# **Electronic and Chemical Properties of Interfaces in Organic Photovoltaic**

# Devices



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Master of Nanotechnology

श्रीश्री गुरु-गौराग्डौ जयतः ।

### कर्मण्येवाधिकारस्ते मा फलेषु कदाचन ।

मा कर्मफलहेतुर्भुर् मा ते संगोऽस्त्वकर्मणि ॥ ४७॥\*

\*Śrīmad Bhagavad Gītā, Chapter 2, Verse 47

"We are at the very beginning of time for the human race. It is not unreasonable that we grapple with problems. But there are tens of thousands of years in the future. Our responsibility is to do what we can, learn what we can, improve the solutions, and pass them on."

- Richard P. Feynman

In Loving memory of my beloved chacu late

Mr. Anuj Sharma (1966- 1988)

Dedicated to my grandparents late Mr. C. L. Sharma (1923- 2004) and Mrs. C. V. Sharma (1930-2003)

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### Abstract

Organic Photovoltaics is a promising technology, which can potentially be a cheap source of clean and renewable energy in the near future. Despite tremendous research and development efforts in this field, organic solar cells still take a back stage in the mainstream photovoltaic market. Though the efficiencies have gradually increased to up to 12 %, device stability still remains a challenge limiting large-scale commercialization of this technology.

This dissertation is devoted primarily to the study of stability and performance-limiting electronic properties of device interfaces in both conventional and inverted OPVs. Given the importance of electrode workfunction in interfacial charge transport in devices, special focus was on better understanding the workfunction measurements on heterogeneous surfaces and precise measurement of lateral variations in workfunction on a nanoscale.

In particular, the interfacial instability of ITO-PEDOT:PSS interface in conventional OPVs was investigated and it was shown for the first time that the migration of indium and tin into the PEDOT:PSS was strongly driven by the presence of moisture and is not merely a diffusive process, as prior beliefs. It was systematically demonstrated that indium and tin contaminants can adversely affect the device performance by increasing the interfacial dipole at the ITO-PEDOT:PSS interface.

For inverted OPVs, a strong correlation between the processing conditions of ZnO and the device performance has been established. Changes in the electronic or structural properties of ZnO were demonstrated to be the driving force behind the strong dependence of device performance on the processing conditions of ZnO.

ZnO prepared via a range of techniques was studied and for all cases a minimum of 25 nm layer thickness was found to be essential to achieve optimum device performance. For solgel prepared ZnO, the workfunction was found to be independent of the layer thickness, whereas for ZnO layer casted from a colloidal solution, post annealing temperature was found to be critical and a minimum temperature of 200 °C was found to be essential in order to achieve desirable workfunction and electron affinity. As in case of pulsed laser deposited ZnO, stoichiometric ratio of Zn and O was also found to be dependent on the layer thickness and thicker layer (up to 100 nm) were found to get oxygen deficient with

increasing thickness. A fully evolved band structure of ZnO was found to be absent for layers of thickness 12 nm or less, which explains the poor performance of such devices.

This work also establishes a clear understanding of workfunction measurements of heterogeneous surfaces with UPS. Surfaces with heterogeneity on a nanoscale were artificially created with a combination of energetically different materials. It was demonstrated that materials having relatively low workfunction have an enhanced secondary electron emission, which can be misleading in deriving absolute workfunction values from UPS measurements. This behaviour was found to be valid even for polycrystalline materials with nanoscale variations in workfunction such as ZnO. While nano-domains of different workfunctions across a nano-roughned ZnO surface were clearly demonstrated using KPFM, UPS results were found to be more representative of the domains corresponding to low workfunction regions.

# Declaration

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

------

Anirudh Sharma

# Acknowledgement

The last four years have been an incredible phase of my life, which witnessed a transition of an inquisitive student to an independent scientist. My PhD journey was full of stirring experiences with fascinating science around me. As this enriching and unique PhD journey comes to an end, I would like to take this opportunity to acknowledge and thank all those who helped me either towards the completion of this dissertation or those who made my Australian odyssey, a memorable journey.

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> Anirudh Sharma Flinders University July 2014

### **List of Publications**

#### **Refereed Journal Articles**

- 1. *Anirudh Sharma*, Rüdiger Berger, Gunther Andersson, David A. Lewis. Nanoscale heterogeniety and workfunction variations in ZnO thin films, *Submitted*.
- Anirudh Sharma, Joseph B. Franklin, Birendra Singh, Gunther Andersson, David A. Lewis. Electronic and chemical properties of ZnO in inverted OPV's, *Submitted*.
- 3. *Anirudh Sharma*, Rüdiger Berger, Gunther Andersson, David A. Lewis. Invisible high workfunction materials on heterogeneous interfaces. *Applied Surface Science*, *Accepted*.
- 4. *Anirudh Sharma*, Scott Watkins, Gunther Andersson, David Lewis. Effect of annealing temperature of ZnO on the energy level alignment in inverted organic photovoltaics (OPVs). *Energy Technology*, 2014, 2 (5) pp. 462-468.
- Anirudh Sharma, Mihail Ionescu, Gunther Andersson and David Lewis. Role of zinc oxide thickness on the photovoltaic performance of laminated organic bulk hetero-junction solar cells. Solar Energy Materials and Solar Cells, 2013, 115 pp. 64-70.
- Anirudh Sharma, Scott Watkins, David Lewis and Gunther Andersson. Effect of indium and tin contamination on the efficiency and electronic properties of organic bulk hetero-junction solar cells. *Solar Energy Materials and Solar Cells*, 2011, 95(12) pp. 3251-3255.
- 7. *Anirudh Sharma*, Gunther Andersson and David Lewis. Role of humidity on indium and tin migration in organic photovoltaic devices. *Physical Chemistry Chemical Physics*, 2011, 13 pp. 4381-4387.

 Lee Hoffman, Gunther Andersson, *Anirudh Sharma*, Stephen Clarke, and Nicolas Voelcker. New insights into the structure of PAMAM dendrimer/gold nanoparticle nanocomposites. *Langmuir*, 2011, 27(11) pp. 6759-6767.

#### **Conference Proceedings**

- Anirudh Sharma, Gunther Andersson and David Lewis. Effect of ZnO layer thickness on the photovoltaic performance of laminated solar cells. Nanomaterials for Green Technology, Proceedings of the 3<sup>rd</sup> ISESCO International Workshop and Conference on Nanotechnology (IWCN 2012) Selangor, Malaysia. Dec 2012, pp. 57-57.
- Anirudh Sharma, Scott E. Watkins, Gunther Andersson, and David Lewis. Instability of ITO-PEDOT:PSS interface in organic bulk hetero-junction solar cells and its effect on the efficiency and electronic properties of the device. *Thin Films and Nanomaterials* (Macmillan Advanced Research Series, India) edited by S. Jayakumar, M.D. Kannan, R. Balasundaraprabhu, S. Prasanna, Proceedings of the *International Conference on Advanced Materials* (ICAM 2011) Coimbatore, India. Dec 2011, pp. 212-215.

#### **Presentations and Seminars**

- [Oral] Anirudh Sharma, Rüdiger Berger, Gunther Andersson, David Lewis. Workfunction measurement of heterogeneous surfaces. Flinders Centre for Nanoscale Science and Technology (FCNST) Annual Conference, June 18, 2014, Adelaide, Australia.
- [Oral] Anirudh Sharma, Rüdiger Berger, Gunther Andersson, David Lewis. Nanoscale surface electronic properties of zinc oxide. International Conference on Nanoscience and Nanotechnology (ICONN 2014), February 2- 6, 2014, Adelaide, Australia.
- [Invited Oral] Anirudh Sharma, Scott Watkins, Gunther Andersson and David Lewis. ZnO buffer layer for OPV's: Interfacial energetics and its influence on device performance. International Workshop and School on Nanotechnology (NanoS-E3 2013), September 15-20, 2013, Airlie Beach, Australia.
- 4. [Seminar] *Anirudh Sharma*, Scott Watkins, Gunther Andersson and David Lewis. Role of interfacial layers on the performance of OPV's. *Physics at Interfaces Research Group, Max Planck Institute for Polymer Research*, June 3, 2013, Mainz, Germany.
- [Poster] Anirudh Sharma, Gunther Andersson and David Lewis. Role of ZnO layer thickness on the photovoltaic performance of OPV's. Hybrid and Organic Photovoltaics Conference (HOPV 2013), May 5-8, 2013, Sevilla, Spain.
- [Oral] Anirudh Sharma, Gunther Andersson and David Lewis. Effect of ZnO layer thickness on the photovoltaic performance of laminated OPV's. The 3<sup>rd</sup> ISESCO International Workshop and Conference on Nanotechnology (IWCN2012), December 5-7, 2013, Universiti Kebangsaan (UKM) Malaysia.
- [Seminar] Anirudh Sharma, Scott Watkins, Gunther Andersson and David Lewis. Role of interfaces on the photovoltaic performance of organic bulk hetero-junction solar cells. South Australian Physical Chemistry Symposium, December 3, 2012, University of Adelaide, Australia.

- [Poster Prize] Anirudh Sharma, Gunther Andersson and David Lewis. Understanding the morphological and electronic properties of zinc oxide buffer layers used in inverted organic photovoltaic cells. International Organic Excitonic Solar Cell Conference (IOESC 2012), September 3-7, 2012, Coolum Beach, Australia.
- [Poster Prize] Anirudh Sharma, Scott Watkins, Gunther Andersson and David Lewis. Air-processed organic bulk hetero-junction solar cells fabricated with hot press lamination: A step towards roll-to-roll processing. Flinders Centre for Nanoscale Science and Technology (FCNST) Annual Conference, June 13, 2012, Adelaide, Australia.
- [Oral] Jonathan Campbell, *Anirudh Sharma*, David Lewis, Thermomechanical behaviour of conducting polymer blends. 33<sup>rd</sup> Australian Polymer School, February 12-15, 2012, Hobart, Australia.
- 11. [Oral] Anirudh Sharma, Scott Watkins, David Lewis and Gunther Andersson. Instability of ITO-PEDOT:PSS interface in organic bulk hetero-junction solar cells and its effect on the efficiency and electronic properties of the device. International Conference on Advanced Materials (ICAM) / Indo-Norwegian Workshop on Solar Energy Materials and Applications, December 12-16, 2011, Coimbatore, India.
- 12. [Oral] Anirudh Sharma, Scott Watkins, Gunther Andersson and David Lewis. Degradation of OPV's due to interfacial instability and an alternative approach towards roll-to-roll device fabrication. Flinders Centre for Nanoscale Science and Technology (FCNST) Annual Conference, July 18, 2011, Adelaide, Australia.
- 13. [Poster] Anirudh Sharma, Gunther Andersson and David Lewis. Stability of ITO-PEDOT:PSS interface in bulk hetero-junction solar cells. Australian Research Network for Advanced Materials & Australian Research Council Nanotechnology Network Joint Annual Workshop (ARNAM/ARCNN 2010), July 19-23, 2010, Adelaide, Australia.

### **Awards and Prizes**

2014:	Best Presentation Award
	Flinders Centre for Nanoscale Science and Technology (FCNST) Annual
	Conference, Australia.
2013:	Visiting Research Fellowship
	Max Planck Institute for Polymer Research (MPIP), Germany.
2012:	Conference Travel Grant
	Australian Nanotechnology Network (ANN), Australia.
2012:	Poster Prize
	International Organic Excitonic Solar Cell Conference (IOESC), Coolum
	Beach, Australia.
2012:	University Finalist (2 <sup>nd</sup> prize- Faculty of Sci. & Eng.)
	Flinders University 3MT Competition, Australia.
2012:	Poster Prize
	Flinders Centre for Nanoscale Science and Technology (FCNST) Annual
	Conference, Australia.
2011:	Chancellor's Letter of Commendation for Academic Excellence
	Flinders University, Australia.
2011:	Tuition Fee Waiver
	Faculty of Science & Engineering, Flinders University, Australia.

#### 2010: Postgraduate Research Top-up Scholarship

*Future Manufacturing Flagship, Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia.* 

#### 2010: Privately Funded Postgraduate Research Scholarship

Flinders University, Australia.

#### 2009: Summer Research Scholarship

Faculty of Science & Engineering, Flinders University, Australia.

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### Abbreviations

AFM	Atomic force microscope	
ALD	Atomic layer deposition	
AM	Air mass index	
BHJ	Bulk hetero-junction	
CPD	Contact potential difference	
CSIRO	Commonwealth scientific and industrial research organization	
DI	De-ionized	
FWHM	Full-width-half-maxima	
НОМО	Highest occupied molecular orbital	
ΙΤΟ	Indium tin oxide	
IMFP	Inelastic mean free path	
KPFM	Kelvin probe force microscope	
LUMO	Lowest occupied molecular orbital	
MEH-PPV	Poly(2-methoxy-5-2(2'-ethyl-hexyloxyl)-p-phenylene vinylene)	
NICISS	Neutral impact collision ion scattering spectroscopy	
nm	Nanometer	
OPV	Organic photovoltaic	
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate)	
РЗНТ	poly (3-hexylthiophene)	
РСВМ	[6,6]-phenyl-C61-butyric acid methyl ester	
PPM	Parts per million	
PESA	Photoelectron spectroscopy in air	

#### Abbreviations

p-LED	Polymer light emitting diodes
PET	Polyethylene terephthalate
PLD	Pulsed laser deposition
PEN	Polyethylene naphthalate
RH	Relative humidity
RBS	Rutherford backscattering spectroscopy
SPM	Surface probe microscopy
S. E.	Secondary electron
SKPM	Scanning kelvin probe microscopy
TEM	Transmission electron microscope
TOF	Time of flight
TW	Terawatt
UV	Ultraviolet
UHV	Ultra-high vacuum
UPS	Ultraviolet photoelectron spectroscopy
VBM	Valence band maxima
XPS	X-ray photoelectron spectroscopy
ZnO	Zinc oxide

### **Introduction to Organic Solar Cells**

The 20<sup>th</sup> century has witnessed tremendous amount of development globally with largescale urbanisation and massive industrialisation. The same phase has also been marked by a fourfold increase in world population.<sup>[1]</sup> Increased development and population together contributed to an energy consumption of as high as sixteen times of that in the 19<sup>th</sup> century. Energy requirements by the year 2050 are expected to be around 23 TW compared to the present consumption of over 13 TW.<sup>[1]</sup> Such a tremendous increase in the energy demands cannot be met entirely by relying on the conventional sources of energy such as the finite fossil fuels, which currently supplies around 80 % of the total energy needs.<sup>[2]</sup>

Due to mushrooming population and constantly expanding human activities, one of the biggest challenges that the 20<sup>th</sup> century has seen is the sharp rise in carbon emissions and climate change. As a result, the average temperature of the Earth is expected to be around 1.8 °C to 4 °C higher by the end of this century.<sup>[3]</sup> More frequent occurrence of severe weather is already seen and is expected to worsen in the coming years.

#### **1.1. Renewable Energy**

The constantly increasing cost of oil and gas, limited fossil fuel reserves and their direct and indirect ill effects on the environment are some of the compelling reasons to explore alternative sources of clean energy which are cheap and generated using renewable methods. Among all the renewable energy sources available such as hydroelectric resources, geothermal resources, tides and ocean currents, wind power etc., solar energy striking the Earth is capable of generating maximum power.<sup>[1]</sup> This is because the Earth receives around 3 x  $10^{24}$  J of solar energy annually. This gigantic figure corresponds to over 10,000 times the present energy consumption, globally.<sup>[4]</sup> The solar energy resource available is significantly more than all other renewable energy resources and finite energy resources combined<sup>[5, 6]</sup> as shown in Figure 1.1.



*Figure 1.1*: Comparison of renewable and finite energy reserves (Terawatt-years). Yearly potential is shown for the renewable resources and total recoverable reserves are shown for the finite resources. Taken from Perez et al.<sup>[5]</sup>

Energy generation through concentrated solar thermal, which converts heat to electricity and photovoltaic technologies, which involves the direct conversion of sunlight to electrical power, are potentially the most reliable contenders as a clean, sustainable and an environmentally friendly energy source capable of fulfilling the ever increasing energy demands on this planet.

The increased scientific focus of researchers in improving the existing photovoltaic technology is a reflection of an attempt to tap into this enormous clean and indigenous energy reservoir. The potential of photovoltaic technology has been well realised and is evident by the exponential growth that the photovoltaic industry has witnessed in the last decade both in terms of production<sup>[7]</sup> (Figure 1.2) and installation (Figure 1.3) of PV modules,<sup>[7]</sup> globally.



*Figure 1.2*: Global production of photovoltaic cells and modules from 2000 to 2012. Taken from PV status report, 2012.<sup>[7]</sup>



*Figure 1.3*: *Cumulative installation of photovoltaic cells and modules from 200 to 2012. Taken from PV status report, 2012.*<sup>[7]</sup>

#### **1.2.** Photovoltaic Technology

The photovoltaic effect was first discovered by a young French scientist Edmond Becquerel in 1839,<sup>[8]</sup> in a liquid device. After a long period of over 40 years after discovering the photoelectric effect, first working photoactive device based on selenium was reported by Charles Fritts in 1883.<sup>[9]</sup> In 1953, Gerald Pearson and Calvin Fuller at Bell Laboratories, in an accidental discovery found that doped silicon responds to light. This led

to the first ever silicon based solar cell fabricated by Chaplin et al. and was reported in 1954<sup>[10]</sup> followed by the fabrication of the first silicon solar cell module for outdoor purposes in 1955.<sup>[11]</sup> For the next 20 years after the discovery, spacecraft provided the main application for photovoltaics.<sup>[11]</sup> The potential of solar cells was demonstrated for the first time when 'Vanguard" the first American satellite equipped with solar cells, was launched.<sup>[12]</sup> The mid 1970's witnessed a sudden growth of module technology due to oil embargoes and application of photovoltaics in large telecommunication systems, resulting in the first modern module which was designed in 1976.<sup>[11]</sup> Based on the developments and technology used to design and fabricate solar cells, they can be classified under three different generations, as described below:

#### 1.2.1. First Generation Solar Cells

The silicon based solar cells such as developed at Bell laboratories in 1950's are called as the first generation solar cells. Cells belonging to this category are the most common type of cells commercially available in the present market. As the photovoltaic technology continues to mature, the cost of a solar panel is driven by the cost of raw material, which in this case is ultra-pure silicon. Purifying and crystallising silicon is the most energy intensive part of manufacturing <sup>[13]</sup> which results in high costs of manufacturing and thus an expensive final product. However, the development of this technology continues in the present time, with the cost reduction mainly driven by efficiency improvement, cost reduction by reducing the volume of silicon used and economies of scale. The energy payback time for this technology, considering the expected improvements in performance and lifetime as a result of further technological advancements, has been forecasted to be less than 0.5 years by the year 2020.<sup>[13, 14]</sup>

#### 1.2.2. Second Generation Solar Cells

Soon after the development of silicon based solar cell technology, due to a quest for cost reduction, in the 1990's the photovoltaic industry witnessed a transition towards thin film solar cell technology which is classified as the second generation of solar cells. These devices are mainly made up of CdTe, CdSe, CIGS etc. In these devices, the elimination of silicon with other semiconducting materials has significantly reduced the cost of manufacturing.
### **1.2.3.** Third Generation Solar Cells

In order to achieve solar cells with truly competitive efficiency to cost ratios, a paradigm shift in the concept and technology is desirable. This is where emerging nanotechnology provides hope. Devices incorporating nanostructured semiconductors such as quantum dots, organic-inorganic assemblies and molecular assemblies make up the 3<sup>rd</sup> generation of solar cells.

