Stability and Degradation of Organic Photovoltaics

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Declaration

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision.

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List of Publications

- C. A. Epstein (2013, November). Development and Degradation Testing of Polymer Solar Cells with a Novel Structure. Poster presented at Australian Institute of Physics Industry Day 2013, Sydney, NSW, Australia.
- M. J. Griffith and C. A. Epstein (2015, October). Lighting Up the Future: the Production and Characterization of Printed Flexible Solar Cells. Paper presented at the Smart Future Cities conference, Newcastle, NSW, Australia.
- **C. A. Fenn** (2017, February). Stability of Standard and Inverted OPV Devices with the Same Buffer Layers. Paper presented at the International Conference Asia-Pacific Hybrid and Organic Photovoltaics, Yokohama, Japan.

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Glossary

Cs_2CO_3	Cesium Carbonate
Al_2O_3	Aluminium Oxide
AM 1.5	Air Mass 1.5
AZO	Aluminium-Doped Zinc Oxide
BHJ	Bulk Heterojunction
CMC	Critical Micelle Concentration
СО	Carbon Monoxide
CO ₂	Carbon Dioxide
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DUT	Device Under Test
ESL	Electron Selective Layer
FF	Fill Factor
FFF	Fused-Filament Fabrication
HOMO	Highest Occupied Molecular Orbital
HSL	Hole Selective Layer
I _{SC}	Short Circuit Current
ICBA	Indene-C ₆₀ Bisadduct
IEA	International Energy Agency
IPA	Isopropyl Alcohol
ISOS	International Summit on OPV Stability
ITO	Indium Tin Oxide
IV	Current-Voltage
J _{SC}	Short Circuit Current Density
LabVIEW	Laboratory Virtual Instrument Engineering Workbench

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LBIC	Light Beam Induced Current
LIFA	LabVIEW Interface for Arduino
LUMO	Lowest Unoccupied Molecular Orbital
MEH-PPV	Poly(2-Methoxy-5-(2-Ethylhexyloxy)-1,4-Phenylene vinylene)
MoO ₃	Molybdenum Oxide
MUX	Multiplexer
NO_x	Nitrogen Oxide
NP	Nanoparticle
OPV	Organic Photovoltaic
P3HT	Poly(3-Hexylthiophene)
РСВ	Printed Circuit Board
PCBM	Phenyl-C ₆₁ -Butyric Acid Methyl Ester
PCDTBT	Poly [N-9- heptadecanyl- 2,7-carbazole- alt-5,5-(4,7- di-2-thienyl-2,1,3
	-benzothiadiazole)]
PCE	Power Conversion Efficiency
PEDOT:PSS	Poly(3,4-Ethylenedioxythiophene):Poly(Styrenesulfonate)
PEIE	Polyethylenimine Ethoxylated
PEN	Poly(Ethylene Naphthalate)
PET	Poly(Ethylene Terephthalate)
PTB7	Poly[[4,8-bis[(2-ethylhexyl)-oxy]benzo[1,2-b:4,5-b]dithiophene-2,6-diyl]
	[3-fluoro-2-[(2-ethylhexyl)carbonyl]-thieno-[3,4-b]thiophenediyl]]
PV	Photovoltaic
R _{sh}	Shunt Resistance
R _s	Series Resistance
SDS	Sodium Dodecyl Sulfate
SMU	Source Measure Unit
TiO ₂	Titanium Dioxide
UPS	Ultraviolet Photoelectron Spectroscopy
UV-Vis	Ultraviolet-Visible Spectroscopy
V _{OC}	Open Circuit Voltage
WO ₃	Tungsten Trioxide

XPS X-Ray Photoelectron Spectroscopy

ZnO Zinc Oxide

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Abstract

Organic photovoltaics (OPV)s are a type of renewable energy technology that have gained a large amount of interest in the scientific literature in recent years, motivated by their potential for large scale use as a flexible, semi-transparent and low cost renewable energy alternative. Due to their flexible and semi-transparent nature, there are several potential applications that are not available to conventional photovoltaics, such as use in windows or wearables. However, several key issues remain to be addressed before large scale, cost effective use is possible. Arguably the foremost issue is the lifetime of the devices; which is currently too short for practical use.

There are various degradation processes that can occur in these devices and often numerous such processes occur simultaneously. To improve device stability, their degradation must be investigated and understood. The most common method for investigating degradation of OPVs is lifetime measurements. Thus, this thesis presents details of the construction of an automated degradation system for performing lifetime measurements on small ($5mm^2$) OPV devices.

Using this degradation system, systematic studies on the stability of several OPV architectures under various lighting conditions were conducted. Devices were constructed with a range of material systems, to elucidate degradation behaviour related to materials and interfaces. The stability of OPV devices was shown to be dependent on material and interface stability, as well as illumination conditions. Observed trends changed significantly when different lighting conditions were employed. Furthermore, the degradation behaviour of printed OPVs was found to be dependent on the thickness of buffer layers used, with unexpected trends observed in the degradation for different thicknesses.

Through rigorous degradation measurements presented in this thesis, a more

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extensive picture of the stability and degradation of OPV devices has been obtained. This understanding provides several pathways for fabrication of more stable OPV devices, including avoiding materials observed to cause rapid degradation, and using filters on appropriate structures to reduce photo-active degradation.

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Chapter 1

Introduction

1.1 Outcomes and Thesis Flow

The main scientific contributions of this thesis are as follows:

- A fully automated system for performing lifetime measurements on smallscale organic photovoltaics (OPVs) was constructed. The system was used to perform numerous degradation studies, resulting in a more thorough understanding of the stability of OPV devices.
- 2. The stability of different OPV structures were investigated, and it was found that the observed stability of each structure was significantly dependent on the testing conditions used. Further, the inverted bulk heterojunction structure was less stable than previously reported when tested under constant illumination.
- Different material systems were investigated to elucidate the impact of materials on device stability. Through these investigations, it was observed that UV light was crucial to long-term operation of devices containing ZnO.
- 4. Extensive work has been completed on the stability of devices made with nanoparticle active layers deposited from environmentally-friendly solvents. A greater understanding of the degradation of NP-OPV has been obtained and it was observed that surfactant plays a significant role in the degradation of these devices.
The flow of the thesis is as follows: the remainder of chapter 1 provides a thorough theoretical background for the work presented in this thesis. Details of the experimental techniques that were employed are then provided in chapter 2.

Chapter 3 focuses on initial degradation measurements that were performed on small scale devices (5mm² active area) with two different architectures and two active layers. Fabrication steps for these devices are also outlined for each device type, which are categorised as either standard or inverted architecture. These devices also contained either a NP or bulk heterojunction (BHJ) active layer. The motivation for, and construction of, a more robust degradation testing system is also presented in this chapter.

Chapter 4 describes further experiments performed on the four device types mentioned above, providing a more complete understanding of the degradation. This chapter includes ultraviolet-visible spectroscopy (UV-Vis) measurements performed on both BHJ and NP films over several days, to investigate changes in absorption of the active layer. Lifetime measurements and light beam induced current (LBIC) measurements are also presented in this chapter.

The effect of materials and lighting conditions on lifetimes of OPVs was more closely investigated in chapter 5. Results in chapters 3 and 4 showed that the stability of the studied devices was dependent on the testing and lighting conditions. Thus, chapter 5 outlines further experiments performed to better understand the degradation of these devices under different lighting conditions. Many degradation processes are associated with specific materials. Consequently, experiments were performed to identify degradation related to materials.

Chapter 6 details experiments investigating the stability of different nanoparticle systems and the effect of surfactant on degradation in these devices. Included therein are degradation studies and x-ray photoelectron spectroscopy (XPS) measurements, which were used to gain a more in depth understanding of the degradation processes.

1.2 Global Demand for Energy

Global demand for energy has been exponentially increasing with increasing population and urbanisation since the Industrial Revolution [1]. The International

2

Energy Agency (IEA) projects that energy demand will grow by more than onethird of current demand by 2035 [2]. This growth is due to further increases in population and a projected rise in per-capita energy consumption, particularly in developing nations [2].

The IEA reports that approximately 70% of the world's energy supply is currently being generated by fossil fuels, with 39% of that from burning coal [3]. However, there are many problems associated with the continued use of fossil fuels; the most pressing of these being production of pollutants, such as carbon monoxide (CO), nitrogen oxide (NO_X) and carbon dioxide (CO₂) [1].

Over the last century, the burning of fossil fuels has drastically changed the concentration of atmospheric greenhouse gases which has already had an observable effect on the environment [4,5]. The clear majority of climate scientists agree that climate warming trends over the past century are likely due to greenhouse gases from human activities [6].

Gaseous CO_2 is the most concerning greenhouse gas because it is being produced in the highest concentration and it has the longest atmospheric lifetime [7]. The atmospheric concentration of CO_2 has increased from a pre-industrial value of approximately 280ppm to 405ppm in 2017 [8], greatly exceeding the range of any natural change in CO_2 concentration over the last 650,000 years (determined using ice core measurements) [9]. Further increases in demand are expected by 2035 and will cause a more rapid increase in the concentration of CO_2 , resulting in a greater effect on global climate.

Another major problem associated with the continued use of fossil fuels as the primary source of energy is that they are a finite resource. Recent projections indicate that reserves of fossil fuels will be depleted in approximately 100 years at projected usage levels [10]. Consequently, alternative power sources are necessary to supply the growing demand while minimising environmental impact [11].

1.3 Renewable Energy Technologies

Renewable energy technologies are alternate power sources with the potential to minimise environmental impacts, reduce secondary waste and provide sustainable energy [12]. The defining feature of renewable energy is that its sources are replenished on a human time scale: such as sunlight, wind, geothermal heat and ocean waves [13].

Renewable energy technologies have received increasing interest in recent decades as an alternative to fossil fuels [14]. Of the many available renewable sources of energy, solar energy is perhaps the most promising because of its abundance [15]. Furthermore, solar cells do not contribute to carbon dioxide and other pollutants during operation, meaning they are a clean energy source [16]. However, for solar cells to offer a viable commercial alternative, sunlight must be converted efficiently, and the production and operation of the devices must be cost effective.

Much of the solar technology market (up to 90%) is currently dominated by single junction solar cells based on crystalline silicon [17]. This dominance is due to an entrenched and relatively mature silicon industry and the high stability and efficiency (above 25%) that silicon devices exhibit [18,19]. However, there are many applications for which conventional photovoltaics (PVs) are not suitable [3].

OPVs are an alternative PV technology that are cheap, light-weight and flexible [3]. These advantages over silicon PVs make OPVs an attractive alternative to silicon PV for a range of applications.

1.4 Organic Photovoltaic Devices

OPVs are a category of photovoltaic device which use organic semiconducting polymers and small molecules to generate electricity from sunlight. They have attracted considerable interest as a renewable energy technology due to their potential for large-area fabrication of flexible solar cells at electricity prices comparable to both conventional solar and non-solar alternatives [20]. Low material usage in OPV cell production (compared with silicon PVs) means OPVs can be fabricated more cheaply. They can also be processed using techniques not available for inorganic semiconductors, such as solution and roll-to-roll processing [21,22]. An OPV module with a power conversion efficiency (PCE) of just 2% and a lifetime of three years could be competitive with conventional PVs on cost of electricity, while a PCE of 5% could be competitive with coal and natural gas [23].

Given the success of silicon PVs, it is unlikely they will be replaced as the dominant PV in the foreseeable future [24]. However, OPVs can be fabricated on flexible substrates, they are light-weight and can be made semi-transparent. Consequently, it is possible that OPVs will initially fill applications that silicon is not suitable for [3]: including portable battery chargers [25], and window and facade installations [26].

While OPVs with PCEs above 10% have been produced [27], the associated lifetimes are untenably short. Understanding and preventing the degradation processes that occur in OPVs is thus paramount to their wide-spread success [28].

1.4.1 Device Operation

The active layer is the layer which absorbs light and generates electricity in OPVs. Conversion of light into electrical current in an OPV device consists of four major steps, shown in figure 1.1.

- (a) Light is absorbed in the active layer and an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) creating an exciton (a strongly, Coulombically bound electron/hole pair).
- (b) The exciton diffuses to an interface and,
- (c) is dissociated.
- (d) The electron and the hole are then transported from the active layer to the electrodes through the acceptor and donor materials respectively.

Each of these steps is described in further detail in the remainder of this section.

(a) Optical Absorption

A photon is absorbed in the active layer, which excites an electron in the donor material. Photo-excitation results in an electron transition from the HOMO to the LUMO of the donor material, leaving a hole in the HOMO. The electron and hole produce an electrically neutral quasi-particle known as an exciton which is tightly bound together by Coulombic attraction [30]. Unlike silicon and other inorganic semiconductors, OPVs are complicated by the high exciton binding energy, due to organic materials having a lower dielectric constant [31]. Consequently, the absorption of a photon does not lead directly to free charge carriers and the exciton



Figure 1.1: Illustration of the operation of organic solar cells: (a) light absorption, (b) exciton diffusion, (c) exciton dissociation and (d) charge transport and collection. All steps must be performed efficiently for high performing devices [29].

requires an energy gradient to dissociate. An interface between donor and acceptor materials provides the energy difference needed to dissociate an exciton [30].

(b) Exciton Diffusion

To generate separate charge carriers, an exciton needs to diffuse to an interface between the two materials. Since excitons are electrically neutral, they diffuse via random hops and will decay to the ground state if they do not reach an interface in a certain length. This distance is known as the exciton diffusion length and is between 4 and 15 nm in the materials that are typically used [32].

(c) Exciton Dissociation

The two materials in the active layer set up an effective electric field which can dissociate excitons by causing the electron to move from the LUMO of the donor to that of the acceptor, while the hole stays in the HOMO of the donor. Once the exciton has diffused to an interface it can dissociate, provided the energy levels are

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appropriately aligned [30]. The HOMO of the donor should match the work function of the anode and the LUMO of the acceptor should match the work function of the cathode [33]. It is also necessary that the acceptor material have a lower LUMO than the donor material, which provides the driving force for charge transfer [34].

(d) Charge Transport and Collection

Once the exciton has been dissociated, electrons move into the acceptor phase and holes remain in the donor phase. Subsequently, electrons and holes are transported towards their respective electrodes by the built-in potential of the device, where charge is collected. However, the polymers in the active layer are arranged in a disordered fashion and defects in either material can cause charge carriers to become trapped [35].

Charge carriers which are generated that are not collected must eventually recombine [36]. There are several types of recombination that can take place, however those most relevant to the OPV cells are geminate recombination and bimolecular recombination which are illustrated in figure 1.2 [37].

- Geminate recombination involves an exciton that has already been split at a donor /acceptor interface. The constituent charges form a charge transfer state at the interface, which acts as an intermediate between a bound exciton and a separated pair of charge carriers. In the charge transfer state, the electron resides in the acceptor material and the hole in the donor material. While the charges still experience some weak Coulombic attraction, they may escape the influence of the other through diffusive motion. However, it is also possible that the charge transfer state may recombine to the ground state [37]; this is germinate recombination.
- Bimolecular recombination involves free charges that are moving through the device. As a charge carrier moves through the device it may encounter an oppositely charged carrier. This encounter may result in the formation of an exciton and recombination. The likelihood of this recombination occurring will increase with the thickness of the device, because the carriers must travel further, and the size and degree of mixing of the donor and acceptor domains [38, 39].



Figure 1.2: Illustration of germinate and bimolecular recombination, which are the two types of recombination most relevant to OPVs. Germinate recombination involves an exciton which dissociates but then recombines due to weak Coulombic attraction. Bimolecular recombination is recombination of free charge carriers while diffusing through the device.

Active layer morphology is an important factor for performance of devices [40]. Improved charge transport and reduced recombination can be achieved by optimising the active layer morphology. In addition to optimising the components and composition of the active layer, modification of the electrodes can also lead to higher performance through improved charge collection. Buffer layers can be used to change the effective work function of the electrode or reduce leakage current [41]. Buffer materials are described in detail in section 1.4.4.

1.4.2 Active Layer Morphology

Active layer morphology in OPV devices is critical to device performance [40]. The first devices had a single layer of organic polymer deposited between two electrodes with differing work functions [42], as shown in figure 1.3(a). Since excitons have a relatively short diffusion length, which can vary from 4 to 15 nm [32], all charge must be generated close to the interface. Furthermore, due to the low elec-

tron mobility that most organic polymers exhibit, charge must be generated at the anode interface meaning single layer devices had poor efficiency [43].

A breakthrough occurred when Tang demonstrated that device performance could be greatly improved by building a bilayer structure containing two materials, as shown in figure 1.3(b) [44]. A bilayer heterojunction comprises an electron donor material and an electron acceptor material in two separate layers on top of one another. The key advantage of the bilayer is improved dissociation of excitons compared with just utilising the polymer/anode interface. However, an exciton must still be able to diffuse to an interface before it can be dissociated. As such, the exciton diffusion length determines the optimal domain size for the materials in the active layer. In a bilayer heterojunction, layer thickness must be comparable to the exciton diffusion length otherwise there is material that does not contribute to current generation. However, a thin active layer has poor light absorption and, as a result, the efficiency of bilayer devices is limited [45].

In contrast, a bulk heterojunction (BHJ) consists of two materials mixed together in a single layer, as illustrated in figure 1.3(c). In a BHJ, donor and acceptor materials are blended and deposited as a single layer, typically from a chlorinated solvent. Phase segregation of the materials occurs upon film formation with regions of each material in the layer only separated by several nanometres [46]. This arrangement means that there are multiple interfaces that the exciton can diffuse to and allows for the layer to be thicker (100-300 nm) [47]. Consequently, BHJ active layers exhibit both improved light absorption and efficient separation and charge transport [48].

Another active layer that has been introduced recently is a nanoparticle (NP) active layer [49–51], which is shown in figure 1.3(d). Pre-formed nanoparticles that have a mixture of the donor and acceptor materials are deposited from water. While environmentally harmful solvents are used to produce the nanoparticles, they can be contained and, critically, they are removed from the device fabrication (printing) step. The NP route also uses less harmful solvent (by volume) than the BHJ approach [52]. NP active layers are described in more detail in section 1.8.





Figure 1.3: Examples of (a) a single layer junction, (b) a bilayer heterojunction active layer, (c) a bulk heterojunction active layer and (d) a nanoparticle active layer. This thesis investigates bulk heterojunction and nanoparticulate active layers.

1.4.3 Annealing and Morphological Changes

The performance of OPVs is intimately dependent on the active layer morphology [53]. The active layer in OPV devices commonly described as consisting of three phases: amorphous P3HT, crystalline P3HT and aggregated PCBM [54]. The extent of the P3HT crystallisation and PCBM aggregation dictate charge separation and device performance [55].

Active layer morphology can be improved using post production techniques such as annealing [56]. In devices comprised of P3HT:PCBM¹ blends, device performance is highly dependent on the P3HT crystallinity [40], and the size of PCBM aggregates within the active layer [46], both of which can be thermally activated.

Annealing can either be achieved thermally or via solvent. Thermal annealing is the process of heating films after deposition to allow the materials in the active layer to rearrange [57]. Yang *et al.* attributed increased performance after thermal annealing to improved crystallinity and controlled de-mixing of both P3HT and PCBM [53]. Solvent annealing involves exposing the film to a high solvent vapour environment to increase the film forming time by slowing the solvent evaporation [58]. The use of solvent annealing leads to an increase in the ordering of P3HT

¹poly(3-hexylthiophene):phenyl-C₆₁-butyric acid methyl ester

allowing better charge transport [59].

Spin coating a mixed polymer thin film will usually result in phase separation, i.e. separation of the P3HT and PCBM phases [60]. Phase separation can occur in both the vertical and lateral directions, and these are generally independent of each other [61]. It has been shown that a small amount of phase separation is beneficial for device performance as it increases the interfacial area where excitons may be dissociated [62]. The ideal phase separation, shown in figure 1.4, maintains an interpenetrated network while having donor- and acceptor-rich regions adjacent to the corresponding electrodes. However, large scale phase separation can result in a non-ideal profile in thin films and reduction of interfacial area [63]. Campoy-Quiles *et al.* reported the formation of a non-ideal gradient with PCBM-rich near the anode and P3HT-rich near the cathode due to surface energy of the substrate/film interface and film/air interface [64]. The gradient was altered to that shown in figure 1.4 using a self-assembled monolayer which modified the surface energy of the substrate.



Figure 1.4: Illustration of the desired vertical phase separation in a polymer:fullerene OPV device, resulting in acceptor- and donor-rich domains at the corresponding electrodes while maintaining an interpenetrated network.

There has been much progress in recent years in investigating the effect of numerous other factors on the morphology of OPVs [46]. The most common of these factors include changing solvent, blend ratio and the use of additives [65]. The ideal morphology of the active layer would contain domains that match the exciton diffusion length and provide constant pathways for free charge carriers to travel to the electrodes [66]. In recent years, much progress has been made in understanding and predicting the morphology of these active layers [67]. However, systematic engineering of this morphology is difficult and is often a trial and error process [61].

1.4.4 Device Architecture

An OPV device also be fabricated with a range of different architectures, which determine the materials that are used and alters device performance and lifetime. The two predominant structures are typically called the standard architecture and the inverted architecture [68]. An example of each is shown in figure 1.5.

The standard architecture was named thus because it has been most widely reported on. This architecture contains an active layer between a high work function metal oxide, commonly indium tin oxide (ITO), as the anode and a low work function metal, commonly aluminium, as the cathode. There is also a hole selective layer (HSL) between the ITO and the active layer, typically PEDOT:PSS². An electron selective layer (ESL), which improves the electrical coherence of the device, may also be included. Metal oxides, such as zinc oxide (ZnO), are commonly used as ESLs [69].

To collect charge efficiently, the work functions of the anode and cathode should be matched to the HOMO of the donor and the LUMO of the acceptor respectively [70]. Having a low work function metal as the top electrode allows for matching of the LUMO of the acceptor and, thus, efficient charge collection. However, a low work function metal can be highly susceptible to damage by water and oxygen which can cause the device to degrade rapidly [71]. Aluminium is known to oxidise rapidly, reducing charge transport when it is used as an electrode [72]. Another problem with aluminium as the top electrode is that water and oxygen can diffuse through to subsequent layers [73].

The inverted architecture is electrically inverted when compared with the standard architecture, hence its name [74]. The flow of charge is reversed using careful selection of electrode materials and buffer layers. A typical inverted architecture device uses an ITO electrode which is modified by an ESL, such as ZnO. The ESL is then covered by the active layer, a HSL and a high work function metal, such as silver, as the top electrode.

²poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate)



Figure 1.5: Layer structure of two common architectures of OPV: (a) standard architecture organic solar cell and (b) inverted architecture solar cell. Different structures allow for different materials to be used.

Buffer Layers

A strategy for improving device performance is to incorporate buffer layers into the structure. These layers serve multiple purposes including: tuning the energy levels of electrodes, defining polarity of the device, altering the morphology and improving interfacial stability [75]. There are a wide range of materials used as buffer layers in OPVs [76]. The buffer layers will be referred to as either a hole selective layer (HSL) or a electron selective layer (ESL). The HSL is an anodic buffer layer which improves conductivity of holes, while the ESL is a cathodic buffer layer which improves conduction of electrons [75].

One major function of buffer layers is to create selectivity at the electrodes [75]. These layers are chosen to improve charge transport through the device by being selective to one charge carrier or by improving the energy level matching. Charge selective contacts are important for minimising recombination and maximising efficient charge extraction [77].

The most commonly used buffer material is PEDOT:PSS, which is used as a transparent HSL [77]. PEDOT:PSS as a HSL alters the work function and improves the hole transport to the anode [78]. While PEDOT:PSS performs well as a buffer layer, several degradation mechanisms have been attributed to it including acceler-

ating oxidation of the electrodes and active layer due to its hygroscopic nature and degradation of the active layer due to the acidic nature of PSS [79, 80]. It has also been shown that transition metals, such as molybdenum oxide (MoO_3), can replace PEDOT:PSS as the HSL with a slight improvement in performance [81].

Metal oxide buffer layers are also used as an ESL to modify the work function of ITO to invert the device polarity [82]. Some examples of metal oxides used as an ESL are titanium dioxide (TiO₂) and cesium carbonate (Cs_2CO_3) [83,84].

As mentioned in section 1.4.2, active layer morphology is closely linked to device performance. Buffer layers can be used to ensure that a desirable level of vertical phase separation occurs in the device. Controlling the surface energy of buffer layers has been proposed to improve the phase morphology of the active layer [85]. For example, by changing the surface energy of a ZnO buffer layer, Bulliard *et al.* observed an increase in PCE from 3.2% to 3.7%.

Buffer layer morphology also influences device performance. Ma *et al.* observed a reduction in PCE from 3.9% to 2.7% when the average surface roughness of a ZnO buffer layer was increased from 1.9 nm to 48 nm [86]. Increasing surface roughness increased the number of potential trap sites at the active layer interface. However, Sekine *et al.* observed an increase in performance from 3.2% to 4% when replacing a nanoparticle ZnO layer with a 'nano-ridge' ZnO layer [87]. The improved performance was attributed to change in morphology of the ZnO layer increasing the surface contact between the active layer and ZnO.

1.5 Organic Semiconducting Polymers

Organic polymers are typically insulators; electrons are strongly localised due to sp^3 hybridised orbitals forming σ bonds on the carbon backbone [88]. Organic semiconducting polymers are based on sp^2 hybridised carbon atoms, leading to the formation of π bonds via overlap of electrons in the p_z orbitals [30]. The π bonds are delocalised into a π bonding orbital and a π^* anti-bonding orbital due to Peierls distortion. However, reorganisation also occurs due to alternating bond lengths in the polymer backbone resulting in electrons that are not localised [89]. This structure forms a one-dimensional electronic system with a HOMO and a LUMO, originating from bonding and anti-bonding orbitals respectively.



Figure 1.6: Semiconducting materials, P3HT and PCBM, that were used as donor and acceptor throughout this thesis [90]. These materials were selected as they are widely discussed in the literature [91].

The bandgap is determined by the energy difference between the HOMO and the LUMO and dictates the wavelengths that are absorbed. In semiconducting polymers, the band gap is smaller than in typical organic polymers, allowing strong absorption of visible light, making them suitable for use in PV devices [92].

There are many organic semiconductors which have been used in the active layer of OPVs [93]. Two materials are used; an electron acceptor and an electron donor, which create an energy gradient which is the driving force for exciton dissociation. An electron donor is the primary material that generates the exciton and donates an electron to the electron acceptor material. The two organic semiconductors that were used in this thesis are shown in figure 1.6; P3HT and PCBM, have been heavily reported on in literature [40,91,94,95].

One of the first organic polymers investigated for use as an electron donor was MEH-PPV³ which was developed by Wudl *et al.* [96]. This material was observed to undergo photo-induced electron transfer with C_{60} buckminsterfullerene and was subsequently incorporated into an OPV device with PCBM [97]. After significant optimisation, PCEs above 3% were achieved with PPV-based polymers [98]. However, further improvement of these devices was limited due to low hole mobility and narrow absorption range of PPV-based polymers [99].

³poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene)

Soluble polythiophenes were subsequently investigated because of their higher hole mobility and broader absorption range than MEH-PPV [100]. Optimisation of structures involving P3HT resulted in a further increase in efficiency to approximately 5% [101]. Subsequently, high performance polymers have been developed which have further increased device PCE. He *et al.* investigated both PCDTBT⁴ and PTB7⁵ in devices with PC₇₀BM and observed PCEs of approximately 6.8% and 8.4% respectively [102]. More recently, PTB7 devices have obtained PCEs up to 11% for inverted devices with PC₇₀BM [103].

There are also a variety of acceptor materials used in OPVs, fullerene-derivatives have been most successfully used as acceptors in these devices [104]. As previously mentioned, C_{60} was used in the active layer of OPVs when they were first developed, however the solubility of C_{60} is limited. Wudl *et al.* synthesised a derivative of C_{60} , PCBM, with higher solubility, that is now widely used in OPVs [105]. PCBM also offers higher electron mobility and electron affinity than C_{60} . However, PCBM has weak absorption in the visible range and a low LUMO [106], reducing the fullerenes contribution to light harvesting [21]. Replacing the C_{60} in PCBM by C_{70} has been observed to increase absorption in the visible range which consequently increases the overall light harvesting of devices [107]. Zhang *et al.* observed an increase in PCE from 3% to 3.5% when PC₇₀BM was used, which was attributed to the increased light harvesting [108].

