 helps improve subsequent wetting of the organic blend solution, which enables better contact to be made by the active layer.\[43\]
The surface compositions of ZnO and SU-8 on ZnO were investigated using XPS. The binding energies were calibrated by using C 1s (285.0 eV) as reference. Figure 4.11 shows the survey XPS spectra for pristine ZnO, ZnO/0.08% SU-8, ZnO/0.2% SU-8 and ZnO/1% SU-8.

At the Zn 2p region (~1050 eV) highlighted in the spectra, the mean free path is ~1 nm.[44] The escape depth of electrons is about three times the mean free path, and so could be taken to be ~3 nm in this instance. The spectrum obtained for ZnO/0.2% SU-8 (SU-8 thickness ~5.5 nm), showed a decreased zinc peak although it was still clearly detected. This confirms the non-
conformal coating of SU-8 on ZnO. As expected, the Zn 2p signal in the spectrum obtained for ZnO/1% SU-8 was not present since the SU-8 thickness was much greater than the electron escape depth.

4.5 Evaluation of charge carrier lifetime by transient photovoltage (TPV) measurements

To investigate whether the SU-8 layer influenced the recombination dynamics in the device, carrier lifetimes $\tau$ at $V_{oc}$ were extracted from TPV measurements. Figure 4.12(a) shows typical photovoltage transients for devices with and without an SU-8 interlayer under a white light reference photovoltage of 350 mV. All transients were normalised to the same peak height at time zero. With up to 0.2% SU-8 present, the photovoltage decayed much more slowly than for SU-8-free devices, indicating slower charge recombination. For the device with 1% SU-8 by contrast, the decay was faster than the SU-8-free device.

Fitting the TPV transient to a single exponential decay indicated an increase in lifetime at 350 mV from 0.1 ms without SU-8 to 0.33 ms with 0.08% SU-8 and 0.36 ms with 0.2% SU-8. These are in good agreement with literature values of P3HT-based devices where lifetimes of order 0.1 ms have previously been reported.[45-47] The device with 1% SU-8 however had a shorter lifetime of 0.05 ms, which is attributable to the reduced path length available for electron diffusion as a result of the insulating SU-8 barrier (which increases the probability of meeting an opposite charge carrier in the active layer resulting in an increased rate of recombination).
Plots of $\tau$ versus photovoltage are displayed in Figure 4.12(b) for photovoltages between 200 and 600 mV. The observed reduction in carrier lifetime with increasing photovoltages agrees with previous reports of TPV measurements in OSCs[45, 47, 48] and is in accordance with expectation: the carrier density inside the device increases at higher photovoltage (since photogenerated carriers are swept towards the respective electrodes more slowly due to the reduced internal field strength), resulting in a higher rate of bimolecular recombination. Across the range of photovoltages tested, the lifetime was consistently higher for devices containing 0.08% and 0.2% SU-8 than for devices without, indicating a substantially reduced recombination rate at all biases up to 550 mV.

4.6 Determination of ambipolar charge mobility through double injection (DoI) measurements

The charge carrier lifetime is not wholly responsible for determining the device performance. Instead it is the $\mu t$ product which typically determines the distance charges travel before recombination and which therefore governs the overall efficiency.[49] The ambipolar charge carrier mobility was determined using the DoI method.[50] Figure 4.13(a) shows the measured injection current transients for the devices with pristine ZnO at various applied external voltages. As expected, the measured current values are higher with increased applied voltage. $t_{m}$, the maximum position of the current derivative relative to the cusp, is seen to gradually reduce with increasing voltage.

![Figure 4.13](image.png)

Figure 4.13: (a) Injection current transients for the ZnO device at different applied voltages (b) Magnified view of the rise in current transient of devices (at 5 V applied voltage) with and without an SU-8 interlayer.
Figure 4.13(b) shows the magnified views of the current transients for devices with and without an SU-8 interlayer at 5 V applied voltage. There was no significant change in $t_m$ with the addition of 0.08% SU-8, although the saturation current was slightly lower. With 0.2% SU-8 the saturation current was decreased further and there was an increase in $t_m$, which resulted in a lower ambipolar carrier mobility.

The ambipolar mobilities are plotted versus external field strength in Figure 4.14(a) for devices with and without an SU-8 interlayer. The mobilities for the devices with 0.08% SU-8 were very similar to those without, varying from about $3.5 \times 10^{-3}$ to $1.5 \times 10^{-3}$ cm$^2$/Vs as the electric field $E$ varied from $1 \times 10^5$ to $2.5 \times 10^5$ V/cm, in good agreement with previous reports in the literature.[51, 52] With a 0.02% SU-8 layer, however, a decrease in mobility to $1.0 \times 10^{-3}$ to $1.5 \times 10^{-3}$ cm$^2$/Vs was observed. For the device with a 1% SU-8 layer, we were unable to determine the mobility as the SU-8 was too thick to allow charge injection.

Figure 4.14(b) shows the product of ambipolar mobility and carrier lifetime obtained through DoI and TPV respectively. The $\mu \tau$ product is highest for the device with a 0.08% SU-8 interlayer since the 0.08% SU-8 interlayer has only a weak influence on the ambipolar mobility, the improvement in $\mu \tau$ product (and ultimately the overall device efficiency) is therefore almost wholly attributable to the slower recombination dynamics. For the device with 0.2% SU-8, although the mobility was reduced slightly due to the increased thickness of the insulating SU 8, the longer carrier lifetime still resulted in the $\mu \tau$ product of the device being generally greater than the device without SU-8. The overall trend in $\mu \tau$ product is consistent...
with the trend in measured PCE, which shows an enhancement of performance with the insertion of up to 0.2% SU-8.

While further studies are required to conclusively establish the origin of the increased carrier lifetime, surface traps on the ZnO crystal are known to promote electron-hole recombination in both dye-sensitised[53] and inverted BHJ solar cells.[54] Hence it appears likely that a thin SU-8 layer reduces the rate of interfacial recombination, either by reducing the rate of back electron transfer from the metal oxide to the P3HT:PCBM active layer or by blocking holes from reaching the ZnO, thereby preventing them from coming into proximity with the trapped electrons. Both effects would lead to an increase in carrier lifetime. We note that similar effects have previously been reported using a reduced graphene-oxide/ZnO composite buffer layer.[54]

4.7 Application of SU-8 on ZnO synthesised via zinc complex

We next investigated whether similar enhancements in device performance could be obtained by depositing SU-8 on a ZnO layer with a different surface composition and crystallinity. Polycrystalline ZnO (ZnO\textsubscript{PC}) films were prepared from an ammine-hydroxo zinc (AHZ) complex solution provided by Dr. Tan Mein Jin. The XRD and XPS spectra of both polycrystalline and sol-gel-derived ZnO films (dropcasted) are shown in Appendix Figures A2.1 and A2.2 respectively, which confirm the different crystallinities and surface compositions. More detailed characterisation of the AHZ-derived ZnO film, in terms of AFM and contact angle measurements, are also found in Appendix Figure A2.3 and A2.4 respectively, where a similar planarising effect and increased water contact angle were observed with SU-8 addition. Here, we mainly focus on the effect of 0.08% SU-8 on film transmittance, device performance, carrier lifetime and ambipolar mobility.