Third generation technology can further be divided in group A and group B. Group A comprise of concepts such as thermophotonics, hot carriers, multiple electron-hole pair creation etc.<sup>[15]</sup> Though these technologies still need to mature and could be expensive, their theoretical maximum efficiencies are well in excess of that of single junction devices.<sup>[16]</sup> Devices in group B are focused on achieving moderate efficiencies but at a very low cost. This requires inexpensive materials, low temperature processing compatible with large-scale fabrication. It is in this category that the organic based photovoltaics play a significant role.<sup>[16]</sup> An extensive listing of the latest efficiencies of various types of solar cells can be found in a recent report.<sup>[17]</sup> Figure 1.4 shows a cost and efficiency analysis of the three generations of solar cells, graphically depicting that if efficiency can be substantially improved, third generation technology can potentially result in the lowest module production cost per unit area as well as lowest cost per unit of energy conversion.<sup>[18]</sup>



*Figure 1.4*: Cost and efficiency projections for  $1^{st}$ ,  $2^{nd}$  and  $3^{rd}$  generation solar cells. Taken from reference [18].

Organic solar cells enjoy advantages over their inorganic counterparts due to the inherently inexpensive organic materials required, the range of fabrication techniques which could be potentially cheap and scalable and the possibility of wide range of unconventional applications due to the portability and versatile design of these devices.<sup>[19-21]</sup> In order for these devices to be commercially viable and feed our day to day energy needs, it is of the utmost importance to make them more efficient and have a reasonable life time. Instability and properties of material interfaces in such devices can greatly influence the device performance and lifetime and are a significant current challenge. In-depth understanding of the material interfaces, interfacial energetics and its influence on device performance is of outmost importance and it is in this direction this thesis is focussed.

# **1.3.** Organic Photovoltaic Cells (OPVs)

Since the discovery of electro-luminescence in conjugated polymers,<sup>[22]</sup> this class of materials has been used extensively to design electronic devices such as diodes, transistors<sup>[23]</sup> and organic photovoltaic (OPV) devices.<sup>[12]</sup> As a result, electronic gadgets such as smart phones, screen touch tablet computers, curved television displays and flexible solar cells are no more a science fiction and are some of the latest examples of new generation of electronics in our day to lives.

OPV's made from polymeric materials are promising alternatives to inorganic semiconductors for renewable energy production. In 1906 Pochettino first observed photoconductivity in the organic compound Anthracene, which was also later reported by Volmer in 1913.<sup>[24]</sup> Since then, there has been a tremendous effort to develop the technology behind OPVs as shown in a number of major reviews.<sup>[24-30]</sup>

### 1.3.1. Performance

In the last five years, the power conversion efficiencies of OPVs have increased almost exponentially from around 5 % to upto 12 %.<sup>[31]</sup> A significant improvement with an efficiency of 8.13 % was reported by Solarmer Energy Inc. in July 2010, a record which was soon overtaken by Heliatek and Konarka Technologies later in 2010 with both reporting 8.3 % efficiencies.<sup>[32]</sup> Soon after, Mitsubishi chemicals reported an efficiency of 9.2 %<sup>[32]</sup> and more recently 12 % efficiency was reported by Heliatek in 2013 (Figure 1.5).<sup>[31]</sup>



*Figure 1.5*: *Record efficiencies reported for OPVs in the last three decades. Taken from reference [33].* 

While this improvement in efficiency is encouraging and business opportunities for OPV's are believed to be enormous,<sup>[21]</sup> major challenges still remain in form of simultaneously achieving longer operating lifetime and low fabrication cost,<sup>[21, 34]</sup> inorder to achieve a high power to cost ratio as depicted in Figure 1.6.



*Figure 1.6*: Venn diagram depicting a favourable scenario for successful commercialization of OPVs where the efficiency, stability and processing is optimally achieved. Adapted from reference [35].

Thus, current OPV research has intensified on reducing the fabrication cost by enabling

large-scale manufacturing as well as on achieving more stable devices with longer operational lifetime.

### 1.3.2. Lifetime & Stability

The operational lifetime of OPVs depends on various factors such as the stability of materials as well as that of the interface between various materials and the electrode. Chemical degradation of the polymeric and electrode materials is known to be one of the main reasons for device degradation.<sup>[36-38]</sup> Organic materials and commonly used low workfunction metals such as aluminium are very sensitive to oxygen and water, which are known to be a common cause for device failure.<sup>[38, 39]</sup> The lifetime of OPVs is also known to be affected by light induced degradation of polymeric materials commonly used in active layers.<sup>[40, 41]</sup> Also material properties such as the hygroscopic nature of PEDOT:PSS (which is commonly used as an interfacial layer in OPVs) make devices more prone to degradation on air exposure.<sup>[42]</sup> Increased water absorption in such devices has been shown to increase the interfacial resistance between material layers and hence affect the overall charge transport leading to device degradation.<sup>[43]</sup>

Another major cause of device degradation is the interfacial instability of the electrodepolymer interfaces. Metal-organic interfaces are not atomically sharp and electrode materials such as aluminium and indium are known to diffuse into the polymer layers<sup>[44, 45]</sup> resulting in device degradation.

While device degradation due to exposure to air and moisture<sup>[43]</sup> can be controlled by encapsulating devices using barrier films,<sup>[46, 47]</sup> the degradation due to interfacial instability can only be controlled by better understanding such material interfaces.

### 1.3.3. Processing & Fabrication

The manufacturing cost of OPV's can be reduced by utilizing fabrication methods which are fast and scalable at low cost. This has resulted in various attempts to apply existing roll-to-roll compatible fabrication and coating technologies such as slot-die printing,<sup>[48]</sup> screen printing,<sup>[49]</sup> knife-over-edge coating,<sup>[19]</sup> spray-coating<sup>[50]</sup> and lamination<sup>[51]</sup> to fabricate OPV's. Such alternative fabrication methods for manufacturing light and flexible solar cells<sup>[19]</sup> can not only be less expensive but also enable large area manufacturing of OPV's.<sup>[52]</sup> Various other methods potentially enabling low cost and large scale

manufacturing has also been successfully demonstrated.<sup>[53-63]</sup>

Fabrication methods such as a lamination approach,<sup>[51, 63-67]</sup> which involves sandwiching various material layers by lamination rather than sequential deposition, has also been investigated. Lamination is a promising technique as it not only enables the optimisation of each material layer before lamination, but it also enables roll-to-roll processing and hence large-scale manufacturing. Laminated devices are self-encapsulated and thus by appropriate selection of a barrier substrate, an additional encapsulation step<sup>[47]</sup> could potentially be avoided, making the entire fabrication process relatively quick and low cost method. A laminated OPV with a polymer-polymer bi-layer structure was reported by Granstrom *et al.* in 1998.<sup>[68]</sup> Since then not much research was done in this field until 2008 when Yang Yang's group reported an organic hetero-junction solar cell fabricated by a lamination process.<sup>[64]</sup> As the device performance of OPV's is improving rapidly, various groups around the world have in recent times started focussing on various lamination methods to fabricate OPV devices.<sup>[64, 65, 67, 69-72]</sup> Recently, device efficiencies as high as 3.13% <sup>[51]</sup> and 4% <sup>[73]</sup> have been reported for laminated devices.

### **1.4.** Physics of Inorganic & Organic Photovoltaics

In inorganic semiconductors with a 3D crystal lattice, individual energy levels form conduction and valence bands throughout the material. However, in the case of organic solids, the molecules interact with weak van der Waals interactions, thus the occupied and unoccupied states are usually localised and the electronic structure of a molecule or a single chain is preserved.<sup>[74]</sup> The validity of band theory in such systems is quite limited<sup>[75]</sup> and charge transport proceeds via a hopping mechanism<sup>[76]</sup> between localised states, resulting in poor charge carrier mobility in organic solids compared to crystalline inorganic semiconducting solids. However, most organic semiconductors have relatively high absorption coefficients ( $\sim \ge 10^5$  cm<sup>-1</sup>) and a 100 nm thick layer is usually enough to get sufficient photogeneration in the photoactive organic film for optimum device performance.<sup>[28, 76]</sup> Unlike inorganic semiconductors, due to their low dielectric constant, lead to coulombically bound electron-hole pairs, also called excitons which require strong electric fields to dissociate due to their high binding energy.<sup>[77]</sup>

# **1.5.** Device Structure & Principle of Operation

## 1.5.1. Single Layer OPVs

The first type of OPV's ever reported were fabricated by sandwiching a single organic light absorbing layer between two metal electrodes of different workfunctions,<sup>[30]</sup> where one of the electrodes is transparent (such as indium tin oxide) in order for light to reach the organic layer. The mechanism of light conversion into electricity in excitonic solar cells (Figure 1.7) can be summarised in four main steps:

- Photon absorption & exciton creation
- Exciton diffusion
- Charge separation
- Charge transport and collection



*Figure 1.7*: A schematic depiction of the light harvesting process in an OPV.  $\phi_{ITO}$  and  $\phi_{Al}$  are the workfunctions of the ITO and aluminium electrode, respectively.

When a photon of energy hv incident on the device is absorbed by the active layer, an electron in the highest occupied molecular orbital (HOMO) is excited, and jumps to the lowest unoccupied molecular orbital (LUMO), forming a bound electron-hole pair (exciton) in the conjugated polymer<sup>[78]</sup> with a binding energy of about 0.4 eV.<sup>[79]</sup> The excitons need to dissociate before the charges can be transported to the respective electrodes.

The rectifying behaviour of single layer devices can be explained by a metal-insulatormetal (MIM) model (for insulator) or by the formation of Schottky barrier at the polymerlow workfunction electrode.<sup>[26, 80]</sup> In a MIM device, internal electric fields developed due to the asymmetry in workfunction of the two electrodes helps to separate the charges and results in rectification properties.<sup>[81, 82]</sup>

In the case of single layer OPV's having a Schottky junction, charge dissociation takes place in the depletion region (Figure 1.8) which is created at the interface due to potential distribution (electronic properties of metal-organic interface are discussed in Section 2.3) between the metal electrode and the organic material.<sup>[74]</sup> Thus single layer devices are limited by the fact that exciton diffusion can take place only in the depletion region.<sup>[26]</sup> These devices are most efficient when the active layer is very thin as it avoids unwanted recombination of the negative and positive photoexcited charges travelling through the same material.<sup>[83]</sup>



*Figure 1.8*: Schematic representation of (a) structure of a single layer OPV (b) a Schottky contact at the p-type polymer-Al interface.

### 1.5.2. Bilayer Hetero-junction OPV's

A significant breakthrough was achieved in the field of OPV's in 1986 when Tang introduced the concept of the bilayer hetero-junction and reported an efficiency of ~ 1 % from a device made by sandwiching two organic materials with hole and electron transporting properties between the two electrodes (Figure 1.9).<sup>[84]</sup> The enhancement observed in the device performance on introducing an additional layer of material with electron transporting properties was attributed to improved dissociation of charges at the donor-acceptor interface.



*Figure 1.9*: Schematic of a bilayer OPV with sequential deposition of donor and acceptor material and (on the right) exciton dissociation at the donor acceptor interface.

Because the electron is transferred from a p-type polymer to an n-type material, this is commonly expressed with a notion of donor and acceptor materials with respect to the electron transfer.

### 1.5.3. Bulk Hetero-junction OPVs

The efficiency of bilayer structured devices is limited by the fact that the diffusion length of the exciton is a few nanometres (~5-20 nm),<sup>[76, 85-88]</sup> so only the excitons near the interface can dissociate with a high level of recombination occurring in the bulk of donor material. This limits the thickness of the light absorbing organic layer, which should be 100 nm or more for optimum absorption of light. This problem was subsequently overcome by the concept of bulk hetero-junction (BHJ), which depends on creating a complex morphology of donor and acceptor materials (Figure 1.10) such that the phases are separated by a distance less than the excitonic diffusion length.<sup>[89, 90]</sup> In BHJ devices, the charge dissociation happens at the donor-acceptor interface.

Unlike bilayer devices where the donor and acceptor materials are selectively in contact with the anode and cathode, in BHJ devices, a bicontinous and interpenetrating network of the donor and acceptor materials is responsible for electron and hole transport to the respective electrodes. Therefore the device performance of bulk hetero-junction device is very sensitive to the nanoscale morphology of the active layer.<sup>[91, 92]</sup>



Figure 1.10: Schematic of a BHJ OPV with a blended donor and acceptor organic layer.

Because of the significantly increased interfacial area between the donor and acceptor in BHJ devices,<sup>[93]</sup> compared to the bilayer structures, this method greatly enhances the charge dissociation and is not limited by the active layer thickness. The light absorption in BHJ devices can thus be enhanced by incorporating a thicker active layer compared to the bilayer structures, resulting in higher photocurrent.<sup>[94]</sup>

### 1.5.4. Tandem OPVs

Tandem structured OPVs are fabricated by stacking two hetero-junction devices with different absorption spectra over one another (Figure 1.11). Hiromoto and colleagues first introduced the tandem cell structure<sup>[95]</sup> which is a promising approach to tackle issues such as thermalisation losses and narrow absorption window which are commonly observed in single junction devices.<sup>[6]</sup>



*Figure 1.11*: Schematic of a tandem OPV with two sub cells complimenting the absorption spectral window. Taken from Ameri et al.<sup>[96]</sup>

# **1.6.** Materials in OPV's

### 1.6.1. Donor Materials

In the last decade, organic semiconductors have been a subject of intense study due to their unique electrical and optical properties. The electrical transport property of conjugated polymers originate due to the presence of de-localized π-electrons and is very significant for the operating mechanism of electronic devices.<sup>[97]</sup> As a result, charge carrier mobility is limited due to the inter-chain hopping required to overcome localisation on a specific chain, giving a higher exciton binding energy. Attempts to improve the charge transport properties of such conjugated materials has led to the synthesis of a variety of more complex high molecular weight polymers and this class of materials can therefore be categorised in first, second and third generations with the classic examples of polyacetylene<sup>[82, 97]</sup> representing the first generation which witnessed initial efforts of fabricating organic solar cells. Some of the most studied second generation of semiconducting polymers are poly(paraphenylene), poly(phenylene vinylene) and polythiophenes.<sup>[98]</sup> For example, poly (3-hexyl thiophene) (P3HT) has been reported as the best seller in photovoltaic research.<sup>[99]</sup> More recently, polymers with more complex such poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopental[2,1-b;3,4-b]structure as dithiophene)-alt-4,7(2,1,3-benzothiadiazole)](PCPDTBT) and poly[N-9'-heptadecanyl-2,7carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)](PCDTBT)<sup>[82]</sup> have been reported and they represent the third generation of semiconducting polymers. A detailed list of various semiconducting polymer, their band positions and the device performance has been recently reviewed.<sup>[100]</sup>

### **1.6.2.** Acceptor Materials

Fullerenes are a class of roughly spherical carbon based molecules predominantly made up of sp2 bonds. Molecules such as  $C_{60}$  and  $C_{70}$ , have a high electron affinity and good electron conductance (~  $10^{-4}$  Scm<sup>-1</sup>) making them one of the most used acceptors in heterojunction OPV's. Photoinduced electron transfer from a conjugated polymer to  $C_{60}$  was first reported by Sariciftci et al.<sup>[101]</sup> Morita and colleagues<sup>[102]</sup> later observed that the conductivity in a  $C_{60}$  - conjugated polymer blend improved with  $C_{60}$ . Relatively more soluble derivatives of  $C_{60}$  were then used as an acceptor with a conducting polymer both in a bilayer configuration<sup>[103]</sup> and in BHJ photovoltaic devices.<sup>[93, 104]</sup> A range of fullerene derivatives have since been studied as acceptors in organic photovoltaic devices.<sup>[105, 106]</sup>

### **1.6.3. Transparent Electrode Materials**

The electrodes are a very important component of a device as they act as the interface between the semiconducting/photoactive layer and the external circuit. Ideally, they should be chemically stable and unreactive to the functional material layers, have very low resistance and must possess high transmission to be used as a transparent electrode in an OPV. The majority of OPV devices use a conducting metal electrode and a transparent conducting electrode usually an oxide such as indium tin oxide (ITO) and fluorine doped tin oxide (FTO) which due to their high band gap are transparent to wavelengths of over 400 nm.<sup>[107]</sup> For better performing devices, low sheet resistance of the electrodes is desirable to minimise charge losses, as the direct correlation of device area and degradation in device performance is well known and has been attributed to the high sheet resistance of underlying electrodes.<sup>[108]</sup>

High cost and limited flexibility of ITO have led to significant research efforts focussed on various organic and inorganic alternatives and a wide range of materials such as PEDOT:PSS<sup>[109]</sup>, ZnO, ZnO doped with boron,<sup>[110, 111]</sup> gallium<sup>[112, 113]</sup> and aluminium<sup>[114]</sup> has been explored as transparent electrode materials. However, due to relatively low sheet resistance and high transmittance, ITO is still the most widely used transparent electrodes in OPVs, even though demonstrations of ITO free devices are available.<sup>[115-117]</sup>

A range of new approaches utilising nanocomposites consisting of carbon nanotubes, graphene, conducting polymers and metallic nanowires are also being studied to develop transparent electrode materials with good electrical and optical properties and their compatibility with roll-to-roll processing.<sup>[115, 118-126]</sup> More details about the electrode materials and the electrical properties of various metals can be found elsewhere.<sup>[127]</sup>

### **1.6.4. Interface Materials**

When conjugated polymers are brought into contact with metals, which are commonly used as electrodes, the interfaces are not atomically sharp. Often dissimilar materials such as the polymer and the metals chemically react with some inter-diffusion caused by metals migrating into the polymers,<sup>[128]</sup> which is known to not only affect the charge transport properties of the polymer,<sup>[129, 130]</sup> but also gives rise to leakage currents<sup>[131]</sup> and affect the

lifetime of the photovoltaic device.<sup>[132, 133]</sup> Interfacial layers of both inorganic (such as ZnO, TiO<sub>2</sub> etc) and organic materials (ex. PEDOTPSS) are commonly used between the active layer and the electrode<sup>[134-137]</sup> to not only help in avoiding chemical and physical reactions at the interfaces, but also bridge the barrier heights for charge injection at the interfaces.<sup>[138]</sup> Interfacial layers enable unipolar extraction of photogenerated charges from the active layer to the electrode hence can be used to alter the polarity of a device. This is discussed in further detail in Section 2.3.