Another C_{60} derivative that is gaining interest in recent years is indene- C_{60} bisadduct (ICBA). This electron acceptor possesses better solubility and stronger visible absorption than PCBM, the LUMO level is also higher which results in a higher possible voltage [109]. As such, devices made with ICBA and P3HT have been shown to out-perform PCBM devices [106]. He *et al.* produced a P3HT:ICBA device with a PCE of 5.44% compared with their P3HT:PCBM standard which had a PCE of 3.88% [106].

There have also been many non-fullerene acceptors investigated [110], which address some of the disadvantages of fullerene acceptors; such as weak absorp-

⁴poly [N-9- heptadecanyl-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)]

⁵poly[[4,8-bis[(2-ethylhexyl)-oxy]benzo[1,2-b:4,5-b]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethyl-hexyl)carbonyl]-thieno-[3,4-b]thiophenediyl]]

tion in the visible range and tunability of band-gap and crystallinity [111]. Nonfullerene acceptors have been used to obtain devices efficiencies over 12% [112]. Zhao *et al.* used PBDB-T⁶ and a non-fullerene acceptor, ITIC⁷ to produce devices with an average PCE of 12.4%. The high performance was attributed to the broad optical absorption.

1.6 Stability



Figure 1.7: Generic layer structure of OPV devices illustrating the degradation processes known to occur in each layer.

OPV operation is dependent on all layers performing efficiently as described in section 1.4.1. An ideal solar cell should maintain constant performance over time and show little dependence on environmental changes [71]. Unfortunately, there are a variety of physical and chemical processes that occur in OPVs, both in storage and under illumination, that can damage one or more of the layers in the device. This damage can then cause device performance to decrease [113]. A number of these processes are illustrated in figure 1.7.

OPV stability is often overlooked in favour of improving performance, however longer lifetimes are required for commercial applications [114]. As shown in

⁶Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b]dithiophene))-alt-(5,5-(1,3-di-2-thienyl-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c]dithiophene-4,8-dione)]

⁷3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)dithieno[2,3-d:2,3-d]-s-indaceno[1,2-b:5,6-b]dithiophene



Figure 1.8: The number of papers indexed on Web of Science for each year between 1985 and 2016 which contain either "efficiency" or "lifetime" as a keyword, showing the significant discrepancy in research output focused each factor. The number of papers relating specifically to the lifetime of devices in 2016 was 1350 compared with 6510 papers relating to efficiency.

figure 1.8, degradation of OPVs has only recently started gaining interest. Furthermore, despite the large increase in interest over the last 10 years, the number of peer reviewed scientific reports relating to degradation of OPVs was less than a third the number relating to efficiency in 2016. Focus on efficiency has resulted in a drastic increase in PCE above 12% [115], but stability still poses a considerable problem [116].

Degradation is significantly affected by several factors including high temperature, humidity, electrical stress and UV-light [117]. These processes can be broadly classified as atmospheric, interfacial, morphological or photoactive degradation. Each of these classifications is described in greater detail in the following section.

1.7 Degradation Processes in Organic Photovoltaics

There are a variety of degradation processes that occur in OPVs both under operation and in storage, which are generally classified as either intrinsic or ex-

	Key Stress	Mechanisms	
Extrinsic	Atmospheric	Water reacting with low work function electrodes	
	Contaminants	Photo-oxidation of organic materials	
		Charge blocking layers formation at electrode	
Intrinsic	Temperature	interface	
		Gross phase separation in the active layer	
	Light	Photo-dimerization of PCBM	
		Photo-induced traps	

Table 1.1: Examples of extrinsic and intrinsic degradation mechanisms in OPV devices [118].

trinsic. Extrinsic degradation is caused by outside factors such as reactions with atmospheric water and oxygen [118]. Intrinsic degradation is caused by internal reactions such as phase separation of polymer and fullerene materials in the active layer. Table 1.1 describes examples of both extrinsic and intrinsic degradation.

Degradation process can also be broadly classified as: atmospheric degradation, interfacial degradation, morphological degradation and photoactive degradation. Each of these categories is described in detail below.

1.7.1 Atmospheric Degradation

The most significant of the extrinsic degradation processes that can occur is diffusion of atmospheric contaminants, typically water and oxygen, into the device [80, 119]. Both water and oxygen have been observed to diffuse through the electrode in a completed device, meaning they have the potential to interact with all layers [120]. Atmospheric contaminants can also be introduced to layers during fabrication [113]. Water and oxygen in the device can cause damage to the active layer and the electrodes which disrupts the electrochemical processes required for device performance [71].

The interaction of water and oxygen with a conjugated polymer in a photocell was investigated as early as 1999. Chawdhury *et al.* concluded that it was possible for oxygen to diffuse through both the electrode and active layer, causing a decrease

in photocurrent [121]. More recently, reactions between the P3HT:PCBM active layer and molecular oxygen were investigated by Guerrero *et al.* [94]. They showed that P3HT formed a complex with oxygen when the active layer was exposed to a flow of dry air, reducing the concentration of neutral P3HT causing a reduction in photocurrent. Oxygen has also been shown to readily decrease the conductivity of bulk C_{60} films by orders of magnitude [122].

Oxygen is activated by UV light and will readily react with the active layer oxidising the organic material [123]. When the active layer is damaged, light absorption can be altered, reducing the performance.

The top electrode also presents a significant source of degradation in the presence of atmospheric contaminants. The aluminium electrode in standard architectures is significantly reactive in the presence of oxygen [124]. Oxidation at the interface acts as a barrier to charge carriers and damages the interface between the electrode and active layer. As this process progresses, charge imbalance causes a rapid decrease in PCE [80].

An example of the effect of atmospheric degradation is shown in figure 1.9. The device on the left is a newly made device while the one on the right was produced and kept in dark, ambient conditions for over six months. There are several obvious holes in the aluminium electrode of the older device caused by oxidative corrosion.



Figure 1.9: Comparison of (a) a pristine device and (b) a device which was exposed to ambient conditions for six months. Extensive degradation of the aluminium electrode can be observed due to exposure to ambient conditions, highlighting the significant effect degradation has on devices.

The aluminium electrode also allows the diffusion of both water and oxygen further into the device [125]. Norman *et al.* observed that water diffuses through

the grain boundaries in aluminium causing uniform degradation through the entire device. Further to this, Krebs *et al.* showed that oxygen diffuses both through pin holes in the aluminium and at the grain boundaries [117]. The authors concluded this was the dominant mechanism for oxygen diffusion, with diffusion from the edges of the cell contributing to a much lesser extent. In each case, significant decreases in PCE were observed.

The PEDOT:PSS layer is also highly susceptible to degradation due to atmospheric contaminants. Voroshazi *et al.* showed that devices with a PEDOT:PSS HSL degraded much more rapidly when exposed to a humid environment [79], observing an exponential decrease in the device lifetime with increasing humidity levels. Infiltration of water through the edges of the device was attributed to the hygroscopic nature of PEDOT:PSS.

Furthermore, degradation processes can be induced or accelerated by simultaneous exposure to multiple factors. Reese *et al.* observed that P3HT films and P3HT:PCBM blend films exhibited no change in absorbance spectra after 1000 hours of illumination under nitrogen [126]. However, films that were illuminated under ambient conditions showed changes in absorbance after only 14 hours and experienced total loss of absorption after 700 hours. The etching of ITO by PEDOT:PSS at the interface has been shown to be accelerated by exposure to atmosphere [127]. Consequently, De Jong *et al.* observed a significant increase in the amount of indium in the PEDOT:PSS film after several days in air compared with samples stored in nitrogen.

1.7.2 Interfacial Degradation

Degradation occurring at the interface between two layers in an OPV can also play a major role in device degradation [128, 129]. The interfaces in the standard architecture are ITO/PEDOT:PSS, PEDOT:PSS/active layer and active layer/ electrode. Processes occurring at each of these interfaces cause a decrease in the device performance [119, 130, 131].

ITO / PEDOT:PSS Interface

Interface stability between ITO and PEDOT:PSS was investigated in organic light-emitting diodes in 2000 [127]. Jong *et al.* concluded that device rapid degra-

dation was due to the strong acidic nature of PEDOT:PSS which etched the ITO layer. Subsequently, etch products were observed in the PEDOT:PSS layer and the polymer layer in the device. Chang *et al.* also investigated the interface in light-emitting diodes in 2000 [132]. It was shown that the etch products diffusing into the PEDOT:PSS layer lowers the ionisation potential and reduces performance.

PEDOT:PSS / Active Layer Interface

The PEDOT:PSS/active layer interface can also be a major source of device failure. Kawano *et al.* observed a reduced injection current in OPVs after 70 hours in air [119]. This observation was explained by the formation of insulating domains at the interface from reactions between acidic PSS and water. An increase in resistance in devices with PEDOT:PSS layers has also been observed, when exposed to a humid environment [133]. This increase was attributed to phase separation in the PEDOT:PSS layer affecting charge transport through the interface.

Active Layer / Top Electrode Interface

The active layer/top electrode interface, in the standard structure, is vulnerable to many degradation mechanisms including chemical reactions and delamination [131]. The electrode can form compounds with the organic material, changing the electrical properties of the device [94]. Oxidation of the top electrode can also occur at the active layer interface, hindering charge transport [134].

1.7.3 Morphological Degradation

The spatial organisation of the different materials within a device is another important factor in the long-term performance of OPVs [135]. The composition of the structure of an OPV device is not necessarily static after production; as the materials often have some freedom to diffuse within the device. Detrimental changes in morphology are termed morphological degradation. Indeed, several processes outlined in the previous section (1.7.2) could also be classified as morphological degradation.

A degree of phase separation of the active layer materials into an interpenetrating network of donor and acceptor is required for efficient charge separation and collection [48, 113]. However, gross phase separation can occur in the active

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layer reducing the donor/acceptor interface, hindering exciton dissociation in the active layer [136]. In addition, changes to the active layer morphology may reduce the continuous paths of donor or acceptor to the electrodes which reduces charge transport and may increase recombination [137].

Electrode materials have been observed to diffuse through the polymer materials [138, 139], creating areas where charges may be trapped within the device. Trapped charges can hinder the transport of other charges and do not contribute to the charge extracted. Furthermore, if the diffusion of the electrode through the device is widespread it can lead to the formation of short circuits in the device [140].

The PEDOT:PSS layer may also phase separate, such that there is a PEDOT-rich phase and a PSS-rich phase [120]. Norrman *et al.* used time-of-flight secondary ion mass spectrometry (TOF-SIMS) to identify the phase separated layers in PE-DOT:PSS surfaces. The PEDOT-rich phase underwent selective oxidation, with subsequent layers in the devices then oxidising rapidly.

1.7.4 Photoactive Degradation

Photoactive degradation describes the processes that occur when OPVs are exposed to light. Photo-oxidation of the polymer material in the active layer is the most significant process of this type [126]. Further to this, many other degradation processes may be accelerated by illumination [119]. Hintz *et al.* found that exposing a thin film of P3HT to ultraviolet light and oxygen caused rapid and irreversible degradation of the film quality [141]. Manceau *et al.*, similarly, found significant photo-oxidation of P3HT:PCBM blends [142]. Photo-oxidation results in reduced light absorption, increased series resistance and lower hole mobility, reducing the overall device performance [143].

Another photo-active degradation process that is of importance for inverted OPVs, is the activation of oxygen radicals that are present in a ZnO film [71]. ZnO nanoparticles absorb wavelengths between 280 and 370 nm which gives rise to this effect [144]. The mechanism for photo-active changes in ZnO was proposed by Verbakel *et al.* who investigated the behaviour of ZnO-PEDOT:PSS diodes before and after exposure to UV light [145]. There was a clear transition from diodic to ohmic behaviour after the exposure. They proposed that oxygen desorption in

the ZnO layer frees electrons which initially dopes the layer. However, excessive doping quickly leads to a loss of selectivity of the ZnO layer [144].

Light can also increase the temperature of OPVs, which can initiate and accelerate other forms of degradation, particularly degradation caused by morphological changes [146]. Lilliedal *et al.* investigated the effect of photo-annealing on a largearea inverted device [147]. They showed that degradation processes are accelerated by both light intensity and the temperature caused by the illumination.

1.7.5 International Summit on OPV Stability Procedures

In order to assess performance and degradation processes in OPV devices, a series of standards for device testing have been developed. The International Summit on OPV Stability (ISOS) (2010) defined several procedures for testing stability and operational lifetimes of OPVs and modules [148]. These protocols include specifications for shelf life testing, outdoor testing, laboratory weathering and thermal cycling testing. Each of the procedures specifies environmental and lighting conditions that devices are tested under. The two testing conditions used in this work are ISOS-D-1 and ISOS-L-1 (defined in table 1.2).

Test ID	ISOS-L-1 Laboratory	ISOS-D-1 Shelf
Light source	Simulator	None
Temperature	Ambient	Ambient
Relative humidity	Ambient	Ambient
Environment	Light only	Light & Temp.
Testing light source	Solar simulator	Solar simulator
Load	MPP or open circuit	Open circuit

Table 1.2: Overview of test protocols, developed by the ISOS, used in this thesis [148].

The intent of these standards was to achieve a consensus in OPV stability testing, so that results from different groups may be compared directly. Currently, due to the lack of widely adopted standard protocols, various procedures exist, and lack comparability [149]. As an illustration, figure 1.10 shows testing protocols used by 90 randomly selected papers over eight years (2008-2016). The two most common categories are "not specified" and "none" (where the conditions were specified but did not match any standard). These two categories represent 60% of the papers analysed, making comparison between many papers difficult.



Figure 1.10: ISOS protocol for 90 randomly selected papers published between 2008 and 2016. "Not specified" represents papers that did not contain explicit testing information, and "none" represents papers where the procedure used did not match any ISOS protocol. This chart shows both the lack of consistent testing conditions and lack of reporting of conditions used. Both factors make direct comparison of reported results difficult.

1.7.6 Encapsulation

One method of prolonging device lifetime is to use encapsulation that protects devices from the atmosphere. Encapsulation can also be used to block UV light, which has been linked to degradation of the active materials in these devices [150]. The use of UV blocking layers has been shown to have a significant positive effect on device stability [151].

Thin film barriers have been studied extensively in relation to food packaging [152]. Thus, there are a variety of materials that can be used to encapsulate OPVs, which vary in both cost and effectiveness [153], and many studies have been performed investigating the effectiveness of different encapsulation materials. Dennler *et al.* compared the degradation of solar cells encapsulated in poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) coated in an ultra-barrier material [154]. The ultra-barrier materials were made up of alternating layers of inorganic and organic materials with a low oxygen and water vapour permeation rate. It was shown the devices encapsulated in PET showed a 50% decay in PCE in only 6 hours, while the cells encapsulated in the ultra-barrier material maintained 54% of the initial PCE after 3000 hours.

Aluminium oxide (Al_2O_3) has been investigated as an encapsulation material many times [155, 156]. Potscavage *et al.* used a 200 nm thick film of Al_2O_3 to encapsulate small molecule devices [157]. The authors compared the stability of unencapsulated devices with those encapsulated with Al_2O_3 and a UV epoxy. Unencapsulated devices degraded to 20% of the initial PCE after only 10 hours, while devices encapsulated in UV epoxy maintained 100% in that period and 25% after 250 hours. Devices encapsulated in Al_2O_3 showed significantly higher stability, maintaining over 90% of the initial PCE after over 6000 hours.

Encapsulation was not investigated as part of this thesis. However, it is an important factor in the operational lifetime of OPV devices.

1.8 Nanoparticle Active Layer

An active layer can be produced by depositing a film of semiconducting nanoparticles. Polymer nanoparticles are made as a dispersion in water because the polymers themselves are not soluble in water. Devices made with a NP active layer offer the potential of morphological control while removing harmful organic solvents from device processing [158]. However, device performance is typically lower than devices made with a BHJ active layer [159]. Extensive work has not yet been performed on the stability of NP active layers.

A nanoparticle dispersion is produced using the miniemulsion process [160], which is illustrated in figure 1.11. The miniemulsion process involves dissolving the polymer and fullerene in an organic (typically chlorinated) solvent, forming a solution identical to that used to form a BHJ active layer. The mixture is then added to water in the presence of a surfactant, such as sodium dodecyl sulfate (SDS). The surfactant is necessary to solubilise and mix the two solvents. Stirring is then used

to form spherical micelles with the hydrophilic parts of the surfactant in contact with the water and the hydrophobic parts within the chlorinated solvent. The resulting solution, known as a macroemulsion, is then sheared using ultrasound to form a miniemulsion consisting of stable droplets ranging in size from 30 to 500 nm.



Figure 1.11: Schematic diagram showing the steps of the miniemulsion process: (a) two solutions are mixed together to create a macroemulsion, (b) sonication is used to shear the mixture into a miniemulsion, (c) the solution is heated over several hours to remove chloroform and (d) dialysis is used to remove excess surfactant.

The miniemulsion is then heated over several hours while being stirred to slowly evaporate the chlorinated solvent. Dialysis is then used to remove excess surfactant, leaving nanoparticles of polymer materials suspended in water. The suspension can then be used in place of the BHJ active layer precursor solution in OPVs, which is outlined in greater detail in section 2.1.2.

1.8.1 Morphology Control

Although there has been an increase in the understanding and ability to predict morphologies in BHJ active layers [67], direct morphological control is still very challenging to achieve as there are several influential factors including: solvent choice, materials, spin speed and drying time. Water-based nanoparticle dispersions, as well as replacing chlorinated solvent, allow direct morphological control (via particle size and morphology) over the nanoscale architecture of the active layer in production [160].

Particle size can be manipulated when producing the nanoparticles by varying the amount of surfactant in the initial solution. Since each of the particles contains both materials, the maximum dimension of the phase-separation is governed by the particle size [160]. The domain size can then be tailored to match the exciton diffusion length, allowing for efficient charge transport and minimal recombination [161].



Figure 1.12: Core-shell structure of P3HT:PCBM nanoparticles showing the polymer, fullerene and mixed regions.

Nanoparticles have been observed to form a core-shell structure using scanning transmission X-ray microscopy, with a fullerene-rich core and a polymer-rich shell for P3HT:PCBM [162–164]. This core-shell structure is illustrated in figure 1.12. As with the BHJ active layers, annealing can be used to alter the morphology of the NP active layer allowing the particles to sinter together to produce a more uniform film. The effect of annealing on nanoparticle films is dependent on the material system. Ulum *et al.* observed a decrease in performance of P3HT:PCBM devices, from 1.3% to 1.1%, upon annealing which was explained by extensive phase separation in the nanoparticle film [162]. A subsequent paper by Ulum *et al.* saw an increase in performance for P3HT:ICBA devices, 1.17% to 2.5%, upon annealing [163]. The improvement was attributed to higher miscibility of ICBA in P3HT resulting in a more homogenous blend upon annealing.

1.8.2 Surfactant and Micelle Formation

Surfactants are organic molecules that lower the free energy of surfaces and interfaces [165]. Surfactants can be used to alter the interfacial tension between two dissimilar phases to allow for mixing. The surfactant used throughout this thesis, SDS shown in figure 1.13, has a hydrophilic head group and a hydrophobic tail. Surfactants in solution at the critical micelle concentration (CMC) can self-assemble to form micelles [166], an illustration of the structure of a micelle is shown in figure 1.14.



Figure 1.13: Structure of SDS, which was used as a surfactant in nanoparticle production.

While surfactants are necessary for the formation of the miniemulsion, it is expected that the surfactant may impede charge transport in the thin film [167]. Bag *et al.* observed that removing excess surfactant improved the hole transport in P3HT films, which was attributed to a higher packing density. Vaughan *et al.* observed a decrease in performance with extended annealing that was attributed to surfactant in the layer [168]. A systematic increase in fill factor (FF) was also observed as the amount of surfactant was decreased.

The surfactant is also required to stabilise the droplets in the dispersion against collisions or aggregation [49]. Darwis *et al.* investigated the change in UV-Vis absorption as a function of time for nanoparticles with and without surfactant [169]. Surfactant-containing nanoparticles were more stable over time than surfactant-free particles that were made via precipitation. However, device performance for the surfactant-containing active layer was less than half the surfactant-free active layer.

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Figure 1.14: Illustration of the structure of a micelle; surfactant molecules surround the material such that the hydrophobic tail remains in the dissolved polymer solution while the hydrophilic head remains in the water, forming stabilised nanoparticles.

1.8.3 Precipitation Method

The precipitation method produces polymer nanoparticles, by using a miscible solvent and non-solvent combination [170]. This process is illustrated in figure 1.15. The solvent (chloroform for the purposes of this thesis) is used to dissolve the active materials and the non-solvent (ethanol) is used to precipitate the materials [171]. The solvent and non-solvent must be miscible so that the initial solvent diffuses into the non-solvent and the active materials precipitate when the polymer solution is added to the non-solvent. This process results in a dispersion of polymer nanoparticles in a mixture of solvent and non-solvent.

The major advantage of this method of producing nanoparticles is that synthesis is quick, and no surfactant is required. Excess surfactant in the active layer of devices may be problematic for device function [50, 167], thus eliminating surfactant from the nanoparticle synthesis improves device performance [169]. However, surfactant also acts as a stabiliser against aggregation in solution, which means that the use of surfactant-free nanoparticles are unstable in solution [50]. Work has not yet been presented on device stability using a precipitated NP active layer.



Figure 1.15: Schematic diagram showing the steps of the precipitation process. a) Droplets of the polymer and fullerene solution are added to a non-solvent, b) the solvent diffuses into the non-solvent and the polymer precipitates, c) all the solvent diffuses out leaving a solid nanoparticle.

Chapter 2

Experimental Techniques

This chapter details the procedures, experimental techniques and equipment that were used throughout this thesis. The production of active layer solutions for OPVs is described in the following section. Various techniques, used to characterise the performance of the devices or layers within a device, are described in this chapter. This chapter also includes information on lifetime testing and the equipment used to build the automated lifetime testing apparatus.

2.1 Active Layer Preparation

The active layers in OPVs produced for this project were deposited from solution via spin coating. The process of making both the BHJ and NP active layer solutions are described in this section. The active layers consisted of an electron donor and electron acceptor material. The electron donor material used in this work was P3HT and two electron acceptor materials were used: PCBM and ICxA. ICxA is a low-cost, mixed-fullerene acceptor material [172]. ICxA is a mixture of the mono-, bis- and tris-adducts of indene: C_{60} , shown in figure 2.1, and reduces production costs by removing the need for extensive purification. The chemical structures for P3HT and PCBM is shown in figure 1.6.

2.1.1 Bulk Heterojunction Active Layer

The BHJ active layer solution had a concentration of 18 mg of the polymer materials for 1000 μ L of chlorinated solvent. The P3HT and PCBM were mixed together in a 1:0.8 ratio, 10 mg of P3HT and 8 mg of PCBM were measured using a Mettler Toledo AB204-s scale, accurate to 0.1 mg. The materials were then dissolved



Figure 2.1: Mono-, bis- and tris-adducts of indene: C₆₀ [172].

1000 μ L of chloroform and the solution was placed in an ultrasonic bath for 60 minutes or until the materials were well mixed.

2.1.2 Nanoparticle Synthesis

Miniemulsion Process

Polymer nanoparticles were fabricated using the miniemulsion process which was outlined in section 1.8 (see figure 1.11) [160]. Firstly, 15 mg of P3HT and 15 mg of PCBM were dissolved in 560 μ L of anhydrous chloroform in a 4mL vial. The solutions were heated at 35°C and stirred at 500 rpm for 30 minutes. The solutions were then placed in an ultrasonic bath and the samples were left for another 25 minutes.

An aqueous solution was prepared by adding 33 mg of SDS to 2780 μ L of highly purified water, which was filtered through a 22 μ m PES syringe filter. The SDS solution was then stirred at 1200 rpm until the SDS had completely dissolved.

The two solutions were mixed and heated at 33°C and stirred at 1200 rpm for 60 minutes. The vials were agitated gently by hand if the two phases separated. This mixing step creates a macroemulsion with droplets of the polymer materials in chlorinated solvent surrounded by surfactant suspended in water, with a micelle size in the order of micrometres [173].

Strong ultrasound, from a sonication horn, was then used to shear the macroemulsion into a miniemulsion. A vial was placed in a clamp and the tip of the horn was inserted into the mixture. The vial was placed in a beaker of ice water, to dissipate any heat generated during sonication. The horn was switched on and slowly increased to approximately 20 watts output power and left for 2 minutes for each sample. Subsequently, the vials were heated at 60°C and 1200 rpm for at least 3 hours to evaporate the chloroform from the solution leaving nanoparticles suspended in water. The predicted size of the nanoparticles after this process is approximately 30 nm [162]. An illustration of the micelle is shown in figure 1.14.

The dispersions were then placed into Amicon Ultra centrifuge filter tubes, a small amount of 0.22 μ m filtered, purified water was used to ensure that all the miniemulsion was removed from the vial. The samples were then centrifuged at 4000 rpm for 6 minutes. The excess liquid was removed from the bottom of the dialysis tube and filtered, purified water was added to re-dilute the sample in the tubes. The filters were unblocked by tipping the tube gently back and forth. The samples were centrifuged five times, at 4000 rpm for 7 minutes, removing excess and adding more water after each centrifuge. After the last centrifuge, the expected volume was approximately 500 μ L.

The centrifuging process was necessary to remove excess SDS from the solution. Since SDS is an insulator, leaving too much in the solution would likely reduce charge mobility in the active layer, resulting in poor performing devices [171].

Precipitation Process

Nanoparticles were also fabricated using a precipitation process which involved injection of a solution of active material into a second solvent with poor solubility [169], as described in section 1.8.3. The synthesis of these nanoparticles is rapid and does not require surfactant [174], which is advantageous as the presence of surfactant in films can decrease charge transport [167]. However, without a stabilising agent (surfactant), these NP solutions are unstable [169].

Firstly, 5 mg of P3HT and 5 mg of PCBM (10 mg in total) were dissolved in 670 μ L of chloroform. This solution was stirred at 1000 rpm on a hot plate at 35°C for 25 minutes, until the material was completely dissolved. The remainder of the fabrication process and subsequent layer deposition were performed in a nitrogen glovebox to limit ingress of water. The solution was loaded into a syringe with a 30-gauge needle and dropped into 5mL of anhydrous ethanol which was stirring at 1000 rpm. A drop rate of 5 drops per second was used until all material was added. The solutions were used immediately after synthesis as the nanoparticles are prone

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to aggregate within hours of production [169].

The precipitated NP solutions are very dilute because higher concentrations caused the materials to crash out of solution rather than form nanoparticles. For this reason, multiple layers of the precipitated NP solutions are necessary to form layers of adequate thickness (\sim 100 nm).

2.2 **Device Preparation**

All the small devices in this thesis were made on glass substrates that were pre-patterned with ITO, as shown in figure 2.2. Each substrate had six ITO fingers and a common ITO electrode. The preparation of devices in both architectures is described in the following sections.



Figure 2.2: Illustration of glass substrates pre-patterned with ITO, to form the transparent electrode on six fingers and a common. Once prepared a substrate contains 6 devices each with an area of 5mm².

2.2.1 Standard Device Preparation

The standard structure that was most heavily investigated throughout this thesis is shown in figure 2.3. PEDOT:PSS was used as a HSL and calcium/aluminium were used as the top electrode. The active layer was a 1:0.8 blend of P3HT:PCBM.

The preparation and deposition of each of the layers in these devices is described below. A schematic of the deposition processes for this structure is presented in figure 2.4.



Figure 2.3: Standard structure solar cell used at the outset of this work, with PEDOT:PSS as the HSL and calcium/aluminium as the top electrode.



Figure 2.4: Fabrication process for standard devices: PEDOT:PSS is deposited via spin coating, the layer is dried, and the active layer is deposited on top, calcium and aluminium are then deposited using thermal evaporation.