The UV-Vis transmittance spectra of glass/ITO/ZnO\textsubscript{PC} with and without SU-8 are shown in Figure 4.15 and reveal a similar red-shift in the transmittance spectra after SU-8 insertion to that seen previously for sol-gel-derived ZnO. The average transmittance from 400 nm to 800 nm for glass/ITO/ZnO\textsubscript{PC} was found to be 85.2% while with SU-8 it was 85.1%.
Figure 4.15: UV-Vis transmittance spectra of glass/ITO/ZnO\textsubscript{PC} with and without SU-8.

Devices were prepared from the polycrystalline films in the same way as before. The $J$-$V$ plots for the ZnO\textsubscript{PC} devices are shown in Figure 4.16, and the photovoltaic characteristics are summarised in Table 4.2. As with the previous sol-gel-derived ZnO devices, devices with an SU-8 interlayer had an improved average $V\text{\textsubscript{oc}}$ and FF. The overall PCE enhancement was about 10%.

Figure 4.16: $J$-$V$ curves of ZnO\textsubscript{PC} devices with and without SU-8, in dark conditions and under illumination.
Table 4.2: Photovoltaic characteristics of ZnO\textsubscript{PC} P3HT:PCBM OSCs with and without an SU-8 interlayer, where the active area is 3mm\textsuperscript{2} cf. Appendix Table A2.1 for equivalent sol-gel-derived ZnO P3HT:PCBM devices.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA cm\textsuperscript{-2})</th>
<th>PCE (%)</th>
<th>Shunt Resistance $R_{sh}$ (kΩ cm\textsuperscript{2})</th>
<th>Series Resistance $R_{s}$ (Ω cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO\textsubscript{PC}</td>
<td>604 ± 1 (602)</td>
<td>57.9 ± 0.8 (57.3)</td>
<td>9.0 ± 0.4 (9.3)</td>
<td>3.13 ± 0.09 (3.21)</td>
<td>0.70 ± 0.06 (0.70)</td>
<td>1.2 ± 0.1 (1.1)</td>
</tr>
<tr>
<td>ZnO\textsubscript{PC}/SU-8</td>
<td>611 ± 2 (610)</td>
<td>61.6 ± 0.5 (61.1)</td>
<td>9.2 ± 0.1 (9.3)</td>
<td>3.45 ± 0.02 (3.46)</td>
<td>0.88 ± 0.09 (0.81)</td>
<td>1.5 ± 0.1 (1.4)</td>
</tr>
</tbody>
</table>

The carrier lifetimes determined by TPV are shown in Figure 4.17(a). An increase in carrier lifetime was observed with the addition of SU-8, as seen previously for sol-gel-derived ZnO devices. The ambipolar mobility again remained approximately the same (see Figure 4.17(b)), resulting in an overall greater $\mu\tau$ product for the device with SU-8 (Figure 4.17(c)). From this, we can deduce that a similar reduction in recombination rate occurs when SU-8 is applied on a ZnO\textsubscript{PC} layer.

Figure 4.17: (a) Carrier lifetimes versus light bias; (b) Ambipolar mobilities versus internal field strength; (c) $\mu\tau$ product versus photovoltage of ZnO\textsubscript{PC} devices with and without SU-8.
4.8 Conclusion

In conclusion, the effect of coating sol-gel-derived ZnO films with an SU-8 interlayer on device performance has been studied. Carrier lifetime and ambipolar mobilities were investigated using transient photovoltage and double injection techniques, respectively.

SU-8 was found to planarise the ZnO film and increase the water contact angle, thus improving the wetting of the organic blend solution for better interfacial contact between ZnO and the active layer. When employed in an inverted P3HT:PCBM BHJ solar cell, an ultrathin dielectric layer formed from 0.08% SU-8 was found to both improve device stability and also enhance the PCE by ~14%. The incorporation of an ultrathin SU-8 interlayer resulted in an increased carrier lifetime, but had little effect on the carrier mobility, suggesting the improved device performance is predominantly due to slower recombination dynamics in the presence of SU-8.

When SU-8 was coated on polycrystalline ZnO films, a similar decrease in the recombination rate was observed with the carrier mobility again remaining largely unaffected. This suggests the possibility of enhancing the performance of other inverted BHJ solar cells with electron-transporting layers of different surface compositions and properties.

4.9 References


Chapter 5: Incorporating an SU-8 Dielectric Interlayer in Different Bulk Heterojunction Systems

5.1 Introduction

In this chapter, the use of an SU-8 interlayer is evaluated for two other BHJ systems, namely (I) polythieno[3,4-\(b\)]-thiophene-co-benzodithiophene (PTB7): [6,6]-phenyl-C\(_{71}\)-butyric acid methyl ester (PC\(_{71}\)BM) and (II) a solution-processable small molecule donor-acceptor blend 7,7\-'[4,4-Bis(2-ethylhexyl)-4\(H\)-silolo[3,2-\(b\):4,5-\(b\')dithiophene-2,6-diyl]bis[6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole] (p-DTS(FBTTh\(_2\))\(_2\))\(_{2}\):PC\(_{71}\)BM. Compared to the widely studied P3HT:PCBM, these are more recently studied systems which have shown efficiencies of up to 9.2\%\cite{1} and 8.9\%\cite{2} respectively.

5.2 PTB7: A promising low bandgap polymer

The device performance of P3HT:PCBM devices has reached a plateau of ~5\% PCE\cite{3} despite extensive studies on solvent additives\cite{4, 5} optimising of process conditions\cite{6, 7} and post-processing treatments\cite{8, 9}. This can be mainly attributed to the poor optical absorption of P3HT in the near-infrared (IR) region due to its relatively high band gap of 1.9 eV\cite{10}. In order to overcome this limitation and reach commercially-viable PCEs of 10\%\cite{11}, much focus has been put on the development of low band gap polymers\cite{12, 13} with the highest PCE for a single junction BHJ cells having now reached > 10\%\cite{14}.

Yu et al. synthesised a series of PTB polymers\cite{15-17} containing alternating thieno[3,4-\(b\)]thiophene (acceptor) and benzodithiophene (donor) repeat units, which enabled tuning of the HOMO and LUMO levels of the polymers to attain lower band gaps (~1.6 eV) corresponding to an absorption onset of 700 nm. Within the series, PTB7 (Figure 5.1(a)) has become one of the most promising polymers, triggering much research dedicated to understanding its BHJ morphology for optimisation of device performance.

In optimised P3HT:PCBM BHJs, the degree of polymer crystallisation ranges from 40 to 60\%\cite{7} and the polymer chains tend to order on the substrate in an edge-on orientation\cite{18}. A higher degree of P3HT crystallisation is generally considered to lead to increased device performance. In PTB7:PCBM blends, the optimum morphology has been found to be
drastically different from typical ordered systems. Grazing-incidence X-ray diffraction and polarising light absorption spectroscopy conducted by Hammond et al.[19] have together indicated that the polymer component of the blend has a low degree of structural order (~20%) with the polymer chains mostly ordered in a face-on conformation on the substrate. This observation has been supported by other reports.[20, 21] The polymer orientation has been mainly attributed to the rigidity and planar orientation of the PTB7 backbone. Compared to the edge-on orientation, this planar orientation is more favourable for charge transport along the axis of the device.