#### **1.7.** Characterisation of OPVs

Photovoltaic cells convert the light from the sun into electricity. The power conversion efficiency  $\eta$  of a solar cell is the ratio of the maximum power generated by the device  $(P_{output})$  to the power of light incident on the device  $(P_{input})$  and is expressed as a percentage.

$$\eta = \frac{P_{output}}{P_{input}}$$
Eq. 1.1

The power of the incident light used  $P_{input}$  is a function of the solar spectrum and therefore for accurate and consistent measurements, it is imperative that it represents the actual solar spectrum, reaching the Earth. When the sunlight reaches the Earth via the atmosphere, certain wavelengths are absorbed due to various reasons such as the chemical interactions, scattering etc. Due to this, the solar spectrum that reaches the Earth is strongly dependent on the path length of the light through the atmosphere. The path length of light reaching the Earth is different at different times of the day and year as well as geographic locations. In order to make the solar cell testing consistent, solar cells are tested using a universally accepted reference solar spectrum with an air-mass coefficient (AM) of 1.5, corresponding to a total power density of 100 mWcm<sup>-2</sup>.<sup>[139]</sup>

AM defines the direct optical path length through the Earth's atmosphere which attenuates the intensity of the radiation and is mathematically expressed as,

$$AM = \frac{1}{\cos \theta}$$
 Eq. 1.2

where  $\theta$  is the elevation angle above the horizon i.e. the angle of the sun from directly overhead, and is 41.81° in case of AM 1.5 spectrum.<sup>[139]</sup> Figure 1.12 shows the AMO,

#### AM1.5 global and normal solar spectrum.



**Figure 1.12**: AM0 extra-terrestrial spectrum and American Society for Testing and Materials (ASTM) G159 (direct normal and global, 37° sun-facing tilted) terrestrial spectra as tabulated in the current standard. Taken from Gueymard et al.<sup>[139]</sup>

The output power of the device  $P_{output}$  can be experimentally determined from the current and voltage (I-V) characteristics of the device. For I-V characterisation, an ideal solar cell can be modelled as a current source connected in parallel to a diode. When there is no light, the device acts as a diode and when the device is illuminated, it produces current.

Practically no device is ideal and various factors contribute to series and shunt resistances in the device. Figure 1.13 depicts a simplified equivalent circuit of a solar cell, where  $I_p$  the photogenerated is current,  $R_{sh}$  is the shunt resistance and  $R_s$  represents the parasitic series resistance (both contact and bulk components) originating in the cell and V is the applied voltage.



Figure 1.13: Equivalent circuit of a solar cell.

As the voltage across the load resistance is swept from 0 to  $V_{oc}$ , the I-V curve of a solar cell has the shape shown in Figure 1.14. In the dark, no diode current flows in the circuit until the applied voltage exceed the  $V_{oc}$  making the contacts inject heavily in forward bias, thus contributing to forward current. Under illumination, the current flows in the opposite direction relative to the injected current.

Based on the above device circuit, the I-V characteristics of a photovoltaic device can be described by:

$$I = I_0 \left\{ exp\left(\frac{e}{nkT}\left(V - IR_s\right)\right) - 1 \right\} + \frac{V - IR_s}{R_{sh}} - I_p$$
 Eq. 1.3

Where  $I_0$  is the dark current, *e* is the electronic charge, *n* is the diode ideality factor, and *V* is the applied voltage.

The output power  $P_{output}$  of a solar cell depends on critical parameters such as the open circuit voltage  $V_{oc}$ , short circuit current  $I_{sc}$  and fill factor FF. All these performance parameters can be determined from the I-V characteristics. The short circuit current  $I_{sc}$ corresponds to the maximum current value in the power quadrant (shown in Figure 1.14) when no voltage is applied. In short circuit conditions, no net current flows in the dark and the internal electric field due to the asymmetry in the electrode workfunction is homogenously distributed across the device, depicted by the tilted bands (Figure 1.14). When the device is illuminated, photogenerated charges drifts towards the electrodes (electrons to low workfunction and holes to high workfunction electrode) due to this internal field. In open circuit conditions, a voltage  $V_{oc}$  builds up and is measured by applying an equal and opposite voltage to balance the built-in field, which results in no net current flowing through the device. On applying a forward bias larger than the  $V_{oc}$  the electrodes injects charges into the semiconductor, thus contributing to forward currents. In a reverse bias scenario, current of small magnitude can flow, and under illumination photogenerated charges drift under strong electric fields to the respective electrodes and the device works as a photodetector. This asymmetry observed in the diode behaviour is known to originate due to the different injection of two metal electrodes into the HOMO and LUMO of the semiconducting polymer.<sup>[140]</sup> At  $I_{sc}$  and  $V_{oc}$  points, the power generated by the cell is therefore zero and the maximum power is generated between the two points.



*Figure 1.14*: *I-V* curve of a solar cell under illumination and in dark. The figure relates the *I-V* characteristics of a device qualitatively to the energy level diagrams. The broken line connecting the  $I_{sc}$  and  $V_{oc}$  corresponds to the shape of an ideal device (100 % FF).

The current and voltage at the maximum power point is denoted by  $I_{mpp}$  and  $V_{mpp}$  therefore, total power generated by the cell or  $P_{output}$  can be expressed as:

$$P_{output} = I_{mpp} V_{mpp}$$
 Eq. 1.4

The electrical conversion efficiency  $(\eta)$  of a solar cell can mathematically be expressed as:

$$\eta = \frac{I_{mpp}V_{mpp}}{P_{input}}$$
Eq. 1.5

The fill factor commonly written as FF is a measure of quality of a solar cell. FF is the ratio of the measured maximum power output to the theoretically possible power and is commonly expressed as a percentage. Mathematically, it can be expressed as,

$$FF = \frac{P_{max}}{I_{sc}V_{oc}}$$
 Eq. 1.6

The series and shunt resistance in the device can significantly influence the shape of the I-V curve and hence the FF. The generated photocurrent is often expressed as current per

unit area and thus "J-V" is interchangeably used for I-V characteristics of devices, when current density is expressed.

### 1.7.1. Factors Influencing I<sub>sc</sub>, V<sub>oc</sub>, & FF

#### 1.7.1.1. Short Circuit Current

Extending the spectral sensitivity can enhance the overall device performance of organic solar cells. This can be achieved by using low band gap materials in order to harvest a broader range of the spectrum, thus higher short circuit currents.<sup>[26]</sup> At a given absorption spectrum, the  $I_{sc}$  depends on efficient photoinduced charge generation and efficient charge transport which further depends on factors such as the exciton diffusion length,<sup>[86]</sup> temperature,<sup>[141, 142]</sup> and the electron and hole mobility of the interpenetrating networks.<sup>[97]</sup> Also, at a given absorption spectrum, the optical absorption profile within the active layer must be understood.<sup>[26]</sup> The thickness of various layers should be optimised such that the active layer thickness coincides with the maximum optical electric-field<sup>[143, 144]</sup> and at the same time it does not exceed the free carrier length of the charges to minimise the recombination losses.<sup>[97]</sup> In order to maximise the light absorption without compromising with the recombination losses as in thick layers, the absorption maxima can be shifted using an optical spacer (Figure 1.15) between the reflective electrode and the active layer. Thus in order to obtain optimum short circuit currents, various parameters such as active layer thickness, proper light absorption etc.<sup>[94, 145]</sup> needs careful optimisation.



*Figure 1.15*: Schematic showing the distribution of the square of the optical field strength across various material layers in a conventional OPV with and without an optical spacer. *Taken from Steim et al.*<sup>[137]</sup>

#### 1.7.1.2. Fill Factor

Minimum series and high shunt resistance are desirable in a device to achieve high fill factor. Devices must be defect free in order to avoid electrical shorts, which can otherwise lead to leakage currents and thus low shunt resistance in devices. FF is directly dependent

on the active area of the device and it decreases with increase in the active area as demonstrated by Maennig *et al.*<sup>[108]</sup> Larger active area contributes high series resistance in the circuit such as the one contributed from the transparent electrode (example: ITO have finite sheet resistance).<sup>[108]</sup>

#### 1.7.1.3. Open Circuit Voltage

The actual origin of open circuit voltage in organic solar cells and the contributions to it from various factors is a matter of debate.<sup>[146-149]</sup> According to a simple metal-insulatormetal (MIM) model, the maximum  $V_{oc}$  that is achievable in a device can be determined from the difference between the electrode workfunction.<sup>[140]</sup> However, such a behaviour has not been found to be valid for all organic systems and instead the open circuit voltage was found to be dependent on the offset between the LUMO of the acceptor and the HOMO of the donor polymer in BHJ solar cells,<sup>[147]</sup> and in addition to the built-in potential, the  $V_{oc}$  is also expected to be dependent on the chemical potential gradient across the photoactive layer.<sup>[150]</sup> Interfacial dipoles are known to significantly influence the workfunction of materials,<sup>[151]</sup> which can change the injection behaviour of the electrodes and hence the  $V_{oc}$ . This has led to an increased research focus on understanding the energy level alignment at the metal-organic interfaces<sup>[74, 152]</sup> in order to better understand and control the charge transport across interfaces of dissimilar materials and to achieve higher efficiencies.<sup>[153, 154]</sup> Interfacial energetics will be discussed in more detail in Chapter 2.

### **1.8.** Design of BHJ Devices

As discussed in Section 1.5, OPVs are commonly fabricated by sandwiching various energetically favourable materials between a transparent and a metallic electrode. The combination of materials and the electrode determines the polarity of the device and based on that, OPVs are commonly referred to have a conventional or an inverted structure.

#### **1.8.1.** Conventional Structures

OPVs in which ITO is used as a hole collecting electrode or anode are usually referred to have a conventional structure. Interfacial layers of various organic and inorganic materials are commonly used between the photoactive BHJ layer and the electrodes not only to planarise the surface of the underlying electrode,<sup>[155]</sup> but also to modify its workfunction, thus enhancing charge extraction by adjusting the energy levels between the electrode and

the active layer.<sup>[135, 156, 157]</sup>

In conventional structures, poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate) (PEDOT:PSS) with a workfunction of ~ 5.2 eV<sup>[158]</sup> is commonly used as an anodic buffer layer (Figure 1.16), and has been shown to improve the hole extraction to the anode,<sup>[159, 160]</sup> improving the open circuit voltage,<sup>[161]</sup> power conversion efficiency<sup>[136]</sup> and also in some cases the stability of the device.<sup>[162]</sup> However, the conventional structure has various performance limiting issues. For example, the phase separation within the BHJ layer<sup>[163]</sup>



Figure 1.16: Schematic of a conventional and an inverted device structure.

and the instability of the polymer- electrode interfaces, such as the PEDOT:PSS-ITO interface<sup>[45, 164, 165]</sup> or the BHJ-metal interface<sup>[44]</sup> which are known to degrade the device performance. In order to overcome such issues, an ultra-thin layer of materials such as lithium fluoride (LiF) or calcium (Ca) are commonly used as a cathodic interfacial layer and are known to significantly enhance the device performance.<sup>[166]</sup>

In recent studies vertical phase separation has been found to occur within the active layer composed of commonly used polymer blends such as P3HT and PCBM.<sup>[167-170]</sup> Such a phase separation of the two polymers in known to influence the charge recombination dynamics<sup>[171]</sup> and is particularly detrimental for conventional structures as explained further in Section 1.8.2.<sup>[172]</sup>

### **1.8.2. Inverted Structures**

Inverted devices are "electrically inverted" compared to conventional devices - basically in such devices the function of the electrodes is swapped (anode functions as a cathode and vice versa) as compared to their conventional counterparts. In inverted devices, ITO is

used as a cathode by modifying it properties with low workfunction materials such as zinc oxide (ZnO),<sup>[173, 174]</sup> aluminium doped zinc oxide (AZO), cesium carbonate (Cs<sub>2</sub>Co<sub>3</sub>),<sup>[153]</sup> titania (TiO<sub>2</sub>),<sup>[175, 176]</sup> etc. such that the ITO act as an electron collecting electrode or cathode in inverted devices.<sup>[177]</sup>

As mentioned earlier, phase separation of the donor and acceptor materials is known to occur immediately after spin-coating the active layer (polymer blend), with the enrichment of the donor and the acceptor material towards the top (air interface) and bottom (polymer-substrate) sides, respectively.<sup>[168]</sup> Energetically, such material segregation is not beneficial for device performance in conventional devices, but in case of inverted devices, because the polarity of the devices is opposite, such phase separation benefits the device performance. In fact, in inverted devices additives such as di-bromo-octane are added to the polymer blend to promote further phase separation in the BHJ layer.<sup>[51]</sup>

The inverted structure (Figure 1.16) also helps in avoiding possible chemical or physical reactions at the electrode-polymer interface. For example, the instability of the ITO-PEDOT:PSS interface is overcome by replacing PEDOT:PSS by other functional layers such as low workfunction alkali metal oxides like Cs<sub>2</sub>Co<sub>3</sub> ZnO etc. On the other hand, the cathodic buffer layer can be replaced by PEDOT:PSS or high workfunction metal oxides such as vanadium oxide  $(V_2O_5)$ ,<sup>[173]</sup> molybdenum oxide  $(MoO_3)$ ,<sup>[156]</sup> etc. in order to increase the workfunction of the metal electrode,<sup>[174]</sup> such that it behaves as an anode and collect holes. Various other materials such as copper oxide,<sup>[178]</sup> tungsten oxide (WO<sub>3</sub>),<sup>[179]</sup> nickel oxide (NiO)<sup>[180]</sup> have also been used to replace acidic PEDOT:PSS as an anodic buffer layer. Such metal oxide layers are also compatible with large scale manufacturing due to solution processability of most of these materials.<sup>[153, 173, 174, 178, 181-185]</sup> Besides changing the polarity of the device, thin metal oxide buffer layers avoid any possible chemical reaction between the electrode and the polymer layer,<sup>[186]</sup> and improve the performance and stability of the device.<sup>[179, 187, 188]</sup> Such improvements have mainly been attributed to increased shunt resistance,<sup>[179, 183]</sup> lower series resistance <sup>[156]</sup> and enhancement in device stability, which is believed to be due to the better shielding property of oxide buffer layers, which prevents diffusion of oxygen and moisture into the device.<sup>[187, 188]</sup> For interested readers, further details can be found in some of the detailed reviews on the above concept.<sup>[189, 190]</sup>

Though most of the materials used as buffer layers seem promising and their application in

BHJ OPV devices can be further explored, Cs<sub>2</sub>Co<sub>3</sub> and ZnO seems to be the most prominent contenders. Special interest in Cs<sub>2</sub>Co<sub>3</sub> layers is due to the fact that it has been shown to decompose into metallic cesium<sup>[191]</sup> which can potentially result in an electrode with a workfunction as low as 1.9eV.<sup>[192]</sup> ZnO on the other hand is considered suitable as a cathodic buffer layers for inverted devices, due to its high electron mobility. Moreover, various morphologies such as nanoparticles,<sup>[193]</sup> ridges,<sup>[194]</sup> vertical and well aligned ZnO nanopillars can be grown on the substrates which besides increasing the interfacial area between the donor and acceptor materials, can also act as well defined electronic transport channels towards the cathode.<sup>[195-198]</sup>

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# **Electronic Properties of Interfaces**

### 2.1. Introduction

In addition to discovering new high performing materials,<sup>[1, 2]</sup> the field of organic photovoltaics has also witnessed an increased focus on the understanding of device physics and interfacial energetics at materials interfaces.<sup>[3-5]</sup> As new photoactive and semiconducting materials are explored and used as ultra-thin films for device fabrication, it is important to develop an in-depth understanding of the charge transport process across interfaces between dissimilar materials, as potential barriers between the interfaces can cause charge traps and recombination losses resulting in inferior device performance. Thus the elucidation of the mechanisms that drives the alignment of molecular levels and charge carrier transport states is important for improving the performance of these devices.

Metal-organic interfaces are critical factors affecting various aspects of device performance such as efficiency, operational voltage or device degradation. As the stability of polymer/polymer and polymer/electrode interfaces are critical for device performance,<sup>[6]</sup> better control of such material interfaces can not only improve the device performance but can also help in achieving more stable devices with longer operational times.

# 2.2. Electronic Structure of Organic Semiconductor

When organic electronic devices such as OPV's are fabricated, organic materials are usually deposited sequentially over a metallic electrode, and hence form a metal-organic interface. Important energy levels in such an interface are the Fermi level of the electrode (which defines the electrode workfunction) and the valence and conduction band of the semiconductor. Because polymeric materials have weak van der Waals force of attraction between the molecules, the electronic structure of the organic solid retains the structure

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common to the molecule and the applicability of band theory is known to be limited (Figure 2.1).<sup>[7]</sup> Therefore, unlike metals, where the difference between the vacuum level *VL* and the Fermi level  $E_f$  defines the workfunction  $\phi_m$ , in organic solids, the electron affinity *A* is defined as the energy difference between the LUMO and the *VL*, whereas the separation between the HOMO and the vacuum level is the ionisation energy *I*.