Indium Tin Oxide (ITO) Layer

The pre-patterned ITO substrates, as shown in figure 2.2, were obtained from Xinyan Technology Limited. The substrates were firstly wiped with a lint-free tissue and exposed to a flow of N_2 to remove any large dust or residue. The substrates were then placed in a ProCleaner UV ozone cleaner for 20 minutes to remove any remaining contamination. The substrates were then placed immediately on a Laurell spin coater and secured using a vacuum pump.

SECTION 2.2

Hole Selective Layer

The PEDOT:PSS solution, that was used as the HSL in these devices, was obtained from Heraeus. The solution was filtered using a 0.45 μ m syringe filter and was used immediately after filtering. Cleaned ITO substrates were secured on the spin coater using a vacuum and 75 μ L of solution was deposited via pipette. The deposition spin speed was 5000 rpm for one minute, with an acceleration of 1680 rpm per second, resulting in a 40(±4) nm thick layer. Next, the contacts of the substrate were wiped off with isopropyl alcohol (IPA), as shown in figure 2.4, and the substrate was placed on a hotplate at 140°C for 30 minutes.

Active Layer

Three types of active layer solution were used for this thesis. The first was a BHJ deposited from chloroform. The other two were polymer nanoparticle dispersions deposited from either water or ethanol. The production of these active layers is described in section 2.1.

The BHJ active layer was deposited in a nitrogen glove box, 60 μ L of the active layer solution was deposited on the substrate via pipette. A spin speed of 2000 rpm for 60 seconds was used to deposit the layer. The contacts were wiped off again with chlorinated solvent and the substrates were dried at 50°C for 5 minutes. The resulting thickness of this layer was 90(±6) nm.

The miniemulsion NP solutions were made 1:1 for P3HT:PCBM and 1:0.8 for P3HT:ICxA. These active layers were deposited under ambient conditions, 35 μ L of solution was deposited and spun at 1750 rpm for one minute giving a layer thickness of 130(±7) nm. The contacts were wiped off using IPA and the substrates were then dried at 110°C for 4 minutes. They were immediately transferred to a nitrogen glove box to limit any ingress of water.

The precipitated NP solution required multiple layers to obtain sufficient thickness because the solution was very dilute, as outlined in section 2.1.2. The layers were deposited under ambient conditions, 70 μ L of solution was used with a spin speed of 1000 rpm for 30 seconds. The film was then dried for 3 minutes at 100°C. The spin and dry process was repeated 5 times, to obtain a layer thickness of 110(±6) nm.
Top Electrode

The top electrode in the standard devices involved evaporating a 30 nm layer of calcium and a 100 nm layer of aluminium. The substrates were placed in a metal mask which defined the area of the electrodes. They were then suspended face down in an Angstrom Engineering thermal evaporator which was then pumped down to 10^{-7} Torr. A crucible that contained calcium was heated to above 500°C and the calcium was deposited at a rate of 1Å/s.

A boat containing pellets of aluminium that was fixed between two electrodes then had current passed through it until a deposition rate of 2Å/s was achieved. The deposition was aborted when approximately 100 nm of material had been deposited. The substrates were then left in the evaporator under vacuum to cool for at least half an hour. It was important to allow the crucible to cool to below 100°C before venting the chamber to avoid it cooling too quickly and cracking. The chamber was then vented, and the devices were transferred to a nitrogen glove box inside a clean room for characterisation.

2.2.2 Inverted Device Preparation

The inverted structure that was used for this phase of the thesis is shown in figure 2.5. This particular inverted architecture is the most commonly used architecture in the literature [175–177]. ZnO was used as a ESL, MoO₃ was used as a HSL and silver was used as the top electrode. The active layer was a 1:0.8 blend of P3HT:PCBM.

The fabrication process for the inverted devices is outlined in figure 2.6 which shows each of the layers. The process of depositing each of these layers is described below.

Indium Tin Oxide (ITO) Layer

The pre-patterned ITO substrates were prepared in the same way as for the standard devices outlined in section 2.2.1.

Electron Selective Layer

The material that was used as an ESL for this part of the thesis was ZnO. A ZnO solution, obtained from Nanograde, was used as is without any dilution. For



Figure 2.5: Inverted structure solar cell used at the start of this thesis: ZnO was used as an ESL, MoO_3 was used as a HSL and silver was used as a top electrode.



Figure 2.6: Inverted structure fabrication process: ZnO and active layer are deposited via spin coating with a drying step after each layer, and MoO₃ and silver are subsequently deposited via thermal evaporation.

this solution, 75 μ L was deposited on the surface and the films were deposited at 5000 rpm for 1 minute. The substrates were then dried at 100°C for 20 minutes and the resulting thickness of this layer was 35(±2) nm.

Active Layer

The procedure for depositing the active layers in the inverted devices was the same as those presented in section 2.2.1.

Hole Selective Layer

In the inverted structure, an evaporated layer of MoO₃ was used as a HSL. The substrates were placed in a mask and put in the evaporator, which was pumped

down. A boat containing MoO_3 powder was fixed between two electrodes in the evaporator. An increasing current was then passed through the electrodes until a deposition rate of 0.5Å/s was achieved and 10 nm was deposited.

Top Electrode

The metal that was used as the top electrode for this study was silver. After the MoO_3 evaporation, silver pellets were placed in a boat and 100 nm silver was at evaporated 2Å/s. The substrates were then left in the evaporator under vacuum to cool for at least half an hour. The chamber was then vented, and the devices were removed for characterisation.

2.3 Characterising Performance

A variety of methods were used to characterise the performance of OPVs. The techniques most relevant to this thesis are described in detail in this section.

2.3.1 Current-Voltage Characterisation

The performance of a photovoltaic device is measured by how efficiently the device converts light to electrical charge and is denoted by the power conversion efficiency (PCE). The current-voltage (IV) curve for an OPV provides the information necessary to see how well the device is performing. The important characteristics of the device which can be obtained from the IV curve are the open circuit voltage (V_{OC}), the short circuit current (I_{SC}), the short circuit current density (J_{SC}) and the fill factor (FF). These characteristics are shown on a typical IV curve in figure 2.7. The open circuit voltage (V_{OC}), short circuit current (I_{SC}) and FF along with I_{light} , the incident solar radiation in W/m^2 , are used to calculate the PCE according to equation 2.1.

$$PCE = \frac{FF \cdot V_{OC} \cdot I_{SC}}{I_{light}}$$
(2.1)

The FF of a device can be calculated according to equation 2.2. Where I_{max} and V_{max} are the current and voltage at the maximum power point of the IV curve in the 4th quadrant. The FF is the ratio of the two dashed rectangles shown in figure 2.7.

$$FF = \frac{P_{MAX}}{P_{\tau}} = \frac{I_{max} \cdot V_{max}}{I_{SC} \cdot V_{OC}}$$
(2.2)

The FF gives a comparison for the performance of the device relative to the theoretical maximum performance of the device and is generally given either as a percentage or a value between 0 and 1. The FF is dependent on the resistances in the device: the series resistance (R_s) and the shunt resistance (R_{sh}). The R_s , which is shown in figure 2.7, is given by the inverse of the slope of the IV curve at the V_{OC} and describes the total resistance of the cell. The R_s is composed of [178]:

- The resistances of the layers and electrodes
- The various contact resistances

The R_{sh} is a parallel resistance in the circuit of the OPV and represents the resistance against leakage current, it is the inverse slope of the IV curve at the J_{SC} . A high R_{sh} value is necessary for the FF to be high and results in a higher PCE [179]. In an ideal device R_s would be zero and R_{sh} would be infinite [180].



Figure 2.7: IV curve for a typical solar cell, showing the open circuit voltage (V_{OC}), the short circuit current density (J_{SC}), the series (R_S) and shunt (R_{SH}) resistances, along with the maximum power point (P_{MAX}) and theoretical maximum power (P_{τ}) which are used to calculate the fill factor (FF).

The IV properties of the device were tested using a Keithley 2400 source measure unit (SMU) throughout this thesis. The Keithley is a single-channel voltage and current source and measure unit which provides four-quadrant operation, with an operating range of ± 20 V and ± 100 mA.

An IV curve is produced by applying a bias voltage between the two electrodes of the device and measuring the current either in the dark or under air mass 1.5 (AM 1.5) illumination. Each of these IV measurements are described in detail in the following sections.

Dark IV Curve

The first part of characterising the performance of an OPV device is to measure the response in the dark. Dark IV measurements provide an effective way to examine the diode properties of a device, which can be used to determine R_s and R_{sh} . For these measurements charge carriers are injected into the system by the SMU. The current is then measured as the voltage is increased through a range. In the dark, a solar cell should act as a large flat diode.

Devices were placed in sample holder and covered to exclude all light. IV measurements were then performed using the Keithly SMU.

Light IV Curve



Figure 2.8: AM1.5 is the standard used for testing the performance of solar cells. (a) Examples of air mass conditions for different angles (AM1.5 is defined at solar zenith angle 48.19) through the atmosphere along with (b) the spectra for AM0 and AM1.5 [181].

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Solar simulators are generally used to perform IV characterisation. The solar industry uses the AM 1.5 standard for testing of solar panels because it represents the overall yearly average of sunlight intensity for mid-latitudes [182]. Air mass refers to the relative path length of light from the sun through the atmosphere, as shown in figure 2.8. When the angle increases from zenith, the path length through atmosphere increases, which increases the amount of scatter and absorption that occurs and alters the light spectrum and intensity [183]. The difference in spectra between AM0 and AM 1.5 is also shown in figure 2.8, where AM0 is the solar spectrum outside the Earth's atmosphere.

For light IV curves, the cell is illuminated under open circuit conditions and electrons and holes separate and diffuse towards the low and high work function electrodes respectively. The photocurrent in the device without any applied voltage is referred to as I_{SC} , which approximates the maximum current available from the device. A forward bias can be applied to compensate the reverse photocurrent. When the voltage is increased, the current will eventually go to zero, the voltage at this point is the V_{OC} .



Figure 2.9: A solar simulator can be used to characterise device performance. (a) A Newport AM1.5 solar simulator used to characterise OPV performance and (b) the spectrum of the Newport solar simulator compared with AM1.5.

Devices were tested while being irradiated with light from a Newport solar simulator, similar to the one shown in figure 2.9(a). The solar simulator used in this thesis provides a class A spectral match to AM 1.5, allowing for accurate determination of PCE. The spectrum of the lamp used is shown in figure 2.9(b), compared with AM 1.5.

2.3.2 Lifetime Measurements

The stability of OPV devices is the primary focus of this thesis, meaning that lifetime measurements were relied on heavily throughout. Measuring the electrical characteristics of a device repeatedly over several hours or days can give information about the lifetime of the device. An example of a decay curve is shown in figure 2.10. The degradation of an OPV is generally categorised by a rapid burn-in phase and a longer-term decay behaviour [118]. The initial period of steep decay is typically referred to as the burn-in and is generally associated with photochemical reactions in the active layer reducing charge transport [184–186]. If the burn-in is not too severe, OPVs then exhibit long-term behaviour; which is slower, and a more linear degradation [187]. Long-term degradation can be caused by many factors, including photo-oxidation of the active layer and water reacting electrodes [118].



Figure 2.10: Example of typical device degradation behaviour showing the burn-in and long-term behaviour. This two-phase behaviour is typical of degradation of OPVs.

Figure 2.10 also shows several quantities that have been defined to describe the lifetime of devices. These quantities are T_{80} , T_{50} , T_S and T_{S80} [148]. The values of

 T_{80} and T_{50} are defined as the time it takes for the device to degrade to 80% and 50%, respectively, of the initial value which depend heavily on the severity of the initial burn-in. For this reason, T_S and T_{S80} are also defined based on the more stable region after the burn-in. T_S is the time when the degradation became more linear and T_{S80} is the time taken to degrade by a further 20%.

The normalised decay curves can generally be fit with a two-term exponential curve, as shown in equation 2.3 [113,123]. In equation 2.3, η_0 is the initial efficiency, A and B are weighting constants, and λ_1 and λ_2 are time constants for dominant degradation processes. The two-term exponential suggests two degradation processes act in parallel [124].

$$\eta(t) = \eta_0 (Ae^{-\lambda_1 t} + Be^{-\lambda_2 t}) \tag{2.3}$$

It has been suggested that if data can be fit with simpler (i.e. one-term exponential or linear) expressions, then fewer degradation effects are occurring simultaneously [188]. Consequently, eliminating stress factors should result in simpler temporal dependency of the PCE.

2.4 LCR Meter



Figure 2.11: E4980A Precision LCR Meter, used to perform impedance and capacitance-voltage measurements [189].

The Keysight E4980A Precision LCR meter (shown in figure 2.11) can perform measurements of inductance (L), capacitance (C) and resistance (R). The primary purpose of the LCR meter for this thesis was to measure the capacitance of OPVs as a function of bias voltage. The LCR meter was also used to perform impedance spectroscopy on pristine and degraded OPVs. Each of these techniques, and how they were applied throughout this thesis, is described in the remainder of this section.

2.4.1 Mott-Schottky Analysis

Mott-Schottky measurements involved sweeping through voltages between -1V and 1V, while measuring the capacitance at each point. Subsequently, this information can be used to determine the doping density in the OPV device as described below. These measurements can provide valuable information about the device physics in OPVs [190].

The relationship between capacitance and voltage is given by equation 2.4; where C is the capacitance, V is the voltage, q is electron charge, ε_0 is the vacuum dielectric constant, ε_R is the relative dielectric constant of the doped semiconductor, A is the area and N_D is the doping density [190].

$$\frac{1}{C^2} = \frac{2V}{q\varepsilon_0\varepsilon_R A^2 N_D} \tag{2.4}$$

The slope of the linear section, marked by the dashed line in figure 2.12, allows the doping density to be determined according to equation 2.5.

$$Gradient = \frac{2}{q\varepsilon_0 \varepsilon_R A^2 N_D}$$
(2.5)

This technique was used in chapter 5 to investigate electrical changes in devices containing ZnO due to exposure to UV illumination.

2.4.2 Impedance Spectroscopy

The LCR meter was also used to performance impedance spectroscopy which has been widely used to study the operation of solar cells [191]. This method measures the current response of electronic devices to the application of an AC voltage as a function of frequency [192]. Impedance spectroscopy has been used on OPVs to determine properties; such as charge carrier lifetime, electronic density of states and carrier concentrations [193–195].

Impedance spectroscopy data is then modelled by an equivalent circuit, a commonly used equivalent circuit is shown in figure 2.13. The model can then be used to identify; the series resistance (R_S), transport resistance (R_1), recombination resis-



Figure 2.12: Example of a Mott-Schottky plot, used to determine doping density from the slope of the linear fit, shown as the dashed line.



Figure 2.13: Equivalent circuit used to analyse impedance spectroscopy data. Fitting data according to this circuit, as shown in figure 2.14, allows the value of each component to be calculated.

tance (R_2), device capacitance (C_g) and a chemical capacitance (C_μ). The values for each of these parameters is selected to fit the data (as shown by the solid lines in figure 2.14), allowing the information to be extracted. Impedance spectra are commonly plotted as the real part of the impedance versus the imaginary part [113]. For OPVs, plotting the impedance spectra in this way results in semi-circles, as shown in figure 2.14 [196].



Figure 2.14: Example impedance spectra for OPV cells under different wavelengths, showing the expected semi-circles [196]. The solid lines represent the data fit using the equivalent circuit, shown in figure 2.13.

2.5 Light Beam Induced Current Mapping

LBIC involves scanning a focused beam of light from a laser source over the active area of a solar cell and measuring the current generated [197]. A 2D map can then be generated of the amount of current at each point, giving an indication of how well the solar cell is working. This map can be used to identify electrical defects in the cell, making it a valuable tool to investigate degradation of OPVs [77].

Examples of LBIC maps for two different OPVs (before and after degradation) are shown in figure 2.15. Lloyd *et al.* observed that devices containing PEDOT:PSS experienced localised current loss, while devices without PEDOT:PSS exhibited more significant and uniform current loss.



Figure 2.15: LBIC maps for OPV devices before and after prolonged exposure to illumination. Degradation of the device shown in (c) is due to localised current loss while the device in (d) exhibits significant, uniform current loss over the entire active area [77].

2.6 **Profilometry**

A profilometer is an instrument that can be used to measure the profile of a surface and the heights of structures such as steps or trenches on a surface [198]. A contact profilometer consists of a sharp stylus which is pressed against the surface of the sample vertically with a set force. The stylus is then moved laterally across the sample and the vertical and lateral positions of the stylus are recorded producing a graph of the variations in the surface is produced.

A Bruker DektakXT profilometer was used throughout the course of this thesis, shown in figure 2.16. This profilometer has a vertical resolution of 1 Å over a range of 6.55 μ m.

Profilometry was used throughout this thesis to measure the thickness of layers that were deposited via spin coating, figure 2.17 illustrates the method and an example graph. A glass slide was cleaned using an ozone cleaner and then a layer was deposited using the spin conditions of interest. Subsequently, a scalpel was

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Figure 2.16: Bruker DektakXT profilometer, used to perform film thickness measurements throughout this work.

used to scratch the surface in several places, so that multiple measurements could be taken. The Bruker DektakXT profilometer was then used to measure the depth of the scratches and, therefore, the thickness of the layer. A minimum of nine measurements were performed on each film to produce an average thickness value and an error estimate. The thickness of all spin coated films in this thesis were measured using this technique.



Figure 2.17: Schematic of profilometry measurement of film thickness with an example graph showing the layer thickness [198]. A scratch is made in the film and a stylus is moved across the surface to generate a profile. The profile can then be used to determine the film thickness.

2.7 Ultraviolet-Visible Spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) is used for analysis and characterisation of samples by measuring the absorption and transmission of radiation over a large range of wavelengths. Absorption occurs when an incident photon's energy is equal to the energy for an electronic transition within the molecule. The excitation of electron to π^* orbitals in organic molecules is the cause of most UV-Vis light absorption. An example of the UV-Vis spectra for P3HT, PCBM and a blend is shown in figure 2.18.

UV-Vis is used mainly to investigate the optical properties of active and interfacial layers which is governed by Beers' law, shown in equation 2.6.

$$A = \epsilon c l \tag{2.6}$$

In equation 2.6, A is the absorbance, ϵ is the absorption coefficient, c is the concentration and l is the path length. Beers' law states that, for a given wavelength, the amount of light absorbed by a medium is proportional to the number of absorbing molecules. UV-Vis measurements were used throughout this thesis to in-



Figure 2.18: Thin film UV-Vis absorption spectra of P3HT, PCBM and a P3HT:PCBM blend [199].

vestigate changes in active layer absorption with time. All the UV-Vis spectra were collected over the wavelength range 300 to 800 nm, using a Varian Cary 6000i UV-Vis-NIR spectrophotometer, as shown in figure 2.19. Measurements were taken on a film that was spin cast onto glass substrates.



Figure 2.19: Varian Cary 6000i UV-Vis-NIR spectrophotometer [200], used throughout this thesis to investigate the absorption of different active layers.

2.8 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) uses X-rays to eject electrons from the surface of a sample using the photoelectric effect. Measuring the kinetic energy of the photoelectrons can be used to obtain information about the chemical composition of the samples surface. The kinetic energy of a photoelectron is given by equation 2.7 where hv is Planck's constant multiplied by the frequency of incident light, *BE* is the binding energy and ϕ_s is the work function of the material.

$$KE = h\nu - BE - \phi_s \tag{2.7}$$

A typical XPS spectrum, as shown in figure 2.20, is a plot of the number of electrons detected against the binding energy of the electrons. Since each chemical has characteristic binding energies, the position of the XPS peaks can be used to map the chemical composition of the material being analysed.



Figure 2.20: XPS survey scans of P3HT:PCBM blend films [201], showing slight differences in surface composition. XPS surface scans were used to investigate changes in BHJ and NP films over time.

XPS spectra for this thesis were collected by illuminating the samples with an Omnivac X-Ray Source, and the photoemission collected by a Scienta SES2002 anal-

yser. Survey scans were carried out with a pass energy of 100 eV, while regions scans were performed using a pass energy of 20 eV. The pressure in the analysis chamber with sample under X-ray illumination was typically 2.5×10^{-9} mBar, with a base pressure of 4×10^{-10} mBar.

2.8.1 Depth Profiling

When used in conjunction with ion etching, XPS can detect elemental composition as a function of depth into a film. An example of an XPS depth profile scan is shown in figure 2.21, data is generally presented with the component percentage as a function of sputtering time. These measurements were used to investigate changes in the structure and composition of devices post-fabrication. Depth profile measurements were performed on a Kratos AXIS Ultra DLD X-ray photoelectron spectroscopy system with an imaging hemispherical analyser, monochromated Al and Ag X-ray sources, and argon gas cluster ion gun.



Figure 2.21: XPS depth profile scan of a P3HT: TiO_2 solar cell, showing the composition of the device and allowing the layers to be identified [202].

2.9 Degradation Testing Equipment

The degradation testing apparatus involved serval pieces of software and hardware. To create automated testing capabilities, controllers and specialised software were required. Each of these is described in detail below. Further details of the degradation testing system are provided in chapter 3.

2.9.1 Source Measure Unit

In the degradation apparatus, IV measurements are performed by an Agilent U2722A modular source unit, shown in figure 2.22. The U2722A is a 3-channel SMU that is capable of four-quadrant operation of up to ± 20 V. The maximum current that can be provided per channel is 120mA. The Agilent was chosen because it was more cost effective than the Keithley (less than one-third the cost), while providing the necessary functionality.



Figure 2.22: Agilent U2722A source measure unit used to perform IV measurements in the degradation system [203].

The U2722A also has remote sensing capabilities which involve a second set of wires, called sense wires, to be connected directly to the device under test (DUT), as shown in figure 2.23. When the U2722A is operating in source voltage mode, the sense wires can account for voltage drop due to lead resistance by measuring the voltage directly at the load. The voltage at the DUT can drop due to resistances in the wires. This voltage drop is given by equation 2.8, where V_{DUT} is the voltage at the device, V_{out} is the voltage output by the Agilent, R_{DUT} is the resistance of the DUT and R_1 and R_2 are the resistance of the leads.

$$V_{DUT} = V_{out} \times \frac{R_{DUT}}{R_{DUT} + R_1 + R_2}$$
(2.8)

If the remotely sensed voltage at the load is lower than the programmed voltage, the output voltage will compensate until the sensed voltage matches the programmed voltage. Remote sensing is particularly useful when there is significant resistance in the system, or low resistance in the DUT, to ensure that the device sees the exact programmed voltage.



Figure 2.23: Illustration of the remote 4 wire sensing used by the Agilent U2722A to account for resistance in the system and provide the correct voltage at the device.

The IV measurements were performed in the same way as described in section 2.3.1. In source voltage mode, the Agilent sweeps through a range of voltages and measures the current from the device. Each finger of each device that is being tested is connected to the U2722A through a multiplexer (MUX). The U2722A then sends the results to the Laboratory Virtual Instrument Engineering Workbench (LabVIEW) which outputs the data to a spreadsheet.

2.9.2 Software Control

LabVIEW is a system-design and development environment for a visual programming language from National Instruments. LabVIEW was suitable for this application because it includes support for interfacing with a range of devices. For the degradation apparatus, LabVIEW was used to interface with both the U2722A for the IV measurements and the Arduino microcontroller for several other processes, including environmental monitoring and device selection.

SECTION 2.9

2.9.3 Hardware Controller

The Arduino Mega 2560 is a microcontroller that has 54 digital input/output pins, a USB connection, a power connector and several other features that allow it to completely support the microcontroller. The Arduino has several ways to communicate with a computer including hardware serial ports and a USB connection that can be used as a virtual communication port with the appropriate software. The Arduino can be programmed using the Arduino software environment. However, for this thesis much of the Arduino control was performed using LabVIEW.

To allow the Arduino and LabVIEW to communicate the LabVIEW Interface for Arduino (LIFA) toolkit was used with several modifications. LIFA is a free toolkit that allows data to be acquired from several different sensors by the Arduino and subsequently processed in LabVIEW. It also allows LabVIEW to send commands to the Arduino, for example to switch an I/O pin to select a MUX output or obtain data from a sensor.

2.9.4 Custom Component Fabrication

To fabricate several plastic pieces for the degradation apparatus, an Ultimaker 3D printer was used. The Ultimaker is a fused-filament fabrication (FFF) 3D printer that melts plastic and deposits it on a glass plate in an additive process. It has a build volume of 223x223x205mm. The parts that were fabricated using the 3D printer are described in detail in section 3.3.3.

Chapter 3

Degradation of Different Organic Photovoltaic Structures

This chapter describes the motivation for, and construction of, an automated degradation testing apparatus. Initial results presented in this chapter compare the stability of devices with BHJ and NP active layers, in the standard and inverted architecture, using existing degradation testing apparatus. This system was modified to perform constant illumination measurements on four devices at once, and shelf-life tests were performed concurrently using a separate system. Given the relatively recent nature of NP devices [204], systematic studies on degradation of these devices have yet to be presented. In order to perform systematic degradation measurements, a fully-automated system was designed and built that could perform degradation measurements on up to eight substrates, perform both constant and shelf-life testing and monitor the environmental conditions (temperature and humidity).

The long-term stability of OPV devices under operational conditions is crucial to their commercial viability [75]. However, these devices are prone to degradation through many processes, as outlined in section 1.6. While the primary research focus in literature has been achieving higher efficiencies, in recent years there has been more research into the stability and lifetime of OPV devices [28, 205].

A detailed background of the stability of OPVs was provided in section 1.7 which focused on the stability of the standard structure, where holes are collected at the transparent electrode [22]. However, the inverted architecture (which is elec-

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trically inverted when compared to the standard structure [206]) has been identified as more stable [74]. Consequently, the first part of this chapter explores the reported benefits of the inverted structure and the degradation processes that have been observed.

Following this review of literature, degradation measurements that were performed on these architectures are described and their results are then presented. The focus of this study was the stability of the inverted structure compared with the standard structure, as well as the stability of BHJ compared with NP active layers.

Lifetime measurements are necessary to gain a thorough understanding of the stability of OPVs. Section 3.2 outlines preliminary lifetime measurements that were performed on a crude apparatus (see figure 3.4). Due to the complex nature of the degradation of OPVs, a reliable system to perform lifetime measurements on a larger number of samples was necessary. Consequently, the decision was made to design and build a more robust degradation testing apparatus before performing any subsequent measurements, to ensure meaningful results were obtained. The goal was to produce a simple, fully automated degradation testing system, that performed quality lifetime measurements under ambient conditions. To maintain the simplicity of the system, the decision was made to monitor environmental factors (temperature and humidity) rather than control them. This approach also meant that production costs could be kept low.

Once the testing system was constructed preliminary measurements were performed as quality assurance before further degradation studies were performed. These quality assurance measures included temperature and humidity measurements and resistance measurements. The steps taken to design and construct the system are outlined in sections 3.3 and 3.4. Quality assurance measurements performed on the more robust testing apparatus are presented thereafter.

Absolute irradiance measurements presented in this chapter and subsequent chapters were performed by Mr Alaa Al-Ahmad.

3.1 Stability of the Inverted Structure

The PCE of OPVs has increased steadily in recent years, towards values that are thought to be commercially viable [118]. Concurrently, there has been an increase in interest in the stability of OPVs [71, 113]. The inverted structure has been presented as a method of improving the stability of OPVs, with a substantial amount of research implying that the inverted architecture is inherently more stable than the standard architecture (see Zhang *et al.* for a comprehensive review [74]). The active layer used in the majority of these reports is P3HT:PCBM with a blend ratio of 1:1, when other blend ratios or materials were used it has been noted.

The inverted structure allows the use of different materials for electrodes and interfacial layers which can be less vulnerable to damage by water and oxygen than materials used in the standard structure [82]. One factor that improves the stability of the inverted devices is the use of a high work function metal as the top electrode. Many degradation processes are associated with the low work function metal typically found in the standard architecture. For example, aluminium, commonly used as an exposed electrode in standard architecture OPVs, is known to readily oxidise, reducing charge transport, and can allow the diffusion of oxygen and water into the device, which can damage the active layer [125, 131, 207].