Addition of 1,8-diiodooctane (DIO) to the PTB7:PCBM solution leads to the formation of a much finer and smoother morphology due to smaller domain sizes in the films (Figure 5.1(b) and (c)),[22] without changing the crystallite size or the orientation of PTB7. It has been widely observed that the device performance significantly improves with the addition of DIO.[19, 20, 22, 23]

**Figure 5.1:** (a) Chemical structure of PTB7; Transmission electron microscopy image of PTB7:PCBM films prepared (b) without and (c) with DIO (scale bar represents 200 nm); figure adapted from [22] with permission. Copyright 2010 John Wiley & Sons, Ltd.

Aside from the use of additives, interlayers have also been used to improve the efficiency of PTB7:PCBM devices.[1, 24-26] In the work here, we investigate the effect of incorporating an
SU-8 dielectric layer into PTB7:PC$_{71}$BM devices, as previously used in P3HT devices. In particular, we study the effect of the SU-8 interlayer on stability, carrier lifetime and charge transport.

5.2.1 Experimental

ZnO and SU-8 interlayers were prepared in the same manner as in Chapter 4. Fabrication of PTB7-based OSCs and electron-only devices will be described in this section.

5.2.1.1 Fabrication of PTB7-based devices

Preliminary testing indicated that an SU-8 layer made from a 0.08% SU-8 solution yielded non-optimised PCEs. The whole range of SU-8 concentrations was therefore investigated to determine the influence of SU-8 thickness on PCE.

The blend solution was formulated in accordance with reference [22]. The blend of PTB7 (1-Material) and PC$_{71}$BM (Solenne BV) was prepared in the ratio 1:1.5 in chlorobenzene (CB) at a total concentration of 25 mg/mL. 3% DIO (Aldrich) was added to the solution as an additive, and stirred at 50 °C overnight. The solution was filtered with a 0.45 µm PTFE filter before spin coating at 1000 rpm for 120 s in N$_2$. The film was dried overnight in the evaporator to give a thickness of approximately 85 nm, after which 10 nm of MoO$_3$ and 100 nm of Ag were thermally evaporated. The active area of each of the four pixels per substrate was 3 mm$^2$.

5.2.1.2 Fabrication and characterisation of electron-only devices

The effect of SU-8 on the electron extraction properties and electron mobility of PTB7:PC$_{71}$BM were investigated by fabricating electron-only devices, and by analysing the $J$-$V$ characteristics in terms of the space-charge limited current (SCLC) model. The device structure employed was ITO/ZnO/(SU-8)/blend/Ca (20 nm)/Al (100 nm). A low work function Ca/Al electrode was selected for the purpose of electron injection through the top of the device. The bottom electrode was maintained as (electron-extracting) ZnO to ensure the same blend morphology in the active layer as in the OSC devices. Devices were illuminated for 10 s under AM 1.5 G simulated conditions. 10 s was chosen because it is the average illumination duration used for testing OSCs.
5.2.2 Effect of SU-8 interlayer on PTB7-based device performance

Figure 5.2 shows $J-V$ curves of PTB7:PC$_{71}$BM BHJ solar cells with and without SU-8 interlayers (of varying thickness), under illumination and in dark conditions, with the typical photovoltaic characteristics summarised in Table 5.1.

![Graph showing $J-V$ curves](image)

**Figure 5.2:** $J-V$ curves of PTB7-based devices without SU-8 and using varying concentrations of SU-8 in dark conditions and under illumination.

The control devices without SU-8 had an average $V_{oc}$ of 717 ± 1 mV, a FF of 66.9 ± 0.5% and a $J_{sc}$ of 13.4 ± 0.1 mA cm$^{-2}$. These values correspond to a PCE of 6.43 ± 0.08%. The greatest PCE enhancement was found with a 0.2% SU-8 interlayer, where devices had a slightly improved average $V_{oc}$ of 729 ± 2 mV, an increased FF of 71.6 ± 0.7% and a slightly increased $J_{sc}$ of 13.9 ± 0.1 mA cm$^{-2}$. The overall PCE improved by 13% to 7.28 ± 0.05%. The shunt resistances also increased with thickness of SU-8 from 1.11 kΩ cm$^2$, in the SU-8-free device, to 1.34 kΩ cm$^2$ in the device with 0.2% SU-8. Above this concentration, the shunt resistance decreased significantly. Interestingly, the series resistance remained fairly constant throughout all concentrations of SU-8. This could be an indication that there were improvements in BHJ microstructure with increasing thicknesses of the insulating SU-8 interlayer, since the insulating SU-8 is expected to lead to an increase in overall series resistance should the bulk resistance remain unchanged.
Table 5.1: Device characteristics of PTB7:PC71BM OSCs without SU-8 and using varying concentrations of SU-8 interlayer.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>PCE (%)</th>
<th>$R_{sh}$ (k$\Omega$ cm$^{2}$)</th>
<th>$R_s$ (k$\Omega$ cm$^{2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>717 ± 1</td>
<td>66.9 ± 0.5</td>
<td>13.4 ± 0.1</td>
<td>6.43 ± 0.08</td>
<td>1.11 ± 0.14</td>
<td>1.6</td>
</tr>
<tr>
<td>(717)</td>
<td>(67.4)</td>
<td>(13.5)</td>
<td>(6.51)</td>
<td>(1.02)</td>
<td>(1.6)</td>
<td></td>
</tr>
<tr>
<td>ZnO/0.08% SU-8</td>
<td>723 ± 2</td>
<td>70.2 ± 0.5</td>
<td>13.8 ± 0.1</td>
<td>6.99 ± 0.02</td>
<td>1.26 ± 0.20</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>(722)</td>
<td>(69.7)</td>
<td>(13.9)</td>
<td>(7.01)</td>
<td>(1.16)</td>
<td>(1.8)</td>
<td></td>
</tr>
<tr>
<td>ZnO/0.2% SU-8</td>
<td>729 ± 2</td>
<td>71.6 ± 0.7</td>
<td>13.9 ± 0.1</td>
<td>7.28 ± 0.05</td>
<td>1.34 ± 0.27</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>(727)</td>
<td>(71.6)</td>
<td>(14.1)</td>
<td>(7.33)</td>
<td>(1.27)</td>
<td>(1.4)</td>
<td></td>
</tr>
<tr>
<td>ZnO/1% SU-8</td>
<td>731 ± 2</td>
<td>52.7 ± 0.8</td>
<td>12.1 ± 0.3</td>
<td>4.66 ± 0.15</td>
<td>0.38 ± 0.04</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td>(729)</td>
<td>(53.5)</td>
<td>(12.4)</td>
<td>(4.83)</td>
<td>(0.42)</td>
<td>(2.1)</td>
<td></td>
</tr>
</tbody>
</table>

Note: The average PCE and standard deviations were obtained from 4 cells and the values in parentheses correspond to the best performing device.