*Figure 2.1*: *Electronic structure of (a) an organic solid (b) simplified version of its energy levels. Taken from Ishii et al.*<sup>[8]</sup>

В

# 2.3. Metal-Organic Interfaces

Α

When a metal comes in contact with an organic semiconductor, the alignment of energy levels can be driven by many factors such as chemical reactions, intrinsic dipole of the organic material etc.<sup>[3, 5]</sup> Traditionally, such interfacial energetics were often understood based on a simple model of vacuum level alignment with both materials sharing a common vacuum level at the interface (Figure 2.2). However, with improved understanding of different vacuum levels of a sample at a finite and an infinite distance<sup>[9]</sup> complimented with more experimental insight into the interfaces, an interface dipole model has been proposed by Seki *et al.*<sup>[10, 11]</sup> The dipole at the interface causes an abrupt shift of the potential across the dipole layer and is commonly denoted by delta ' $\Delta$ '. A schematic representation of a Schottky barrier formed between a metal-organic interface with and without a dipole is shown in Figure 2.3. This model has since been widely accepted and
supported by a range of experimental findings<sup>[12-14]</sup> where such a shift is also called as the change in surface potential or workfunction.



*Figure 2.2*: Electronic structure of a metal-organic interface depicting a scenario with vacuum level alignment between the two materials. Taken from Seki et. al.<sup>[10]</sup>



**Figure 2.3**: Schematic depiction of a metal-organic interface in electrical equilibrium (Fermi levels aligned) with the band bending assuming (a) common VL (b) interface dipole formation between the metal and organic layer resulting in VL shift.  $\Phi_B^n$  and  $\Phi_B^p$  are the electron and hole injection barriers, respectively and the organic layer is charged positive, thus making the  $\Delta$  negative. Taken from Ishii et al.<sup>[8]</sup>

The formation of a dipole could take place due to various reasons such as charge transfer across the interface, chemical reactions between the materials or redistribution of the electron cloud.<sup>[8, 15, 16]</sup> An interface dipole due to charge transfer is schematically depicted in Figure 2.4.

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Due to the different workfunction of a metal and an organic semiconductor, charge distribution takes place when they come in contact in order to achieve electrical equilibrium (as denoted by a common Fermi level). Redistribution of charge across the interface results in a diffusion layer with band bending and leads up to a build-in potential drop  $eV_{bi}$  in the organic layer (Figure 2.3).<sup>[5, 8]</sup> Though it must be mentioned that for band bending to occur, significant density of charge carriers is required in the organic layer.<sup>[5]</sup> Thus for very thin organic layers, Fermi level alignment is not easily achieved and flat band situation (similar to Figure 2.2) can be expected.<sup>[8]</sup>



*Figure 2.4*: Schematic depicting charge transfer induced dipole formation resulting in (a) downshift or (b) upshift of the vacuum level by electronic charge transfer to or from the substrate, respectively. Taken from Braun et al.<sup>[5]</sup>

The charge transport across such metal-organic interfaces mainly depends on the electron and hole injection barriers between the electrode and the semiconducting material.

For an ideal Schottky junction, the Schottky-Mott rule applies<sup>[17]</sup> and the barrier heights of the electron  $\phi_B^n$  and hole  $\phi_B^p$  injection depends on the workfunction of the metal and the ionisation energy of the organic material. These can be expressed as,

$$\Phi_B^p = I - \Phi_m$$
 Eq. 2.1

$$\Phi_B^n = \Phi_m - A = E_g - \Phi_B^p$$
 Eq. 2.2

However, in the presence of an interfacial dipole, the barrier height is influenced (hence the metal workfunction) due to the shift in the vacuum level and for a negative shift as shown in Figure 2.3 b, barrier heights can be expressed as:

$$\Phi_B^p = I - \Phi_m - \Delta \qquad \text{Eq. 2.3}$$

$$\Phi_B^n = \Phi_{\rm m} - A + \Delta \qquad \text{Eq. 2.4}$$

#### **2.3.1. Interface Engineering**

From Section 2.3, it can be realised that chemical or electronic changes in the interfacial properties has a significant impact on the charge injection barriers at the interface and hence can significantly influence the device performance. Modification of such interfaces also called as interface engineering has been widely used in recent years to improve device performance by favourably tuning the surface properties.

A well-established example in the literature is the use of self-assembled monolayers (SAM) for improving charge injection in organic electronic devices via workfunction modification of electrodes.<sup>[18]</sup> Ganzorig *et al.* has demonstrated an increase in ITO workfunction of as high as 0.9 eV by chemically inducing permanent dipoles on the surface.<sup>[19]</sup>

Surface treatment such as oxygen plasma cleaning is another example of a commonly used method to modify the ITO workfunction. Oxygen plasma cleaning of ITO has been reported to increase the workfunction from ~ 4.6 eV to 5.2 eV leading to changes in hole injection barrier.<sup>[20]</sup> A variety of other approaches such as deposition of thin film of carbon, polyanelene, PEDOT on ITO surface to tune its properties, have been reported.<sup>[21, 22]</sup>

In OPVs, surface modification has been used at both the anode and cathode interfaces. As reviewed in Section 1.8, a range of oxide materials such as vanadium oxide  $(V_2O_5)$ ,<sup>[23]</sup> molybdenum oxide  $(MoO_3)$ ,<sup>[24]</sup> copper oxide,<sup>[25]</sup> tungsten oxide  $(WO_3)^{[26]}$  and nickel oxide  $(NiO)^{[27]}$  has been used to modify the ITO workfunction to enhance hole transport. Similarly, at the cathodic interface, thin layers of lithium fluoride (LiF) or calcium (Ca) are commonly deposited between the polymer and the low workfunction metal electrode such as Al, to enhance device performance.<sup>[28]</sup> Shaheen *et al.* have shown that thin layer of LiF can significantly reduce the electrode workfunction.<sup>[29]</sup> By introducing a thin layer of LiF

between the active layer and the cathode, a favourable dipole can be introduced resulting in enhanced electron transport and hence better performing devices.<sup>[30, 31]</sup> Various other low workfunction oxide materials such as  $ZnO^{[32]}$  and  $Cs_2Co_3^{[33]}$  have also been effectively used as interfacial layers to modify the cathode.

Changes in the interfacial energetics such as the electrode workfunction and interfacial dipoles due to surface modification can be experimentally determined using spectroscopic techniques such as ultraviolet photoelectron spectroscopy (UPS). The analysis of interfacial properties using UPS and experimental determination of such physical quantities is discussed in Section 2.4.2. For interested readers, the interfacial energetics of metal-organic, organic-organic interfaces has been comprehensively reviewed in the literature.<sup>[3, 5, 8, 34]</sup>

## 2.4. Experimental Techniques Used in This Thesis

#### 2.4.1. Neutral Impact Collision Ion Scattering Spectroscopy (NICISS)

NICISS is a spectroscopic method used for investigating concentration death profiles of elements up to a depth of 20 nm in the interfacial region of soft matter, with a depth resolution of few Å in the near surface region.<sup>[35, 36]</sup> It has been demonstrated as a useful technique to investigate the composition of the interfaces in organic electronic devices.<sup>[36, 37]</sup> The major components of the setup are an ion source, an electrostatic deflection unit to pulse the ion beam and the time of flight detector, as shown in Figure 2.5 and a detailed design is described elsewhere.<sup>[35]</sup> In a typical NICISS experiment, sample is bombarded with a pulsed beam of rear gas ions such as helium with energy in the range of 1 - 5 keV, as projectiles.<sup>[35]</sup>

The incident beam of ions is back-scattered after hitting the sample, with majority of the back-scattered ions being in the neutral state.<sup>[35]</sup> The interaction of the projectile and the target involves charge transfer as well as elastic and inelastic transfer of energy between the two and the projectile loses energy by two separate mechanisms. The trajectory of a helium ion is known to consist of a number of small angle scatterings and only one back-scattering process.<sup>[35]</sup> The small angle scatterings and the electronic excitations of the target atoms contribute to the inelastic or the continuous energy loss over the trajectory of



the projectile, whereas the elastic energy loss is due to the back-scattering event.

*Figure 2.5:* A schematic depicting the basic setup of NICISS instrument. Projectiles backscattered at about 168° from normal are detected with the TOF detector.

The energy transfer in the elastic collision can therefore be calculated from conservation of energy and momentum while the inelastic energy loss has to be measured, e.g. by measuring the gas phase spectra of the respective element.<sup>[35]</sup> The inelastic energy loss per depth interval is called stopping power.<sup>[38]</sup> Therefore, the mass of the target atoms can be determined from the elastic energy loss and the depth profiles can be obtained from the energy spectrum, once the stopping power is known.<sup>[38]</sup> This second mechanism of energy loss corresponds to the depth of the atom from which the projectile is backscattered.

The sensitivity of the detector increases with the increase in the kinetic energy of the projectile. The energy of the back-scattered atoms is determined from the recorded TOF: the longer the TOF, the lower the energy. The relationship between TOF spectrum and the energy spectrum is given by:

$$I(E) = I(t) \frac{\Delta t}{\Delta E} \frac{1}{\frac{d\sigma}{d\Omega(E)}} \frac{1}{\det(E)}$$
 Eq. 2.5

where t is the time of flight, E the energy,  $\frac{d\sigma}{d\Omega(E)}$  is the differential cross-section, and det(E) is the detector sensitivity. The factor  $\frac{\Delta t}{\Delta E}$  has to be taken into account for the fact

that equal intervals on the TOF scale are not equal on the energy scale due to the nonlinear relation between the TOF and the energy.

The concentration depth profiles are obtained from the energy spectrum<sup>[39]</sup> using the following relation:

$$I(d) = I(E)\frac{\Delta E}{\Delta d}f$$
 Eq. 2.6

where *d* is the depth, *f* relates the concentration to the yield of back-scattered projectiles. The low energy of the projectile used in NICISS, enables a higher depth resolution near the surface, thus making it a superior choice over the Rutherford back-scattering (RBS). However, as the incident beam travels through the bulk, it gets widened due to multiple low-angle scatterings, thus limiting the depth to about 30 nm that can be analysed with high precision, and this uncertainty increases with an increase in depth.<sup>[35]</sup> Therefore in order to obtain concentration depth profiles of thicker layers, RBS is usually the method of choice.<sup>[40]</sup> It uses a similar setup as NICISS, however the energy of the incident projectile is in the order of few MeV, which enables investigation deeper into the surface though the first layer sensitivity is lost as compared to NICISS.

#### 2.4.2. X-ray & Ultraviolet Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is a surface sensitive technique that can quantitatively measure the elemental composition of a material with specific information about the chemical and electronic state of elements present in the material. XPS was developed by Kai Siegbahn in 1950's at the University of Uppsala,<sup>[41]</sup> for which he was later awarded the Nobel Prize for Physics in 1981.

The working operation of the XPS technique is based on photoelectric effect, where the sample is irradiated with monoenergetic soft X-rays and the number of photoemitted electrons and their kinetic energy is measured. The basic elements of an XP instrument are a light source (X-ray source, a hemispherical electron energy analyser and an electron detector (Figure 2.6). As photons have limited penetrating power in solids (1-10 micrometers),<sup>[42]</sup> they interact with atoms in the surface region causing electrons to be emitted. Due to high probability of electron interaction with matter, the inelastic mean free path (IMFP) in solids is very small (tens of Angstrom), so the detected electrons originate only from the surface region, making XPS a surface sensitive technique.



**Figure 2.6**: A schematic depicting the working principle of a photoemission spectrometer. Monochromatic photons with certain energy hv are incident at certain angle  $\Psi$  on the sample surface. Adapted from Reinert et al.<sup>[43a]</sup>

The primary electrons which escape the surface without losing energy are seen as sharp peaks in a typical XP spectrum, while the inelastic scattering results in a step like background with onset at each of the sharp peaks and low energy secondary electrons. XPS background also has photoelectron contributions due to continuous Bremsstrahlung radiations<sup>[43b]</sup>.

The emitted electrons pass through the spectrometer (Figure 2.6), which detects the emitted electrons according to their kinetic energies. The energy range at which the analyser operates at, also known as the pass energy is usually fixed at a certain value such that only electrons with kinetic energy in the range as defined by the pass energy can pass through the analyser and reach the detector. From the electrons emitted from the sample, the electrostatic lens system forms an image of the sample at the entrance slit of the hemispherical analyser. The electrons entering the analyser are accelerated or deaccelerated by applying a floating potential,<sup>[44]</sup> such that only electrons with energy as defined by the fixed pass energy, reach the channeltrons and are detected as discreet events. Thus intensity of electrons reaching the chaneltrons is recorded against the applied accelerating or de-accelerating voltage. The resolution of the hemispherical analyser

The kinetic energy of the electrons when it just leaves the surface can mathematically be expressed as,

where *KE* is the measured kinetic energy, *hv* is the energy of incident photon, *BE* is the binding energy of the atomic orbital from which the electron originates and  $\phi_{sample}$  is the sample workfunction. Here *BE* is usually the difference between the final and the initial states after the photoelectron has left the atom. Since the channeltron also has a workfunction  $\phi_{analyser}$ , a contact potential of  $\phi_{sample}$ - $\phi_{analyser}$  exists between the sample and the analyser when they are electrically connected.<sup>[45, 46]</sup> As  $\phi_{analyser}$  is usually lower than  $\phi_{sample}$ , it creates an acceleration of the electrons and increases the *KE* of electrons by  $\phi_{sampe}$ - $\phi_{analyser}$ .<sup>[46]</sup> Therefore, the measured *KE* can be expressed as:

$$KE = hv - BE - \phi_{sample} + \phi_{sample} - \phi_{analyser}$$
 Eq. 2.8

$$KE = hv - BE - \phi_{analyser}$$
 Eq. 2.9

Because each element has a unique set of binding energies, by measuring the kinetic energy of the emitted electrons and knowing the analyser workfunction, XPS can thus be used for identifying the elemental composition of a given sample. A shift in the binding energy can be due to the difference in chemical potential of various compounds, and hence are used to identify the chemical state of elements being analysed. However, for quantitative analysis, due to different probability or cross-section for each final state, the spectral intensity is corrected for the cross-section using the relative sensitivity factor.

About the same time when Kai and his group was working on XPS, David W. Turner, a physical chemist at Imperial College was working on a spectroscopic technique capable of measuring ionisation potential of materials and published his first paper on UPS in 1962.<sup>[47]</sup> The working principle of UPS is similar to that of XPS, however for UPS measurements, samples are irradiated with low energy photons such as He I line (with an energy of 21.2 eV) as compared to high-energy X-ray photons of energies ranging from 1253.6 eV (Mg K $\alpha$ ) to 1486.7 eV (Al K $\alpha$ ) used in XPS measurements.

By measuring the kinetic energy spectrum of the photoemitted electrons from molecules, which have absorbed the UV photons, the molecular orbital energy can be determined. As in case of XPS, the UV photons impinging on the surface are absorbed and impart kinetic energy to electrons, creating large number of low energy electrons which subsequently loose energy on their path through the material and constitute the secondary electrons.<sup>[48]</sup> However, due to low energy of the incident photons and small electron mean free path of

the emitted electrons, in case of UPS the photoemitted electrons are only from the valence region.

In a UPS measurement, workfunction is determined from the lowest kinetic energy electrons escaping from the surface. As the strength of the potential barrier, which the secondary electrons need to overcome at the surface, is not only dependent on material but also on the crystalline structure, lattice orientation and surface contamination and hence, so does the workfunction. Single crystals have a unique workfunction and these are specific to the crystal face.<sup>[49]</sup>

Workfunction of a sample can be determined from a typical UP spectrum (Figure 2.7). As seen from Eq. 2.9, the measured kinetic energy is independent of the material workfunction.<sup>[46]</sup> Therefore, after correcting for the analyser workfunction, kinetic energy can be expressed as;

$$KE = hv - BE$$
 Eq. 2.10



Figure 2.7: UP spectrum of a clean Au surface. Adapted from Helander et al.<sup>[45]</sup>

As the fastest electrons (i.e. electrons having maximum kinetic energy) are the ones emitted from the Fermi level ( $BE = 0 \ eV$ ), they have the maximum energy  $K_{\text{max}}$  which is equal to the excitation energy hv and the slowest electrons will have the minimum kinetic energy.

$$KE_{max} = hv$$
 Eq. 2.11

The kinetic energy scale can therefore be calibrated relative to the Fermi edge of the

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sample using the Fermi edge of a metal surface. Thus the secondary electron (S.E.) cut-off of a calibrated spectrum defines the workfunction, as it represents the secondary electrons at the surface which had just enough energy to overcome the workfunction.<sup>[46]</sup>

The workfunction of the sample can therefore be expressed as the difference between the excitation energy and the length of the spectrum.

$$\phi = hv - (KE_{max} - KE_{min})$$
Eq. 2.12

where  $\phi$  is the workfunction. However, this is only true in case of metals where the Fermi edge can be measured. In case of semiconductors, the workfunction can be measured by calibrating the analyser to a metal. When semiconducting materials is electrically connected to the analyser, its pseudo Fermi level equilibrates with the Fermi level  $E_f$  of the analyser and the workfunction can thus be calculated as,

$$\Phi = hv - (E_f - KE_{min})$$
 Eq. 2.13

It must be noted that in order to acquire a UP spectra with a discreet secondary electron cut-off, an external bias is usually applied to the sample, thus enabling precise measurement of the secondary electron cut-off.<sup>[45]</sup> It also helps in measurement of samples, which have a workfunction less than the spectrometer workfunction.

When this layer of organic materials is deposited on a metal surface (electrode), the spectrum becomes dominated by the photoelectrons from the organic layer, with increasing thickness.

Unlike in metals, where the maximum kinetic energy electrons are emitted from Fermi level, for organic semiconductors, the fastest electrons are emitted from the. HOMO. UP spectra can therefore be used to determine the HOMO position (ionisation energy  $I_{org}$ ) of the organic material and the formation and strength of dipoles at interfaces,<sup>[8]</sup> as depicted in Figure 2.8.