One of the first reports of the stability of the inverted structure compared the change in performance with that of standard structure devices when both were stored under ambient conditions in the dark [208]. Devices were fabricated using P3HT:PCBM in a blend ratio of 1:0.6. The authors observed that inverted devices re-tained over 80% of the initial PCE after 40 days stored in ambient conditions while standard structure devices showed negligible activity after only 4 days. The silver electrode in the inverted structure oxidised when exposed to atmosphere, increasing the effective work function at the interface. The higher work function resulted in improved charge transport. It was also suggested that the PEDOT:PSS layer acts as a barrier preventing oxygen entering the active layer which also improved the stability, however no supporting evidence was provided.

The air-stability of inverted devices was also investigated by Li *et al.* [209]. Inverted and standard devices were stored under ambient conditions for 400 hours.

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The inverted devices maintained over 70% of the initial PCE after that period, while the standard devices showed minimal performance after only 175 hours. The superior stability of the inverted structure was attributed to the stability of the buffer layers.

Song *et al.* investigated the effect of buffer layers on device stability by measuring the change in performance in air of inverted devices with and without a MoO_3 HSL [210]. Standard devices were also investigated for comparison. Devices were stored under ambient conditions for 72 hours and the performance was measured regularly. The standard devices and the inverted devices without a HSL degraded relatively rapidly, both experiencing almost complete loss of PCE in 72 hours. Conversely, the inverted devices with the MoO_3 layer maintained 60% of the initial PCE over the same period, which was attributed to the barrier effect of MoO_3 protecting the active layer.

Two important studies have been performed which compare the degradation of standard and inverted devices with the same materials. Kundu *et al.* investigated the stability of devices with ZnO and MoO₃ buffer layers that were stored in ambient conditions [211]. The inverted devices were shown to be much more stable, maintaining 80% of the initial PCE after 240 hours. In comparison, the standard devices showed negligible activity after 75 hours. The superior stability of the inverted structure was again attributed to MoO₃ acting as a barrier. Subsequently, Han *et al.* performed a similar experiment using TiO₂ and MoO₃ buffer layers, and aluminium electrodes [212]. Devices were fabricated using PCDTBT and PCBM in a blend ratio of 1:4. The inverted devices showed no activity after only 228 hours. The degradation of the standard device was attributed to degradation of the TiO₂ layer at the top of the device. This study also showed that the top aluminium electrode did not lead to an inherently unstable device, despite the high humidity (90% RH) in the experiment.

Lee *et al.* also investigated the stability of inverted devices with an aluminium electrode [213]. Devices were kept under ambient conditions for 40 days and the normalised PCE remained over 90%. A similar experiment was performed in which the ESL was a tin oxide (SnO); devices maintained over 95% of the initial PCE after

60 days [214]. These studies further confirmed that aluminium as a top electrode is not inherently unstable.

Bao *et al.* compared standard devices to inverted devices with a silver electrode [215]. The standard devices exhibited minimal photovoltaic activity after two days, while the inverted devices retained over 70% of the initial PCE after ten days. The improved stability was attributed to the stability of the TiO_2 . Furthermore, oxidation of the silver electrode increasing the effective work function to better match with the HOMO of MoO_3 , which improved the electrical properties of the interface [215].

The thermal stability of the inverted structure with three different HSLs and a silver electrode were investigated by Greenbank *et al.* [216]. Samples were kept in an inert atmosphere at 85°C for 500 hours. After this period, the PCE of the device with a MoO₃ HSL decreased to 50% of the initial value while the PEDOT:PSS and tungsten trioxide (WO₃) devices maintained 85% and 90% respectively. As a result, the degradation was attributed to degradation of the MoO₃/silver interface. This study was also performed on devices with an aluminium top electrode. The devices with MoO₃ and WO₃ HSLs showed high stability, each maintaining more than 70% of the initial PCE after 500 hours. Conversely, the device with the PE-DOT:PSS HSL showed rapid degradation, dropping to below 25% normalised PCE after only 1 hour. This degradation was attributed to the formation of aluminium oxide at the PEDOT:PSS/aluminium interface. These observations highlight the effect of interfacial degradation on device performance.

Studies have also been performed to investigate the effect of humidity on degradation. Drakonakis *et al.* exposed devices with a PEDOT:PSS HSL to 85% RH over 300 hours [133]. The performance of the inverted devices reduced to 80% of the initial PCE over that time, while standard devices degraded below 80% in only 10 hours. Similarly, Voroshazi *et al.* investigated the effect of humidity on the degradation rate of inverted devices with two different HSLs [217]. Inverted devices with PEDOT:PSS or MoO₃ HSLs were stored in environments with <5% RH, 40% RH and 75% RH over 5000 hours. Interestingly, the increase in humidity did not have a negative effect on the stability of the PEDOT:PSS device. It did, however, accelerate the degradation of the MoO₃ device, with final normalised efficiencies of 80%,

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60% and 50% for <5% RH, 40% RH and 75% RH respectively. The rapid degradation at higher humidity was attributed to a change in hole mobility resulting in more bimolecular recombination.

Venkatesan *et al.* investigated the stability of inverted devices with ZnO, polyethylenimine ethoxylated (PEIE) or aluminium-doped zinc oxide (AZO) ESLs [114]. Devices were stored under ambient conditions for 178 days and were measured periodically. The degradation behaviour of the devices with ZnO and AZO was quite similar, each showing approximately 57% of the initial PCE. In contrast, the PEIE device exhibited rapid degradation over the first week and only maintained 20% of the initial PCE after 178 days. This observation was attributed to a drop in V_{OC}, however no root cause was suggested.

All the studies mentioned so far have focused on the storage of inverted devices in the dark. They show that the inverted structure is, in general, superior to the standard structure for storage lifetime. However, there has also been work examining the degradation of inverted devices under illumination.

Krebs *et al.* tested the performance of inverted devices in different model atmospheres and compared them with standard devices [218]. The environments used in this study were nitrogen, humid nitrogen, oxygen and ambient. Devices were subjected to constant illumination while being stored in one of the four environments. The inverted devices showed superior stability in the nitrogen and humid nitrogen, maintaining over 80% of the initial PCE. However, the inverted devices were significantly less stable than the standard devices in the dry oxygen and ambient environments. Inverted devices in these environments lost all photovoltaic activity in less than 50 hours, while their standard counterparts maintained 20% and 70% normalised PCE in the ambient and dry oxygen, respectively, after 200 hours.

The stability of the inverted structure under constant light when exposed to humidity or oxygen independently was investigated by Norrman *et al.* [120]. Inverted devices were exposed to an oxygen free environment, with 65% RH, and a dry oxygen environment, with <0.5% RH. Both environments lead to rapid degradation, with the devices reduced to 50% of their initial PCE in 2.2 hours for the high humidity environment, and 0.3 hours for the oxygen environment. The degradation in the humid environment was attributed to water absorption in the PEDOT:PSS layer: confirmed by measuring the variation in conductivity with humidity. Degradation in the oxygen environment was attributed to the P3HT:PCBM active layer reacting with oxygen.

The degradation of an inverted device with a silver/aluminium electrode was investigated by Tanenbaum *et al.* under constant illumination over 1500 hours [219]. The devices were tested under accelerated full sun simulation, a sharp decrease to approximately 40% normalised PCE over the initial 50 hours of the illumination was observed. The performance then stabilised until 1200 hours, when a gradual decrease was observed.

A similar experiment was repeated by Rösch *et al.* over 600 hours [146]. The PCE initially decreased rapidly, reducing to 30% normalised efficiency in 23 hours. However, after this initial decrease, the PCE was reasonably stable up to 618 hours. The nature of degradation was investigated further using several imaging techniques and the mechanism was identified as silver penetrating into the MoO₃ layer, causing a drop in V_{OC} .

More recently, the widely observed rapid degradation under constant illumination has been attributed to the diffusion of oxygen into inverted devices [205]. Diffusion of oxygen occurs but does not cause significant damage to devices in the dark. The presence of light accelerates reactions with oxygen, which causes degradation [141].

The degradation of OPV devices is very dependent on the environmental and testing conditions. This literature shows that the observed stability of the inverted structure changes significantly depending on the lighting conditions, with a very long shelf-life but a short operational life generally observed. There are many factors that affect the degradation of these devices, including light, environment and atmosphere. Consequently, despite the many degradation studies reported, the variety of testing procedures used in literature make it difficult to obtain a clear picture of degradation.

3.2 Preliminary Degradation Testing

As outlined in sections 1.6 and 1.7, there are a number of degradation processes which can occur that are activated by different factors. Section 3.1 also showed that observed degradation behaviour can be altered by lighting conditions. For these reasons, the initial degradation testing of devices was undertaken in two ways. The first was to measure the shelf life of the devices; after fabrication devices were kept in dark, ambient conditions and tested periodically over several days. Constant illumination tests were also performed, where the devices were kept in ambient conditions, constantly illuminated, and tested every hour. Each of these degradation tests was performed at the same time with devices of both standard and inverted structures, with BHJ and NP active layers containing P3HT:PCBM.

Table 3.1: Average initial IV characteristics (with standard deviations) of devices selected for preliminary degradation measurements. All devices contain P3HT:PCBM and NPs were fabricated via the mini-emulsion process.

	Eff. (%):	V _{OC} (V):	I _{SC} (mA):	FF (%):
Standard BHJ	2.74 (±0.10)	0.580 (±0.002)	8.02 (±0.43)	0.589 (±0.008)
Inverted BHJ	2.69 (±0.06)	0.510 (±0.036)	8.12 (±0.25)	0.651 (±0.066)
Standard NP	0.44 (±0.12)	0.480 (±0.067)	2.35 (±0.27)	0.393 (±0.033)
Inverted NP	0.91 (±0.06)	0.480 (±0.021)	4.35 (±0.34)	0.302 (±0.010)

Four of each kind of device, with 6 cells each (a total of 24 individual devices), were produced using methods outlined in sections 2.2.1 and 2.2.2. These devices were then tested under AM 1.5 according to procedures outlined in section 2.3.1. Two of each device type were selected; one for the shelf life test and one for the constant illumination test.

Typical IV characteristics for each device, that were degradation tested in the following sections, are shown in table 3.1 with typical IV-curves shown in figure 3.1. The NP devices have lower performance than the BHJ devices, as expected [220].

The inverted NP devices show a strong s-shape in the IV curve which is gener-



Figure 3.1: Typical IV-curves of a (a) standard BHJ, (b) inverted BHJ, (c) standard NP and (d) inverted NP device, tested in nitrogen under a class A Newport solar simulator.

ally attributed to charge transport barriers [221]. This observation may be related to surfactant hindering charge transport within the device [169].

3.2.1 Shelf Life

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For the shelf life test one of each type of device was placed in a small environmental chamber which kept the temperature and humidity constant at 25°C and 50% RH respectively. These conditions meet the ISOS-D-1 conditions as outlined in table 1.2. The environmental chamber was covered in aluminium foil to exclude ambient light. The devices were removed from the environmental chamber and transferred to nitrogen glove box once a day and tested under AM 1.5. The normalised efficiency for each of the devices over a number of days is shown in figure 3.2.



Figure 3.2: Comparison of the shelf life of standard BHJ, inverted BHJ, standard NP and inverted NP over 8 days. Devices were kept in an environmental chamber with a temperature of 25°C and a humidity of 50% RH. The superior stability of the inverted BHJ devices under these conditions can be seen.

The inverted structure devices with the BHJ active layer performed the best in this test. After 9 days in the environmental chamber the inverted BHJ device was the only device that was still exhibiting 90% normalised efficiency. Conversely, for the standard structure, both the BHJ and NP devices stopped working after the first day in the environmental chamber. The results of this study show that the inverted NP device was significantly less stable than the inverted BHJ. However, the inverted NP devices lasted significantly longer than the standard devices, maintaining 30% of their initial efficiency after 8 days.

The inverted BHJ device was tested again after 68 days in the environmental chamber. The device retained approximately 20% of the initial PCE after that extended period. The initial IV curve and the IV taken after 68 days in the environmental chamber are shown in figure 3.3. These measurements further illustrate the stability of this structure under shelf life conditions.

Under shelf-life conditions, inverted structures are observed to be significantly more stable than standard structures [212, 222]. The results presented here are con-



Figure 3.3: Comparison of an initial IV curve and a curve after 68 days in an environmental chamber for an inverted BHJ device, showing the long-term stability of this structure under shelf-life conditions.

sistent with these observations, as the inverted devices were most stable. The NP devices of each architecture were observed to be less stable than the corresponding BHJ devices. These observations indicate that further investigation and development may be required to produce stable devices using the NP active layer.

3.2.2 Constant Illumination

The constant illumination test involved taking each type of device and placing them under ISOS-L-1 conditions; constant illumination from a light source in ambient conditions. The devices were then tested every half hour for approximately 90 hours. This type of measurement is important as there are many degradation processes that are activated or accelerated by light [223], making it impossible to obtain an accurate picture of device degradation using only shelf life measurements. Consequently, it was expected that the results of this test would be different from the results of the shelf life test.

Previous to this experiment the testing apparatus was only capable of testing one substrate at a time, due to the sample holders and wiring set-up that were used. To perform measurements on four devices concurrently, a make-shift apparatus had to be created by arranging and securing single substrate holders under a light

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source. The experimental set up that was used is shown in figure 3.4.



Figure 3.4: Make-shift apparatus constructed to perform constant illumination measurements on four substrates at once, individual substrate holders were arranged and secured under a single light source.

The experiment ran for approximately 90 hours and the results are presented in figure 3.5. Some interesting trends were identified. The inverted structure degraded rapidly under constant illumination. Unlike in the shelf life test, the performance of the inverted BHJ device dropped to below 10% of its initial efficiency after approximately 15 hours; indicating that photoactive degradation mechanisms are significant for this architecture.

The inverted NP device also degraded much more rapidly than when tested under shelf-life conditions. Under shelf-life conditions the inverted NP devices maintained 50% after 5 days, conversely under constant illumination the PCE decreased below 50% in less than 5 hours. These results further indicate that photoactive degradation mechanisms dominate for the inverted structure.

For the initial 20 hours of the experiment, the degradation of the BHJ and NP



Figure 3.5: Normalised efficiency as a function of time for standard BHJ, inverted BHJ, standard NP and inverted NP under constant illumination, the value presented is the average of a minimum of 4 fingers with the standard deviation represented by the shaded region.

devices of the standard structure were very similar. After approximately 20 hours, the change in PCE was much more rapid for the NP device. The NP device dropped below 10% normalised efficiency after 90 hours, while the BHJ device maintained over 20%.

These results were somewhat contrary to expectations at the time. As of 2014 when these data were collected, the prevailing notion was that inverted devices were superior to standard devices [74]. However, these results strongly indicated that the testing conditions dictated the observed stability. Consequently, a more robust testing apparatus was constructed to further investigate these results. The design and construction of the testing system are described in section 3.3. The results of degradation studies performed using the system are presented in subsequent chapters.

3.2.3 Decay Curve Modelling

As mentioned in section 2.3.2, the degradation of PCE can generally be fitted with an exponential function that describes the decay [188]. Furthermore, time constants for different decay mechanisms can be obtained through one- or two-term exponential fitting, which provide information about potential mechanisms [123,124]. After the burn-in, the degradation rate reduces, and the devices exhibit long-term degradation behaviour. The inverted architectures exhibited more severe burn-in then the standard architectures.

The long-term degradation for each decay curve was fitted with a single exponential and is shown in figure 3.6. The time constants for each fit are then shown in table 3.2.



Figure 3.6: Long-term degradation behaviour fitted with one-term exponential curves, showing similarity in the long-term degradation of devices with NP active layer in both architectures.

The long-term degradation behaviour of the two architectures with NP active layers exhibit very similar time constants. These results suggest that the long-term degradation is dictated by the active layer rather than the architecture for the NP devices. However, the long-term degradation of the two architectures with BHJ active layers show significantly different time constants. Further investigation of degradation time constants is presented in section 4.2.5.

Further degradation measurements that were performed to understand these effects are outlined in chapter 4.

Architecture	Active Layer	$\lambda (h^{-1})$
Standard	BHJ	0.013
Inverted	BHJ	0.067
Standard	NP	0.032
Inverted	NP	0.037

Table 3.2: Degradation time constants, λ , for each structure based on $I/I_0 = Ae^{-\lambda t}$.

3.3 Degradation Testing Apparatus

In order to perform more thorough degradation measurements, a new system was designed that was capable of testing more devices in parallel. When designing the system, a trade-off needed to be made between circuit complexity, and therefore signal quality, and device testing capability. Accordingly, the system was designed such that eight substrates, with six cells each, can be tested simultaneously. These design constraints allowed for 48 cells to be tested simultaneously, while maintaining simplicity and signal quality.

An aluminium frame was purchased from Misumi and assembled which encased the whole system. The assembled frame is shown in figure 3.7a. It was important to install the lights so that experiments running in parallel did not affect each other. Accordingly, the lights were installed in an opaque plastic layer with custom holes, cut such that no light passed through into the testing chamber.

3.3.1 Testing Conditions

The testing conditions were another important consideration when designing the system. The degradation of devices depends heavily on exposure to light and the environment, as outlined in section 1.7.4. The system was designed so that constant illumination and intermittent illumination (shelf-life) tests could be performed simultaneously. Furthermore, it was also important to perform dark IV curves with each measurement. The ability of the testing system to perform different types of test, and the dark IV curves (at the same time) meant that each testing position needed to be isolated from the others. PVC pipe with a diameter of 90mm, cut to 210mm, was used to enclose each testing position. These were placed in the

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Figure 3.7: A case was constructed to enclose the system. (a) Aluminium frame from Misumi which house the lights and device testing positions for the degradation testing system, and (b) schematic showing the dimensions of the frame and enclosure.

system with coupling (100mm) so that the height could be adjusted to ensure a tight fit and to make removing the pipe easy (shown in figure 3.8).

3.3.2 Lighting

The lighting for the system is supplied by eight individually controlled Osram Decostar 12V 50W warm white halogen globes. These globes were chosen due to their low cost and size. Given the compact nature of the system, it would have not been possible to accommodate as many larger lamps. The lighting was powered using the 12V line on a ZM-600GV power supply. The globes were placed in mesh down-light housings, in order to reduce heat build-up. Moreover, the top of the system was also left open to allow heat from the lamps to dissipate.

Absolute irradiance of these lamps was measured using an Ocean Optics spectrometer USB 400, with a spectral range of 200 to 1100 nm. The spectrum of the 50W lamp is shown in figure 3.9, compared with the Newport AM 1.5 lamp that was used for IV measurements and the global AM 1.5 spectrum. The spectral mis-

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Figure 3.8: Length of PVC pipe used to separate individual experiments, such that lighting conditions from each experiment would not be affected by ambient light or experiments running in parallel.



Figure 3.9: Comparison of the absolute irradiance of a 50W halogen lamp and the AM1.5 solar simulator used for determination of the IV characteristics.

match was quantified but not corrected for as the purpose of this system was to measure relative degradation of performance not to accurately determine device

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PCE. However, it was important to consider how the altered spectrum might affect degradation.

Figure 3.10: Percentage of total irradiance for seven wavelength ranges of the 50W lamps used in the degradation testing system, compared with AM1.5 along with the ranges for class A and B solar simulators.

In order to quantify the spectral mismatch, the percentage of total irradiance of the lamps was compared to AM 1.5 in seven wavelength ranges. These results are shown in figure 3.10, along with the ranges for class A and B solar simulators. The halogen globes also had an irradiance that was 12% higher than AM 1.5, over the region of interest (350-1100 nm). The lamp also had a significantly lower UV component than the solar spectrum. Given that UV is known to play a significant role in degradation [123, 224, 225], the low UV content may affect degradation. However, the effect of UV on degradation is investigated thoroughly in chapter 5.

3.3.3 3D Printed Components

Several components for the degradation testing apparatus were printed using an Ultimaker 2 3D printer. Components were designed using 3D drawing program Inventor and a program called Cura to create the code for the 3D printer to run.

The components that were 3D printed were a sample holder and a base for the sample holder to sit in. The sample holders, shown in figure 3.11a, were placed on

top of push pins to contact the device.



(a) Sample holder that was 3D printed for small scale devices.



(b) Base plate that was 3D printed to hold the sample holders in place in the tube.

Figure 3.11: 3D printed components for degradation testing system.

The bases, shown in figure 3.11b, were designed in such a way so that the substrate would sit in the same spot in the tube each time the system was used. There was a groove that was slightly larger than the sample holder so that it would sit in place. The base was also designed with holes to allow air flow at the bottom of the tube and a small hole for a pin to secure the sample holder in place.

3.4 System Control and Monitoring

Several custom written visual instruments (VI)s in LabVIEW and an Arduino Mega 2650 are used to control the system. A schematic of the final control system design can be seen in figure 3.12. The substrate and finger control and environmental measurements, are performed by a series of MUXs on a custom printed circuit



board (PCB). The lights are controlled, through 12V relays, by the Arduino.

Figure 3.12: Schematic diagram illustrating how the system is controlled.

Much of the code used as part of the testing system was purpose written. The VIs interface with the Arduino controlling the MUXs or relays based on the inputs provided from LabVIEW. The user panel of the degradation system is shown in figure 3.13. An Agilent U2722A Data Acquisition System performs the IV measurements, and the IV curve is displayed in real time on the front panel of the VI along with the characteristics. The collected data is then analysed and split into raw IV data and characteristics, which are written to separate spreadsheets by LabVIEW along with the environmental measurements that are taken by the Arduino, and the time-stamp.

Each of the possible device testing positions can be individually turned on or off by the user. If the position is switched on the system will control the light appropriately, take temperature and humidity measurements, select the appropriate substrate and finger and perform IV measurements. If the position is switched off, no measurements are performed. A flow chart of the process is shown in figure 3.14 and each of the steps are described in detail below.



Figure 3.13: User control panel for the degradation system that allows device information to be entered and which displays IV data and environmental conditions in real time.

3.4.1 Light Control

It is possible to select one of two modes of illumination; constant and intermittent illumination. In constant illumination mode, the light is switched on for the first measurement and kept on for the duration of the degradation test. Conversely, in intermittent illumination mode, the light is switched on before each device is tested and switched off afterwards.

Dark IV tests are also performed with each set of IV measurements. If constant illumination is selected, the light is switched off for the duration of the dark IV and switched back on afterwards. If intermittent illumination is selected, the light is already off, the dark IV is performed.

The lights are controlled using a 16-channel 12V relay module from Sainsoft, which was chosen because it was compatible with the high current drawn by the eight lights. The ZM-600GV power supply provides the power to the relay module and power lines are connected to the lights through the relays. The Arduino micro-controller interfacing with LabVIEW was used to switch the relays at appropriate times.



Figure 3.14: Flow diagram of the degradation testing procedure for both constant and intermittent testing. If the cell is switched on, the light is controlled appropriately, and measurements are performed. The system then waits the given amount of time before performing measurements again.

3.4.2 Substrate and Finger Control

Substrate and finger control is performed using a custom PCB containing a series of MUXs. The MUXs that were used for this system were the CD4052B 4:1 MUX and the CD4051B 8:1 MUX from Texas Instruments. They are digitally controlled analogue switches, a schematic of these MUXs is shown in figure 3.15. As mentioned in section 2.9.1, the devices were tested using a 4-wire set up to account for resistance in the system due to the MUXs.

For the common pins, an 8:1 MUX is used which inputs the common pins from each device, and outputs one directly connected to the ground line on the Agilent.



Figure 3.15: Functional diagram for the CD4051B and CD4052B MUXs which were used to switch between devices and fingers in the degradation testing system [226].

Another 8:1 MUX is used for the sense line from the Agilent and works in the same way. The selector pins of each of these MUXs are connected to the same digital pins of the Arduino. The sense and reference pins for the temperature sensors were connected and controlled in the same way.

The set up for the fingers required switching between all fingers on 8 devices, 96 in total for both measurement and sense lines (see section 2.9.1 for a description of the U2722 wiring). A cascading set up of 4:1 MUXs are used because it was the most cost-effective solution. Each of the fingers from the device is connected to a pin on one of twelve 4:1 MUXs, making up the first level of the cascade. The output of each of these MUXs is then passed into the second level of the cascade, three 4:1 MUXs. Finally, the output is fed into a 4:1 MUX which is connected to the Agilent. The sense wires were connected in the same way.

A PCB was also designed such that the sample holder could be placed on to the pins, as shown in figure 3.11b. The board contained the temperature and humidity sensor, it was connected to the main board by a 20-way ribbon cable allowing for 14 connections to the substrate and 3 connections to the temperature and humidity sensor.

3.4.3 Environmental Monitoring

After the light is set appropriately, temperature and humidity measurements are taken. To maintain an accurate picture of the environment each of the devices was exposed to, temperature and humidity measurements were taken separately for each device in each isolated testing environment. A DHT22 sensor is present

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in each of the testing environments in close proximity to the sample (which can be seen in figure 3.11b). It was also necessary to wire the sensors through a MUX. For simplicity, the sensors were wired in the same way as the ground pins for each device. Thus, two CD4051B MUXs were used for the DHT sensor data and ground. The power for each sensor was directly connected to a 5V line from the ZM-600GV power supply.

The DHT22 temperature and humidity sensor was selected for this application due to its high precision and long-term stability. The operating range of these devices for temperature is -40°C to 80°C and for humidity is 0% RH to 100% RH. The accuracy in the operating range for temperature is $\pm 0.5^{\circ}$ C and for humidity is $\pm 2\%$ RH.

3.4.4 Timing

Given the variety of device architectures and material systems to be investigated, it was likely that a wide range of decay rates would be observed. For this reason, it was important to individually control the measurement frequency. If a device is unstable there may be drastic changes in the performance in the first hours of the test, meaning it is beneficial to have frequent tests. However, more stable devices change very slowly over many hours meaning that frequent tests would provide a large amount of superfluous data.

For the sake of simplicity, the user can select the time between scans. This function works by monitoring the number of cycles which have taken place and skipping a certain number of cycles depending on the value given as the time between scans. It was found that each device IV test took approximately one minute to test and so the time between scans could change drastically depending on how many devices were testing in each cycle. To accommodate any timing discrepancies, the time-stamp for each scan is printed to the spreadsheet with the IV data so the exact time between each scan is easy to determine.

3.5 Preliminary Temperature and Humidity Measurements

The system design involved a light illuminating the small area enclosed by the PVC pipe for extended periods of time, which was likely to have a significant ef-

fect on the environment inside the tube. For this reason, it was important to closely monitor the environment. The temperature and humidity that OPVs are subjected to throughout operation has been observed to have a significant effect on the life-time of the devices [113]. Consequently, ISOS developed several procedures for stability testing which include directions for shelf-life testing, outdoor testing and weathering as well as a standard temperature and humidity for ambient conditions (see section 1.7.5) [148].

After the system was operational, two small fans were added to the sides of the testing chamber to maintain air flow. All eight lights were switched on and a temperature and humidity sensor in each of the tubes was used to measure the change in temperature of the tube over approximately 18 hours. The results, shown in figure 3.16, are the average for all eight tubes. The shaded region represents the standard deviation at each point.



Figure 3.16: Change in temperature and humidity caused by a lamp over a 20-hour period. The temperature quickly rose and stabilised at approximately 33°C and the humidity stabilised at 29% RH. While these environmental conditions do not match any ISOS protocol, given that the conditions were consistent for each testing position, they are appropriate for comparison.

These measurements showed that the temperature and humidity of the system plateaued at approximately $33(\pm 2)^{\circ}$ C and $29(\pm 3)^{\circ}$ RH. Furthermore, the amount of variation between the tubes is relatively small. These conditions were consistent for each testing position meaning that degradation rates can be meaningfully compared and are consistent with keeping the system simple. All results presented from here on use these conditions.

3.6 Quality Assurance

The electrical properties of the system were also tested by measuring the IV characteristics of a $4.7k\Omega$ resistor at each of the device positions. The results for four of the eight device positions are shown in figure 3.17. There was minimal variation in the characteristics between the different testing positions. Furthermore, the resistance was measured to be $4.7k\Omega$ with a variation of less than 1% between the eight measurements. These results indicate the electrical measurements that are taken at different device positions are equivalent and accurate.



Figure 3.17: IV characteristics of a resistor measured at four different device positions showing no variation in electrical measurements, indicating that precision IV-characterisation is possible.