The EQE spectra of the devices are shown in Figure 5.3. The ratios of the measured $J_{sc}$ values agreed to within 4% with the ratios of the integrated EQE spectra. The EQE between 340 nm and 700 nm was increased in the presence of 0.08% and 0.2% SU-8. With a 1% SU-8 interlayer, the EQE was considerably reduced in the region 450 nm to 700 nm, which accounts for the reduced $J_{sc}$.

Figure 5.3: EQE spectra of PTB7:PC71BM devices without SU-8 and using varying concentrations of SU-8.

5.2.3 Device stability with and without SU-8 interlayer

The stability in ambient conditions of encapsulated devices with and without SU-8 was investigated (see Table 5.2). After 8 weeks, the 0.08% and 0.2% SU-8 devices showed
improvements in $J_{sc}$ under AM 1.5 G conditions, while the control SU-8-free device suffered an 11% reduction. The series resistance for the SU-8-free device increased by more than 60% while the other devices saw a decrease in series resistance with time. The shunt resistance also decreased most significantly in the device without SU-8 post-storage.

Overall, the SU-8 devices retained ~94% of their initial PCE after 8 weeks, while the control device retained only 89% of its initial PCE, consistent with the previously observed behaviour for P3HT:PCBM devices.

**Table 5.2:** Device characteristics of PTB7:PC$_{71}$BM OSCs without and with varying concentrations of SU-8 after storing in ambient conditions for 8 weeks.

<table>
<thead>
<tr>
<th>SU-8 Concentration</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>PCE (%)</th>
<th>Shunt Resistance $R_{sh}$ (kΩ cm$^2$)</th>
<th>Series Resistance $R_s$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>712 ± 1 (-0.6)</td>
<td>65.0 ± 0.8 (-2.8)</td>
<td>12.4 ± 0.2 (-8.0)</td>
<td>5.72 ± 0.03 (-11.0)</td>
<td>0.71 ± 0.07 (-36.5)</td>
<td>2.6 ± 0.3 (+61.2)</td>
</tr>
<tr>
<td>ZnO/0.08% SU-8</td>
<td>730 ± 1 (+1.0)</td>
<td>71.0 ± 0.5 (+1.1)</td>
<td>12.6 ± 0.2 (+8.4)</td>
<td>6.54 ± 0.06 (-6.4)</td>
<td>1.16 ± 0.23 (-7.8)</td>
<td>1.4 ± 0.1 (-20.3)</td>
</tr>
<tr>
<td>ZnO/0.2% SU-8</td>
<td>741 ± 1 (+1.6)</td>
<td>72.0 ± 0.2 (+0.5)</td>
<td>12.8 ± 0.1 (+8.4)</td>
<td>6.81 ± 0.04 (-6.4)</td>
<td>1.20 ± 0.04 (-10.6)</td>
<td>1.4 ± 0.1 (-2.2)</td>
</tr>
<tr>
<td>ZnO/1% SU-8</td>
<td>739 ± 1 (+1.1)</td>
<td>52.4 ± 1.0 (-0.5)</td>
<td>11.3 ± 0.4 (-6.5)</td>
<td>4.38 ± 0.20 (-5.9)</td>
<td>0.44 ± 0.03 (+16.0)</td>
<td>2.1 ± 0.1 (-2.8)</td>
</tr>
</tbody>
</table>

Note: The average PCE and standard deviations were obtained from 4 cells and the values in parentheses correspond to the % change compared to the as-fabricated devices.

**5.2.4 UV-Vis absorption of films**

To investigate if the slight enhancements in $J_{sc}$ observed with 0.08% and 0.2% SU-8 might be due to an increase in active layer absorption as a result of the SU-8, we compare the UV-Vis absorption spectra of the stacks till the PTB7:PC$_{71}$BM active layer (Figure 5.4). The spectra are found to be very similar to each other. We therefore conclude that any enhancement or deterioration in $J_{sc}$ is not caused by a change in absorption with addition of SU-8, and that changes in the EQE are likely to be due to differences in active layer morphology, charge generation, charge transport or extraction at the electrode.
Figure 5.4: The absorbance spectra of the stacks of films up to and including the PTB7:PC$_{71}$BM active layer, without and with different concentrations of SU-8.

5.2.5 Evaluation of carrier lifetimes and charge transport

In Figure 5.5, an increased carrier lifetime relative to the SU-8-free device was observed for both 0.08% and 0.2% SU-8 devices over the range 250 mV to 650 mV, with the 0.2% SU-8 device showing substantially longer lifetimes at higher photovoltages. The increased carrier lifetimes imply slower rates of bimolecular recombination and are consistent with the observed improvement in FF.

Figure 5.5: Carrier lifetimes determined from TPV measurements of PTB7-based devices without SU-8, and with 0.08% and 0.2% SU-8.
We first attempted to study charge transport in SU-8 and SU-8-free devices by acquiring the current transients from DoI (Figure 5.6) measurements. Unlike in previous P3HT-based devices, the ambipolar mobilities could not be accurately determined in the presence of SU-8, due to there being no rise in the current transient (see Figure 5.6(b)). The DoI measurement technique is only applicable to devices in which there are no significant barriers to electron and hole injection. The observed behaviour however is characteristic of devices in which injection barriers exist[27] and further investigation is required to elucidate the existence of a barrier in PTB7-based devices but not in P3HT-based devices.

We note that although there was an injection barrier with the insertion of SU-8, this need not pose a problem in the normal operation of the PTB7-based OSC where it is current extraction that is of concern. The observed enhancement in J-V characteristics confirm that extraction is still efficient after insertion of the SU-8.

![Graphs](image)

**Figure 5.6:** DoI transients measured from PTB7-based device (a) without SU-8 and (b) with 0.08% SU-8.

As an alternative to DoI, we employed electron-only devices to study the electron transport and extraction in devices containing different thicknesses of SU-8. A “light-soaking” effect has previously been reported,[28, 29] in which a low dark current density is observed for as-fabricated unilluminated electron-only devices with a TiOₓ electron-selective layer due to inefficient electron extraction through the TiOₓ-active layer interface. After exposing the devices to AM 1.5 G illumination, the dark current density is found to increase significantly as a presumed consequence of trap-filling by photo-generated carriers (as a result of the UV component present in the AM 1.5 G spectrum).
It is well-known that there is a different mechanism for the photoconductivity of ZnO. [30, 31] As-prepared ZnO contains a high concentration of surface-adsorbed oxygen which traps electrons, causing a depletion region with low conductivity near the surface. (Equation 5.1)

\[ O_{2(g)} + e^- \rightarrow O_{2(ad)}^- \]  

(5.1)

The generation of holes due to photoexcitation leads to the desorption of these adsorbed oxygen ions, as shown in Equation 5.2, while the photo-generated electrons increase the ZnO conductivity.

\[ O_{2(ad)}^- + h^+ \rightarrow O_{2(g)} \]  

(5.2)

The decay of photo-induced conductance has been reported to be rapid in air and slow in vacuum or inert environments. [30, 32] In our experiments, where the devices are stored, illuminated and tested in the glovebox, we have found the photoconductance to persist for days.