*Figure 2.8*: Schematic of UP spectra depicting photoemission from a metal, an organic layer and the corresponding shift in the vacuum level and at the Fermi edge. Taken from Ishii et al.<sup>[8]</sup>

$$I_{org} = hv - KE_{max}^{org}$$
 Eq. 2.14

The hole injection barrier  $\Phi_B^p$  can be obtained as the difference between the energy of the electron coming from the Fermi level of the metal and HOMO of the organic layer, as shown by a shift  $E_v^F$  between the two spectra. Also, the vacuum level shift  $\Delta$  between the organic layer and the metal electrode can be determined by the shift of the high binding energy cut-off before and after depositing the organic layer.<sup>[8]</sup>

#### 2.4.3. Atomic Force Microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM)

In 1981, G. Binnig and H. Rohrer from the IBM research laboratory in Ruschlikon invented a new type of imaging instrument called a scanning tunnelling microscope (STM) and received the Nobel Prize in 1986.<sup>[50]</sup> Binnig went on for further application of SPM work with Quade and Gerber in 1986 and the collaboration resulted in a new technique called AFM.<sup>[51]</sup>

Atomic force microscopy is a very high resolution scanning probe microscopy (SPM) capable of characterising the surface morphology at the atomic level. It employs a sharp tip/probe (usually made of hard material such as silicon nitride) at the end of the cantilever that is scanned across the surface. AFM images are obtained by measuring the force on its sharp tip created by its proximity to the surface of the sample, as defined by Hooke's law:

$$F = -kx$$

Where, *F* is the force exerted on the cantilever in the displacement position, *k* is the spring constant and *x* is the displacement of the cantilever form its equilibrium position. By applying a laser at the top surface of the cantilever, interaction of the tip and the surface can be monitored through the reflection of the laser into the array of photodiodes as shown in Figure 2.9. When the tip approaches the surface, forces such as van der Waals force, dipole attraction, etc. acts on the cantilever. Mounting the sample on a piezoelectric scanner and employing a feedback loop enables the manipulation in the x and y directions for surface scanning and adjust the z direction of the sample in order to minimise these forces of attraction and maintain a constant oscillation.<sup>[52]</sup> The resolution of the AFM tip is defined by its radius of curvature, which can vary from few nanometres to several tens of nanometres.



Figure 2.9: Basic schematic of an AFM. Taken from Butt et al.<sup>[52]</sup>

AFM can mainly operate in three different modes, namely the contact mode, non-contact mode and the intermediately or tapping mode. In contact mode, the tip touches the sample surface and the deflection of the cantilever due to tip-sample repulsive force is monitored using the feedback loop. In tapping and non-contact mode, the cantilever is externally oscillated close to the samples surface. As the tip-sample distance changes, their interaction also changes, leading to a change in the resonant frequency and the oscillation amplitude in non-contact and tapping mode, respectively. Therefore, tapping mode and non-contact mode are also known as amplitude modulation and frequency modulation

modes. The changes in the frequency and amplitude relative to the reference values are used as feedback signal to obtain topographic image of the surface.<sup>[53]</sup>

Based on the work of Bennig's and his colleagues,<sup>[51]</sup> many AFMs have now been commercialized and further modifications to the basic AFM setup has led to techniques such as conducting AFM<sup>[54]</sup> for example, which enable mapping of surface conductivity on a nanoscale.

In 1991, Nonnenmacher *et al.* introduced Kelvin Probe Force Microscopy (KPFM) technique<sup>[55]</sup> to measure the local contact potential difference between the conducting AFM tip and the sample surface, enabling the mapping of workfunction of the sample with high spatial resolution. Since then, KPFM has been extensively used as a unique method to characterize the nanoscale electronic properties of a variety of semiconductor, organic and biological materials.<sup>[56-60]</sup> KPFM is primarily based on the instrumentation of an AFM, with an additional bias applied between the tip and the sample.

When the tip and sample are at a distance d apart, their Fermi levels are not aligned, as shown in Figure 2.10.



**Figure 2.10**: Energy level alignment of the AFM tip and sample when (a) tip and sample are at a distance 'd' (b) when tip and sample are electrically in contact (c) when an external bias equal to the  $V_{CPD}$  is applied between the tip and the sample. Taken from Melitz et al.<sup>[53]</sup>

However, when the tip and sample comes into electrical contact, electron flow takes place between the sample and the tip in order to align the Fermi level and attain a state of equilibrium, thus giving rise to contact potential difference  $V_{CPD}$  which results in an electrical force on the contact area.<sup>[53]</sup> This  $V_{CPD}$  can be measured by applying an equal and opposite bias  $V_{DC}$  to nullify the  $V_{CPD}$  and thus it gives the difference in the workfunction of the tip and the sample surface.

The  $V_{CPD}$  between the tip and the sample is mathematically expressed as,

$$V_{CPD} = \frac{\Phi_{tip} - \Phi_{sample}}{-e}$$
 Eq. 2.16

where  $\phi_{sample}$  and  $\phi_{tip}$  are the workfunction of sample and tip respectively and *e* is the electronic charge. The tip workfunction can be calculated using a reference sample such as HOPG, whose workfunction is well known in the literature.<sup>[61]</sup>

$$\phi_{tip} = e \ CPD_{HOPG} + \phi_{HOPG}$$
 Eq. 2.17

Further details about KPFM and its applications in a variety of characterisation studies can be found in the literature.<sup>[53, 62-64]</sup>

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# **Research Project**

#### 3.1. Introduction

From previous chapters, it is clear that interfacial energetics control charge transport across the metal-organic interfaces and the design of the device. The main emphasis of this project is on understanding the electronic properties of interfacial layers, and in particular, correlating interfacial properties with the processing conditions and its impact on the device performance. Special emphasis has been placed on the role of scale, in which the role of micro and nanoscale heterogeneity is examined.

As this work is focused on studying the electronic properties of interfacial layers, all devices were fabricated with the commonly used P3HT:PCBM BHJ active layer.

### **3.2. ITO-PEDOT:PSS Interface In Conventional OPVs**

As earlier reviewed in Chapter 1, ITO is commonly used as a transparent electrode in OPVs. However, the inorganic-organic interface formed between ITO and polymer layer is not sharp and diffusion of indium into the polymer layer is known to occur.<sup>[1]</sup>

The use of PEDOT:PSS as an interfacial layer between the ITO and the active layer has been found to improve the device lifetime,<sup>[2]</sup> however, earlier XPS studies have reported the presence of indium in the PEDOT:PSS layer as well<sup>[3]</sup> and has been shown to diffuse through the PEDOT:PSS layer into the active layer.<sup>[4]</sup>

While indium from ITO has been reported to be detected in the PEDOT:PSS layer and was assumed to have diffused, little was known about the concentration profile and the root cause. In Chapter 4, I report the first quantitative study of indium and tin migration from the ITO electrode (Figure 3.1) into the PEDOT:PSS layer. Using a depth profiling technique, neutral impact collision ion scattering spectroscopy (NICISS - described in Section 2.4.1), the detailed concentration depth profiles of migrated indium and tin into the

polymer layer were obtained and provides a basis to understand the concentration dependence on various processing and storage conditions such as cleaning, relative levels of humidity etc. X-ray photoelectron spectroscopy (XPS) confirmed that indium was present as an ion rather than a neutral atom. Exposure of PEDOT:PSS coated ITO substrates to humidity was found to be one of the main factors responsible for enhancing indium and tin migration in the PEDOT:PSS layer.



*Figure 3.1*: Schematic of a conventional OPV depicting indium and tin migration across the ITO-PEDOT:PSS interface.

In order to determine the impact of indium and tin contamination in the PEDOT:PSS layer on device performance, controlled amounts of migrated indium and tin contamination from the ITO electrode was systematically introduced in the PEDOT:PSS layer through exposure to humidity in controlled environments as described in Chapter 5. We have found that high levels of indium and tin contamination in the PEDOT:PSS layer results in significantly poor performing devices compared to the ones without indium and tin contamination.

The impact of indium migration on device performance as a result of humidity confirms previous observations of the need for device encapsulation to prevent water from reducing the lifetime of devices. The results presented in Chapters 4 and 5 indicate that this is a fundamental challenge for conventional OPVs which are extremely difficult to overcome especially for flexible devices on polymeric substrates.

## **3.3.** ZnO-Polymer Interface in Inverted OPVs

Issues such as the instability of the ITO-PEDOT:PSS interface could be avoided in case of devices fabricated with an inverted geometry as discussed in Section 1.8.2.

This can be achieved by the intelligent selection of materials and by using alternative fabrication techniques which enable optimisation of these material layers during fabrication.

As discussed in Section 2.3.1, the electronic properties of interfaces can be engineered by modification using materials having electron transporting or electron blocking properties. Zinc oxide in particular, has been demonstrated as a promising electron acceptor material in hybrid OPVs or an electron selective layer in inverted OPVs.<sup>[5-7]</sup> Due to its promising electronic properties,<sup>[8, 9]</sup> transparency and ability to be synthesised using various methods,<sup>[6, 10-14]</sup> ZnO continues to attract significant research focus as an electron transport material. Use of ZnO in inverted device structures as a replacement of low workfunction metal has also been shown to improve the stability of devices.<sup>[15]</sup>

While the process to deposit ZnO is quite simple, the literature reports a range of ZnO layer thickness, morphologies and wildly varying values for device performance and comparatively little information on the optimal processing conditions for what is the first layer deposited.<sup>[16-20]</sup>

Chapter 6, 7 and 8 are therefore focussed on understanding the co-relation between the processing conditions of ZnO buffer layers and the device performance. A systematic study relating the ZnO (sol-gel derived and pulsed laser deposited) layer thickness, chemical nature, processing conditions such as the post deposition annealing temperature and their influence on the device performance is presented.

Detailed XPS and UPS studies were performed on ZnO layers to understand the dependence of electronic properties of the resultant ZnO on the layer thickness and processing conditions.

For sol-gel processed ZnO as reported in Chapter 6, a model where the ZnO-P3HT:PCBM inter-diffuse is proposed concluding that the thickness of the ZnO layer plays a crucial role in device performance.<sup>[21]</sup> The influence of the layer thickness (4 nm - 100 nm) of ZnO

deposited using pulsed laser ablation (which would result in ZnO film with different porosity than that of sol-gel derived films) on the device performance of inverted OPVs, was studied in detail and is reported in Chapter 8. Particular attention was paid to the morphological and chemical properties of ZnO and parameters important to photovoltaic devices; such as the workfunction and the Zn:O stoichiometric ratios in the resultant ZnO films. As found for sol-gel derived ZnO (Chapter 6), a strong dependence of device performance on the thickness was also found in the case of laser deposited ZnO.

Low temperature processing is generally required for the fabrication of OPVs on flexible/plastic substrates due to the low glass transition of commonly used substrate materials, such as polyethyleneterephthalate (PET) and polyethylenenaphthalate (PEN). Therefore, it is important to optimize and understand the impact of annealing temperature of ZnO particle layers on the electronic properties of ZnO. Chapter 7 reports the investigation of the effect of post deposition annealing temperature of ZnO on the device performance.

#### **3.4.** Electronic Properties of Heterogeneous Surfaces

Findings of Chapter 4 to 8 clearly suggests that precise understanding of the electronic properties of materials and more specifically their workfunction is very essential for tailoring the device properties. Conventional techniques such as UPS have been commonly used for workfunction measurement of materials, where the absolute value of workfunction is defined by the S.E. cut-off of a UP spectrum as described in Section 2.4.2.

Close examination of a number of UP spectra showed significant variation of the slope and shape of the S.E. cut-off region of the spectrum. The slope of this region is due to both instrumental factors such as analyser resolution as well as multiple environments within the sample - or heterogeneity of the sample - but this is largely ignored in the literature.

Chapter 9 investigates the electronic properties of a range of artificially created binary heterogeneous surfaces fabricated from materials having distinctly different workfunction with features in the order of a few microns. The results indicate that the properties of the high workfunction component in a heterogeneous surface are underestimated in UP spectra. Detailed examination of the spectrum shows a range of workfunction corresponding to the energetically different species in the sample, are present.

Recent advances in nanotechnology have shown that systems that appear "uniform" at a macroscale become more variable at the nanoscale. Thus the interpretation of UPS measurements on heterogeneous surfaces and the subsequent understanding developed in Chapter 9 was applied to study thin films of sol-gel prepared ZnO comprised of nanoparticles and the influence of ZnO morphology on its electronic properties, using KPFM (Chapter 10).

Chapter 11 summarises the key understanding of interfacial structure, stability and electronic properties on the performance of OPVs, bringing a new level of understanding of the materials used for key layers in these devices.

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# **Role of Humidity on Indium and Tin Migration in Organic Photovoltaic Devices**

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Author Contribution:

Anirudh Sharma: Designed & performed experiments, data analysis & interpretation, prepared the first draft of the manuscript.

*Prof.* David Lewis & Prof. Gunther Andersson: Intellectual contribution in conceptualising experiments, data interpretation & revision of manuscript.

Some of the experimental results presented here were obtained as part of my Master of Nanotechnology research dissertation. Significant intellectual contributions to understanding & interpretation of results were made during my PhD, which justifies inclusion in this dissertation.

## 4.1. Abstract

The stability of a common interface used in organic photovoltaic cells, between the transparent electrode of indium tin oxide (ITO) and a buffer layer of poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate) (PEDOT:PSS) is strongly influenced by the presence of humidity during processing, leading to significant migration of indium and tin species into the PEDOT:PSS layer. The interface was studied using neutral impact collision ion scattering spectroscopy (NICISS) and X-ray photoelectron spectroscopy (XPS), to determine migration of indium and tin into the polymer layer. It was found that the migration starts almost instantly after spin coating of the aqueous PEDOT:PSS solution and it reaches a saturation level within twenty four hours. The indium and tin was found always uniformly distributed over the sampling depth of almost one-third of the thickness of the PEDOT:PSS layer. Exposure to humidity following annealing resulted in the highest concentration  $(1.8 \times 10^{-3} \text{ mol cm}^{-3})$  of indium or tin species, corresponding to about one indium or tin moiety per 4.7 monomer units in the PEDOT:PSS. The maximum bulk concentration of indium is about two orders of magnitude higher after exposure to humid conditions compared to vacuum dried conditions. XPS measurements confirms the presence of both indium and tin into the PEDOT:PSS and the formation of salts with the metal ions as cations.

## 4.2. Introduction

In the last few decades, the development of electronically conductive organic materials and the synthesis of inorganic-organic assemblies have enabled the design of next generation photovoltaic cells.<sup>[1]</sup> Polymer based hetero-junction solar cells, can be a key alternative to the existing silicon based cells due to their potential to be flexible, semi-transparent, light weight and financially viable.<sup>[2]</sup> The promise of low cost and ease of fabrication of such cells has generated significant research and commercial interest around the world.

Organic solar cells, with power conversion efficiency of 8.1 % have been realised,<sup>[3]</sup> but still their efficiency and their lifetime needs to be further increased in order to make them commercially viable.

The structure of an organic cell consists of polymeric active layer sandwiched between the metallic electrodes. The interfaces between metals and organic substances are typically not atomistically sharp with some inter-diffusion caused by metals migrating into the polymers,<sup>[4]</sup> which can cause leakage currents,<sup>[5]</sup> influence the charge transport properties of the polymer<sup>[6, 7]</sup> and can also effect the lifetime of the photovoltaic device.<sup>[8, 9]</sup>

ITO is commonly used as the transparent electrode in opto-electronic devices such as hetero-junction solar cells and polymer light emitting diodes (p-LED) due to its optical and electrical transport properties, but the ITO-polymer interface is known to not be stable with indium migrating into the organic layer.<sup>[10]</sup> X-ray photoelectron spectroscopy (XPS) used to study an ITO-poly(2-methoxy-5-2(2'-ethyl-hexyloxyl)-p-phenylene vinylene) (MEH-PPV) interface also confirms the presence of indium throughout the 100 nm thick polymer layer.<sup>[11]</sup> Jong *et al.* has even reported an increase in indium migration into poly(phenylene vinylene) with increased annealing time.<sup>[12]</sup> Migration of indium into the active layer has been found to have an adverse effect on the quantum efficiency of the device.<sup>[13]</sup>

In order to overcome the problems at the interface between the hetero-junction polymer and ITO described above, poly(3,4-ethylenedioxythiophene) :poly(4styrenesulfonate) (PEDOT:PSS) is commonly used as a buffer layer. Adding the PEDOT:PSS layer also improves the electronic properties like the open circuit voltage,<sup>[14]</sup> power conversion efficiency,<sup>[15]</sup> and lifetime of the device.<sup>[16]</sup>

#### Chapter 4

However, Norrman *et al.* recently found that the performance of devices using PEDOT:PSS as a buffer layer significantly decreases in the first 10 hours when exposed to humid conditions. Humidity dependence of the conductivity of PEDOT:PSS films has also been observed.<sup>[17]</sup> In a further study, Norrman *et al.* used TOF-secondary ion mass spectroscopy to investigate various interfaces of a polymer cell and found water being present at the ITO-PEDOT:PSS interface. Also, particle formation at the hetero-junction-PEDOT:PSS interface was observed involving at least carbon, sulphur and indium suggesting that ITO and PEDOT:PSS play a role in particle formation.<sup>[18]</sup> Though the effect of particle formation was not studied as a function of device performance.

In particular it was found that the ITO-PEDOT:PSS interface is not stable as indium is found in the PEDOT:PSS layer as contamination.<sup>[19]</sup> The cleaning of the ITO surface with plasma treatment,<sup>[20]</sup> exposure of ITO-PEDOT:PSS sample to air,<sup>[21]</sup> and annealing treatments<sup>[22]</sup> has been found to enhance the migration process.

Different approaches to reduce the migration of metal ions have been suggested such as the introduction of a thin diamond like carbon layer,<sup>[19]</sup> or a self-assembled monolayer of alkylsiloxanes<sup>[23]</sup> between the ITO-PEDOT:PSS interface. However, these extra interfacial layers make the system more complex and potentially increase the overall series resistance of the cell. Therefore, it is imperative to understand the migration process and the rate of migration for developing methods to stabilise the interface through device processing and appropriate surface treatments.