3.7 Conclusions

This work demonstrated that the observed stability of OPV devices is heavily dependent on the testing conditions. The starkest difference in the degradation trends between the two lighting conditions occurred in inverted BHJ devices. These devices maintained 20% of the initial PCE after 68 days when tested under intermittent illumination. However, under constant illumination they dropped below 20% normalised PCE within 10 hours. When these results were collected, there was little existing work comparing the stability of the inverted structure under constant illumination and shelf life conditions. Furthermore, the magnitude of this difference was surprising and highlighted the need for more degradation measurements to be performed on each structure (see chapter 4).

The performance of standard devices in both the shelf life and constant illumination tests indicates that the dominant process is atmospheric degradation. In the shelf life test the temperature and humidity were kept at 25°C and 50% RH, under which diffusion of water into devices represents a significant source of degradation, as outlined in section 1.7.1. Under shelf-life conditions, the standard devices were significantly less stable than the inverted devices.

The performance of standard BHJ devices in the constant illumination test provides further evidence of the effect of humidity on degradation. Subsequent experiments, presented in section 3.5, showed that constant illumination can have a drastic effect on the environment around it. A drop in the relative humidity in the environment around the lamp as the temperature increased was observed. Humidity is a known factor in the degradation of OPVs, particularly of the standard architecture [79,133]. The difference in humidity in the shelf-life and constant illumination measurements may explain the more rapid degradation of the standard devices under shelf-life conditions. While the rapid degradation of the inverted structure under constant illumination suggests that the dominant degradation mechanisms for this structure are photo-active rather than atmospheric.

The degradation of NP devices was also investigated for the first time. Given the relatively recent nature of NP OPVs, extensive work on the stability of these devices does not exist. Results in this chapter indicated that NP devices are less

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stable than their BHJ counterparts. However, further experiments were required to obtain a more comprehensive understanding of the degradation of these devices, which is addressed in chapter 6.

As outlined in section 1.7, there are many degradation processes that can occur simultaneously. Consequently, obtaining a complete picture of the degradation of devices using lifetime measurement can be difficult. To obtain a more thorough understanding of the degradation of these devices, a new, fully-automated degradation testing apparatus was constructed. The system was designed to test more devices concurrently, in order to increase the reliability of results. Quality assurance measurements were performed, indicating that the system can reliably perform electrical characterisation.

This chapter has demonstrated that inverted devices are not inherently more stable than standard devices, and that observed degradation behaviour is a product of both architecture and testing conditions. The work in this chapter also highlighted the need for more in-depth degradation experiments involving multiple devices concurrently under varying lighting conditions and describes a low-cost testing environment which meets these requirements.

Chapter 4

Degradation of Bulk Heterojunction and Nanoparticulate Films

The purpose of this chapter was to fully characterise the degradation of standard and inverted OPV devices with BHJ and NP active layers. After designing a fully automated degradation characterisation system, lifetime measurements were recorded for BHJ and NP devices in both standard and inverted architectures. To further characterise the changes in the two active layers, UV-Vis, lifetime measurements and LBIC measurements were performed.

The first part of this investigation involved performing measurements to quantify the change in absorption of the active layer with time through UV-Vis measurements. The UV-Vis spectra of films of the BHJ and NP solutions were measured repeatedly over 24-hour intervals to observe how the absorption evolved with time in ambient and inert environments, both in the presence and absence of illumination. The purpose of these experiments was to understand the degree to which the degradation of devices was related to changes in the absorption of the active layer. Additionally, it was important to compare the change in absorption of the two active layer types. The NP active layer films exhibited a more rapid decrease in absorption, suffering almost complete loss of absorption after 9 days in ambient conditions under illumination, whereas the BHJ film took 36 days under the same conditions.

In an inert environment and in the dark, the absorption of both active layers was stable over 36 days. These experiments showed that the combination of am-

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bient conditions and illumination results in significant loss of absorption for both active layers. However, given the long-time scale of the loss of absorption when compared with the observed device degradation which was less than 5 days for the most stable devices (see section 4.2), it is likely not the dominant degradation process.

Lifetime measurements of device performance were also recorded on standard and inverted devices, with BHJ and NP active layers. These measurements were performed using the automated degradation characterisation system developed in chapter 3. The results also indicate that the inverted structure was less stable than the corresponding standard structure, for each active layer. In addition, the NP devices were less stable than the BHJ devices. In this experiment, the inverted BHJ devices were more stable than observed in figure 3.5, which highlights the need for multiple device testing capabilities since a single device may be susceptible to failure that is unrelated to the devices intrinsic stability.

Data fitting of the long-term degradation of these devices suggests that the behaviour is dictated by the active layer irrespective of architecture. However, the length and severity of the burn-in changes for each architecture resulting in different lifetimes.

LBIC measurements were performed on both standard and inverted devices, with BHJ and NP active layers. Current maps were produced for pristine and degraded devices, to identify changes in current generation as the devices degraded. The results suggest that the architecture was the dominant factor in current loss, as the standard BHJ and NP devices exhibited similar changes in current generation. The LBIC measurements, along with lifetime measurements, suggest that the burn-in degradation is dictated by the architecture and the long-term degradation is dictated by the active layer for the systems studied here.

4.1 Evolution of UV-Vis Absorption Spectra

One method for investigating the degradation of the active layer is to observe the change in the UV-Vis absorption spectrum with time [113]. While this method is not perfectly reflective of the operating conditions in a device, as the active layer may be protected by other layers, it does provide some useful insights. Manceau *et* *al.* used UV-Vis spectroscopy to investigate the changes in P3HT:PCBM films due to prolonged light exposure [227]. A significant decrease in the UV-Vis absorbance was observed after prolonged illumination due to aggregation of PCBM in the active layer. Hintz *et al.* investigated degradation of polymer films in oxygen under illumination using UV-Vis spectroscopy [141]. Irradiation of P3HT films was observed to cause a decrease in the absorbance with time, which was attributed to photo-oxidation of the P3HT.

The evolution of the UV-Vis absorption spectrum was investigated for films that were kept in the dark and under illumination in both ambient conditions and a nitrogen environment. The active layer solutions were prepared using the methods described in sections 2.1.1 and 2.1.2. The films were deposited on glass slides and subsequently dried using the conditions outlined in sections 2.2.1. All films were deposited and dried in an ambient environment.

Before UV-Vis measurements were performed on the films, zero and baseline measurements were taken. The baseline measurements involved taking the UV-Vis spectrum of a piece of glass with no film present, which allowed the system to account for any absorption by the glass. The zero-measurement involved blocking the beam entirely using a metal plate, allowing for any stray light entering the chamber to be accounted for. The UV-Vis measurements were then taken for the wavelength range between 300 nm and 800 nm, with a step-size of 1 nm.

4.1.1 Bulk Heterojunction Films

The initial UV-Vis spectra of two of the films is shown in figure 4.1. After the initial UV-Vis measurements, one film was placed in a dark chamber, and designated sample a), while another film was placed in a tube under constant illumination from an Osram Decostar 12V 50W warm white halogen globe, and designated sample b). The substrates were stored under ambient conditions for this experiment.

There are some slight differences in the spectra for each film, likely due to minor variations or defects in the films. However, it is still possible to observe the expected absorption structure in each spectrum. The expected P3HT absorption has three features at 600, 550 and 515 nm respectively [199], shown as dashed lines in figure 4.1, which are attributed to the $\pi - \pi^*$ transition [228]. The peaks at 550 and 600 nm are vibronic bands associated with the crystallinity of the P3HT [229]. The contribution of PCBM is a distinct peak at 335nm [230], also shown by a dashed line in figure 4.1.



Figure 4.1: UV-Vis spectra of two active layer films after deposition and drying, showing the expected features at 335, 515, 550 and 600 nm. Sample a) was then stored in the dark while sample b) was stored under illumination.

The spectra shown in figure 4.1 contain the expected features for each material [199]. The PCBM peak at 335 nm and the P3HT peak at 515 nm exhibit strong agreement for each of the active layer materials. The features expected at 550 nm and 600 nm are not particularly distinct from the main peak at 515 nm. However, these observations are in accordance with expectations and the intensity of these peaks is known to be a function of the crystallinity of the polymer [199].

Ambient Conditions

The films were stored under ambient conditions and UV-Vis measurements were performed for each film repeatedly at 24-hour intervals over 36 days. The change in UV-Vis absorption over 36 days for the films is shown in figure 4.2.

Sample a), shown in figure 4.2a, exhibited a slight decrease in the overall inten-

sity over the course of the experiment. The intensity of the main peak at 515 nm decreased to 93% of the initial value for sample a). This slight decrease is likely due to the small amount of time that the substrates were exposed to illumination over the testing period causing very slight photo-degradation. The substrates were exposed to incidental light when they were transported from storage to the spectrophotometer and when they were tested.

The film that was kept under illumination, sample b), showed a continuous decrease in overall absorption as shown in figures 4.2b. However, looking at the change in shape with time also provides valuable information about material degradation. There is a slight shift in the peak absorption towards shorter wavelengths suggesting a reduction in the conjugation length of the polymer, leading to photobleaching of the polymer [225].

The intensity of the main P3HT peak reflects the degree of interchain order in the polymer [90]. Consequently, the decreases in peak intensity indicate a loss of order in the domains of P3HT due to photo-oxidation [231].

Interestingly, there is almost complete degradation in the PCBM peak at 335 nm, which suggests that as the film degrades the nature of the PCBM in the layer changes [232]. As the film is illuminated, PCBM may diffuse out of the polymer matrix and aggregate into larger clusters which would account for the decreased UV-Vis intensity [233].

After 27 days of storage there is a visible difference in samples a) and b), as shown in figure 4.3. Sample b) has a significantly lighter colour than sample a), which corresponds with the UV-Vis absorption decreasing by almost 50%. After 36 days, sample b) still showed some slight absorption features, however the absorption had reduced to 30% of the initial value.

These results show that the combination of ambient conditions and illumination cause a decrease in absorption. Loss of absorption would lead to a loss in current generation and an overall decrease in device performance.

Inert Environment

Active layer films were also stored in a nitrogen environment inside of a Pure Lab He GP-1 glovebox, with an oxygen level of less than 50ppm and a moisture



Figure 4.2: Evolution of UV-Vis spectra for active layers films kept in ambient conditions, showing the significant change in absorption of films kept under illumination while the absorption of the film stored in the dark was relatively stable.

level of less than 5ppm. One film was stored in the dark, designated sample c), and one film was stored under illumination, designated sample d). The UV-Vis spec-

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Figure 4.3: Films stored (a) in the dark and (b) under illumination for 27 days show a significant difference in colouration. The film stored under illumination has undergone substantial photo-bleaching.

trum was measured daily over 37 days. The UV-Vis spectra are shown in figure 4.4.

Sample c) showed a 5% decrease in the absorption at the main P3HT peak and a 10% decrease in intensity in the PCBM peak. These results suggest that PCBM may be diffusing out of the polymer matrix, resulting in lower PCBM absorption throughout the film.

Comparing these results to those in figure 4.2 shows a significant difference in the change in absorption caused by the storage environment. Sample d) experienced less than a 10% decrease in absorption, which suggest that photo-degradation still occurs at a much slower rate in a low oxygen/water environment. UV-Vis measurements were performed under ambient conditions, meaning that devices were exposed to oxygen for the duration of the measurements. This brief exposure to ambient conditions, followed by storage under illumination, may be the cause of the small amount of photo-degradation observed for sample d).

The combination of illumination and exposure to ambient conditions can have a significant impact on the absorption of the active layer. Similar behaviour has been observed for both P3HT and P3HT:PCBM blend films [141,142]. Devices kept in inert conditions or in the dark under ambient conditions were significantly more stable, experiencing less than 10% loss in absorption over 36 days which was attributed to slight morphological changes. These results show that both illumination and an oxidative environment are required for substantial degradation of the



Figure 4.4: Evolution of UV-Vis spectra for active layers films stored in a nitrogen environment, showing the absorption of these films was relatively stable. Comparing this with figure 4.2 suggests that the combination of illumination and ambient conditions causes loss of absorption.

active layer to occur.

4.1.2 Nanoparticle Films

Four NP films were prepared using the methods described in section 2.2.1. Samples a) and b) were P3HT:PCBM films and samples c) and d) were P3HT:ICxA films. The initial UV-Vis spectra of the nanoparticle films are shown in figure 4.5. The expected features for P3HT and PCBM are all clearly visible. The absorption features that would be expected from ICxA occurs below 300 nm and therefore was not observed [106]. The difference in initial spectra between the films containing PCBM and those containing ICxA is likely due to slight differences in the concentrations of the two NP solutions and the relative extinction coefficients of the fullerene materials.



Figure 4.5: UV-Vis spectra of the four active layer films with two types of nanoparticles after deposition and drying. Samples a) and b) are P3HT:PCBM nanoparticles and samples c) and d) are P3HT:ICxA nanoparticles.

Ambient Environment

After the initial UV-Vis measurements were performed; one P3HT:PCBM film, sample a), and one P3HT:ICxA film, sample c), were kept in the dark under ambient conditions. Another P3HT:PCBM film, designated sample b), and P3HT:ICxA film, designated sample d), were placed under a lamp in ambient conditions. The UV-

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Vis spectra of each of the four films was measured repeatedly over different lengths of time, 21 days for samples a) and c) and 9 days for samples b) and d). The change in UV-Vis for films kept under the ambient environment are shown in figures 4.6 and 4.7.

As with the BHJ films, the NP films that were kept in the dark under ambient conditions showed significantly greater stability than devices that were illuminated. The results in figure 4.6 show only slight change over the 21 days, there is a decrease of less than 10% in the intensity of the PCBM peak. For the P3HT:ICxA film, shown in figure 4.6c, there is also a 10% increase in the absorption at 550 nm.

The effect of exposure to illumination under ambient conditions on the absorption, shown in figure 4.7, is significant. After 3 days, there is a 15% decrease in the intensity of the main peak at 550 nm. After only 9 days, the spectra lost most of the defining peaks. These results indicate that, like the BHJ films (see section 4.1), the combination of oxygen and illumination significantly reduces the absorption of the active layer. However, the change in absorption of the nanoparticle films occurs over a much shorter time frame than the BHJ films, which took over 36 days to reach a similar level of degradation (see figure 4.2). The more rapid loss of absorption of NP films may be related to the speculated higher water content of the nanoparticulate active layer initiating degradation [120].

Inert Environment

In this series of experiments, active layer films were stored in a nitrogen environment inside a glovebox, as described in section 4.1.1. A film of each type of nanoparticle blend was stored either in the dark or under illumination and the UV-Vis spectrum was measured daily over 36 days. The results of this experiment are presented in figures 4.8 and 4.9.

There was no significant decrease in absorption of the films that were stored in the dark over 36 days, as shown in figure 4.8. Both films exhibited an intensity variation in the main P3HT peak of less than 5% over the 36 days.

The films that were stored under illumination over 36 days, shown in figure 4.9, both exhibited slight decreases in absorption. The film containing PCBM experienced a decrease of approximately 10% in the main peak at 550nm. The film con-



Figure 4.6: Evolution of UV-Vis spectra for active layer films with two types of nanoparticles kept in the dark, under ambient conditions, over 21 days. The absorption of each film remained stable.

taining ICxA exhibited a decrease of approximately 12% in absorption at 550nm. These slight decreases in the optical absorption may be caused by the effect of il-

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Figure 4.7: Evolution of UV-Vis spectra for active layer films with two types of nanoparticles kept under illumination, in ambient conditions, over 9 days. A significant loss of absorption was observed for both films.

lumination, however, it is also possible that the NP films kept under illumination were more sensitive to ambient exposure when UV-Vis measurements were performed due to the higher water content in the films when compared with the BHJ



Figure 4.8: Evolution of UV-Vis spectra for active layer films with two types of nanoparticles kept in a dark, inert environment for 36 days, showing that the absorption was stable.

films. It was observed that the decrease in absorption for these films was significantly slower than that observed in figure 4.7. These observations indicate that the degradation in the optical absorption of the active layer films (both BHJ and NP) is



Figure 4.9: Evolution of UV-Vis spectra for active layer films with two types of nanoparticles kept under illumination, in an inert environment, for 36 days, showing a slight decrease in absorption.

caused by the combination of oxygen/water and illumination. These results agree with investigations presented for different material systems ([143,150,227]), which

show that the combination of oxygen and illumination cause rapid photodegradation.

4.2 Lifetime Measurements of Devices with Different Active Layers

The first degradation study that was performed on the new degradation testing system reproduced the constant illumination measurements presented in section 3.2.2. The devices types that are presented in this chapter are defined as either standard or inverted, depending on the polarity, and BHJ or NP, depending on the active layer. Thus, the four devices are described as standard BHJ, standard NP, inverted BHJ and inverted NP.

Five substrates of each type, with six cells each, were tested simultaneously. For each device type, five devices were made using the procedures outlined in section 2.2. Subsequently, these devices were tested using the procedure outlined in section 2.3.1. Finally, four representative devices were selected from the five and placed on the degradation apparatus. The devices were set to be tested every 15 minutes and left until the devices all showed negligible photovoltaic activity. The average IV characteristics of each device type are presented in table 4.1.

	Eff. (%):	V _{OC} (V) :	I _{SC} (mA):	FF (%):
Standard BHJ	2.10 (±0.09)	0.577 (±0.042)	7.41 (±0.23)	0.492 (±0.020)
Inverted BHJ	1.83 (±0.09)	0.493 (±0.012)	7.88 (±0.19)	0.470 (±0.051)
Standard NP	0.41 (±0.14)	0.401 (±0.031)	3.07 (±0.43)	0.331 (±0.013)
Inverted NP	0.52 (±0.11)	0.516 (±0.045)	3.45 (±0.38)	0.290 (±0.017)

Table 4.1: Average initial IV characteristics (with standard deviations) of devices selected for degradation measurements.

The results of degradation measurements on each of the device types are presented in figures 4.10, 4.11, 4.12 and 4.13. The normalised value of the key cell parameters (PCE, V_{OC} , I_{SC} , FF) are displayed as a function of time, normalised to the starting value. The PCE is the most important parameter since it directly de-

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scribes overall device efficiency. PCE is often directly the result of I_{SC} and the trends for these two parameters generally correlate well. The shape of these curves will be different depending on whether burn-in or long-term degradation mechanisms dominate in the device. The curves presented are an average of a minimum of 15 cells along with the error bound (shaded area).

4.2.1 Standard Bulk Heterojunction

The average degradation of the standard BHJ devices are shown in figure 4.10 over 220 hours. The drop in PCE is driven almost entirely by a drop in the I_{SC} of the device, with a smaller decrease in FF.



Figure 4.10: Average change in characteristics for standard BHJ devices kept under constant illumination for 220 hours.

A decrease in I_{SC} is generally attributed to the changes in the active layer; such as loss of polymer conjugation, decrease in donor/acceptor interfaces and a loss of percolating paths hindering charge transport [80]. The small decrease in FF indicates that there was a slight deterioration of charge extraction at an interface [222]. The aluminium electrode in this structure readily oxidises under ambient conditions [124]. Consequently, charge transport at the active layer/electrode interface may be restricted causing a drop in FF [222].

4.2.2 Standard Nanoparticle

The average change in the characteristics of the standard NP devices over 60 hours are shown in figure 4.11. In-depth degradation studies, as presented here, have yet to be reported on in literature. The degradation of this structure is driven entirely by degradation of the I_{SC} . The FF remains more constant than was observed with the BHJ devices. A possible explanation for this difference is that the factors causing the NP device to degrade happen on a much shorter time scale, so longer time-scale degradation effects are not observed. In 60 hours, the FF of the BHJ device still maintained over 85% of the initial value. It is possible that the I_{SC} of the NP device degraded too rapidly to observe the phenomenon responsible for the FF degradation. However, it is also possible that the observed decrease in FF is related to the BHJ active layer.



Figure 4.11: Average change in characteristics for standard nanoparticle devices kept under constant illumination over 45 hours.

The standard NP devices degraded much more rapidly than the corresponding BHJ devices, either suggesting additional degradation mechanisms are occurring or the degradation processes are accelerated in the NP active layer. Residual water in the active layer may degrade the interfaces [234], as water is known to be a

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significant source of degradation [73, 120]. SDS has also been observed to degrade under illumination [235], however it is not yet known what effect SDS degradation would have on device performance. Results of more thorough investigation of the degradation of NP devices are presented in chapter 6.

4.2.3 Inverted Bulk Heterojunction

The degradation in characteristics for the inverted BHJ devices are shown in figure 4.12 over 150 hours. Unlike the standard architecture devices, the degradation in the inverted BHJ device was caused by significant decreases in both I_{SC} and V_{OC} , with a smaller decrease in FF. The degradation of all the characteristics indicates that multiple degradation pathways occur in these devices. This structure also exhibits a significant burn-in period, characterised by rapid decreases in I_{SC} and FF in the first three hours of the experiment, which in turn cause the normalised PCE to decrease to 65% of the initial value.



Figure 4.12: Average change in characteristics for inverted BHJ devices kept under constant illumination for 150 hours.

As mentioned in section 4.2.1, a decrease in I_{SC} suggests degradation in the active layer [222]. A decrease in V_{OC} is generally indicative of electrode or active layer/electrode interface degradation [236]. A drop in V_{OC} has been observed repeatedly in devices containing a MoO_3 /silver electrode [146,216], in each case this drop in V_{OC} was attributed to changes in the work-function at the interface.

Rapid degradation of this structure under constant illumination was also observed in the preliminary degradation measurements (see chapter 3). The devices tested here degraded more slowly than those presented in chapter 3. The results in section 3.2.2 were the average of cells on a single device, while these results are the average of cells from 4 devices, making the measurements statistically more reliable. Despite the differences, these results further confirm that photo-active degradation is a dominant process for the inverted architecture.

4.2.4 Inverted Nanoparticle

The degradation of the inverted NP devices occurred over a very short period. Figure 4.13 shows that the performance dropped below 50% of its initial value within 2 hours of the test commencing. The performance continued to decrease rapidly, with devices showing negligible activity after 16 hours.



Figure 4.13: Average change in characteristics for inverted nanoparticle devices over 18 hours under constant illumination.

The rapid decrease in PCE was driven by I_{SC} and V_{OC} , which both decreased below 40% in 16 hours. The degradation of these devices was similar to that of the

inverted BHJ devices, however over a much shorter period. These results again suggest that either additional degradation mechanisms are operating or that the degradation processes are accelerated by the NP active layer. Given that the water content in the NP devices is likely to be higher than BHJ devices, more rapid degradation is not surprising since water and oxygen in devices has been observed to lead to some of the most significant degradation mechanisms. Diffusion of water within devices has been observed to lead to oxidation of the aluminium electrode in the standard architecture [73,79], changes in conductivity of the electrodes [133] and changes in the electronic structure and morphology of the active layer [237].

4.2.5 Comparison

The change in normalised PCE for each of the device types is shown in figure 4.14. Overall, the results of the degradation measurements confirmed that the inverted architecture was less stable than the standard structure under constant illumination conditions. This observation held for both BHJ and NP active layers and agrees with results presented in section 3.2 for devices of the same structures.



Figure 4.14: Change in efficiency over 200 hours for each device architecture. For both active layers, the inverted architecture was less stable than the standard architecture.

The difference in degradation behaviour between the standard and inverted ar-

chitectures appears to be the length and severity of the initial burn-in. The key mechanism in the burn-in are changes in the active layer, including photo-dimerisation of PCBM and increased disorder in the polymer [118]. This degradation has also been associated with impurities in the polymers [184], differences in poly-dispersity and oxygen trapped in the films [186]. These factors reduce charge generation and transport in the active layer, reducing I_{SC} [238].

The degradation occurs approximately four times faster for the NP devices than the corresponding BHJ architecture. This increased rate may be due to the presence of water and SDS in the active layer. Each of these materials could be acting as impurities and sites for degradation to initiate [239].

It has been stated that the burn-in is related to the active layer and is independent of electrode used [184]. However, the rate of degradation in the burn-in was approximately 3 times faster for the inverted architecture than the standard architecture, suggesting another process must be occurring in the inverted architecture. It has been observed that devices that contain ZnO experience a rapid loss of V_{OC} in the first hours of illumination [185]. The loss of V_{OC} was explained by the formation of shunts in the ZnO layer. These observations agree with the degradation of the inverted architectures, which experience loss in V_{OC} initially regardless of active layer. The loss of V_{OC} may also be related to the MoO₃/silver electrode, which may be caused by diffusion of silver into the MoO₃ altering the work-function [216].

In order to obtain information about the long-term degradation, each curve was fitted with a one term exponential after the rate stabilised. The change in I_{SC} was plotted on a log-linear scale along with the fit for each device type, shown in figure 4.15.

The fit for the long-term degradation appears to be dependent only on the active layer used. Both architectures with a BHJ active layer show very similar longterm degradation, as do both architectures with a NP active layer. To quantify this observation, the degradation time constant for each structure is shown in table 4.2.

For each active layer, the time constants for standard and inverted are within 95% confidence intervals of each other. Similar trends were observed in results presented in section 3.2.3 for the NP active layer, although the time constants were slightly lower. These results suggest that the degradation processes that dictate the



Figure 4.15: Change in current over 200 hours for each device architecture, with exponentials fitted to long-term degradation behaviour showing similar rates from both active layer types.

Architecture	Active Layer	$\lambda \left(h^{-1} ight)$
Standard	BHJ	0.011
Inverted	BHJ	0.012
Standard	NP	0.044
Inverted	NP	0.049

Table 4.2: Degradation time constants, λ , for each structure based on $I/I_0 = Ae^{-\lambda t}$.

long-term degradation behaviour are independent of buffer and electrode materials, and are only dependent on the active layer. Moreover, the NP devices degrade approximately 4 times faster than the corresponding BHJ devices. Again, this rapid degradation must be due to the presence of water and SDS in the active layer.

4.3 Light Beam Induced Current Mapping

LBIC mapping was used to further investigate the degradation of these structures. The LBIC measurement process is described in section 2.5. LBIC measurements were performed at Commonwealth Scientific and Industrial Research Organisation (CSIRO) by Dr Krishna Feron.

Given that the degradation in PCE was driven most strongly by J_{SC} in every case, LBIC was a powerful tool for determining the nature of the current loss in each structure. Devices were made using the methods described in section 2.2, LBIC measurements were then performed on pristine devices and devices that were subjected to ambient conditions for 12 hours (degraded). Blue light (405 nm, a wavelength where the absorption is shared between the polymer and fullerene [230]) from a laser source was used and measurements were performed with a resolution of 0.04mm.

The LBIC maps for pristine and degraded standard BHJ devices are shown in figure 4.16. The LBIC map of the pristine device shows variations in current generation over the active area. There are three significant dark spots in the current generation in figure 5.1a, which are likely related to defects in the active layer. The degraded device shows that much of the degradation in current is located around the defects that were observable in the pristine device. Each of the dark spots observed in the pristine device increase in area by approximately three times, the active area of the device is also smaller indicating that edge effects are significant. These results suggest that the degradation in these devices is localised and originates at defect sites, which has previously been observed for devices containing PEDOT:PSS [77].

The LBIC maps for the standard NP device are shown in figure 4.17. The pristine device exhibited relatively uniform current generation, with some minor defects. As with the standard BHJ device, the degraded device shows a significant number of dark spots where no current is being generated. Similar degradation was observed in figure 4.16, with the formation of significant areas where current was not generated, suggesting that this degradation is related to the standard architecture rather than the active layer. Diffusion of atmospheric contaminants through pinholes in the aluminium electrode has been identified as a source of degradation in standard devices [240], which would explain the localised degradation observed here. The degradation observed here is more significant than observed in figure 4.16. This observation agrees with previous results (see section 4.2), that the NP devices are less stable than the BHJ devices.









Figure 4.16: LBIC maps of pristine and degraded standard BHJ devices, indicating that the reduction of performance for this structure is caused by pinhole degradation.

The LBIC maps for the inverted BHJ device are shown in figure 4.18. The LBIC map of the pristine device shows uniform current generation over the entire active area. The degraded map also shows uniform current generation, with no significant dark spots. The maximum current generated over the active area decreases by almost one third, which would cause a significant decrease in performance. This observation suggests that the loss of current is not dominated by degradation at




⁽b) Degraded.