In our SU-8-free electron-only devices, we observed a substantial increase in dark current density, from 20 A m\(^{-2}\) before illumination (Figure 5.7(a)) to 3.7 \(\times 10^4\) A m\(^{-2}\) after illumination (Figure 5.7(b)) at an applied voltage of 5 V. For devices with 0.08% and 0.2% SU-8, the dark current density was increased from about 1.4 \(\times 10^2\) A m\(^{-2}\) to about 4.5 \(\times 10^4\) A m\(^{-2}\) after illumination for the same applied voltage, implying improved electron extraction in devices with SU-8 compared to pristine ZnO, consistent with the slightly improved \(J_{sc}\) in the OSCs.

**Figure 5.7:** Dark current density of PTB7-based electron-only devices without SU-8 and using different concentrations of SU-8 (a) before and (b) after AM 1.5 G illumination.
The charge transport in the devices after illumination was determined by fitting the $J-V$ characteristics to a unipolar SCLC model, assuming the characteristics to be governed by the Mott–Gurney law:[33]

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{(V_{app} - V_{BI})^2}{L^3}$$  \hspace{1cm} (5.3)

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the dielectric permittivity of the active layer (taken to be 3), $\mu$ is the electron mobility, $L$ is the thickness of the active layer, $V_{app}$ is the applied bias and $V_{BI}$ the built-in potential, which is the difference in electrode work functions (in this case taken to be $\sim$1.15 eV).

By fitting $J^{1/2}$ versus $(V_{app} - V_{BI})$ to a straight line, the mobility can be extracted from the slope and $L$:

$$\mu = \frac{slope^2 \delta L^2}{9 \varepsilon_0 \varepsilon_r}$$  \hspace{1cm} (5.4)

Table 5.3: Slopes of $J^{1/2}$ vs $(V_{app} - V_{BI})$ plot for each electron-only device and its corresponding mobility.

<table>
<thead>
<tr>
<th>Slope ($A^{1/2}/(Vm)$)</th>
<th>Mobility ($m^2/Vs$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>30.22</td>
</tr>
<tr>
<td>ZnO/0.08% SU-8</td>
<td>32.41</td>
</tr>
<tr>
<td>ZnO/0.2% SU-8</td>
<td>32.72</td>
</tr>
<tr>
<td>ZnO/1% SU-8</td>
<td>3.16</td>
</tr>
</tbody>
</table>

Table 5.3 shows the slopes of $J^{1/2}$ vs $(V_{app} - V_{BI})$ for each device and the corresponding mobilities. The mobilities increased slightly with up to 0.2% SU-8 but reduced by two orders with the insertion of a 1% SU-8 layer. To attain SCLC conditions in unipolar devices, Ohmic contacts are required for both the injecting and extracting electrodes. In the case of the device with 1% SU-8, a non-Ohmic contact might have resulted from the thicker SU-8 at the cathode side, hindering the tunnelling of charges and so resulting in much poorer electron extraction and apparent mobility.

Ideally, hole transport should also be investigated by fabricating hole-only devices to verify the balance of electron and hole mobilities. However, in order to ensure hole selectivity, the ZnO layer would have needed to be replaced with a hole-transporting/electron-blocking layer...
Since doing so would result in a drastic change in surface properties and morphology, the BHJ properties in the hole-only device would not then have been representative of the BHJ in the OSC (with a ZnO or ZnO/SU-8 interlayer). The hole transport was therefore not studied in this instance. However, on the basis of hole mobilities for PTB7:PC$_{71}$BM blends reported in the literature of $5 \times 10^{-9}$ m$^2$/Vs to $1 \times 10^{-8}$ m$^2$/Vs,[34, 35] we may expect a good balance of carrier mobilities in devices with up to 0.2% SU-8.

5.2.6 Postulations on enhancement in device performance

On the basis of the results obtained thus far, it appears likely that the polymer orientation may have been affected by the underlying SU-8. Murray et al., for instance, have previously reported enhanced PTB7 π-π stacking when the polymer/fullerene blend is deposited on graphene oxide instead of PEDOT:PSS.[36] We speculate that the SU-8-coated-ZnO offers a different surface energy and reduced surface roughness, leading to better ordering of PTB7 in the bulk as seen in Figure 5.8.

![Figure 5.8: Schematic diagram depicting illustrative cross sectional morphologies for (a) ZnO; (b) ZnO/0.08% SU-8; and (c) ZnO/0.2% SU-8; figures to the right of each cross section illustrate the possible PTB7:PCBM BHJ packing on the surface within the marked region and likely throughout the BHJ.](image-url)
In Figure 5.8(a), the PTB7 on rough pristine ZnO ($R_{\text{rms}} \sim 4.1$ nm, see Figure 4.9) while mainly possessing face-on stacking, could have had a high degree of random ordering throughout the BHJ. With 0.08% SU-8 deposited (Figure 5.8(b)), the $R_{\text{rms}}$ is reduced to $\sim 2.6$ nm, potentially leading to slightly improved face-on stacking. In Figure 5.8(c), the roughness is further reduced with a thicker SU-8 (while still being thin enough for charge transport), further enhancing the polymer packing. Such behaviour would account for the improved carrier transport and extraction observed in our devices with up to 0.2% SU-8.

The improved device performance with up to 0.2% SU-8 could also be due to a favourable vertical phase separation. However, further characterisation e.g. grazing incidence wide angle X-ray scattering (GIWAXS), resonant soft X-ray scattering (RSoXS) or secondary ion mass spectroscopy (SIMS)) would be required to confirm the above postulates.

It is interesting to note that we achieved a similar enhancement ($\sim 13\%$) in device performance with PTB7-based devices as we did with P3HT-based devices despite the polymer systems being inherently different in terms of morphology. The PCE versus SU-8 concentration for both systems are plotted in Figure 5.9. The general form of these two curves is strikingly similar. While further characterisation of the PTB7 BHJ is required to elucidate the enhancement to device performance, it is possible that the inclusion of SU-8 is beneficial to polymer systems in general.

![Graph](image)

**Figure 5.9:** PCE versus SU-8 concentration for P3HT-based devices (black squares) and PTB7-based devices (red circles). (Lines are drawn as a guide for the eye.)
5.3 p-DTS(FBTTh$_2$)$_2$: A solution-processable small molecule

Small molecule organic semiconductors have attracted increasing attention over the years due to the advantages they offer over polymers: for example the facile purification processes,[37] their well-defined structures which ensure reproducibility[38] and generally higher $V_{oc}$[39] and mobility[40] compared to polymer semiconductors.

Vapour-deposited small molecule OSCs have been extensively studied for many years, while solution-processable small molecule BHJ OSCs only started receiving attention in 2006. The latter have now achieved ~9% PCE for a single junction cell,[41] making them comparable to their polymeric counterparts. The film forming properties of small molecules however, are often inferior, leading to reduced FF and $J_{sc}$ in devices.