However, the nature of the migrated species remain controversial<sup>[19, 22]</sup> and the parameters that influence the migration are not yet known. Until these issues are better understood it is difficult to control the composition and thus the properties of the PEDOT:PSS layer, resulting in significant process unknowns and risks in durability and device lifetime limiting the commercialisation of this technology.

In this paper, important process parameters that influence the stability of the ITO-PEDOT:PSS interface, including surface cleaning, annealing and exposure to humidity are examined to understand the time dependent changes in the concentration of migrating species and to determine their role in indium and tin migration. Concentration depth profiles of the migrated indium and tin in the PEDOT:PSS layer are obtained by Neutral impact collision ion scattering spectroscopy (NICISS) and XPS measurements were employed to confirm the nature of the migrated indium and tin. The results of this paper have important implications on the understanding of OPV properties.

#### 4.3. Experimental

ITO-coated glass substrates with a sheet resistance of 15 ohms square<sup>-1</sup> were purchased from Kintek. Pyroneg was supplied by Johnson Diversey. Pyroneg forms a caustic solution in water. Deconex PA neutral detergent was supplied by Borer. PEDOT:PSS (CLEVIOS P VP AL4083) was purchased from H.C. Starck and was used as received without any dilutions. Copper sulfate pentahydrate with 99.5 % purity was supplied by Chem Supply. Sodium bromide was supplied by Sigma Aldrich.

A standard procedure was followed to clean the ITO coated glass. The glass was cleaned by standing it in a solution of 5 % pyroneg at 50 °C for 20 minutes or 5 % deconex PA neutral detergent at 90 °C for 20 minutes. Samples were rinsed in deionized (DI) water followed by successive sonication for 10 minutes each in DI water, acetone and isopropanol. An ozone treatment was performed using an exposure to UV radiation (G8W SYLVANIA uv lamp) for 20 minutes. Samples were placed approximately 2.5 cm away from the lamp inside a covered chamber. The cleaned substrates were stored in wafer containers supplied by Kintek, when transported to the spin-coater, or to the vacuum chamber of the analyser.

The PEDOT:PSS solution was filtered using 0.2 micron RC filter supplied by Sartorius. The PEDOT:PSS was deposited on the substrates by spin coating (PWM 32 spinner, from Headway Research, Inc.) the solution at 5000 rpm for 1 minute. This procedure results in approximately 40 nm thick polymer films. After depositing PEDOT:PSS, the samples were annealed in air on a pre-heated aluminium block inside an oven at 145 °C for 10 minutes. Controlled humidity chambers were assembled in a desiccator using a saturated solution of sodium bromide (NaBr) for 56 % relative humidity (RH) and hydrated copper sulphate (CuSO<sub>4</sub>.5H<sub>2</sub>O) for 95 % RH. RH was measured using data logger U12-011 supplied by HOBO and shown to vary by less than 2 % when opened for a short time and required around 100 minutes to recover to the standard RH.

The design of the NICISS equipment is described in reference.<sup>[24]</sup> NICISS is a technique able to obtain the concentration depth profiles of the elements of soft matter surfaces up to

a depth of about 20 nm and a resolution of a few Å in the surface-near area.<sup>[24, 25]</sup> In a NICISS experiment the target is bombarded with a pulsed beam of inert gas ions - mostly helium ions - with a kinetic energy of several keV.<sup>[24]</sup> The energy of the projectiles backscattered from the atoms in the target is determined by their time of flight from the target to the detector. The projectiles lose energy during the backscattering process, and the energy transfer depends on the mass of the target atom. This first type of energy loss is used to identify the element from which a projectile is backscattered. The projectiles also lose energy on their trajectory through the bulk due to small angle scattering and electronic excitations of the molecules constituting the target (stopping power).<sup>[26]</sup> This energy loss is used to determine the depth of the atom from which a projectile is backscattered. In combination, these two types of energy losses are used to determine the concentration depth profiles of the elements. The data evaluation to obtain the concentration depth profiles is described in detail in reference.<sup>[27]</sup>

For the NICISS measurements shown here, helium ions with energy of 3 keV were used as projectiles. The samples were mounted on a rotating disc. The surface of the samples was investigated in concentric circles with a total surface area of about  $1 \text{ cm}^2$ . The ion dose was kept below  $2 \times 10^{13}$  ions cm<sup>-2</sup>.

XPS measurements were performed with UHV equipment built by SPECS. The instrument is equipped with a source for meta-stable helium atoms and UV light, with an X-ray source for Al K $\alpha$  and Mg K $\alpha$  and with an ion source for rare gas ions with kinetic energy of 1 to 5 keV. The instrument is equipped with a sample holder for solid samples and a sample holder for liquid samples. Solid samples can be cooled to liquid nitrogen temperature and heated to 800 °C. For the analysis of insulating samples with ionising radiation a facility for charge compensation can be used. High resolution XP spectra were obtained to identify elements and their chemical state in the surface near region of the PEDOT:PSS layers.

#### 4.4. **Results and Discussion**

A typical TOF spectrum of PEDOT: PSS obtained using NICISS is given in Figure 4.1(a). The spectra of the PEDOT:PSS spin-coated on a silicon wafer shows signals due to the constituents of PEDOT:PSS, namely sulphur, oxygen and carbon. The arrows indicate the onset of the signals from the different elements. The steps with onsets at 4.7, 6.1 and 7.3  $\mu$ s correspond to the back-scattering of helium from sulphur, oxygen and carbon, respectively. Page 74

A slight step in the TOF spectra around 5.2  $\mu$ s is due to traces of residual sodium present in the PEDOT:PSS. These elemental steps are superimposed on a broad background of sputtered hydrogen atoms. Figure 4.1(b) was recorded from a sample with a thin film of PEDOT:PSS spin-coated on an ITO substrate. The sample was annealed in air at 145 °C for 10 minutes followed by exposure to a 56 % RH environment for 48 hours. A new step with an onset at 3.9  $\mu$ sec is found showing the presence of indium/tin in the polymer layer. Due to the large difference in atomic mass between the incident helium ion and both In and Sn, NICISS cannot distinguish between these species and techniques such as XPS are necessary. Therefore, the notation indium/tin (In/Sn) is used.



Figure 4.1: NICIS spectra of PEDOT:PSS spin-coated on (a) silicon substrate (b) ITO and exposed to 56 % RH for 48 hours. To the spectrum of PEDOT:PSS on ITO an offset is added for clarity.

The contribution of different elements in spectra of Figure 4.1 is converted to a concentration depth profile and is shown in Figure 4.2. The procedure is described in Andersson et al.<sup>[27]</sup> However, there is a concentration gradient over the first 2 nm for In/Sn and sulphur (Figure 4.2 a) with a constant increase in concentration up to the constant bulk concentration. It must be noted here that the slope of the In/Sn profiles is not due to the depth resolution of the method but due to the concentration depth profile of In/Sn. The concentration depth profiles thus show a reduced In/Sn concentration in the outermost layer and a constant concentration in the bulk. These profiles are different to those of carbon and oxygen shown in Figure 4.2(b). The slope of carbon and oxygen profile is only due to the energy resolution, i.e. deconvolution of these profiles with the energy resolution

of the method would result in a step function of the concentration depth profile. A higher concentration of carbon could be due to adventitious carbon. However, this is unlikely given the fact that all polymers have low surface energies. So far the different gradient for oxygen and sulphur is not understood, as both PEDOT and PSS are the only organic species present and both have oxygen and sulphur in the same monomer unit. The gradient in the In/Sn concentration profile over this range corresponds closely to the sulphur profile over the same range.

Beyond the top 2 nm, the In/Sn concentration is constant for up to 12 nm (Figure 4.2 c), before spectral interference in the TOF due to the presence of other elements. The measurement depth is almost one-third of the total thickness of the approximately 40 nm PEDOT:PSS layer, giving clear evidence of a lack of concentration gradient of In/Sn through the PEDOT:PSS layer that would be consistent with a conventional diffusion limited migration process.

Importantly, the concentration depth profile remains constant at all sampling times and under all processing conditions (with the concentration changing), with the apparently rapid diffusion of species throughout the 40 nm PEDOT:PSS film suggesting that the generation / liberation of mobile species at the ITO interface is the rate determining step in the migration process.

Using the constant concentration region of the depth profile between 2 nm and 12 nm to define the concentration of In/Sn species observed under a range of conditions, In/Sn was observed at some concentration in PEDOT:PSS coated onto ITO in all cases, regardless of surface treatment, annealing conditions and exposure to humidity. The concentration depth profile was also similar to Figure 4.2 in all cases, indicating that these conditions did significantly alter the underlying mechanism of migration, however, the amount of In/Sn found was strongly dependent on processing conditions.

The NICISS measurements show that In/Sn is found in a concentration of about  $1.8 \times 10^{-03}$  mol cm<sup>-3</sup> or 1 metal ion per 4.7 monomer units of the polymers. The error bar for the In/Sn concentration is given by the uncertainty in evaluating the step height of the In/Sn step in the NICIS spectra.
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*Figure 4.2:* Concentration depth profiles of (a) indium/tin and sulphur (b) oxygen and carbon (c) indium/tin migrated into the PEDOT:PSS thin film. The PEDOT:PSS film was

#### spin-coated on ITO and exposed to 56 % RH for 48 hours.

The time dependence of migration is shown in Figure 4.3 under three humidity conditions and with various surface cleaning treatments. A summary of the combinations of humidity conditions and surface treatments is listed in Table 4.1. In all cases, the time dependence of migration was similar with a non-zero concentration observed initially, which increased over the following 20 hours while stored at room temperature. Subsequently the concentration remained constant for a period of at least a week, while the sample was stored under the same conditions.

Set No.	<b>Relative Humidity</b>	Cleaning agent	Annealing	
A1	0 % (Vacuum drying)	Pyroneg at ~ 50 °C	~ 145 °C	
A2			Without annealing	
A3		Without pyroneg	~ 145 °C	
A4			Without annealing	
B1	56 %	Pyroneg at ~ 50 °C	~ 145 °C	
B2			Without annealing	
B3		Neutral detergent (deconex) at 90 °C	~ 145 °C	
C1	95 %	Pyroneg at ~ 50 °C	~ 145 °C	
D1	56 %	Neutral detergent (deconex) at 90 °C)	~ 145 °C	
D2	95 %	Neutral Detergent	~ 145 °C	
		(deconex) at 90 °C)		

**Table 4.1**: Summary of various NICISS experiments performed to study the effect of different processing conditions on the migration process.

When the PEDOT:PSS coated ITO was stored in vacuum at room temperature immediately following annealing (see Set A, Table 4.1), the saturation concentration of In/Sn in the upper 12 nm was  $1.3 \times 10^{-04}$  mol cm<sup>-3</sup> or 1 metal ion per 64 monomer units. Considering

the magnitude of the error bars, it can be concluded that the effect of detergent cleaning and the annealing of the sample after spin coating does not affect the migration process when the samples are stored in vacuum.

When exposed to higher humidity levels following annealing, the saturation level of In/Sn increases to  $1.5 \times 10^{-03}$  mol cm<sup>-3</sup> of In/Sn (1 metal ion per 5.6 monomer units) for exposure at 56 % RH (see Set B, Table 4.1) at room temperature (Figure 4.3(b)) and to  $1.8 \times 10^{-03}$  mol cm<sup>-3</sup> of In/Sn ions (1 metal ion per 4.7 monomer units) following exposure to 95 % RH (see Set C, Table 4.1) at room temperature (Figure 4.3(c)). These concentrations are about a factor of 10 to 15 higher than in case the samples were stored in vacuum.

As can be seen in Figure 4.3(b), the cleaning agent, either the caustic solution or deconex (neutral detergent), is benign and does not have a significant influence on the overall In/Sn migration.

Compared to the 56 % RH exposure both the migration of In/Sn is faster and the maximum bulk concentration is higher in case of 95 % RH. In Table 4.2 the bulk concentration of In/Sn is summarised for the various sample treatments.

Measuring the concentration of In/Sn in the PEDOT:PSS layer after various treatments of the samples show that exposure to humidity has the largest influence on the migration of the metal ions from the ITO into the polymer layer. All results can be grouped according to the level of humidity: the larger the humidity the stronger and faster is the migration. Choosing a detergent for cleaning the ITO or not, varying the detergent and varying the annealing of the samples is of secondary importance.

The migrating moiety could be clusters of ITO that have been etched from the surface, since ITO has a granular structure, or it could be individual atoms or ions. ITO is known to be etched in acid.<sup>[28]</sup> Since PEDOT:PSS has a pH of about 2 in solution, it can be assumed that the PEDOT:PSS solution is etching the surface of the ITO.

To understand the role of humidity at a much later stage after the fabrication, two samples were vacuum dried for twenty-four hours (set D, see Table 4.1). One sample was then exposed to 95 % RH and the other to 56 % RH.



Figure 4.3: Time dependence of indium/tin migration into thin PEDOT:PSS films. The concentration shown is the bulk concentration in the PEDOT:PSS film. In (a) the

concentration of films stored under vacuum are shown, in (b) of samples exposed to 56 % RH. In (c) the bulk concentration of samples exposed to various RH are compared.

NICISS measurements were obtained for both the samples before and after they were stored in humid conditions. After each NICISS measurement, samples were immediately replaced in their respective controlled humidity setup. Figure 4.4 shows the time dependence of the migration process after twenty four hours of vacuum drying. It can be seen that considering the magnitude of errors in Figure 4.3 a, the concentration under vacuum conditions agrees well with that found in the set A of the experiment, which shows the reproducibility of the measurements. It can also be seen that similar to set A, B and C measurements, the concentration of migrated indium/tin in the PEDOT:PSS film reaches a constant level within approximately 20 hours following the exposure to humid atmosphere, irrespective of the humidity levels and then become constant. It must also be noted that even after vacuum drying the samples immediately after annealing, the concentration of migrated indium and tin is non-zero, however by introducing an initial vacuum drying step, the overall concentration of the migrated indium/tin into the PEDOT:PSS reaches only 6.0E-04 mol cm<sup>-3</sup> (incase of 95 % RH ) and 4.0E-04 mol cm<sup>-3</sup> (incase of 56 % RH) as compared to 1.3E-03 mol cm<sup>-3</sup> in set B and 1.8E-03 mol cm<sup>-3</sup> in set C of the experiments. This finding could potentially be important for the fabrication of OPVs.



*Figure 4.4: Time dependence of the indium/tin migration into PEDOT:PSS thin films after the films have been dried for 24 hours in vacuum.* 

Due to presence of indium/tin in the PEDOT:PSS layer immediately after the spin-coating,

irrespective of the humidity levels, it can be assumed that the ITO surface is etched with the acidic PEDOT:PSS while the spin-coating process. It is found that humidity plays significant role in the migration process and vacuum drying can be a potential way to control the indium/tin migration into the PEDOT:PSS film.

It must be noted that atmospheric oxygen can diffuse into the devices and possibly affect the ITO-PEDOT:PSS interface. Therefore the role of oxygen in the indium/tin migration process cannot be excluded but is not within the scope of this paper.

*Table 4.2*: Summary of bulk concentrations of indium/tin measured after different treatments.

Set No.	A1	A2	A3	A4	B1	B2	B3	C1	D1	D2
Conc/mol cm <sup>-3</sup>	1.3E-04	8.2E-05	9.0E-05	9.9E-05	1.5E-03	1.2E-03	1.6E-03	1.8E-03	3.9E-04	6.0E-04

In order to determine whether both indium and tin migrate into the polymer layer and in what chemical state they are present in the polymer layer, we investigated the polymer films with XPS. Figure 4.5 shows spectra of indium and tin both as component of ITO and after migration into the PEDOT:PSS layer. The XP spectra were referenced to the C1s peak which is due to adventitious hydrocarbons adsorbed on the ITO in case of the bare ITO. For the PEDOT:PSS coated ITO, the C 1s is due to the C-C bond in the backbone of the polymer.

The XP spectra show that both indium and tin are migrating into the PEDOT:PSS, which is contrary to some of the previous reports.<sup>[22]</sup> The signal due to tin is small with low signal to noise ratio, which may explain why it has not been observed in some cases previously.

The ratio of indium to tin for bare ITO is  $10.7 \pm 0.5$ , which is consistent with suppliers specifications, however, the ratio of indium to tin in PEDOT:PSS is  $16 \pm 2$ . The change in ratio indicates a slight preference for indium to migrate to the upper half of the polymer layer.

The indium peak for bare ITO has two components, with the In 3d5/2 and Sn 3d5/2 peaks found at 444.7 eV and 486.9 eV respectively corresponding to the characteristic lines of  $In_2O_3^{[29]}$  and  $SnO^{[30]}$  respectively. The peak positions for both indium and tin in the

polymer layer are different to that of the bare ITO, whereas the peak shape of indium was found to change as well. It must be noted that the major component of In 3d5/2 is not found at 444.7 eV as in the case of bare ITO. Instead, there is only one component at 446.3 eV.

The peak position in the XP spectrum of indium in the polymer layer at 446.3 eV corresponds to indium ions in a salt. For example, the binding energy found for indium in indium(III) trifluoride is 446.2 eV<sup>[31]</sup> and in indium(III) chloride is 446 eV.<sup>[32]</sup> The XPS peak position of tin 3d (5/2) in the polymer layer was found at 487.8 eV. It corresponds to a tin salt as for example, the binding energy reported for tin in pyrazil tin tetrachloride [Sn(C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>)Cl<sub>4</sub>] is 487.8 eV,<sup>[33]</sup> and in trichlorophenyl(pyrazine-N1) tin [SnCl<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)(C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>)] is 487.9 eV.<sup>[34]</sup>



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**Figure 4.5**: XP spectra of (a) indium at the surface of pristine ITO and (b) indium found in a PEDOT:PSS film spin-coated on ITO and exposed to 56 % RH. The pristine ITO has a large peak at 444.7 eV and a small peak at 446.0 eV. In the spectrum of the PEDOT:PSS film the peak at 444.7 eV has disappeared and only a peak at 446.3 eV is found. In (c) XP spectra of tin of pristine ITO (broken line spectrum) and of tin in the PEDOT:PSS (bold line spectrum) is shown. The count rate of the tin spectra is much lower due to the lower concentration in ITO compared to indium. Thus no fits to the spectra are shown. However, a shift in the peak position of tin can clearly be identified.