Figure 4.17: LBIC maps of pristine and degraded standard NP devices. As with the standard BHJ devices, the performance decrease appears to be due to pinhole degradation.

pinholes or defects, as was the case for the standard devices.

The LBIC map for the pristine inverted NP device is shown in figure 4.19. This map shows variations in current generation, which may be due to the device beginning to degrade. The rapid degradation of the device meant that it was not possible to perform a degraded LBIC map as the device was no longer generating current. The experiment was repeated for devices that were degraded for as little









Figure 4.18: LBIC maps of pristine and degraded inverted BHJ devices, showing a uniform decrease in current generation over the entire active area.

as three hours, however it was not possible to obtain a meaningful LBIC map. It is also likely that the "pristine" device had undergone some degradation before the map (shown in figure 4.19) was taken. As a result, it is not possible to draw meaningful conclusions about the nature of the current loss for this structure. However, rapid degradation to zero current generation for inverted NP devices agrees with lifetime measurements presented in section 4.2.



Figure 4.19: LBIC maps of a pristine inverted NP device. Devices of this structure degraded too drastically to obtain a meaningful LBIC map of a degraded device.

The LBIC data suggest that the degradation is more dependent on the architecture than the active layer type in the burn-in phase of degradation. Both devices of the standard architecture degraded through localised current loss, originating at defect sites. Conversely, the inverted BHJ device experienced uniform current loss over the entire active area, suggesting different degradation mechanisms.

4.4 Conclusions

The change in absorption of the active layer was investigated using a series of UV-Vis measurements. The NP active layer was found to be less stable than the BHJ when exposed to ambient conditions and illumination, indicating that the NP active layer is much more susceptible to photo-bleaching than the BHJ. However, the absorption of the NP active layer was stable when stored in the dark or in an inert environment, indicating this active layer is not intrinsically less stable than the BHJ active layer. For both BHJ and NP films, the decrease in absorption occurred over a much longer timescale than the decrease in I_{SC} typically seen in such devices. These results suggest that the decrease in absorption of the active layer is not the dominant process driving current loss in these devices.

The constant illumination experiments in section 3.2.2 were reproduced with a larger number of sample devices. Furthermore, similar trends were observed;

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inverted devices were, again, less stable than standard devices with both BHJ and NP active layers. However, the inverted BHJ devices were observed to be more stable than measured in section 3.2.2, while standard NP devices were observed to be less stable.

Rapid degradation was again observed for inverted devices under constant illumination, confirming the conclusion in chapter 3 that photo-active degradation mechanisms are dominant for this structure. In order to better understand degradation under different lighting conditions, another test was designed involving a wider range of illumination conditions. These experiments are presented in chapters 5 and 6.

Using modelling it was possible to identify that long-term degradation profiles seen in this chapter are primarily dependent on the active layer used. After the initial burn-in, devices with a BHJ active layer exhibited the same degradation rate regardless of architecture. Devices with a NP active layer also exhibited the same degradation in both structures. These observations are consistent with long-term processes being related to the active layer.

LBIC measurements were performed on pristine and degraded devices of the four structures, to probe the nature of current loss as devices degrade. Devices of the standard architecture exhibited localised, but significant, current loss originating at defect sites in the active layer, while current loss in the inverted BHJ device was uniform over the entire active area, suggesting different degradation mechanisms within each architecture. These results suggest that the architecture, and not the active layer, is the dominant factor for short-term current loss. The conclusion is that, for the systems studied, burn-in is a function of device architecture, while long-term degradation is a function of the active layer.

Chapter 5

Effect of Materials on Degradation of Organic Photovoltaics

The degradation results presented in chapters 3 and 4 showed that the stability of OPVs was significantly affected by the lighting conditions. Under constant illumination, the inverted structure devices were repeatedly shown to be less stable than standard devices. Conversely, under intermittent lighting (or shelf-life) inverted devices were significantly more stable. Several recent papers point to the interfacial layers as being the cause of more rapid degradation of these devices under illumination [217,236]. However, there is not a consensus on which layer is the origin of this photoactive degradation. The purpose of this work was to elucidate if one layer was the cause or if it was caused by compound degradation of several layers.

The degradation testing apparatus (developed in chapter 3) was used to compare a range of standard and inverted device structures under constant and intermittent illumination directly. To identify the cause of the accelerated degradation under constant illumination, filters and LEDs were used to modify the spectrum of the lamps by removing or adding light in the UV range. Degradation measurements were then performed and compared with the unmodified light.

Degradation measurements were performed on standard and inverted devices with several material systems. For standard devices, two typical HSL materials, two ESL materials and two electrodes were employed to make eight different device structures. The inverted structures were limited by processing techniques and

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thus only two inverted structures were employed with two electrode materials, see tables 5.1 and 5.2.

This chapter shows that the degradation behaviour under different lighting conditions is dependent on the buffer materials used. The effect of UV-light on devices was also found to be determined primarily by whether the structure contained ZnO. Structures containing ZnO experienced rapid degradation in the absence of UV-illumination. Further experiments indicated that this degradation was almost entirely reversible and likely related to electronic changes in the ZnO ESL.

5.1 Lighting Conditions

To investigate the effect of lighting conditions on the degradation of OPVs, further degradation experiments under a range of illumination conditions were undertaken. These degradation measurements involved testing the different structures, listed in tables 5.1 and 5.2, under one of four lighting conditions. Most devices were made using the methods that were outlined in sections 2.2.1 and 2.2.2. For the other structures, the production is described in section 5.2. The devices were characterised under an AM 1.5 lamp and the eight best devices were selected, two of each structure were then tested under each of the four lighting conditions. The IV characteristics of the devices were measured every 30 minutes over several days. All lighting experiments for a given structure were performed simultaneously to reduce the effect of outside factors.

The lighting conditions that were used were constant illumination, intermittent illumination, UV-filtered illumination and additional UV illumination. Both UV-filtered and additional UV illumination were under constant illumination conditions where the spectrum of the lamp was altered. The spectrum of the lamp, unfiltered, with the filter and with the UV LED, was measured; these spectra are shown in figure 5.1.

The filter that was used as part of this investigation was a GG455 coloured glass filter, which filters out light below 455 nm as well as causing a slight (less than 10%) decrease in intensity of the whole spectrum. It was important to quantify the difference in intensity and spectral profile caused by the filters. Since, the highenergy light in the UV end of the spectrum is thought to initiate several degradation mechanisms [142]. For this reason, it was expected that devices tested under this filtered light would degrade more slowly than devices tested under the unfiltered light.

The LED that was used to supplement the UV-light intensity was a Bivar Tight Tolerance Ultraviolet LED with a peak wavelength of 390 nm and a viewing angle of 30°. The LED was wired in series with a 120 Ω resistor to regulate the current and a 5V supply. The circuit was set up on a small piece of prototyping board so that it could be inserted into the top of a testing tube with minimal intrusion. The spectrum of the light with additional UV is also shown in figure 5.1. Although the change in spectrum was minimal (approximately 1%) due to the low wattage, the LED had a significant effect on device degradation (see section 5.3).

The effect of modifying the illumination spectrum for each device structure are outlined in the following sections. Degradation results presented in the following sections are average values from a minimum of 10 cells, the shaded area represents the standard deviation in the data at each point.



Figure 5.1: Spectrum of the 50W globe that was used. The lamp was used with no modification, through a UV filter and in conjunction with a UV LED.

5.2 Device Structures

To gain a more thorough understanding of degradation, ten functional OPV structures were investigated. The standard structures, as shown in table 5.1, were

investigated and the results of degradation measurements are outlined in the following sections. The structures were chosen to provide every electronically viable combination of ESL, HSL and electrode in order to gain a better understanding of the degradation of each material. For this study P3HT:PCBM was used as the active layer through out to reduce additional degradation variations and simplify the results.

Table 5.1: The standard structures selected for investigation.

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Anode	ITO							
H.S.L.	PEDOT:PSS	PEDOT:PSS	PEDOT:PSS	PEDOT:PSS	MoO_3	MoO_3	MoO_3	MoO_3
A.L.	P3HT:PCBM							
E.S.L.	Ca	Ca	ZnO	ZnO	Ca	Ca	ZnO	ZnO
Cathode	Al	Ag	Al	Ag	Al	Ag	Al	Ag

The inverted structures that were investigated are shown in table 5.2. The possible inverted structures were limited due to processing problems of depositing the water-based PEDOT:PSS layer on top of the hydrophobic active layer (outlined in section 2.2.2). Calcium was also unsuitable due to the instability of the material in the presence of water and oxygen [241]. The conductivity of thin films of calcium is known to decrease rapidly in the presence of small amounts of water and oxygen [242], making it unsuitable as a buffer layer without an evaporated layer on top [243].

Table 5.2: The inverted structures selected for investigation.

	(i)	(j)
Anode	Al	Ag
H.S.L.	MoO_3	MoO_3
A.L.	P3HT:PCBM	P3HT:PCBM
E.S.L.	ZnO	ZnO
Cathode	ITO	ITO

All of the layers were deposited and dried in the way described in section 2.2,

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with the exception of the ZnO which was dried for 5 minutes at 100°C to minimise the effect of heat on the active layer.

5.2.1 IV Characteristics

The average IV characteristics of 10 cells of each structure are shown in table 5.3, along with the standard deviations. There was a range in performance observed due to the difference in electrical coherence of the various material systems, issues in processing and device fabrication and the inherent effects of the materials on charge generation, transport and collection within the devices.

Table 5.3: Initial IV Characteristics of devices of each structure in tables 5.1 and 5.2.

Structure	Eff. (%)	\mathbf{V}_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)
Standard				
(a)	2.55 (±0.14)	0.546 (±0.003)	7.64 (±0.26)	61.3 (±3.1)
(b)	0.98 (±0.18)	0.500 (±0.015)	4.76 (±0.82)	40.5 (±3.2)
(c)	1.95 (±0.15)	0.519 (±0.003)	8.22 (±0.52)	45.7 (±2.6)
(d)	1.31 (±0.14)	0.511 (±0.011)	6.51 (±0.50)	39.5 (±3.4)
(e)	1.86 (±0.20)	0.571 (±0.015)	5.88 (±0.80)	55.9 (±4.1)
(f)	1.00 (±0.05)	0.529 (±0.030)	4.02 (±0.26)	47.2 (±1.7)
(g)	1.46 (±0.23)	0.550 (±0.003)	6.92 (±0.79)	38.5 (±4.1)
(h)	1.16 (±0.04)	0.513 (±0.005)	4.21 (±0.19)	53.8 (±1.8)
Inverted				
(i)	0.40 (±0.06)	0.207 (±0.014)	4.48 (±0.42)	42.8 (±1.4)
(j)	2.42 (±0.20)	0.551 (±0.002)	6.50 (±0.60)	67.7 (±1.5)

Some of the device structures (those presented in sections 5.3.6, 5.3.8 and 5.3.10) exhibited significant decreases in performance after annealing. Consequently, for this study, none of the devices were annealed before degradation testing to avoid influencing the degradation results, given that relative degradation of materials

was the focus of this investigation.

5.3 Degradation Measurements

The device parameter decay curves for each structure are presented in the remainder of this chapter. All characteristics (PCE, I_{SC} , V_{OC} and FF) quoted for the remainder of this chapter are a value normalised to 100% at the start of the degradation measurements, from table 5.3. Additionally, all structures investigated contained a P3HT:PCBM active layer and an ITO electrode, but employed different combinations of HSL, ESL and electrode. Ideally, degradation measurements were performed until negligible photovoltaic activity was observed. However, in several cases the experiments were stopped early due to unforeseen issues with equipment.

Tables 5.4 and 5.5 show the T_{80} and T_{50} of each structure under each lighting condition. The T_{80} and T_{50} represent the time taken for devices to reach 80% and 50% of the parameter initial value, in this case PCE. As expected, the lighting used had a significant effect on the degradation of most structures. Grossiord *et al.* identified light as one of the major triggers for extrinsic degradation in OPVs [80].

It is also possible to identify trends using T_{80} and T_{50} . The general trends that can be observed are that inverted architectures are more stable under intermittent illumination and structures that contain ZnO require some UV-light to maintain performance. The decay curves for each structure under the four lighting conditions are presented in the following sections and are discussed in detail in the following sections.

5.3.1 PEDOT:PSS, Calcium and Aluminium

The first structure investigated was the standard structure presented in chapters 3 and 4. The decay curves are shown in figure 5.2. As the data presented in table 5.4 indicated, very different degradation behaviour is observed under different lighting conditions.

Under each illumination condition the decrease in PCE is initially driven completely by a decrease in I_{SC} . This decrease in I_{SC} may be related to chemical degradation in the active layer or at the electrode interface [80]. However, constant illumination and the experiment with additional UV also exhibit a decrease in the

	Al				Ag				
	PEDC	T:PSS	Mo	D ₃	PEDC	T:PSS	Мо	O ₃	
Lighting	ZnO	Ca	ZnO	Ca	ZnO	Ca	ZnO	Ca	Time
Intermittent	73	19.5	8.5	48	1	1.5	3.5	6.5	
UV Filter	4	38	0.25	3	0.5	1	< 0.5	0.5	T ₈₀
Constant	3	4	2	2	4	< 0.5	29	1.5	
UV LED	40	1	2	2	4	1	90	< 0.5	
Intermittent	123.5	113	25.5	83	4	5.5	13.5	15	
UV Filter	23	>120	10	10	1	5	2	2.5	T ₅₀
Constant	40	41	13	6	48	3	400	3.5	
UV LED	>150	6	17	7	40	5	>460	0.5	

Table 5.4: Time (in hours) for PCE to decrease to 80% (T₈₀) and 50% (T₅₀) of the initial value for each standard structure in table 5.1, under each lighting condition.

Lighting	Al	Ag	Time	
Intermittent	262	151		
UV Filter	1.5	< 0.5	T ₈₀	
Constant	4	2.5		
UV LED	6	1.5		
Intermittent	>262	>163		
UV Filter	5	1	T ₅₀	
Constant	10	13		
UV LED	15	5		

Table 5.5: Time (in hours) for PCE to decrease to 80% (T₈₀) and 50% (T₅₀) of the initial value for the two inverted structures in table 5.2, under each lighting condition.

FF. Reductions in FF are caused by any processes which hinder charge transport through an interface, such as oxidation of the aluminium electrode or degradation of the active layer/electrode interface [134].

Devices exposed to unmodified light degraded to less than 15% PCE after 215 hours. This decrease in PCE was driven most strongly by I_{SC} with an accompanied, slower decrease in FF to approximately 70%. The decrease in I_{SC} is likely related to processes causing a decrease of absorption in the active layer (as observed in section 4.1.1), loss of conjugation in the P3HT, radical-induced cross-linking or chain scission in the P3HT and migration of the fullerene out of the polymer into large aggregates have all be observed to reduce the absorption and charge generation [141, 150, 244]. Additionally, the decrease in FF is likely related to oxidation of the aluminium electrode blocking charge transport [72].

The effect of increased UV on this structure was also significant. There is a steep degradation in I_{SC} , which drops below 20% in the first 60 hours, resulting in a rapid degradation of the PCE. The V_{OC} remains constant and there does not



Figure 5.2: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with PEDOT:PSS, calcium and aluminium that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, for 200 hours.

appear to be a consistent trend in the degradation of the FF, although, there is a decrease in FF in the first 20 hours of the experiment before the results became noisy due to decreased performance. The reduced stability of this structure under additional UV-light was expected as UV-light has been observed to accelerate several degradation processes [141,224,245], including oxidation of the active layer which can cause the observed decrease in I_{SC} .

Under intermittent illumination, devices showed a slower rate of degradation, which was driven entirely by I_{SC} . The devices tested under filtered light also exhibited a stable FF. These observations indicate that the process causing the decrease in FF is photo-activated by UV-light, such as degradation of the active layer/electrode

interface hindering charge transport [80].

Significantly slower degradation was observed when the UV filter was used. The I_{SC} of devices under unmodified light decreased below 40% in 120 hours while the device under filtered light remained above 70% over the same period. This observation suggests that the dominant degradation processes occurring in this structure are accelerated by UV-light. Photo-bleaching is known to be accelerated in P3HT and P3HT:PCBM blend films by UV-light [142]. Consequently, the decrease in I_{SC} exhibited by devices under intermittent and filtered illumination is likely due to a slower rate of photo-bleaching [245].

5.3.2 PEDOT:PSS, Calcium and Silver

The next structure investigated replaced the aluminium electrode with silver. As outlined in section 1.6, aluminium has been identified as a cause or factor in many degradation processes. Silver has been observed to protect against water and oxygen as it has smaller grain boundaries than aluminium [246]. However, as shown in figure 5.3, these devices were significantly less stable than the aluminium devices shown in figure 5.2, dropping below 10% PCE after less than 20 hours.

This rapid degradation is driven almost entirely by a decrease in I_{SC} and is presumably related to the calcium/silver interface as it was not seen for the calcium/aluminium case in figure 5.2. After 15 hours, a decrease in V_{OC} is observed, however by this time, the devices were already showing minimal photovoltaic activity. Interestingly, it was not possible to observe any difference in degradation rate under different lighting conditions suggesting that total incident photons and UV-light do not affect the dominant degradation process. This structure has been previously investigated with different active layer materials, PTB1¹ and PCBM [247]. Rapid degradation was observed for all devices tested under ambient conditions, which was attributed to the reactivity of calcium with water. Clearly, the calcium cannot be the whole reason for the rapid degradation since a much-reduced degradation rate was observed for the analogous device with an aluminium electrode. This degradation may be related to penetration of silver into the active

¹poly[[4,8-bis (octyloxy) benzo [1,2-b:4,5-b] dithiophene-2,6-diyl] [2-[(dodecyloxy) carbonyl] thieno[3,4-b] thiophenediyl]]

layer, hindering hole injection into the HOMO of P3HT [146]. Furthermore, these results suggest that the calcium is not acting as an effective interlayer in this structure.



Figure 5.3: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with PEDOT:PSS, calcium and silver that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, for 25 hours.

5.3.3 PEDOT:PSS, ZnO and Aluminium

The next structure investigated contained PEDOT:PSS, ZnO and an aluminium electrode. The results of this degradation study are shown in figure 5.4. For the devices tested under constant illumination, the reduction in PCE is driven most strongly by a drop in I_{SC} , with a smaller drop in FF in the first 5 hours. The similarity with trends observed in figure 5.2 suggests that the observed degradation is not

related to the ZnO interlayer. As mentioned previously, oxidation of the aluminium electrode could cause a drop in FF as observed here [72]. Furthermore, given that the devices were more stable when tested under intermittent illumination, degradation of PEDOT:PSS is unlikely as it is generally associated with water. Considering the humidity is higher under intermittent illumination, more rapid degradation would be expected if PEDOT:PSS was the cause [73, 248]. Again, photo-bleaching of the active layer could be causing a decrease in I_{SC} [141].



Figure 5.4: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with PEDOT:PSS, ZnO and aluminium that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, over 200 hours.

Under intermittent illumination there is an increase in performance up to approximately 110% PCE over the first 24 hours. The initial increase in PCE is driven

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by slight increases in FF and V_{OC} , which both remain above 100% over the 200 hours of the experiment. The conductivity of ZnO is known to increase upon exposure to UV containing light, since photo-induced doping of the ZnO layer has been observed to increase the free electron density [236]. It is possible that intermittent exposure to light slowly changes the conductivity and work-function of ZnO layer increasing V_{OC} and FF. After the initial increase, the PCE decreases are then driven entirely by the I_{SC}.

The devices tested under the UV filter exhibited the most rapid degradation. The PCE of these devices dropped below 20% after only 10 hours. The degradation is driven by a drop in I_{SC} and FF with a slight drop in V_{OC} . Contrastingly, the results for devices tested under additional UV show higher stability than devices tested under constant illumination. Devices maintained 60% PCE even after 150 hours, which is driven by the I_{SC} with a slight decrease in FF. These observations agree with a mechanism based on changes to ZnO conductivity, causing a decrease in both I_{SC} and FF.

The absence of UV-light has a significant, detrimental effect on the stability of this structure. Furthermore, the degradation of this structure shows the opposite reaction to UV-light than the structure containing PEDOT:PSS, calcium and aluminium investigated in section 5.3.1 (see figure 5.2), which demonstrates the prevalent understanding of degradation. The difference between these two structures is the ESL, indicating that the phenomenon is related to changes in the ZnO layer.

5.3.4 PEDOT:PSS, ZnO and Silver

The next structure involved replacing the aluminium electrode in the previous structure with Ag. The effect of the same set of lighting conditions on the stability of this structure are shown in figure 5.5.

There is a significant difference in the degradation of devices tested under the UV filter when compared with those tested under constant illumination. Under the UV filter there is a rapid decrease in PCE to below 10% in the first 5 hours. This degradation is driven by significant decreases in both I_{SC} and V_{OC} . Another structure with ZnO, investigated in section 5.3.3, showed similar poor stability in the absence of UV-light, however the decrease in characteristics is different. Devices



Figure 5.5: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with PEDOT:PSS, ZnO and silver that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, over 280 hours.

with aluminium showed significant degradation in FF with only a slight decrease in V_{OC} , while devices with silver exhibit a considerable decrease in V_{OC} . These observations suggest that degradation in FF and V_{OC} may be related to the electrode material. In this case, the likely cause is oxidation of the silver electrode altering the work function and lowering the V_{OC} [222].

The degradation under intermittent illumination is also rapid, decreasing below 10% PCE in 15 hours. As with the devices tested under the UV filter, the degradation is driven predominantly by I_{SC} and V_{OC} , with a smaller decrease in FF. Given the decrease in all parameters, it is likely that multiple degradation processes occur in this structure under this lighting condition [80]. As mentioned previously, oxidation of the silver electrode would cause the observed reduction in V_{OC} [222].

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Moreover, the conductivity of PEDOT:PSS has been observed to decrease under atmospheric conditions [249], which may cause the reduction in FF.

Devices tested under constant illumination and under additional UV exhibited similar and slower degradation, with a significant overlap of the error bounds for each condition. Furthermore, the degradation under both conditions is driven almost entirely by decreases in the I_{SC} , which is indicative of photodegradation in the active layer [80]. There was also a decrease in V_{OC} , to approximately 70%, over more than 200 hours. Oxidation of the silver electrode may cause this behaviour, since oxidation of silver increases the work-function from 4.3 to 5.0eV [74]. Consequently, the electrodes ability to extract electrons deteriorates [222]. The fact that both constant illumination and UV added light exhibit the slowest degradation suggest that constant UV-illumination is required to activate the ZnO layer and that the changes in the ZnO electronic state dominate the device performance.

5.3.5 MoO₃, Calcium and Aluminium

The next structure investigated was MoO_3 , calcium and aluminium. The results for all lighting conditions are shown in figure 5.6.

This structure had a relatively short lifetime under all conditions, the most stable were the devices tested under intermittent light which still degraded to below 10% PCE within 70 hours. The degradation in PCE of these devices was driven initially by a decrease in I_{SC} , after approximately 20 hours the FF also begins to decrease. Reduction of FF indicates a decrease in charge transport at one of the interfaces, which may be related to oxidation of the aluminium electrode at the active layer/electrode interface [134]. MoO₃ is also known to undergo changes in work function and optical response upon exposure to heat or UV-light [250], which may decrease the performance of devices under constant illumination.

Under the other lighting conditions, there is decrease in all parameters, which indicates multiple failure mechanisms occur in this structure. The failure is likely related to failure of both MoO₃ and calcium, both of which are reported to be unstable [146,241], as well as a slower degradation in the active layer. Due to the overlap of the error ranges for these three lighting conditions, it is not possible to say that any lighting conditions resulted in higher stability. Furthermore, the degrada-



Figure 5.6: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with MoO₃, calcium and aluminium that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, for 70 hours.

tion behaviour observed for this structure suggests that the dominant mechanisms are not accelerated by the amount of UV-light the devices were exposed to. These results are consistent with photo-oxidation of the MoO_3 layer being a significant degradation pathway in these devices

5.3.6 MoO₃, Calcium and Silver

The degradation of devices with MoO₃, calcium and silver is shown in figure 5.7. As with other devices which employed a calcium/silver electrode (results presented in section 5.3.2), the degradation is rapid and showed only slight dependence on lighting conditions.

The devices of this structure tested under intermittent illumination exhibited



Figure 5.7: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with MoO₃, calcium and silver that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, over 100 hours.

the highest stability. These devices show an increase in PCE, to almost 120%, in the first two hours of the experiment, driven by an increase in I_{SC} . Similar increases in PCE were observed for other structures (see sections 5.3.3 and 5.3.7), however these were driven by V_{OC} indicating distinct processes are occurring. After the initial increase, the degradation is driven by FF and I_{SC} . The change in FF may be related to changes in the work function of the MoO₃/active layer interface reducing hole extraction [146]. Given that this structure was most stable under intermittent illumination, it is likely that the total photon flux is a significant factor in the degradation rate.

Devices tested under additional UV showed the most rapid degradation. The PCE of these devices decrease below 10% within 6 hours. The degradation of this

structure highlights the damaging effect of UV-light on device lifetime for some structures. MoO₃ strongly absorbs UV-light and is a known photo-catalyst [251], which may explain this rapid degradation. Photo-degradation of MoO₃ has also been observed to cause rapid decreases in FF and I_{SC} [252]. However, given that devices containing MoO₃, calcium and aluminium (investigated in section 5.3.5) did not experience the same degradation, it is likely not the only process being accelerated by UV-light.

The devices tested under constant illumination and the UV filter show similar degradation in PCE. However, the change in characteristics between the two test conditions is slightly different, which indicates degradation processes are occurring at different rates and may be different processes.

5.3.7 MoO₃, ZnO and Aluminium

The next structure investigated was MoO_3 , ZnO and aluminium. The degradation results for this structure under each lighting condition are shown in figure 5.8.

Under intermittent illumination there was an increase, in the first 20 hours of the experiment, to above 120% PCE. The increase is most strongly driven by V_{OC} and to a lesser extent FF. Similar results were observed in section 5.3.3 for devices containing PEDOT:PSS, ZnO and aluminium. These results suggest that the increase in V_{OC} is related to the ZnO. After the initial increase, degradation is driven by I_{SC} suggesting reduction in absorption of the active layer; which could be caused by photo-bleaching of the polymer or aggregation of the fullerene [141, 244]. Additionally, there is a slight decrease in FF, which is likely related to MoO₃ as it has been observed in other devices with MoO₃ (see figures 5.7 and 5.6).

The stability of this structure, when tested under both constant illumination and additional UV, was similar. The degradation is driven by a decrease in I_{SC} , while both FF and V_{OC} maintain more than 80%. No acceleration in degradation was observed due to exposure to additional UV-light.

The degradation under the UV filter is slightly more rapid than under additional UV-light. The degradation of this structure is driven entirely by a decrease in I_{SC} , while in section 5.3.3 there was also a decrease in FF which is likely to be related to the PEDOT:PSS. Again, the absence of UV is detrimental for the stability



Figure 5.8: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with MoO₃, ZnO and aluminium that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, for 180 hours.

of devices that contain ZnO. This observation is likely related to adsorption of oxygen in the ZnO layer creating charge traps [236]. This effect is investigated further in section 5.4.

5.3.8 MoO₃, ZnO and Silver

The next structure that was investigated was MoO_3 , ZnO and silver, which was of particular interest as it contains the same materials as the inverted structure investigated in chapters 3 and 4. The degradation curves of devices under the four different lighting conditions are shown in figure 5.9.

As observed for other structures containing ZnO (presented in sections 5.3.3, 5.3.4 and 5.3.7), the devices that were tested under the UV filter degraded most



Figure 5.9: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with MoO₃, ZnO and silver exposed to constant illumination, intermittent illumination, UV Filtered illumination and additional UV, for 460 hours.

rapidly. Degradation of this structure was driven by a rapid decrease in I_{SC} and a decrease in V_{OC} , resulting in negligible photovoltaic activity after less than 20 hours. Rapid degradation in V_{OC} was also observed in section 5.3.4, indicating that the V_{OC} degradation is likely related to oxidation of the silver electrode accelerating electrical changes in the ZnO layer [253].