The modification of surface chemistry to control the morphology of solution-processed small molecule organic semiconductor films[42] has previously been investigated in field effect transistors. In films processed via solution, the crystal formation has been found to be highly dependent on the wetting behaviour of the solvent on the substrate surface.[43, 44] Having a rough underlying substrate is also detrimental to the formation of semiconductor films as it results in the formation of in smaller crystals with poor long-range order, which significantly lowers the carrier mobility in devices.[45]

p-DTS(FBTTh$_2$)$_2$ (structure shown in Figure 5.10) is a promising small molecule donor material, which after extensive optimisation with DIO, has achieved a PCE of 8.9% in conventional OSCs[2] and 7.8% in inverted cells.[46] Following the studies in the previous chapter, we hoped that inclusion of an SU-8 interlayer would be beneficial for small molecule inverted OSCs based on p-DTS(FBTTh$_2$)$_2$. In particular, we study the effect of the SU-8 interlayer on the electron mobility and recombination dynamics, crystallinity and d-spacing of the small molecule in the bulk.

![Figure 5.10: Molecular structure of p-DTS(FBTTh$_2$)$_2$.](image-url)
5.3.1 Experimental

Preliminary devices fabricated showed optimum performance with a 0.08% SU-8 layer, therefore the studies in this section were focused on this concentration of SU-8.

The blend solution was formulated in accordance with reference [46]. p-DTS(FBTTh$_2$)$_2$ (1-Material) and PC$_{71}$BM (Solenne BV) were mixed in the ratio 1.5:1 in CB at a total concentration of 35 mg/mL. 0.4% DIO was added, and the solution was stirred at 50 ºC overnight. The solution was heated at 90 ºC for 15 mins before deposition for improved solubility and wetting. Spin coating was performed at 2000 rpm for 45 s. The film was annealed at 70 ºC for 10 mins and 80 ºC for 5 mins to give a thickness of approximately 110 nm. Subsequently, 5 nm of MoO$_3$ and 100 nm of Ag were thermally evaporated to complete the device.

Electron-only devices based on p-DTS(FBTTh$_2$)$_2$ were fabricated as previously done for PTB7, but replacing the active layer blend.

5.3.2 Effect of SU-8 interlayer on p-DTS(FBTTh$_2$)$_2$-based device performance

The $J$-$V$ curves of the best performing p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM BHJ solar cells with and without 0.08% SU-8, under illumination and in dark conditions, are shown in Figure 5.11, with the typical photovoltaic characteristics summarised in Table 5.4.

![Figure 5.11: $J$-$V$ curves of p-DTS(FBTTh$_2$)$_2$-based devices with and without 0.08% SU-8 in dark conditions and under illumination.](image)
Table 5.4: Device characteristics of p-DTS(FBTTh₂)₂:PC₇₁BM OSCs without and with a 0.08% SU-8 interlayer.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Voc (mV)</th>
<th>FF (%)</th>
<th>Jsc (mA cm⁻²)</th>
<th>PCE (%)</th>
<th>Shunt Resistance Rsh (kΩ cm²)</th>
<th>Series Resistance Rs (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>510 ± 14</td>
<td>46.8 ± 6.5</td>
<td>11.2 ± 0.1</td>
<td>2.73 ± 1.16</td>
<td>0.35 ± 0.23</td>
<td>2.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>(719)</td>
<td>(54.8)</td>
<td>(11.3)</td>
<td>(4.44)</td>
<td>(0.66)</td>
<td>(2.6)</td>
</tr>
<tr>
<td>ZnO/0.08% SU-8</td>
<td>762 ± 3</td>
<td>60.5 ± 0.3</td>
<td>13.3 ± 0.1</td>
<td>6.13 ± 0.07</td>
<td>1.27 ± 0.08</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>(764)</td>
<td>(60.6)</td>
<td>(13.4)</td>
<td>(6.21)</td>
<td>(1.28)</td>
<td>(2.7)</td>
</tr>
</tbody>
</table>

Note: The average PCE and standard deviations were obtained from 4 cells and the values in parentheses correspond to the best performing device.

SU-8-free devices had an average Voc of 510 ± 14 mV, a FF of 46.8 ± 6.5% and Jsc of 11.2 ± 0.1 mA cm⁻². The device had a PCE of 2.73 ± 1.16%. With the SU-8 interlayer added, devices had a significantly better Voc of 762 ± 3 mV, an increased FF of 60.5 ± 0.3% and a 19% increment in Jsc to 13.3 ± 0.1 mA cm⁻². The overall PCE improved to 6.13 ± 0.07% with SU-8. Series resistance increased slightly with SU-8 addition and the shunt resistance increased considerably from 0.35 kΩ cm² to 1.27 kΩ cm² with the addition of SU-8. The leakage current was reduced significantly with SU-8. The insertion of an SU-8 interlayer not only improves most device characteristics but also their consistency with a substantially reduced standard deviation for all parameters except the Jsc.

Figure 5.12: EQE spectra of p-DTS(FBTTh₂)₂:PC₇₁BM devices with and without SU-8.

The EQE spectra of the best performing devices SU-8 and SU-8-free devices are shown in Figure 5.12. The ratios of the measured Jsc values agreed to within 5% with the ratios of the integrated EQE spectra. The shapes of the spectra are very different between 380 nm to 480 nm,
and the EQE values are much higher with SU-8 between 450 nm and 700 nm. With the significant increase in $J_{sc}$ and change in shape of spectral response we postulate that there was likely a substantial change in the initial wetting and subsequent morphology or crystallinity of the active layer.

5.3.3 UV-Vis absorption of films

To determine whether the substantial enhancement in $J_{sc}$ might be due to an increase in absorption by the active layer, we compared the UV-Vis absorption spectra of both stacks of films up till the active layer (Figure 5.13). The two spectra were very similar implying that the increase in $J_{sc}$ is not caused by a change in absorption by the active layer with the insertion of an SU-8 interlayer.

![Figure 5.13: The absorption spectra of the thin-film stacks with and without SU-8.](image)

5.3.4 Evaluation of carrier lifetimes and charge transport

Figure 5.14 shows the carrier lifetime versus photovoltage for devices with and without SU-8. There was almost no change in carrier lifetime from 200 mV to 450 mV, but the SU-8 device showed substantially higher lifetimes at higher white light biases. The enhanced lifetime above 450 mV can be attributed to the increase in $V_{oc}$ in the SU-8 device, possibly due to a morphological change in the BHJ which may also account for the reduced shunting. The lower dark current implies reduced shunt paths in the device that may have contributed to the increased carrier lifetime.
Figure 5.14: Carrier lifetimes determined from TPV measurements of p-DTS(FBTTh$_2$)$_2$ devices with and without SU-8.

DoI measurements with SU-8 gave similar current transients to the PTB7-based devices, preventing us from obtaining ambipolar mobility values from these devices. As before, electron-only devices were fabricated to study the electron transport in more detail.

The dark current densities measured after exposure to AM 1.5 G simulated light showed a similar increase to that observed with the PTB7 devices (see Figure 5.15(a)). After light exposure, the dark current density measured at an applied voltage of 5 V was $2 \times 10^4$ A/m$^2$ for SU-8-free devices, and about $4 \times 10^4$ A/m$^2$ for SU-8 devices, indicating that insertion of an SU-8 interlayer enhances charge extraction.
Using Equation 5.4, the slopes of the SU-8-free device from Figure 5.15(b) (26.1 A$^{1/2}$/V$m$) and SU-8 device (29.7 A$^{1/2}$/V$m$), the electron mobilities were then calculated for the devices to be $3.0 \times 10^{-8}$ m$^2$/V$s$ and $3.9 \times 10^{-8}$ m$^2$/V$s$ respectively. To elucidate the origin of increased electron mobility in the SU-8 device, we investigated the surface morphology and crystallinity.