It can therefore be concluded that the In/Sn observed in the PEDOT:PSS layer is in the form of individual metal ions which form salts in the polymeric layer. The most likely counter ion is the sulphonate functionality in PSS as this is the only anion present in the polymer layer, although there is no direct evidence to support this.

The proposed reaction scheme occurring at the surface can be represented as Equation 4.1, below.

$$RSO_{3}H + H_{2}O \rightarrow RSO_{3}^{-} + H_{3}O^{+}$$
  
$$In_{2}O_{3} + 6RSO_{3}^{-} + 6H_{3}O^{+} \rightarrow 2(RSO_{3})_{3}In + 9H_{2}O$$
  
Eq. 4.1

For tin a reaction equation applies accordingly. In this proposed reaction, water absorbed from the atmosphere by the hygroscopic PSS component plays a key role in the initial liberation of indium and tin from the ITO and the concentration can be expected to be highly dependent on the humidity of the atmosphere surrounding the sample. Since PEDOT:PSS is spin-coated from water, it can also be expected that some reaction will occur almost immediately, consistent with the observations in the time dependence.

Once the indium and tin salt are formed at the ITO surface, the ions can subsequently diffuse relatively rapidly throughout the 40 nm thick polymer layer.

The implications for the OPV devices are twofold. Firstly, the presence of indium and tin ions can influence the charge transport through the PEDOT:PSS buffer layer. Salt ions can act as traps for the charges and decrease the charge transport. Indium and tin ions also could further migrate into the hetero-junction layer in a photovoltaic device and affect the charge separation and charge transport in this layer. Since previous studies have shown conformational changes in the PEDOT:PSS films and phase separation of PEDOT:PSS,<sup>[17, 35]</sup> therefore it can be speculated that the formation of a salt with the PSS could possibly cause changes in conformation of the PEDOT:PSS and hence influences the charge transport also in this way. Even though the reaction affects in first instance only the PSS and not the PEDOT as the actual charge transporting polymer, this can have influence on the charge transport; PSS is used in this polymer blend as matrix for the PEDOT. The separation of PEDOT and PSS could generate islands of PEDOT polymer molecules and thus interrupt the pathway for hopping charge carriers. It must be emphasized, however, that from the findings here there is no evidence for either of these effects on the charge transport. The influence on the charge transport will have to be investigated separately. Whether or not the change of the PSS deteriorates or improves the performance of OPVs will have to be investigated separately. The second implication relates to the surface properties of ITO. The workfunction of ITO will always be changed when spin coating of PEDOT:PSS on ITO from an aqueous solution as the PEDOT:PSS solutions chemically reacts with the ITO through etching. As a consequence, the workfunction of ITO measured before spin coating the PEDOT:PSS is not representative for the workfunction of the ITO in an OPV.

In a real device, the reactions at the interface found here could continue after finalising the photovoltaic device and cause deterioration over time.

# 4.5. Conclusions

Indium and tin from ITO have been found to migrate into PEDOT:PSS when the polymer is spin-coated onto the transparent metal oxide electrode. Both indium and tin migrate into the polymer in ionic form and appear to form a salt, probably with the sulfonate group in poly(styrenesulfonic acid). The concentration depth profiles show that a constant concentration of the metal ions is found in the upper 12 nm of a 40 nm thick polymer layer in all cases, with no evidence of concentration gradients that would be expected for a diffusion controlled process. The cleaning procedure of the substrate had no significant effect on the level or rate of migration, while humidity has a very strong influence on migration. This implies that the surface reaction to liberate In and Sn are the rate determining steps, with water and the subsequent acid generation from the PSS playing a significant role in the initial liberation of the salt throughout the 40 nm thick film appears to cease after approximately 20 hours, where the concentration of In and Sn in the polymer layer layer become constant.

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# Effect of Indium and Tin Contamination on the Efficiency and Electronic Properties of Organic Bulk Hetero-Junction Solar Cells

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# 5.1. Abstract

Organic photovoltaic devices using an electrode of indium tin oxide (ITO) coated with a buffer layer of poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) exposed to controlled humidity during fabrication showed a 65 -75 % decrease in efficiency and displayed s-shaped J-V curves, changes which are attributed to different levels of indium and tin migration into the PEDOT:PSS film. A distinct shift in the secondary electron cut-off in the UV photoelectron spectra (UPS) of ITO/PEDOT:PSS samples exposed to controlled humidity indicate an increase of the dipole at the ITO/PEDOT:PSS interface, which could explain the appearance of s-shaped J-V curves. Additionally, the electron density at low binding energies is reduced for the humidity exposed PEDOT:PSS suggesting a second mechanism for decreased device performance.

## 5.2. Introduction

Organic photovoltaic devices (OPVs) made from polymeric materials are promising alternatives to inorganic semiconductors for renewable energy production. The bulk hetero-junction (BHJ) OPV technology is of increasing interest due to its potential of being low cost in production, mechanically flexible, light weight and production scalability,<sup>[1]</sup> with power conversion efficiencies of up to 8 % achieved.<sup>[2]</sup> Both novel donor<sup>[3]</sup> and acceptor<sup>[4]</sup> materials as well the modification of the interfaces have contributed to this increase in efficiency.<sup>[5, 6]</sup>

Typically an OPV consists of an active layer of conjugated polymers sandwiched between two electrodes. The polymer layer is usually comprised of an electron donor and an electron acceptor forming a BHJ layer. Frequently used compounds are poly (3hexylthiophene) (P3HT) as electron acceptor and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) electron donor. Light absorbed in the polymer leads to the generation of excitons which separate into electrons and holes at the donor-acceptor interface. The charge transport over the polymer/polymer and polymer/electrode interfaces are critical factors that affect the device parameters such as the short circuit current  $J_{sc}$ , open circuit voltage  $V_{oc}$ , efficiency and the fill factor *FF*. Potential barriers between the interfaces can cause charge traps and high recombination losses resulting in inferior device performance. The total parasitic series resistance in OPVs is a combination of both the bulk resistance of the functional layers and the contact resistance between them.<sup>[7]</sup> In-order to achieve high  $J_{sc}$ ,  $V_{oc}$  and high efficiencies it is therefore desirable to use materials with high charge carrier mobility and low barriers between the electrodes and the BHJ layers.

Interfacial layers are used between the photoactive BHJ layer and the electrodes in order to adjust the energy levels between the electrode and the active layer and to enhance charge extraction<sup>[8]</sup> electrode.<sup>[9]</sup> and planarise the surface of the underlying Poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate) (PEDOT:PSS) is commonly used as an anodic buffer layer to improve hole extraction to the anode<sup>[10]</sup> improving the open circuit voltage,<sup>[7]</sup> power conversion efficiency<sup>[11]</sup> and also in some cases the stability of the device.<sup>[12]</sup> However, the ITO/PEDOT:PSS interface has been shown to be unstable, with both indium and tin ions migrating into the PEDOT:PSS layer.<sup>[13-15]</sup>

We have recently shown that humidity is one of the critical factors influencing the migration of indium and tin from the ITO electrode into the PEDOT:PSS, probably due to the reaction of the acidic PEDOT:PSS with the ITO.<sup>[14]</sup> After exposure to high humidity for 24 hours, concentrations of up to  $1.8 \times 10^{-3}$  mol cm<sup>-3</sup> of indium and tin ions, corresponding to 1 indium or tin moiety per 4.7 monomer units, have been found in the PEDOT:PSS layer by measuring concentration depth profiles with neutral impact collision ion scattering spectroscopy (NICISS).<sup>[14]</sup> It is important to note that OPVs used in other studies will have similar levels of ions in the PEDOT:PSS layer due to the processing environment, or changes in the device over time. Therefore, while the exposure of devices to a humid atmosphere does not occur under normal fabrication conditions, the changes induced in the device by humidity may be the same as those induced by normal operation over time. The direct impact of ion migration on the cell efficiency and electrical performance has not been systematically studied. The findings from this work will therefore have implications for all devices where ITO/PEDOT:PSS is used as an electrode.

Though water induced degradation of organic solar cells have previously been mentioned in the literature,<sup>[16, 17]</sup> the aim of this paper is to fully characterise OPV's fabricated with known concentrations and profiles of indium and tin in the PEDOT:PSS layer. The electronic properties of the doped PEDOT:PSS layer are investigated with UV photoelectron spectroscopy (UPS) and correlated to the J-V characteristics of the completed device.

### **5.3.** Experimental

#### Sample preparation

OPVs based on normal device structure ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al were fabricated as shown in Figure 5.1.

ITO-coated glass substrates with a sheet resistance of 15 ohms sq<sup>-1</sup> (purchased from Kintek) were used. A standard procedure was followed for cleaning the ITO-coated glass. The glass was cleaned by standing it in a solution of 5 % deconex PA neutral detergent (supplied by Borer) at 90 °C for 20 minutes. Samples were then rinsed in deionised (DI) water followed by successive sonication for 10 minutes each in DI water, acetone and isopropanol. Subsequently UV-ozone cleaning of the ITO substrates was applied using a Novascan PDS-UVT UV/ozone cleaner with the lamp intensity being greater than Page 94



36 mW cm<sup>-2</sup> at a distance of 100 cm, giving ozone output greater than 50 ppm at ambient conditions.

#### Figure 5.1: Schematic representation of the fabricated device structure.

Aqueous solutions of PEDOT:PSS were spin-coated in air using a Laurell WS-400B-6NPP Lite single wafer spin processor. The optimised fabrication conditions of the PEDOT:PSS films were similar to those in Sharma *et al.*<sup>[14]</sup> PEDOT:PSS (CLEVIOS P VP AL4083) was purchased from H.C. Starck and was used as received. The films were then annealed on a hot plate in a nitrogen filled glove box at 140 °C for 10 minutes. The BHJ layer of P3HT-PCBM was then spin-coated in the glove box at 3000 rpm for 60 seconds using a SCS G3P spin-coater followed by annealing on a hot plate at 110 °C for 10 minutes. PCBM was purchased from Nano-C and P3HT was generously donated by Merck. The samples were transferred to the vacuum evaporator without exposure to air and thermal evaporation of Ca and Al was carried out at pressures below 2 x  $10^{-6}$  mbar resulting in layer thicknesses of 20 nm and 100 nm respectively. Calcium pellets were purchased from Sigma Aldrich and aluminium pellets were purchased from KJ Lesker. A shadow mask was used for patterning of the metallic electrode and the device active area defined by the mask was  $0.1 \text{ cm}^2$ .

Following annealing, samples were stored under three different conditions for 48 hours: (A) vacuum; (B) controlled humidity at 56 % RH and (C) controlled humidity at 95 % RH. These were the same conditions as in a previous study in which the profiles and concentrations of indium and tin migrated into the PEDOT:PSS layer were quantified.<sup>[14]</sup> A

summary of various exposure conditions used for different samples is given in Table 5.1.

 Table 5.1: Summary of various exposure conditions used for different samples.

Sample A	Stored under vacuum for 48 hours
Sample B	Stored in a closed chamber with 56 % RH for 48 hours
Sample C	Stored in a closed chamber with 95 % RH for 48 hours

All the samples exposed to humidity were annealed at 140 °C for 10 minutes inside the glove box immediately prior to spin-coating the BHJ layer to ensure all samples had been exposed to similar thermal treatments and had similar moisture levels. OPVs prepared from samples A, B and C are named device A, device B and device C respectively.

#### Electron spectroscopy

The investigations of the polymer samples with UPS were performed in a UHV apparatus built by SPECS (Berlin, Germany). The apparatus is equipped with a two stage cold cathode gas discharge from MFS (Clausthal-Zellerfeld, Germany) to generate simultaneously metastable helium atoms (He\*  ${}^{3}S_{1}$ ) and UV light (He I line). The spectra of the electrons emitted from the samples are recorded with a hemispherical Phoibos 100 energy analyser from SPECS. Spectra obtained by Metastable Induced Electron Spectroscopy (MIES) and UP spectra were recorded at pass energy of 10 eV; however, as the MIE spectra are not relevant for the current study they are not shown here. At the pass energy of 10 eV the analyser has an energy resolution of 400 meV as evaluated from the Fermi edge of polycrystalline silver. The apparatus is further equipped with a non-monochromatic X-ray source for Mg and Al K $\alpha$  radiation and an ion source for rare gas ions with kinetic energy from 1 to 5 keV. The angle between the He\*/UV light irradiation and the analyser and the X-ray irradiation and the analyser are both 54°. The base pressure of the UHV chamber is a few 10<sup>-10</sup> mbar. However, UHV conditions are not required for the experiments shown here.

In a UPS experiment the sample is irradiated with UV photons leading to photoionization via the photoelectric effect. The energy of emitted electrons is given by

$$E_{kin,hv} = E(hv) - E_{bin} - \Phi_{spec}$$

where  $E_{kin,hv}$  is the kinetic energy of the emitted electron, E(hv) the photon energy (21.22 eV for the He I line used here),  $E_{bin}$  the binding energy of the electron before excitation and  $\Phi_{spec}$  the spectrometer workfunction. With UPS the electron density in the surface near area is determined. The information depth is limited by the electron mean free path of the emitted electrons. At the used excitation energy the electron mean free path in organic compounds is around 10 Å.<sup>[18]</sup> UP spectra can be used to determine the workfunction or, in case of organic compounds, the ionisation energy of samples as well as the position of the highest molecular orbital (HOMO) and the formation and strength of dipoles at interfaces. The workfunction or ionisation energy of the samples is determined as the difference between the excitation energy and the length of the spectrum. The latter is given as the difference of the high binding energy cut-off and the cut-off of the spectrum at the lowest binding energy. The formation of dipoles at the interface between an organic layer and its supporting substrate can be determined by the shift of the high binding energy cut-off before and after depositing the organic layer.

Photoelectron spectroscopy in air (PESA), which is a relatively new technique was used as independent measure of the ionisation energy of the PEDOT:PSS films with different levels of migrated indium and tin. PESA uses a low power (5–10 nW), monochromated UV source to scan an energy range. Above the ionisation potential, photogenerated electrons ionise oxygen molecules in the air that are in turn detected by an open counter.<sup>[19]</sup>

#### Electronic characterisation

After fabrication, the devices were encapsulated using optical cement inside a glove box and tested in air. The cells were tested with an Oriel solar simulator fitted with a 1000 W Xe lamp filtered to give an output of 100 mW cm<sup>-2</sup> at AM1.5. The lamp was calibrated using a standard Si cell from Peccell Limited, which was subsequently cross-calibrated with a KG5 filtered reference cell traceable to the National Renewable Energy Laboratory. The devices were tested using a Keithley 2400 sourcemeter controlled by Labview software.

The device parameters open circuit voltage  $V_{oc}$ , short circuit current  $J_{sc}$  and fill factor *FF* were derived. Fill factor reflects the diode properties of a cell and is determined as,

$$FF = \frac{V_{mpp} J_{mpp}}{V_{oc} J_{sc}}$$
Eq. 5.2

where  $J_{mpp}$  and  $V_{mpp}$  are the current and voltage at the maximum power. The performance of an OPV can be determined by its efficiency at the standard conditions such as 1000 Wm<sup>-2</sup> irradiance with a AM1.5 solar spectrum. The efficiency  $\eta$  can numerically be calculated as,

$$\eta = \frac{V_{oc} J_{sc} FF}{I_{light}}$$
Eq. 5.3

where  $I_{light}$  is the intensity of the irradiated light.

### 5.4. **Results and Discussion**

The J-V curves for devices A, B and C are shown in Figure 5.2. Device A had an efficiency of  $2.9 \pm 0.1$  % and a fill factor of  $0.54 \pm 0.05$  with a typical exponential J-V response, consistent with carefully prepared OPVs using these materials.

In contrast, devices B and C show an s-shaped plateau in the J-V curves. Instead of an exponential current-voltage ratio, a plateau is observed in the conducting direction between an applied voltage range of 0.4 to 0.5 V and beyond that, the current is found to increase again. The plateau can be interpreted as a saturation of the current.

Efficiencies of  $0.6 \pm 0.1$  % and  $1.0 \pm 0.1$  % were measured for devices B and C respectively which is a significant reduction in photovoltaic efficiencies compared to that of device A. It should be noted that the efficiency of device B is reduced to a greater extent than that of device C despite device C having a significantly higher level of indium and tin ions in the PEDOT:PSS layer. This result is reproducible over five devices. It is important to note that humidity results in migration of indium and tin, but it has also been reported that humidity can affect the morphology of PEDOT and PSS,<sup>[20]</sup> so these results cannot be solely attributed to indium and tin migration.

The appearance of an s-shaped J-V curve of OPVs has been previously reported in the literature.<sup>[21, 22]</sup> The cause has not been directly established, but appears to relate to the degradation of the PEDOT:PSS layer and the cathode-polymer interface.<sup>[23]</sup> This behaviour clearly has a significant role in device performance and has recently become the focus of a number of investigations.

Kumar *et al.* attribute s-shaped features in the J-V curves to the presence of interfacial Page 98

dipoles,<sup>[24]</sup> while Schulze *et al.* attribute them to a hole injection barrier between the active polymer layer and the hole transport layer.<sup>[25]</sup> Tress *et al.* have suggested that the mismatch in the charge carrier motilities in the donor and acceptor materials is a potential reason for the appearance of an s-shaped J-V curve.<sup>[26]</sup>



Figure 5.2: J-V characteristics of device A, B and C.

Wagenpfahl *et al.* recently developed a model to describe s-shaped J-V curves<sup>[27]</sup> in which charge transfer across the metal-semiconductor interface plays an important role. Their model demonstrates that a local depletion region is created within the devices in case the surface recombination velocity for holes (majority charge carriers) at the anodic interface is reduced.<sup>[27]</sup>

Importantly, all these proposed mechanisms for the s-shaped J-V curve relate to interfacial phenomena and affect the charge transport over one of the interfaces in the device.

In order to better understand the mechanisms leading to the decrease of the efficiency of the devices and the formation of the s-shaped J-V curve the electronic properties of the PEDOT:PSS layer and of the ITO/ PEDOT:PSS interface after exposure to humidity were investigated.