Devices tested under intermittent illumination degraded to below 10% PCE after 100 hours. The decrease in PCE was driven by decreases in all characteristics, indicating multiple degradation processes. Additionally, the degradation behaviour of this structure was different to that of the inverted structure with the

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same materials-which was stable under intermittent illumination - suggesting the deposition order dictates stability to some extent. This degradation is similar to what was observed in section 5.3.4, indicating it is likely related to ZnO and silver layers. Further to this, oxidation and interpenetration of silver into subsequent layers has been observed to reduce the V_{OC} [146].

The devices tested under additional UV were observed to be more stable than the devices tested under constant illumination. The degradation under constant illumination is more rapid than under the UV LED, dropping to 40% PCE by 450 hours. However, the degradation under both lighting conditions is driven almost entirely by a decrease in I_{SC} , suggesting a decrease in absorption in the active layer becomes the dominant degradation pathway when there is sufficient UV available to condition the ZnO [80].

The devices that were tested under additional UV exhibited excellent stability; maintaining greater than 70% PCE after 450 hours. This stability is significant as the devices are unencapsulated and standard calcium/aluminium devices (section 5.3.1) degraded to 50% PCE in only 50 hours under constant illumination. Devices of this structure and others containing ZnO (sections 5.3.3 and 5.3.4), exhibited significantly greater stability when exposed to UV-light and significantly poorer stability in its absence. Thus, UV-light must play a critical role in maintaining device performance for some structures. This result is most likely related to ZnO and is investigated further in section 5.4.

5.3.9 ZnO, MoO₃ and Aluminium

The first inverted structure investigated, ZnO, MoO₃ and aluminium, exhibited the lowest performance of all structures tested in this thesis. The initial PCE for these devices was approximately 0.4%, table 5.3 shows that this poor performance is caused by a low V_{OC} which was less than half the value of any of the other structures. The low V_{OC} was likely due to poor matching of electrode work-function with the HOMO of the donor in this structure [22].

All devices of this structure exhibited an initial increase in V_{OC} , above 120%. The increased V_{OC} is likely due to photo-induced doping of the ZnO layer increasing the free electron density [236]. However, this does not follow with previous



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Figure 5.10: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with ZnO, MoO_3 and aluminium that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, for 250 hours.

results on the effect of the UV filter on ZnO (section 5.3.10), suggesting the observed trend may be caused by another mechanism. After the initial increase, the PCE began to decrease for all devices that were tested under constant illumination, UV filter and UV LED, driven largely by I_{SC} . The decrease in I_{SC} suggests photooxidation of the active layer especially since the most stable devices where those illuminated only when they were tested. [143].

Conversely, the change in performance for the device tested under intermittent illumination is initially positive. There is a significant increase in the V_{OC} and a smaller increase in FF, resulting in a two-fold increase in PCE in the first 30 hours of the experiment. After this, the degradation in I_{SC} causes the PCE to decrease. At approximately 200 hours it decreases back to the initial value. Similar increases

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in performance has been observed by Lloyd *et al.*, who observed a 2.8 and 1.5fold increase in V_{OC} and FF respectively, for devices containing ZnO, PEDOT:PSS and silver [77]. The authors attributed these increases in V_{OC} and FF primarily to changes in the electrical properties of the ZnO ESL.

5.3.10 ZnO, MoO₃ and Silver

The second inverted structure investigated under the four lighting conditions was the inverted BHJ presented in chapters 3 and 4. The degradation of this structure is shown in figure 5.11.

In line with observations made in section 4.2.3, the degradation in performance under constant illumination is caused by a degradation in all key parameters. This observation indicates that several of the layers or interfaces within the device underwent degradation on similar time-scales, pointing to multiple processes [80]. Furthermore, illumination is known to accelerate reactions with oxygen and diffusion of oxygen is known to be stronger in inverted devices [205]. Photo-oxidation of the active layer is likely the dominant process, as I_{SC} decreases most rapidly [141].

This structure was most stable under intermittent lighting, with the PCE maintaining approximately 75% after 160 hours. The degradation in PCE is driven most strongly by a decrease in the FF to 80%, with a smaller decrease in I_{SC} to 85%. These decreases are likely due to photo-oxidation progressing at a much slower rate due to lower total photon flux.

After only 2 hours there was a significant difference in the degradation of devices tested under the UV filter and the others, with the UV filters resulting in more rapid degradation. To highlight this difference the data was plotted over the first 20 hours of the experiment in figure 5.12. Figure 5.12 shows the PCE drops below 20% after 5 hours. The degradation is driven by a rapid decrease in both I_{SC} and the FF, while the V_{OC} is largely unaffected. Standard devices containing ZnO also degraded rapidly when tested under a UV filter, providing further evidence that this behaviour is related to ZnO.

Although these devices are sensitive to UV-light, the ZnO ESL requires some component of UV-illumination to maintain optimal conducting properties [254]. The degradation results show that the small change in the spectrum of incident



Figure 5.11: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for devices with ZnO, MoO₃ and silver that were exposed to constant illumination, intermittent illumination, UV filtered illumination and additional UV, over 180 hours.

light caused by the additional LED (see figure 5.1) has a drastic effect on the device performance.

The addition of UV-light did not have a significant effect on the PCE degradation of these devices when compared with devices tested under unmodified light. The change in characteristics is slightly different for the two lighting conditions, however there is significant overlap of the error bounds. This observation suggests that any increased stability caused by the ZnO and UV is being dominated by the photo-degradation of the active layer [205].



Figure 5.12: Degradation of efficiency for devices containing ZnO, MoO_3 and silver over the first 20 hours of data presented in figure 5.11.

5.3.11 Decay Curve Modelling

As in section 4.2.5, the decay curve of I_{SC} for each structure was fitted with either a one- or two-term exponential. Several of the structures were able to be fit with one-term exponentials, indicating that a single degradation process is dominating the decrease in performance [124]. Comparing the long-term behaviour of several structures showed similar time constants, which may indicate a similar or the same degradation mechanism.

Degradation can be generally categorised, as mentioned in section 2.3.2, as burn-in and long-term behaviour. The initial rapid decay is generally referred to as burn-in [118]. After the burn-in, the degradation becomes slower which is referred to as the long-term degradation [187]. The exponential fitting was analysed with these two categories in mind.

One-Term Exponentials

Several structures under different lighting conditions were fitted with a single exponential, which represented the data to a high degree. This observation suggests a single degradation process is dominant, rather than the typical burn-in and long-term behaviour [118].

The structure containing PEDOT:PSS, calcium and silver exhibited one-term exponential decay with the same time constant for all lighting conditions, excluding the initial degradation behaviour under constant illumination, which is shown in figure 5.13. The degradation of devices under constant illumination could not be fit with a single exponential. However, the long-term degradation behaviour had the same time constant as degradation under the other lighting conditions. These observations reinforce the notion that degradation of this structure was driven by the same mechanism regardless of lighting conditions. Furthermore, there are several degradation processes that are associated with both PEDOT:PSS and calcium upon exposure to ambient conditions. Balderrama *et al.* observed rapid degradation of devices containing calcium/silver electrodes, due to the reactivity of calcium under ambient conditions [247]. PEDOT:PSS is also known to react in the presence of water, which reduces the conductivity of the layer and interface with the active layer [255].

Half of the structures that were investigated under intermittent illumination were fitted well with a single exponential. The exponential fit for the standard structures is shown in figure 5.14. These results suggest that eliminating illumination as a stress factor results in one degradation process being dominant for several structures. These results agree with expectations, as less complicated temporal dependence of the PCE indicates fewer degradation effects [188].

The major stress factor under intermittent illumination is exposure to ambient conditions. However, each of the structures have a different time constant, indicating that ambient conditions affect them differently [79]. In this case, both structures containing calcium/silver electrode degraded more rapidly than the corresponding ZnO/aluminium devices, which is likely due to the reactivity of the calcium/silver electrode [247]. The time constants for the two devices with the ZnO/aluminium electrode are within error bounds, which suggests the same dominant process. This degradation is likely related to processes in the active layer or the aluminium electrode [134].



Figure 5.13: Exponential fits for structures containing PEDOT:PSS, calcium and silver over 30 hours. Single-term exponential fits were adequate for devices tested under intermittent illumination, additional UV and UV filtered illumination. A two-term exponential fit was required to model the initial degradation of devices tested under constant illumination. Each fit was found using degradation data from sixteen devices and the shaded region represents the 95% confidence interval.

Two-Term Exponentials

Most of the decay curves exhibited two-term exponential decay, which is indicative of two degradation processes which each dominate at different times in the degradation [123]. As observed previously, the initial degradation behaviour is significantly affected by the materials used. Several trends were observed in the long-term degradation behaviour of structures with some of the same materials.

Under constant illumination, each of the structures containing PEDOT:PSS (excluding the structure containing calcium/Ag) degraded at a similar rate, as shown in figure 5.15. The degradation observed here is likely dominated by processes in or at the interface of the PEDOT:PSS layer. There are several degradation processes that are associated with PEDOT:PSS, including loss of conductivity in humid environments [119] and accelerating corrosion of adjacent layers [134].

Under intermittent illumination, devices containing PEDOT:PSS, ZnO and sil-



Figure 5.14: One-term exponential fit for different standard structures under intermittent illumination over 180 hours. Each fit was found using degradation data from sixteen devices and the shaded region represents the 95% confidence interval. These devices showed less complicated degradation behaviour when illumination is removed as a stress factor.

ver and those containing MoO₃, ZnO and silver exhibited similar long-term degradation behaviour. The two-term exponential for each structure is shown in figure 5.16. This observation suggests that the long-term degradation process is related to the ZnO/silver electrode. Oxidation of the silver electrode or adsorption of oxygen in the ZnO layer are potential causes of this long-term degradation [146,236].

Under the UV filter, the long-term degradation behaviour of all devices containing MoO₃ is similar, as shown in figure 5.17. Except for the structure containing ZnO and silver, all structures had a similar time constant. This observation indicates that the primary degradation mechanism is related to MoO₃ [146]. The burn-in degradation of devices with calcium/silver electrode is likely dominated by degradation of the electrode [247]. However, the device containing MoO₃, ZnO and silver experienced more rapid degradation than the others, indicating additional degradation mechanisms. The rapid degradation of this structure may be associated with adsorption of oxygen in the ZnO hindering charge transport [145].



Figure 5.15: Two-term exponential fit for devices containing PEDOT:PSS under constant illumination over 160 hours. Each fit was found using degradation data from sixteen devices and the shaded region represents the 95% confidence interval. Similar degradation behaviour was observed initially.



Figure 5.16: Two-term exponential fit for different structures under intermittent illumination over 180 hours. Degradation data from sixteen devices was used for each fit and the shaded region represents the 95% confidence interval. These structures exhibited similar long-term behaviour.



Figure 5.17: Two-term exponential fit for different structures with MoO_3 under the UV filter over 80 hours, showing similar long-term behaviour (with the exception of the devices containing ZnO and silver). The two-term exponential fit for each structure was found using degradation data from sixteen devices and the shaded region represents the 95% confidence interval.

5.4 UV Exposure

The degradation of some structures in the presence and absence of UV-light, presented in section 5.3, did not agree with initial expectations [141]. The degradation study of various structures showed that this phenomenon is related to ZnO. The time constants for all the devices containing ZnO were observed to significantly increase (at least two-fold) when tested under the UV-filter, as shown in figure 5.18. The standard structures all exhibited slower degradation under the UV LED when compared with constant illumination. Conversely, the inverted structures exhibited slightly faster degradation under the UV LED, which is likely related to activation of oxygen in the active layer: a significant factor in the degradation of inverted devices [205].

Exposure to UV-light has previously been observed to increase performance for devices containing ZnO [221, 256, 257]. Trost *et al.* tested devices under a UV filter before they were exposed to UV-light. A 3- to 5-fold increase in FF and a substantial increase in I_{SC} were both observed after UV illumination. Subsequently, Cowan *et al.* aged devices for 30 days in the dark and observed the formation of a prominent s-shape in the IV curve. The FF was then recovered after 30 minutes of light soaking. In both cases, the desorption of oxygen from the ZnO layer was identified as the cause.

Boa *et al.* investigated the changes in the surface electronic structure and chemical states of ZnO films upon exposure to UV-light [258]. XPS and ultraviolet photoelectron spectroscopy (UPS) measurements were performed on films that had been exposed to UV-light for different lengths of time. The authors observed a decrease in oxygen defects with increasing exposure time, which was attributed to desorption of oxygen.

The proposed mechanism for the interaction of ZnO with UV-light and oxygen is illustrated in figure 5.19, since adsorbed oxygen molecules act as electron traps [259]. Oxygen desorption changes the ZnO electronic properties after UV illumination [260]. When a hole is generated in ZnO by UV illumination, it causes neutral oxygen desorption from the layer. When the oxygen is released, a previously bound electron is freed in the ZnO conduction band [236].


Figure 5.18: Degradation time constants, obtained from exponential fitting, for each of the standard structures containing ZnO, under each of the four lighting conditions.



Figure 5.19: Proposed interaction of ZnO with UV-light and oxygen, causing changes in the degradation behaviour of devices.

When devices are not exposed to UV-light (when the UV filter is used) this process stops, and oxygen re-adsorbs to the ZnO. The oxygen traps free electrons and the conductivity of the layer drops again. It is proposed that this process is reversible [144].

To investigate this further, devices were covered with a UV filter to degrade. If the proposed mechanism was causing the degradation, the PCE should recover when the filter was removed. The structure that was used was ITO/MoO₃/Active Layer/ZnO/Ag, because this structure exhibited the greatest difference in degradation between the UV filter and UV LED.

Devices were produced using the methods outlined in section 5.2, and degradation measurements were performed with the devices under UV filters until substantial degradation was observed. The filter was then removed, this process was then repeated several times. The results of this experiment are shown in figure 5.20. The devices were tested under the filters initially for 2 hours. Subsequently, the filter was removed, and devices were illuminated with additional UV-light. After 60 hours, the filter was placed back over the devices and the process was repeated.

The results shown in figure 5.20 are an average of six cells, with the shaded region representing the error for each curve. The three grey shaded areas - at 0, 68 and 90 hours - represent the time that the cells were covered with the UV filter. The devices were covered with the UV filter for approximately 8 hours of the experiment. For the rest of the experiment, the devices were illuminated with the light



Figure 5.20: Recovery of device performance using UV-light. The shaded grey sections represent periods when the device was covered with a UV filter. Otherwise the device was illuminated with constant light and additional UV.

and LED providing additional UV.

In the first two hours of the experiment, when the device was covered with the filter, the PCE decreases to approximately 40%. The rapid degradation is most strongly driven by I_{SC} , but the V_{OC} also decreases to approximately 70%.

The effect of removing the filter and illuminating the devices with additional UV is significant. The change in characteristics caused by exposure to UV illumination is shown in table 5.6. The FF increases to 180% and the J_{SC} increases to 116%, along with a less significant increase in V_{OC} . The change in light intensity, caused by switching from the filter to the LED, would account for a less than 20% change in device PCE. When the filter was removed the PCE increased from 40% to 170%, an almost four-fold increase. The device was relatively stable when it was being illuminated with UV. Over the next 60 hours, the PCE decreased to approximately 140%, driven by J_{SC} .

The sample was the covered with the filter and, again, significant degradation was observed. The PCE decreases from 140% to approximately 45% in two hours. This degradation is driven mostly by the I_{SC} , with smaller contributions from both

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	Eff. (%)	V _{OC} (%)	J _{SC} (%)	FF (%)
Pre-UV	44	77	51	112
Post-UV	170	81	116	180
% Increase	386	105	227	161

Table 5.6: Normalised characteristics before and after initial exposure of UV illumination, along with percentage increase.

FF and V_{OC} . The degradation that occurs is observed to be, almost, entirely reversible. When the filter is removed again, the sample recovers much of the PCE. The PCE before the filter was 140%, but it only increases to 130%. Repeating the filter process again results in slightly less of the PCE being recovered, a decrease from 120% to 100% was observed.

5.4.1 Decay Curve Modelling

To confirm that the degradation observed here was the same as was observed in section 5.3.8, two sections of the data were fit was exponentials and compared with the relevant curves from section 5.3.8. The initial degradation under the UV filter was fit with a single exponential and is shown in figure 5.21 along with the first three hours of a previous experiment.

There is significant agreement between the two degradation rates. Furthermore, the degradation rate constants lie within the 95% confidence interval of each other, which provides evidence that the same degradation process is occurring.

The section of the curve where the device was illuminated with the UV LED was fit with a two-term exponential. This is shown in figure 5.22, with the data from section 5.3.8.

There are small differences in the burn-in of the two, however degradation time constants for the long-term behaviour fall within the 95% confidence interval. This observation may indicate that intermittently exposing the devices to UV-light alters the initial degradation processes that occur in this structure.

This data analysis confirms that the degradation processes observed for this structure under the UV filter are reversible. The devices measured here degraded in the same way as devices that were only exposed to the UV LED (in section 5.3.8)



Figure 5.21: One-term exponential fit for ITO/MoO₃/A.L./ZnO/Ag under the UV filter compared with data presented in figure 5.9, along with 95% confidence intervals represented by the shaded region, showing similar degradation.

and showed no long-term effect from the initial or subsequent degradation under the UV filter.

5.4.2 Capacitance-Voltage Analysis

Desorption of oxygen in the ZnO would alter the doping density in the material. Capacitance-voltage measurements were used to quantify the electrical changes in this structure before and after exposure to UV-light. These measurements were performed at two points in the degradation measurements, as shown in figure 5.23a. Before degradation measurements started, capacitance-voltage measurements were performed in the dark. Degradation measurements were then performed for approximately 3 hours before devices were exposed to UV-light. After the initial exposure, capacitance-voltage measurements were performed again. The results of the capacitance-voltage measurements are presented in figure 5.23b.

The linear trend-lines were used to calculate the doping density before and after exposure to UV-light [12]. The doping density of the device before exposure to UV-light was $7.96 \times 10^{19} cm^{-3}$, while after exposure the doping density is $1.38 \times 10^{20} cm^{-3}$. This almost two-fold increase in the doping density corresponds with the almost two-fold increase in performance observed after the initial exposure to

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Figure 5.22: Two-term exponential fit for $ITO/MoO_3/A.L./ZnO/Ag$ under the UV LED compared with data presented in figure 5.9, along with 95% confidence intervals represented by the shaded region. This shows the rate of degradation in the presence of UV is not altered by periods of UV filtering.

UV-light. This increase in doping density also provides further evidence of the mechanism (in figure 5.19) altering both the performance and degradation of these devices.



(b) Mott-Schottky characteristics of a device before and after exposure to UV-light

Figure 5.23: Effect of exposure to UV-light on PCE and capacitance. Linear fits (shown in black) were used to calculate the doping density before and after UV exposure. Coloured lines in (a) correspond to the times at which measurements in (b) were performed.

5.5 Impedance Study

Impedance spectroscopy is a powerful tool for measuring electronics properties of these devices [191, 195]. As part of a larger study, performed in collaboration with Dr Matt Griffith and Mr Mohammed Al-Mudhaffer, impedance measurements were performed on devices containing PEDOT:PSS, ZnO and aluminium. These impedance measurements were performed on devices before and after exposure to UV-light. The purpose was to investigate how exposure to UV-light effected the impedance and capacitance of this structure. Devices were produced using the methods described in section 2.2. Impedance measurements are described in section 2.4.2.

Devices were initially IV tested under AM 1.5 with a GG455 UV filter. Impedance measurements were then taken on a Keysight E4980A Precision LCR meter by Mr Mohammed Al-Mudhaffer. Both IV and impedance measurements were then repeated under full AM 1.5 illumination on the same set of devices. Devices were subsequently exposed to 5 minutes of UV illumination, followed by a final set of IV and impedance measurements under AM 1.5. Impedance measurements were taken for the frequency range from 20Hz to 1MHz, the capacitance was then calculated for each frequency value.

The resulting impedance spectra and capacitance response are shown in figure 5.24. The device showed a decrease in capacitance to approximately 60% of the initial value when it was exposed to full AM 1.5 illumination, but no subsequent change after the UV-light soaking. The decrease in capacitance indicates that less charge is trapped in the device after exposure to AM 1.5 illumination. While, these results agree with expectations, they suggest that either the UV soaking period was insufficient or that only a small amount of UV illumination is required to observe the full effect. These results provide further evidence for the mechanism proposed in figure 5.19. Adsorption of oxygen in the ZnO layer occurs when devices were exposed to ambient conditions, which traps charge within the device. Exposure to some component of UV illumination desorbs oxygen from this layer. This desorption frees the trapped charges reducing the charge in the device and, thus, the capacitance as observed.



Figure 5.24: Impedance spectrum and capacitance response for a device with a 100nm thick active layer and 40nm ZnO layer under illumination with no UV, full AM1.5 spectrum and after 5 minutes of UV-light soaking. These results show a change in capacitance upon exposure to full AM1.5 but no change after additional UV-light soaking.

5.6 Conclusions

Degradation of OPVs with a variety of material structures, were investigated under four different lighting conditions. For most structures, degradation was found to depend on both the material combinations and the lighting conditions. The dominant degradation mechanisms for each device type are proposed based on results presented in this chapter and are presented in table 5.7. The most commonly proposed mechanisms are changes in ZnO, photo-oxidation of the active layer and photo-degradation of MoO_3 .

The two structures containing calcium/silver as the electrode exhibited rapid degradation irrespective of the lighting condition, indicating that this electrode material is inherently unstable. Calcium is known to be unstable upon exposure to ambient conditions. However, devices with calcium/aluminium electrodes were notably more stable than those with calcium/silver, indicating additional degradation mechanisms specific to calcium/Ag. It would be reasonable to conclude that calcium/silver electrodes are not a suitable candidate for OPVs.

Most notable, the degradation of all structures containing ZnO were dominated by electronic changes in the ZnO, caused by UV-illumination. Surprisingly, results for devices containing ZnO showed that a small amount of UV-light is required for stable operation. In every case, devices with ZnO exhibited significant, rapid degradation when tested with a UV filter in place. This rapid degradation was also observed to be almost entirely reversible: removing the filter and continuing the degradation measurements resulted at least 80% recovery of PCE, even after multiple filtering cycles. Despite the damaging nature of UV-light for OPVs, these results indicate that devices containing ZnO require regular exposure to some UVillumination in order to maintain performance over time.

To further examine the odd behaviour of ZnO, capacitance measurements were performed on two of the ZnO containing structures already investigated. Capacitance-voltage measurements and capacitance-frequency measurements both showed UV-induced changes. Capacitance-voltage experiments showed a significant increase in the doping density after a short exposure to UV-light. Further to this, capacitance-frequency measurements showed a significant drop in the trapped charge Materials **Dominant Degradation Process** Standard PEDOT:PSS, Ca, Al Photo-oxidation of active layer, active layer/electrode degradation PEDOT:PSS, Ca, Ag Degradation of Ca/Ag interface PEDOT:PSS, ZnO, Al Electronic changes in ZnO, oxidation of Al electrode PEDOT:PSS, ZnO, Ag Electronic changes in ZnO, oxidation of Ag electrode MoO₃, Ca, Al Photo-degradation of MoO3, oxidation of Al electrode Photo-degradation of MoO3, degradation of Ca/Ag interface MoO₃, Ca, Ag MoO₃, ZnO, Al Electronic changes in ZnO, photo-degradation of MoO3 MoO₃, ZnO, Ag Electronic changes in ZnO Inverted ZnO, MoO₃, Al Photo-oxidation of active layer ZnO, MoO₃, Ag Electronic changes in ZnO, photo-oxidation of active layer

Table 5.7: Proposed dominant degradation processes occurring in each architecture investigated in this chapter.

upon exposure to the full AM 1.5 spectrum, suggesting that only a small component of UV illumination is necessary to observe the effect. Both results support the proposed mechanism of oxygen desorption.

These experiments have allowed for a more comprehensive understanding of the degradation of OPVs. The degradation behaviour was found to be dependent on the materials and combinations thereof. Mechanisms were also proposed for the degradation observed for each structure investigated. UV-illumination was shown to play a critical role in the stability of devices containing ZnO, with unencapsulated devices maintaining more than 70% of their initial PCE after 20 days of continuous UV exposure. Thus, the standard structure containing ZnO, MoO₃ and silver would be well-suited for stable OPVs.

Chapter 6

Degradation of Nanoparticle Systems

Nanoparticulate based OPV devices are a rapidly growing area of research [163]. However, beyond speculation that their water-based fabrication may lead to long term instability, very little is known about their longevity or degradation pathways. The degradation of the nanoparticle devices, presented in chapter 4, showed that they exhibited significantly lower stability than the corresponding BHJ devices. Subsequently, further experiments were performed to obtain a more thorough understanding of the degradation of nanoparticle devices. The degradation measurements performed in this chapter focus on NP devices with the standard structure.

The initial experiment was to reproduce the degradation measurements of standard nanoparticle devices, presented in chapter 4. Additionally, ICxA was investigated as an acceptor in place of PCBM. However, it has been observed that multiadduct-fullerene blends can accelerate the photo-bleaching of polymers [261]. Hoke *et al.* investigated the role of electron affinity in the fullerene in photobleaching of the polymer. The authors observed that the rate of photobleaching in the polymer was inversely proportional to electron affinity, with higher adduct-fullerenes causing more rapid photodegradation [261]. This rapid photo-bleaching was attributed to the fact that ICBA has a lower electron affinity than PCBM, making electron transfer from ICBA to oxygen more likely, oxygen radicals then initiate polymer degradation [143]. Furthermore, Tromholt *et al.* observed destabilisation of P3HT in blends with ICBA causing more rapid photodegradation when compared with P3HT:PCBM blends [262]. Extensive work has yet to be reported for ICxA or NP devices. Consequently, degradation measurements were performed on devices containing PCBM and ICxA (blended with P3HT), under the four lighting conditions described in section 5.1. These experiments were performed to determine if the use of ICxA had a drastic effect on degradation in the NP devices.

The low stability of the NP devices, initially observed in chapter 4, raised the question of whether the rapid degradation was related to the surfactant in the NP active layer. SDS is known to undergo several degradation reactions, including photo-oxidation [235]. Bandala *et al.* and Lea *et al.* both observed significant photo-oxidation of SDS in aqueous solution under UV illumination [235, 263]. In each case, the photo-oxidation resulted in the formation of sulphate ions in solution, which could lead to a rapid decrease in the performance of the NP devices [50]. XPS depth profiling measurements were performed on the two architectures with BHJ and NP active layers, to obtain a clearer picture of the location and role of the surfactant in the structure.

A small amount of SDS was also incorporated in a BHJ solution to observe any effect on the performance or stability of the devices. For this reason, IV and lifetime measurements were performed on BHJ devices with and without added SDS. Furthermore, XPS measurements were used to observe changes in the surface SDS content of these films upon annealing.

Finally, precipitated NP were incorporated into devices and degradation measurements were performed under the four lighting conditions: constant illumination, intermittent illumination, UV-filtered illumination and additional UV illumination (as described in section 5.1). The purpose of these measurements was to investigate and contrast degradation of nanoparticles with and without surfactant in order to establish the role surfactant plays in device degradation.

Surfactant-containing NP solutions that were used to produce devices in this part of the thesis were made by Ms Melissa Marks and Mr Furqan Almyahi.

6.1 Lifetime Measurements of Nanoparticle Devices

Two sets of devices were produced with the standard structure shown in figure 2.3: one set of devices containing P3HT:PCBM nanoparticles and one containing P3HT:ICxA nanoparticles. Devices were produced using the procedures described in section 2.2.1. Subsequently, the IV characteristics of these devices were measured using the method outlined in section 2.3.1. The average characteristics of 15 cells for each device type are shown in table 6.1. A representative IV curve for each device type is shown in figure 6.1. The performance of the devices with P3HT:ICxA nanoparticles is significantly higher than the P3HT:PCBM nanoparticles, as expected due to the higher LUMO of ICxA and when compared with PCBM [106].

Table 6.1: Performance characteristics of devices with P3HT:PCBM and P3HT:ICxA nanoparticles fabricated via the miniemulsion process.