5.3.5 Probing surface morphology

AFM images of the BHJ films on pristine ZnO and ZnO/SU-8 are shown in Figure 5.16. Fibrillar structures of similar lengths (~1 µm) are observed in both films and their $R_{rms}$ are comparable: 1.59 nm for the BHJ on ZnO and 1.66 nm for the BHJ on ZnO/SU-8. It therefore appears that the SU-8 has only a weak influence on the surface morphology of the BHJ.

![Figure 5.16: Tapping mode AFM topography image of p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM on (a) pristine ZnO and (b) SU-8 coated ZnO.](image)

5.3.6 Evaluation of crystallite size and d-spacing

Aside from the surface morphology, the crystallinity in the bulk is of great interest since the performance of small molecule BHJ OSC has been found to improve with increased crystallinity. With larger crystallite sizes up to the order of the exciton diffusion length (to maintain efficient exciton dissociation), higher conductivity is expected for crystalline domains as compared to amorphous domains.[47]

To determine the crystallite sizes, BHJ films were spin coated onto ITO/ZnO and ITO/ZnO/SU-8. XRD spectra for the films are shown in Figure 5.17 for $2\theta \approx 2.5^\circ$ to $20^\circ$. The XRD spectrum of an uncoated ITO/ZnO film did not give any peaks in this region, indicating
that all detected peaks originate from the BHJ. The out-of-plane X-ray scans show a sharp peak at $2\theta \approx 4^\circ$. Higher order reflections at $2\theta \approx 8^\circ$ and $12^\circ$ are also evident, indicating the highly crystalline nature of the BHJ films. The spectrum for the film with underlying SU-8 shows peaks with higher intensity and smaller full width at half-maximum (FWHM), consistent with larger crystal sizes.

The coherence length, and hence estimated crystal size $D$, is given by the Scherrer formula as:

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (5.5)$$

where $K$ is the shape factor ($\sim 0.9$), $\lambda$ is the wavelength of the X-ray, $\beta$ is the FWHM and $\theta$ is the Bragg diffraction angle.

![Figure 5.17: XRD spectra of ITO/ZnO, ITO/ZnO/p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM and ITO/ZnO/SU-8/p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM.](image)

From the data in Figure 5.17, the crystallite size is estimated to be $11.2$ nm for the BHJ film on ZnO and $13.9$ nm for the BHJ film on ZnO/SU-8. These values are smaller than reported in the literature ($\sim 26$ nm)[48] for the same blend system on PEDOT:PSS which can be attributed to the roughness of the underlying ZnO affecting the crystallite formation. The addition of SU-8 resulted in larger average crystallite sizes in our BHJ, consistent with the increased mobility and efficiency in the device.
Peaks are seen to slightly shift from $2\theta \approx 3.98^\circ$ for the BHJ film on ZnO to $4.06^\circ$ for the BHJ film on ZnO/SU-8. The $d$-spacing can be calculated from Bragg’s Law (Equation 2.4).

The $d$-spacing for the film on ZnO was found to be approximately 2.23 nm and that for the film on ZnO/SU-8 was found to be 2.18 nm. Hence we see the packing density increases slightly for the film on ZnO/SU-8, which we would also expect to be beneficial for the carrier mobility in the device.

5.4 Conclusion

In this chapter, the effect of an SU-8 interlayer on the performance of devices based on two different semiconductor BHJ systems have been studied, each of which is quite distinct from P3HT.

In PTB7 devices, the PCE improved by ~13% and stability was improved with the insertion of SU-8. Carrier lifetimes measured from TPV and electron extraction from electron-only devices were improved by the insertion of up to 0.2% SU-8, while the electron mobility was maintained. We postulate that the SU-8 leads to a better polymer orientation or polymer-fullerene phase separation although further characterisation is required to confirm.

In p-DTS(FBTTh$_2$)$_2$ devices, the average PCE increased more than two fold to 6.2%, with contributions from all device characteristics. The carrier lifetime was slightly increased at high white light bias and electron extraction and mobility both increased significantly with the insertion of an SU-8 interlayer. Analysing the XRD spectra, we estimated a larger crystallite size and a slightly smaller $d$-spacing for the BHJ deposited on SU-8-coated-ZnO. These changes along with reduced shunting in the device are considered the likely causes of the substantial enhancement in device performance and consistency.

With the results presented, we have found SU-8 to also an effective interlayer for low crystallinity PTB7. SU-8 was also found to significantly enhance the performance of small molecule devices. On the basis of these findings, it seems likely that the SU-8 interlayer will be beneficial in many other BHJ OSCs as well.
5.5 References


Chapter 6: Conclusions and future work

6.1 Conclusions

The two main aims of this work were: i) to develop a fabrication protocol for ITO-free OSCs based on AgNWs capable of delivering performance and yields comparable to equivalent ITO-based devices and ii) to study the effect of applying an insulating interlayer on ZnO in different BHJ systems.

In the first results chapter, preliminary inverted devices based on AgNWs and ITO were first fabricated. AgNW-based devices had substantially poorer performance and yields than ITO-based devices. This was attributable to the roughness of the AgNW electrode, which adversely affected the film formation of all layers in the device. An optimised fabrication protocol was developed for AgNW devices. For the patterning of the AgNW electrode, employing water to remove excess AgNWs from the glass substrate was found to give the best consistency and minimal height difference at the edge. After deposition and baking of the AgNWs on glass, their adhesion was improved by removing the binders present in the film by prolonged immersion and agitation in DI water. A polymeric butyl titanate solution was coated on the AgNWs for improved subsequent wetting of the ZnO sol-gel precursor. The optimal concentration for the ZnO precursor was found to be 0.5 M. Spin coating of a filtered blend of P3HT:PCBM at 1000 rpm (which gave a film thickness of ~200 nm for the specified blend formulation) resulted in the best device performance. PEDOT:PSS, containing 1 vol% Zonyl surfactant and heated to 90 ºC before deposition, reasonably wetted the active layer, and greatly enhanced the yield of devices compared to unheated surfactant-free PEDOT:PSS. Devices were completed by evaporating 80 nm of Ag. Using the optimised fabrication protocol, the performance, consistency and yield of AgNW-based devices was significantly improved and close to that of equivalent ITO-based devices.

In the next results chapter, the effect of coating an SU-8 interlayer on sol-gel-derived ZnO was investigated for P3HT:PCBM BHJ OSCs. SU-8 had a planarising effect on ZnO and also led to an increased water contact angle compared to ZnO, resulting in better interfacial contact of the active layer and ZnO. A 0.08% SU-8 layer (~2.5 nm thickness) enhanced the PCE by ~14% and improved the device stability. Inclusion of a 0.08% SU-8 layer caused an increase in carrier lifetime but had minimal effect on the carrier mobility, implying that slower recombination dynamics accounted for the improvement in device performance. When SU-8
was deposited on polycrystalline ZnO, a similar effect on device performance, recombination dynamics and carrier mobility was observed, which suggests SU-8 can be used to enhance the performance of devices with electron-transporting layers of varying surface compositions and properties.

In the final results chapter, the effect of an SU-8 interlayer on device performance was studied in two other BHJ systems, namely PTB7 and p-DTS(FBTTh$_2$)$_2$. In SU-8-containing PTB7 devices, the PCE saw a ~13% enhancement. The device stability also improved compared to control SU-8-free devices. Carrier lifetime and electron extraction improved with up to 0.2% SU-8 inserted. SU-8 is postulated to create a more favourable polymer orientation or polymer-fullerene phase separation, but this requires further investigation. In SU-8-containing p-DTS(FBTTh$_2$)$_2$ devices, the PCE was significantly increased, mainly attributable to an increase in crystallite size, smaller d-spacing and reduced shunting with SU-8. These findings suggest that addition of an SU-8 interlayer will be beneficial in other BHJ systems.

6.2 Future work

In this work, AgNWs were found to have great potential as a replacement for ITO. The suitability of AgNWs for flexible OSCs has been reported elsewhere, suggesting they are an ideal candidate for solution-processable flexible electrodes. While AgNWs might address the concerns of the scarcity of indium which is needed to produce ITO, the cost of AgNWs are still considerably high, with commercial conductive AgNW inks costing up to US$15,000 per litre.

The first direction for future work could be to employ copper nanowires, a cheaper alternative to silver nanowires, to reduce the cost of such conductive inks considerably. The optimisation studies conducted in this work could also be applied to copper nanowire inks for incorporation into large area, flexible and stretchable optoelectronic devices and even wearable electronics.

Further work should also seek to investigate the source of the enhancement in PTB7 device as a result of SU-8 addition. Based on previous reports of similar work, we expect that this is likely due to a more preferential BHJ phase separation or polymer orientation for charge transport caused by an underlying SU-8 layer which could be studied with SIMS and X-ray scattering techniques, respectively. Having identified the reason for device enhancement, SU-8 could be applied to other high performance polymers systems.
Appendix 1

The work function of the ITO electrode was calculated from UPS spectra using Equation 2.6. The normalised UPS spectra in Figure A1.1 showed bare ITO to have a work function of 4.7 eV, which was shifted to 4.15 eV upon deposition of the sol-gel-derived ZnO layer, both of which are in agreement with literature values. [1]

Figure A1.1: The normalised secondary cutoff region in the UPS spectra of ITO and ZnO coated on ITO.

Figure A1.2: Valence band edge of ZnO.
Based on the spectral width (difference between the valence band edge shown in Figure A1.2 and the secondary cutoff) of 13.85 eV, the ionisation potential (IP) of ZnO (Equation 2.7) was found to be 7.35 eV.

Figure A1.3: UV-Vis absorbance spectrum of ZnO, the inset shows the Tauc plot.

Figure A1.3 shows the UV-Vis absorbance spectrum of ZnO on quartz. The optical band gap $E_g$ of ZnO was determined from the spectrum using the Tauc relation:[2]

$$ (ahv)^n = C(hv - E_g) \quad \text{(A1)} $$

where $\alpha$ is the absorption coefficient, $hv$ is the photon energy, $n$ is 2 for a material with a direct band gap and $C$ is a constant.

$E_g$ was estimated to be 3.3 eV by extrapolating the plot to the x-axis, which then gives the ZnO conduction band edge level of 4.05 eV.

References

Appendix 2

The XRD spectra of sol-gel-derived ZnO and ZnO<sub>PC</sub> were compared with peaks obtained from the JCPDS powder diffraction file 75-576 for ZnO in Figure A2.1. The three diffraction peaks observed for ZnO<sub>PC</sub> at 2θ = 31.7° (100), 34.4° (002) and 36.2° (101) correspond to pure ZnO crystalline phase. In the sol-gel-derived ZnO, however, the peaks characteristic of ZnO were broader and less defined. Since the crystallite size is inversely related to the broadness of the peaks, the ZnO<sub>PC</sub> can be considered to be much more crystalline than the sol-gel-derived ZnO.

![Figure A2.1: XRD spectra of sol-gel-derived ZnO and ZnO<sub>PC</sub>, compared to the peaks from JCPDS file 75-576.](image)

Figure A2.2 shows the O 1s XPS spectra of sol-gel-derived ZnO and ZnO<sub>PC</sub>. The deconvolution of the O 1s peaks for both samples showed the presence of 3 components at 530.4 eV (corresponding to the O<sup>2-</sup> surrounded by Zn in the ZnO lattice), 531.6 eV (oxygen deficiencies) and 532.4 eV (oxygen from adsorbed water and carbon dioxide on the sample surface). The ratio of oxygen atoms in the lowest binding energy component to those in the oxygen deficient component was 1:0.4 in the sol-gel-derived ZnO and was found to be 1:0.2 in the ZnO<sub>PC</sub>. This indicates a greater proportion of Zn-O bonds and fewer oxygen deficiencies in the ZnO<sub>PC</sub> than in the sol-gel-derived ZnO, and confirms the different surface compositions in each ZnO.
Figure A2.2: O 1s XPS spectra of (a) sol-gel-derived ZnO and (b) ZnO_F.

The AFM topographic images in Figure A2.3 of ITO/ZnO_F and ITO/ZnO_F/SU-8 show the SU-8 has a planarising effect causing the R_{rms} to decrease from 4.8 nm to 3.1 nm after SU-8 deposition.

Figure A2.3: AFM topographic images of (a) ITO/ZnO_F (b) ITO/ZnO/SU-8.

Static water contact angle measurements on the films in Figure A2.4 showed an increase in hydrophobicity when SU-8 was applied to the ZnO_F, with the contact angle increasing from 55.3 ± 2.1° to 78.7 ± 1.2°.

Figure A2.4: Static water contact angle measurements on (a) ITO/ZnO_F (b) ITO/ZnO_F/SU-8.
**Table A2.1:** Photovoltaic characteristics of sol-gel-derived ZnO P3HT:PCBM OSCs with and without SU-8 (when fabricated to an active area of 3 mm$^2$).

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>PCE (%)</th>
<th>Shunt Resistance $R_{sh}$ (kΩ cm$^2$)</th>
<th>Series Resistance $R_s$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>602 ± 1 (603)</td>
<td>59.2 ± 0.8 (59.3)</td>
<td>8.8 ± 0.1 (8.9)</td>
<td>3.12 ± 0.06 (3.16)</td>
<td>1.03 ± 0.17 (1.04)</td>
<td>1.3 ± 0.1 (1.2)</td>
</tr>
<tr>
<td>ZnO/SU-8</td>
<td>610 ± 2 (609)</td>
<td>64.1 ± 0.4 (64.4)</td>
<td>9.0 ± 0.1 (9.0)</td>
<td>3.51 ± 0.04 (3.53)</td>
<td>1.39 ± 0.14 (1.23)</td>
<td>1.7 ± 0.1 (1.7)</td>
</tr>
</tbody>
</table>