Acceptor:	Eff. (%):	V _{OC} (V) :	I _{SC} (mA):	FF (%):
PCBM	0.516 (±0.06)	0.458 (±0.03)	2.98 (±0.18)	38.6 (±0.5)
ICxA	1.001 (±0.09)	0.540 (±0.01)	5.03 (±0.37)	37.1 (±1.6)

Degradation measurements were performed on the two sets of devices under the four lighting conditions outlined in section 5.1. The results of these degradation measurements are shown in sections 6.1.1 and 6.1.2. These results are an average of a minimum of 10 cells with the lighter shaded region representing the standard deviation at each point.

6.1.1 P3HT:PCBM Nanoparticles

The change in characteristics for the devices made with P3HT:PCBM nanoparticles are shown in figure 6.2. The change in degradation rate for these devices was not significant for the lighting conditions that involved constant illumination. The device tested under intermittent illumination exhibited more rapid degradation than the others, which was driven by a reduction in the I_{SC} . These results agree with previous degradation of NP devices, presented in chapter 3, which indicated that the shelf-life of standard NP was very low.

The degradation of devices under the three other lighting conditions was similar, with the error bounds overlapping in all cases. Again, this degradation is driven by the I_{SC} which can be attributed to changes in the NP active layer mor-



Figure 6.1: IV-curves of representative devices made with (a) P3HT:PCBM and (b) P3HT:ICxA nanoparticles in the standard architecture.

phology, such as PCBM aggregation or changes in P3HT crystallinity [40,46].

The lighting conditions, excluding intermittent, all resulted in similar degradation rates, which indicates the processes most damaging for these devices were



Figure 6.2: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for P3HT:PCBM standard nanoparticle devices that were exposed to constant illumination, intermittent illumination, UV Filtered illumination and additional UV, over 210 hours.

not affected by the changes in intensity of UV light. Given that photo-oxidation is accelerated by UV light [142, 263], the observed decrease in I_{SC} is likely related to morphological changes in the film. Both the FF and V_{OC} were relatively stable, remaining above 80% and 90% respectively, over the 200 hours. This observation suggests that the interlayers and electrodes were not affected by degradation, providing further evidence that the observed degradation is related to morphological changes to the active layer.

Comparing the results presented in figure 6.2 with standard BHJ devices (figure 5.2), shows that the NP active layer has a significant effect on the observed degradation. For the standard BHJ devices, the degradation is greatly altered by the presence or absence of UV light. Furthermore, devices tested under the UV filter were significantly more stable than for a standard BHJ device. In figure 6.2, the filter did not have a noticeable effect on the degradation behaviour of NP films. These observations suggest that the NP active layer is not as susceptible to the same photo-oxidation as the BHJ active layer, given that photo-oxidation should be accelerated by the presence of additional UV light [80].

6.1.2 P3HT:ICxA Nanoparticles

The change in characteristics for the devices made with P3HT:ICxA nanoparticles are shown in figure 6.3.



Figure 6.3: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for P3HT:ICxA standard nanoparticle devices that were exposed to constant illumination, intermittent illumination, UV Filtered illumination and additional UV, over 140 hours.

Under all the lighting conditions, the degradation is driven almost exclusively

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by a drop in I_{SC} , which decreases below 25% under all lighting conditions in 125 hours. The V_{OC} is extremely stable, the final values under each lighting condition are between 99% and 105% of the initial value at the end of the experiment. The FF for devices tested under constant illumination and with the UV filter show an improvement over the first 10 hours of the experiment, while the UV LED and intermittent both showed slight decreases.

Under three of the lighting conditions, the degradation of devices with ICxA was similar to those with PCBM. However, there was a significant difference in degradation behaviour for ICxA devices and those with PCBM (section 6.1.1) tested under intermittent illumination. The devices containing PCBM were observed to degrade significantly more rapidly under intermittent illumination than devices containing ICxA. Given that the humidity is higher under intermittent illumination, the rapid degradation may be related to interactions between PCBM and atmospheric water. Bao *et al.* observed strong degradation in electronic structure of PCBM upon exposure to water vapour [237].

6.1.3 Decay Curve Modelling

For a direct comparison of the degradation rates, the decay curves for devices made with P3HT:PCBM and P3HT:ICxA were fitted with exponential functions, as in chapters 4 and 5. The degradation time constants for each material and lighting condition are presented in table 6.2. This data shows two important trends.

First, the decay curves for the devices containing PCBM nanoparticles all exhibited a single exponential decay. As mentioned previously, single exponential decay suggests that a single degradation process dominates. Furthermore, the decay of these devices under intermittent illumination occurs almost five times faster than the other lighting conditions, as shown by the time constants in table 6.2. Devices tested under intermittent illumination generally experience higher humidity (approximately 10% RH higher for these experiments) than devices tested under constant illumination. These results indicate that PCBM is more sensitive to damage by water than ICxA, as the ICxA devices were stable under intermittent illumination (see figure 6.3). The effect of water vapour on PCBM films has been investigated [237]. Bao *et al.* found exposure to water vapour caused rapid and ir-

	А	$\lambda_1 (h^{-1})$	В	$\lambda_2 (h^{-1})$		
Constant	79.51	0.010				
Intermittent	90.78	0.053			рсрм	
Filter	81.99	0.013			PCBM	
LED	88.84	0.010				
Constant	25.61	0.85	75.57	0.009		
Intermittent	10.74	0.14	88.49	0.013	ICvA	
Filter	17.95	0.34	80.39	0.009	ICXA	
LED	11.37	0.29	87.48	0.008		

Table 6.2: Degradation time constants, λ_1 and λ_2 , for two different nanoparticle compositions based on $I/I_0 = Ae^{-\lambda_1 t} + Be^{-\lambda_2 t}$.

reversible changes to the electronic structure of PCBM. The authors concluded that these changes would significantly alter transport properties in the film.

The second important trend is that the devices containing ICxA nanoparticles show very different burn-in behaviour but the same long-term behaviour as those containing PCBM. Under different lighting conditions, there is a difference in the initial degradation rate of almost eight times. This observation indicates either that different processes are occurring, or one process proceeds differently depending on the lighting conditions. By contrast, the rate constants for the long-term behaviour are very similar for each lighting condition, indicating that this second degradation process is unaffected by the lighting condition.

Excluding the PCBM devices tested under intermittent illumination, the degradation constants for the PCBM devices are similar to the long-term degradation constants (shown in table 6.2) for the ICxA devices. This similarity suggests that the degradation process is unaffected by substituting ICxA in place of PCBM, providing evidence that the mechanism may be P3HT-based. The degradation constant of the long-term degradation for these devices were a quarter of the value previously observed for devices of this type (see section 4.2.5). Differences in degradation rates may be caused by differences in environmental conditions when devices were produced.

6.2 X-Ray Photoelectron Spectroscopy to Identify Surfactant

XPS depth profile measurements were performed on standard and inverted devices with BHJ and NP active layers. These measurements were used to map the chemical composition through the device, in order to identify the position of SDS within the NP active layer. Surfactant build-up at an interface would indicate that the surfactant could diffuse through the layer after deposition, which may make nanoparticle devices more susceptible to morphological degradation and could result in the formation of insulating layers at interfaces.

XPS measurements presented in figures 6.4, 6.5, 6.6 and 6.7 were performed and analysed by Dr Kane O'Donnell at Curtin University.

The SDS in these results is best shown by the sodium peaks since SDS (sodium dodecyl sulphate) is the only source of sodium in the devices. The results for the inverted devices are shown in figures 6.4 and 6.5. The depth profile for the standard devices and the sodium peak are shown in figures 6.6 and 6.7. In each case, BHJ and NP depth profiles are qualitatively similar, except for the sodium peak which is only present in the NP devices.

The sodium peak for the inverted NP device is plotted separately in figure 6.5. For the inverted devices, the sodium peak can be observed most strongly in the active layer. However, there is significant accumulation at the silver interface and diffusion through the interface. Since surfactant is an insulator, a build up at the interface may explain charge extraction issues and the s-shaped appearance of IV curves, in figure 3.1 for example. Furthermore, the build-up also indicates that the surfactant can diffuse within the layer after deposition, since SDS should be evenly dispersed in the solution and throughout the active layer.

The sodium peak for the standard NP device was magnified and is presented in figure 6.7. For the standard devices, it was also observed that the surfactant accumulated at the interface between the top electrode and the active layer, with the sodium penetrating through the calcium into the aluminium electrode. However, the amount of surfactant is roughly half for the standard architecture, when compared with the inverted architecture, which may suggest that more surfactant



Figure 6.4: Results of XPS measurements for inverted devices, showing the composition of devices. Note the distribution of SDS in the NP device (b). The shaded regions represent the layers in the inverted structure.

remains diffuse in the active layer in this structure. Lower surfactant concentration at the interface is likely why no significant charge extraction issues are observed

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Figure 6.5: The sodium peak for the inverted NP device. The layers are represented by the shaded regions.

for this structure and conventional IV curves are observed.

These results suggest that surfactant is free to move within the active layer after deposition, since the surfactant would be dispersed within the solution. Further evidence of the mobility of SDS in the active layer is presented in section 6.3. The diffusion and accumulation of SDS may alter the device performance with time as it acts as an insulator and may also alter the work-function of the electrode [220].



Figure 6.6: Results of XPS measurements for the standard devices, showing the composition of devices. Note the distribution of SDS in the NP device (b). The shaded regions illustrate the layers in the standard structure.



Figure 6.7: The sodium peak for the standard nanoparticle device. Again, the layers are represented by the shaded regions.

6.3 Surfactant and Degradation

Results presented previously in this chapter suggest that the degradation of nanoparticle devices may be related to SDS, which was observed to accumulate at interfaces within the devices. To gain an understanding of the effect of surfactant on device degradation, a BHJ active layer solution was prepared with a small amount of SDS introduced into the active layer. A $18mg/1000\mu$ L active layer solution was prepared using the method described in section 2.1.1. An aliquot of this solution was separated and SDS was added at a concentration of $1mg/1000\mu$ L. The solution was subsequently stirred at 1000rpm at 35°C for an extended time to ensure the solution was well-mixed.

Devices were then prepared with each of these solutions, with SDS and without, according to methods outlined in section 2.2. The devices were characterised under AM 1.5 and degradation measurements were performed. XPS measurements were also taken of annealed and non-annealed active layer films on glass, to investigate if the surface content of SDS changed upon annealing.

6.3.1 IV Characteristics

The average characteristics for each device type are shown in table 6.3. Unexpectedly, the non-annealed devices that contained SDS significantly outperformed the non-annealed SDS-free devices. However, the way the devices responded to thermal annealing was significantly altered. The average IV characteristics of devices with and without SDS are presented in table 6.3.

Non-Annealed	Eff. (%):	V _{OC} (V) :	I _{SC} (mA):	FF (%):
Without SDS	0.976 (±0.17)	0.472 (±0.013)	5.34 (±0.56)	38.7 (±1.6)
With SDS	1.94 (±0.16)	0.529 (±0.021)	5.87 (±0.31)	59.1 (±1.4)
Annealed				
Without SDS	1.67 (±0.23)	0.549 (±0.124)	5.62 (±0.49)	54.1 (±2.3)
With SDS	0.08 (±0.02)	0.557 (±0.012)	0.76 (±0.03)	22.1 (±0.5)

Table 6.3: Performance of devices, with and without SDS, before and after annealing.

Figure 6.8 shows the IV curves of devices before and after annealing of a standard BHJ device and an SDS-containing BHJ device. The surfactant-free device shows an increase in V_{OC} and an improvement in the overall shape of the IV-curve upon annealing. Conversely, the device containing SDS showed negligible photovoltaic properties after annealing. This observation implies that the SDS was free to move within the layer upon annealing, which had a severe impact on the performance. Consequently, degradation measurements were performed on non-annealed devices of both types.

6.3.2 Degradation of Bulk Heterojunction Devices with Surfactant

Two devices with surfactant and two without were degradation tested under constant illumination over 120 hours, as shown in figure 6.9. Due to the reduction in performance observed when annealing devices containing SDS, devices tested here were non-annealed. The curves are the average of a minimum of 10 cells, with the standard deviation represented by the shaded region.

The decrease of each of the key parameters for each device are shown in figure 6.9. There is a significant difference in the degradation rate between the two devices. The SDS device exhibits less than 10% of the initial PCE after 120 hours, while the device without SDS maintains more than 50% of the initial PCE.

Initially, the SDS containing device exhibits a rapid decrease in all parameters which causes the PCE to decrease to 70% of the initial value in ten hours. After this burn in period, degradation in PCE is driven strongly by I_{SC} until approximately 45 hours when FF also begins to decrease. A decrease in the FF can indicate a reduction in charge transport at an interface. These results further suggest that the SDS migrates and accumulates with time, hindering charge transport at the interface with the active layer. The effect of annealing devices containing SDS provides further evidence of this phenomenon (see figure 6.8).

The degradation of the SDS-free devices is driven most strongly by I_{SC} . This degradation is similar to previous degradation of standard BHJ (figures 5.2 and 4.10), although, the FF was much more stable than was observed previously. This slight change in degradation behaviour may be related to defects in the aluminium electrode accelerating oxidation [240].



Figure 6.8: IV-curves of standard BHJ devices with and without SDS, showing the adverse effect of annealing on the performance of devices containing SDS.

Data fitting was, again, used to obtain more information about the degradation. The efficiency data with the fitted curves are shown in figure 6.10. For the devices without SDS a single-term exponential was used, while the fitting for the devices containing SDS was more complicated. The degradation curve exhibited two distinct phases, consequently it was not possible to fit all the data with a single

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Figure 6.9: Change in efficiency, open circuit voltage, short circuit current and fill factor of standard BHJ devices, with and without surfactant, over 120 hours, under constant illumination.

exponential function. Two exponential functions were used: on which described the data from 0 to 50 hours and one which described the data from 50 to 120 hours. Each of the exponential functions that were used to fit the data of the devices containing SDS were two-term exponentials. As mentioned in section 2.3.2, the less complicated the fit is, the fewer degradation mechanisms are acting simultaneously [188]. The complicated nature of the fit for the devices containing SDS, compared to devices without SDS, suggests more degradation processes are occurring due to the present of the SDS. Indeed, when coupled with the degradation evidence presented above and the XPS data presented in section 6.2, this data suggests that migration of SDS to the cathode/active layer interface is a significant degradation pathway in NP devices.



Figure 6.10: Change in efficiency over 120 hours for devices with and without SDS, with one- and two-term exponential functions fitted.

There is a distinct change in FF at approximately 50 hours, which indicates a change in interface characteristics within the device. This change in the interface may be related to mobile SDS in the active layer accumulating at one of the interfaces. The response of the devices containing SDS (see figure 6.8b) to annealing provides further evidence of mobile SDS altering device characteristics.

6.3.3 XPS of Active Layer Surface

There was a significant decrease in the performance of the BHJ device with added SDS upon annealing (see figure 6.8). To investigate this effect further XPS was used to observe the change in the surface composition of the active layer upon annealing. For comparison, NP films were also measured as previous results, presented in section 6.2, suggested that the surfactant in a NP film would move to the surface. XPS measurements presented in this section were obtained and analysed by Mr Adam Fahy.

For this experiment four samples were prepared, two BHJ films with SDS added and two NP films. One of each of the films was annealed for 4 minutes at 140°C, while the others were left as spun. The samples were then mounted on a sample holder as shown in figure 6.11. Samples were placed into the analysis chamber, which was then pumped to a working pressure of 2.5×10^{-9} mBar. An Omnivac non-monochromatic X-ray source was used to illuminate the samples, and the photoemission was collected by a Scienta SES2002 analyser.



Figure 6.11: Samples mounted on sample holder for XPS.

The amount of SDS at the surface was quantified by looking at the sodium 1s peak. The peak for the non-annealed and annealed films of each type are shown in figure 6.12. In the case of the nanoparticle film, shown in figure 6.12a, there is

a significant increase in the amount of surfactant at the surface. This observation agrees with the depth profile results shown in section 6.2, further indicating that the SDS has freedom to move within the active layer and that it migrates to the surface upon annealing.

It has been observed repeatedly that annealing has a significant effect on the morphology of NP films. Ulum *et al.* observed changes in photoluminescence upon annealing, which was attributed to a decrease in defects in the film [163]. Thermal treatment has been observed to reduce performance in P3HT:PCBM by Holmes *et al.* [264]. Decreases in performance were attributed to gross phase segregation due to extensive diffusion of PCBM in the P3HT matrix. Subsequently, Ulum *et al.* investigated changes in performance for P3HT:ICBA devices upon annealing [162]. The improvement in performance was attributed to the formation of a highly intermixed film upon thermal treatment. Annealing films of P3HT:PCBM nanoparticles results in significant phase segregation and diffusion of PCBM. These observations highlight the dynamic nature of these films upon annealing, which agree with the observations of this thesis.

For the BHJ film, the size of the sodium peak for the annealed sample is approximately 60% of the peak from the non-annealed sample. The decrease in sodium content at the surface upon annealing shows that the SDS in the BHJ behaves differently than in the NP films. However, in these measurements the interface is open to air rather than to a Ca/Al electrode. Consequently, it is not perfectly reflective of diffusion dynamics in a device and in this case the surfactant may migrate to the active layer/substrate interface.



Figure 6.12: XPS results of the sodium content obtained from a region scan of non-annealed and annealed (a) NP and (b) BHJ active layer films.

6.4 Surfactant-Free Nanoparticles

To further investigate how the presence of surfactant altered the degradation, surfactant-free NP solutions were produced via the precipitation method described in section 2.1.2. Standard devices were then produced using the methods described in section 2.2.1. The average characteristics of these devices are shown in table 6.4.



A typical IV-curve for these devices is shown in figure 6.13.

Figure 6.13: IV-curves of representative devices made with P3HT:PCBM NP using the precipitation method.

Table 6.4: Performance of devices with P3HT:PCBM precipitated nanoparticles.

Eff. (%):	V _{OC} (V):	I _{SC} (mA):	FF (%):
0.557 (±0.17)	0.433 (±0.18)	3.07 (±0.78)	41.9 (±5.8)

Degradation measurements were performed under the four lighting conditions described in section 5.1. The results of this degradation study are presented in figure 6.14. The degradation of devices containing the precipitated NP was significantly more rapid than the surfactant-containing NP. Under all lighting conditions the PCE dropped below 50% in the first hour, and after 8 hours negligible photovoltaic activity was observed.

The degradation is most strongly driven by decreases in I_{SC} , a less significant decrease in V_{OC} was observed for the devices (except for devices tested under intermittent illumination). The results presented in figures 6.2 and 6.3 show a relatively stable V_{OC} under every lighting condition. These results, when compared with



Figure 6.14: Degradation of efficiency, short circuit current, fill factor and open circuit voltage for P3HT:PCBM standard precipitated nanoparticle devices that were exposed to constant illumination, intermittent illumination, UV Filtered illumination and additional UV, for 8 hours.

those presented in figure 6.14, indicate that the initial drop in V_{OC} is related to the precipitated NP active layer. Both the FF and V_{OC} experience a severe amount of noise after the PCE drops below 10% in the first 3 hours.

These results suggest that surfactant may be beneficial to the stability of the devices. The devices that were made with surfactant-containing NP maintained more than 10% PCE over 100 hours (with the exception of the devices tested under intermittent illumination), conversely the devices containing the surfactant-free NP active layers degraded in less than 8 hours. These results show that removing the

surfactant initiated or accelerated very rapid degradation in these devices. Given that the surfactant is known to accumulate at the interface (see section 6.2), it is possible that the surfactant layer may be acting as a barrier, protecting the active layer from water and oxygen. Interestingly, these results suggest that surfactant both inhibits charge transport at the cathode/active layer interface, reducing FF and device performance, and at the same time prevents oxidation of the interface or active layer, thereby improving device lifetime.

6.5 Conclusion

The purpose of this chapter was to investigate the degradation of NP active layers. Two fullerene materials: PCBM and ICxA, were considered and the effect of lighting conditions was examined. Contrary to expectations, substituting PCBM for ICxA did not have a significant effect on device stability. Devices made with PCBM were both less efficient and less stable than ICxA devices when tested under intermittent illumination. Under other illumination conditions, no change in degradation rate was observed between the two, suggesting the degradation is dominated by processes in the P3HT layer or in the interfaces or electrodes. Furthermore, the degradation of these devices was also observed to not be affected by exposure to UV light, indicating photo-oxidation is likely not the dominant degradation mechanism. Overall, these observations provide evidence that degradation of these devices is dominated by processes at the electrodes or interfaces.

NP active layers are known to be dynamic when subjected to annealing. Multiple XPS measurements were used to investigate SDS in the NP and BHJ active layers before and after annealing. The results indicate that SDS diffuses through the active layer, accumulating at interfaces in the NP device. Moreover, the amount of SDS present at the surface of a NP film was found to increase upon annealing. In combination, these observations confirm that the composition of the NP active layer is dynamic, leading to the accumulation of SDS into insulating layers which may contribute to degradation.

The presence of SDS was observed to have a significant effect on the performance of BHJ devices. Unannealed devices were observed to perform well, whereas annealing resulted in substantial loss of photovoltaic activity. These devices also

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degraded at twice the rate of control devices (without SDS). These results further indicated that SDS is a major contributing factor to the degradation of NP devices.

The results of this chapter initially appeared to suggest that surfactant-free NPs may provide a more stable alternative. However, when surfactant-free NP devices were constructed, rapid degradation was observed. Further investigation would be required to fully understand the degradation of these devices, but the results herein show that removing the surfactant did not result in greater stability. SDS at the active layer/electrode interface may be protecting the active layer and electrode from the diffusion of water or oxygen. The overall conclusion is that surfactant plays an important, and complex, role in the stability of NP devices.
Chapter 7

Conclusions and Future Work

7.1 Conclusion

OPVs are a versatile and promising renewable energy technology due to their low cost, solution-processability and flexibility. Furthermore, the maximum PCE of OPVs has consistently increased in the last 10 years and is currently above 10%. One of the key impediments to the widespread use of OPVs is their low stability. Understanding the degradation processes that occur is therefore crucial to manufacturing more stable OPVs and was the primary purpose of this work. The work presented herein characterised the degradation behaviour of a variety of OPV devices, with different architectures, materials and active layers. Several mechanisms are proposed throughout, supported by the relevant literature and experimental investigation.

Initial work focused on comparisons of the standard and inverted architectures and BHJ and NP active layers. The results showed that inverted devices are more stable when tested under intermittent illumination, while standard devices are more stable when tested under constant illumination. These observations are consistent with prevailing theories that the dominant degradation processes are photo-active in inverted architectures and atmospheric in standard architectures. Additionally, these results highlighted the importance of consistent testing procedures when comparing device stability. To this end, a fully-automated testing system was designed, such that multiple devices could be tested concurrently under different lighting conditions. Experiments were performed, using this new testing apparatus, to investigate the standard and inverted architectures with BHJ and NP active layers. Constant illumination experiments confirmed that the inverted architecture was not inherently more stable than the standard architecture. Given that the degradation observed was generally driven by reduction in I_{SC} , two other techniques were used to investigate current loss. UV-Vis measurements were performed which indicated that loss of absorption in the active layer occurred over a much longer timescale than observed current loss, ruling it out as the primary cause. Subsequent LBIC measurements suggested that short-term current loss is related to architecture (standard vs. inverted) and independent of active layer.

Lifetime measurements were performed on devices with different material structures, in order to identify phenomena related to specific materials and several such relationships were identified. Additionally, mechanisms were proposed to explain the observed change in characteristics for different structures. UV-illumination plays a key role in the stability of devices containing ZnO, with unencapsulated devices maintaining performance over several weeks. Of the device-types evaluated, it is concluded that a standard structure containing ZnO, MoO₃ and silver is the most suitable candidate for future stable OPVs.

Subsequent experimentation with varying UV-light levels revealed rapid degradation of structures containing ZnO in the absence of UV-light. This effect was investigated further by intermittently exposing devices to illumination with and without UV-light. The effect of illumination with no UV component was rapid degradation of device performance. When typical UV levels were reintroduced, performance increased to almost double the initial value. This process was repeated on the same device with the same result being observed several times consecutively, indicating that the mechanism is reversible. This observation led to the hypothesis that the causal mechanism for this degradation is oxygen adsorption in the ZnO ESL.

Further investigation of NP systems gave a clearer understanding of the degradation processes dominant in these devices. NP systems with two different electron-accepter materials (PCBM and ICxA) were investigated under four different lighting conditions. The degradation of devices was significantly different for each fullerene type when tested under intermittent illumination. As intermittent illumination typically involves higher humidity, these results indicate that PCBM is likely more sensitive to water than ICxA. The similarity in the results for the two acceptors is promising, as ICxA is lower cost and higher performing than PCBM.

Experiments showed the presence of surfactant in BHJ devices had a significant effect on both initial performance and degradation. Subsequent, XPS measurements revealed the nature of the movement of surfactant through the active layer. It was observed that, in the NP active layers, surfactant accumulates at the interface with the exposed electrode regardless of device structure, which was confirmed by both depth-profile and surface-scan XPS measurements.

Surfactant-free NP solutions were also produced via precipitation to observe the stability and compare with the degradation of devices containing surfactant. Given that earlier results suggested that degradation was related to the movement of surfactant within the device, the surfactant-free devices were expected to be more stable. However, lifetime measurements showed these devices to be significantly less stable than the surfactant-containing devices. These experiments provided novel insight into the degradation of several NP systems and showed that surfactant plays a complex role in the stability of these devices.

Degradation processes, relating to materials or conditions, were identified and investigated using lifetime measurements, in conjunction with a variety of imaging and characterisation techniques. Several materials were identified as causing rapid degradation under certain conditions. Additionally, a material structure was also identified which produced devices that were stable, without encapsulation, over several weeks. The stability of NP OPV devices has been systematically studied, for the first time, showing that mobile surfactant in the active layer plays an intricate role in their degradation. Overall, a more in-depth picture of the degradation of OPVs has been obtained allowing for the production of more stable devices.

7.2 Future Work

The degradation of OPVs is a complex system of processes that are affected by various factors. Thus, there remains a great deal of work necessary to gain a full understanding. Through this thesis, a fully-automated system for performing

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degradation measurements was produced, allowing for any number of further lifetime measurements to be performed.

Further work is required to fully understand the role of ZnO in the degradation of devices, both in the presence and absence of UV-light. Performing degradation measurements under light with a more intense UV component would be informative. The light source used in chapter 5 provided only a small increase in UV intensity, consequently it was difficult to observe changes from unmodified constant illumination in some cases. Additionally, UPS could be used to further investigate the changes in ZnO that were observed upon exposure to UV-light in section 5.4.

There are also a wide variety of other techniques that can be employed to identify degradation processes associated with changes in performance for different structures. The exposed electrode is a significant source of degradation. As such, imaging techniques, such as atomic force microscopy and scanning electron microscopy, are viable candidates for investigating physical changes in the electrode due to degradation.

It is well known that the composition of devices is not static and diffusion of materials throughout the device causes degradation. Changes in chemical composition between pristine and degraded devices could be explored using XPS and depth profile measurements. The identification of materials prone to migrating between layers would facilitate the design of more stable devices. Investigations on physical changes in the layers during degradation, performed using imaging techniques such as scanning electron microscopy (SEM), could be used to identify degradation processes. Specifically, it may be used to further characterised changes in the active layer when stored under different environmental and lighting conditions.

Investigation of encapsulation is also required. As mentioned in section 1.7.6, there are various encapsulation materials that vary in both expense and effectiveness. To investigate the suitability of a material, lifetime measurements can be performed on devices of the same structure which have been encapsulated in different materials. It would also be informative to repeat degradation measurements on devices of different material structures with encapsulation to observe the effect on proposed degradation mechanisms. Another project has already commenced investigating the suitability of various encapsulant materials. The switching system design for the degradation testing system is versatile and is also currently in use to that end.

The primary goal of this thesis was to provide a more comprehensive understanding of the stability and degradation of OPVs, several important questions were answered, and novel phenomena identified and substantiated. The work completed represents a significant step towards the stated goal and will act as a strong foundation for the suggested future work.

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