Figure 5.3 shows the secondary electron cut-offs of the UP spectra obtained from the





Figure 5.3: UP spectra of the PEDOT:PSS films spin-coated on ITO substrates. The secondary electron cut-off of sample B and sample C is shifted for 0.31 eV relative to that of sample A.

It can be seen that the onset of the secondary electron cut-off is the same for both sample B and C, and shifted by  $0.31 \pm 0.07$  eV relative to that of sample A. The shift in the secondary electron cut-off correlates to a shift of the HOMO compared to that of the untreated PEDOT:PSS. The shift in the HOMO position has to be interpreted as a relative shift of the HOMO with respect to the workfunction of the substrate ITO which means that the dipole at the ITO/PEDOT:PSS interface increases leading to an increase in the barrier for the charge transport over this interface.

However, the change of the dipole at the ITO/PEDOT:PSS interface is more complicated since the ITO surface is also modified due to its interaction with the acidic PEDOT:PSS (resulting in significant indium and tin migration), and it is not possible to prepare a representative ITO surface for comparison. Previous studies have shown that acidic treatment of ITO leads to an increase in the workfunction of ITO of 0.1 to 0.7 eV depending on the acid used.<sup>[28]</sup> Thus the interface dipole between ITO and the PEDOT:PSS layer could increase even more than it is given by the observed change in the HOMO position of the PEDOT:PSS alone.

The increase of the barrier at the ITO/PEDOT:PSS interface can explain the appearance of

the s-shape in the J-V curve and the reduction in efficiency of the devices where the ITO/PEDOT:PSS interface was exposed to humidity. In all cases described above s-shaped J-V curves have been related to a decrease in charge transport over one of the interfaces in the OPVs.

Figure 5.4 shows the low binding energy side of the UP spectra of the samples A, B and C. The spectra are very similar to those reported in literature.<sup>[29, 30]</sup> In Figure 5.4 the region from 0 to 7 eV is fitted with a series of Gaussian curves to determine, how the position of the energy levels at low binding energy change due to the exposure to humidity. The fitting is performed even though the nature of the respective orbitals is not known. However, in the context here only the shift of the peak position is important. The full width-half-maximum of the peaks fitted has been kept constant and the relative position of the peaks has been kept the same for all three spectra. Shifts of  $0.12 \pm 0.1$  eV and  $0.14 \pm 0.1$  eV have been found in sample B (exposed to 56 % RH) and sample C (95 % RH), respectively, relative to peaks of the sample dried in vacuum (sample A). This shift at the lower binding energy side of the spectra corresponds to the change in the vacuum level of the sample.<sup>[31]</sup>

The change in the high binding energy cut-off (see Figure 5.3) and the shift observed in the low binding energy levels (see Figure 5.4) are unequal and therefore the ionisation energy of the PEDOT:PSS has changed through the humidity treatment.<sup>[32]</sup> As a consequence, samples B and C show a decrease in ionisation energy of  $0.19 \pm 0.12$  eV and  $0.17 \pm 0.12$  eV respectively. When measured by PESA, samples B and C also showed a statistically significant shift of  $0.1 \pm 0.01$  eV in the ionisation potential when compared with sample A.

The change in ionisation energy of the treated PEDOT:PSS is another factor that impacts on the overall device performance. The change in the ionisation energy of the PEDOT:PSS will lead to a change of the relative position of the energy levels at the BHJ/PEDOT:PSS interface. Depending on the materials used in the BHJ layer this could increase or decrease the mismatch of the energy levels at the BHJ/PEDOT:PSS.

It should be noted that the efficiency of device B has decreased more than that of device C even though the change in the position of the HOMO is the same. This indicates that there is a second mechanism operating which reduces the device performance.



Figure 5.4: Low binding energy side of the UP spectra obtained from samples A, B and C.

The spectra in Figure 5.4 also show a change in the intensity ratios of the peaks. In the spectrum of sample A the ratio between peak 1 and peak 3 is  $0.16 \pm 0.01$ , in that of sample B is  $0.13 \pm 0.01$  and in that of sample C is  $0.17 \pm 0.01$ . It must be noted that the lower the binding energy of the electrons, the more they contribute to the charge transport in the polymer. As a consequence, the decrease of peak 1 will influence stronger the charge transport in the PEDOT:PSS than a reduction of peak 2 or peak 3. While peak 1 has the same height in sample A and C it is found that peak 2 is noticeably smaller in sample B. As a consequence, the charge transport in sample B should be reduced compared to sample A but in particular also compared to sample C even though sample B and C both show the same shift of the high binding energy cut-off. This is confirmed by the J-V characteristics as the efficiency of sample B is lower than that of sample C even though sample B was exposed to a lower level of humidity and also has a lower concentration of indium and tin ions in the PEDOT:PSS layer. So far we do not have an explanation for this result.

### 5.5. Conclusions

J-V curves have been measured for OPVs in which the PEDOT:PSS has been exposed to humidity to generate a known concentration of indium and tin, migrated from the ITO electrode.

OPV's created after the PEDOT:PSS layer was exposed to humidity to generate known concentrations of indium and tin displayed s-shaped J-V curves and had significantly reduced device efficiencies. UPS measurements show that the HOMO of the PEDOT:PSS with indium and tin contamination shifts to a higher binding energy, consistent with an increase of the dipole at the ITO/PEDOT:PSS interface. Since the workfunction of acid treated ITO increases, the strength of the dipole could be even larger than estimated by the UPS measurements. The increase of the dipole at the ITO/PEDOT:PSS interface which leads to an increase of the barrier for the charge transport over this interface, is consistent with both the reduced efficiency of the devices as well as the appearance of an s-shaped J-V curve.

The devices where the ITO/PEDOT:PSS was exposed to 56 % humidity reproducibly showed a lower efficiency than those exposed to 95 % humidity. UPS measurements of the sample exposed to 56 % humidity show a reduction of electron density for the low binding energy states in the PEDOT:PSS. As the low binding energy electrons are critical in charge

transport, a reduction in their density is expected to lead to reduced charge transport through the PEDOT:PSS layer. A reduction in charge transport is a second effect reducing the efficiency of the OPVs upon exposure to humidity.

While the changes in these devices were induced by exposure to controlled humidity, the fundamental understanding that has been demonstrated through these results will be relevant to lifetime testing of devices where similar levels of ion migration may occur through different mechanisms. These results demonstrate that indium and tin migration in PEDOT:PSS significantly reduces the performance of OPVs.

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# Role of Zinc Oxide Thickness on the Photovoltaic Performance of Laminated Organic Bulk Hetero-Junction Solar Cells

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### 6.1. Abstract

A comprehensive study of zinc oxide (ZnO) film thickness and morphology on the electronic properties of inverted cells is reported. The complete conversion of zinc acetate precursor to 3-5 nm particles of ZnO with no residual acetate is obtained after 10 minutes at 300 °C. The workfunction determined by ultraviolet photoelectron spectroscopy (UPS) was 4.3 eV and is independent of the thickness of the ZnO layer or with the planarization of the ITO surface topology. However, the efficiency varies from 0.6 % to 1.7 % as the ZnO thickness varies from 17 to 28 nm (assuming full density for the ZnO layer) in a laminated device, with both the shunt and series resistance showing a strong variation with ZnO thickness. A relatively thick, mixed phase ZnO / BHJ in which the BHJ penetrates into the porous ZnO layer is proposed to explain the observed performance trends.

# 6.2. Introduction

Solution processed BHJ organic photovoltaic (OPV) have attracted extensive research and development due to their potential to be a low cost renewable energy source, mechanically flexible, light weight and their production scalability.<sup>[1, 2]</sup> In the last few years, significant effort has focused on improving the performance and lifetime of these devices resulting in efficiencies of more than 8 % being reported,<sup>[3]</sup> leading to realistic commercialization opportunities of the OPV technology in the near future. However, a number of significant challenges remain, especially regarding interfacial stability, such as the etching of ITO by poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) in which indium and tin migrate into the PEDOT:PSS layer resulting in reduced device efficiencies and lifetimes.<sup>[4, 5]</sup>

Inverted devices, as shown in Figure 6.1, in which the polarity has been reversed, have the potential to overcome the inherent instability of the ITO-PEDOT:PSS interface. This structure is also highly compatible with roll-to-roll manufacturing processes<sup>[6-10]</sup> to enable large scale production through various printing and coating methods.<sup>[7, 11, 12]</sup> Lamination has the added potential to allow optimal treatment of the layers in the device prior to fusing as well as overcoming wetting issues in the sequential fabrication of these devices.



Figure 6.1: Schematic of an inverted device fabricated using lamination technique.

If ITO is to be used as the cathode, the workfunction must be lowered. This can be

achieved by the application of low workfunction materials such as zinc oxide (ZnO),<sup>[13]</sup> cesium carbonate (Cs<sub>2</sub>Co<sub>3</sub>),<sup>[14]</sup> or titania (TiO<sub>2</sub>).<sup>[15]</sup> Recent research has focused on ZnO buffer layers, due to its high transparency, electron mobility<sup>[16]</sup> and more importantly the ability to synthesize ZnO films by solution processing<sup>[16, 17]</sup> making it applicable to roll-to-roll processing of inverted OPV's.<sup>[18]</sup> However, there are no systematic studies of the optimal morphology or understanding of the critical performance parameters for this system, with a wide range of performance being reported due to morphology,<sup>[19, 20]</sup> and film thicknesses of ZnO.<sup>[21, 22]</sup> The final process conditions used in a roll-to-roll process will be limited by the dimensional stability of the substrate (especially PET), so it is especially important to understand the mechanisms limiting optimal device performance degradation.

In this chapter, we report a comprehensive study of the impact of film thickness and morphology of the ZnO layer on the performance of inverted OPV's produced by lamination and propose a mechanism to explain the thickness dependent properties.

### 6.3. Experimental

#### Device Fabrication

ITO coated glass substrates with a sheet resistance of 15 ohm sq<sup>-1</sup> (purchased from Kintec) were used. The ITO glass was cleaned by immersing it in a well-stirred solution of 5 % Pyroneg (supplied by Johnson Diversey) at 80 °C for 20 minutes. Samples were then rinsed in deionized (DI) water and were successively sonicated in DI water, acetone and iso-propanol for 10 minutes each. Subsequently the substrates were then cleaned with UV-ozone for 20 minutes.

Zinc oxide sol-gel was prepared as follows: zinc acetate dihydrate  $(Zn(C_2H_3O_2)_2 (H_2O)_2 99.9 \%$  chemical purity, supplied by Sigma Aldrich) (250 mg) was dissolved in absolute ethanol (5 ml) at room temperature (0.23 M). The resulting mixture was stirred at 70 °C for two hours to form a clear homogeneous solution. Upon cooling to room temperature, undissolved zinc acetate salt was seen to settle at the bottom of the vessel.

The zinc acetate layer thickness was varied by changing the temperature of the zinc acetate solution and thus the solubility of zinc acetate in ethanol. The homogenous solution was
used at 70 °C at different spin speeds as well as the saturated room temperature solution.

The resulting ZnO films were prepared by spin-coating the solution (filtered using a 0.45 micron syringe filter) on cleaned ITO substrates (using a PWM32 spin-coater from Headway Research, Inc.) at various spin speeds followed by annealing at 300 °C for 10 minutes in air, and then cooled at room temperature. The detailed recipes for various experiments are summarized in Table 6.1.

Sample	Spin speeds	Solutions Used
Sample A	5000 rpm	Saturated solution at ambient
Sample B	5000 rpm	Fresh clear (0.23M) solution at 70°C
Sample C	3000 rpm	Fresh clear (0.23 M) solution at 70°C

Table 6.1: Recipes for spin-coating various zinc oxide layers on ITO.

P3HT and PCBM were mixed in a 1:1 weight ratio (20 mg ml<sup>-1</sup>) and dissolved overnight with constant stirring in the dark in cholobenzene with 2 % bromooctane to promote phase separation.<sup>[23]</sup> This solution was then spin-coated on ZnO coated ITO substrates in ambient conditions at 1000 rpm for 30 seconds followed by annealing at 115 °C for 10 minutes (first part of the device).

For the second half of the laminated device, 100 nm thick silver electrodes were sputter coated on a Kapton film and PEDOT:PSS (Clevios P VP AL 4083) doped with d-sorbitol (15 % by weight, purchased from Sigma Aldrich) was doctor bladed. PEDOT:PSS coated substrates were then annealed at 115 °C for 60 minutes in ambient conditions on a laminar flow hood.

The two parts of the device were brought together and laminated for 10 minutes under contact pressure, in a hydraulic hot press preheated at 130 °C. The press was cooled to 40 °C before releasing the pressure and recovering the laminated devices.

#### Atomic Force Microscopy (AFM)

The surface morphology of the samples was studied using VEECO multimode AFM operated in tapping mode.

#### Electron Spectroscopy

The investigations of the ZnO seed layer on ITO substrates with UPS were performed in an ultra-high vacuum (UHV) apparatus built by SPECS (Berlin, Germany). The apparatus is equipped with a two-stage cold cathode gas discharge from MFS (Clausthal-Zellerfeld, Germany) to generate simultaneously metastable helium atoms (He<sup>\* 3</sup>S<sub>1</sub>) and UV light (He I line). The spectra of the electrons emitted from the samples are recorded at a pass energy of 10 and 2 eV, with a hemispherical Phoibos 100 energy analyser from SPECS. At the pass energy of 10 eV the analyser has an energy resolution of 400 meV as evaluated from the Fermi edge of polycrystalline silver.

In a UPS experiment the sample is irradiated with UV photons leading to photoionization via the photoelectric effect. The energy of emitted electrons is given by

$$E_{kE} = E(h\vartheta) - E_{bin} - \phi_{spec}$$
 Eq. 6.1

where  $E_{kE}$  is the kinetic energy of the emitted electron,  $E(h\vartheta)$  the photon energy (21.22 eV for the He I line used here),  $E_{bin}$  the binding energy of the electron before excitation and  $\emptyset_{spec}$  the spectrometer workfunction. UP spectra can be used to determine the workfunction and the density of states in near surface region of a material. The workfunction of the samples is determined as the difference between the excitation energy and the length of the spectrum. The latter is given as the difference of the high binding energy cut-off and the cut-off of the spectrum at the lowest binding energy.

The apparatus is further equipped with a non-monochromatic X-ray source for Mg and Al K $\alpha$  radiation with the first one used in the present study. The angle between the He\*/UV light irradiation and the analyser and the X-ray irradiation and the analyser are both 54°. The base pressure of the UHV chamber is a few 10<sup>-10</sup> mbar. High-resolution XP spectra were obtained to determine the chemical state of zinc and oxygen in the surface near region of the ZnO thin films. The XP spectra were referenced to the carbon 1s peak, which is due to the adventitious hydrocarbons absorbed on the ZnO surface. The carbon 1s peak was set to 285 eV.

## Rutherford Backscattering Spectroscopy (RBS)

RBS was performed on an HVEE 2MV Tandem accelerator with 1.8 MeV He<sup>+</sup> directed perpendicular to the sample surface, with a rectangular beam shape of 2 mm width and 4 mm height and a beam current of around 5 nA. The energy of backscattered He atoms

were measured with a surface barrier detector, in a vacuum environment of less than  $1 \times 10^{-7}$  mbar, and the data was processed using a commercial package (SIMNRA).<sup>[24]</sup> The scattering angle of the He<sup>+</sup> was 170°.

## Thermogravimetric Analysis (TGA)

TGA was performed using a TA Instruments Hi-Res modulated TGA 2950-Thermogravimetric Analyser. For TGA measurements, a fresh clear solution of zinc acetate was placed in the pan. The TG analysis was performed in air by ramping temperature from room temperature to 300 °C at a rate of 20 °C min<sup>-1</sup> under an air flow of 60 mL min<sup>-1</sup>, and an isothermal hold at 300 °C, as shown in Figure 6.4 and Figure 6.5 to mimic device processing.

## I - V characterization

The fabricated devices were tested in air immediately after lamination, without encapsulation. The cells were tested using an Oriel solar simulator fitted with a xenon lamp filtered to give an output of 100 mW cm<sup>-2</sup> at AM1.5. The lamp was calibrated using a reference silicon cell from PV Measurements, Inc. The devices were tested using Keithley 2400 source meter controlled by Labview software.

For all devices the device area was  $0.105 \text{ cm}^2$  as defined by the electrodes. However, as the PEDOT:PSS was doped by d-sorbitol, resulting in higher conductivity,<sup>[25]</sup> an aperture which defined an active area of  $0.09 \text{ cm}^2$ ,<sup>[26]</sup> was used.

## 6.4. Results and discussion

The surface morphology of the resultant ZnO layers confirms a nano-rough surface which appears to be made up of spherical particles in all films, as seen by AFM (Figure 6.2) and is consistent with previously reported images.<sup>[16]</sup> The feature size is about 5 nm diameter, as can be seen in Figure 6.2 (d). As the thickness of the ZnO increases (due to different spin speeds and solution concentrations) from sample A to sample C, the larger scale texture due to the flaky topography of ITO (Figure 6.2 (x)) diminishes until the surface is approximately planar, with ZnO particles superimposed.

The morphology of in-situ produced ZnO is quite different to that produced by some other techniques, in particular atomic layer deposition (ALD) which produces a full density

conformal layer.<sup>[27]</sup>

RBS was used to determine the thickness of the ZnO layers and to obtain the depth profiles of the elements in the bulk layer. Figure 6.3 shows the contributions of In, Sn and Zn to the RBS spectrum. Taking into account cross sections, the coverage of the substrate with specific element can be determined from the total count rate measured for each of the elements constituting a sample. In and Sn have been used as references to determine the coverage in this case. The full density value of  $4.17 \times 10^{22}$  atoms cm<sup>-3</sup> was used for ZnO to determine the thickness of the ZnO layer as summarised in Table 6.2.



**Figure 6.2:** 3-dimensional images of AFM scans (2x2 micron) showing the morphology of (X) cleaned ITO (A) sample A (B) sample B (C) sample C (D) sample C on a 1x1 micron scale.

As can be seen from the AFM, the particulate ZnO layer is likely to have significant porosity due to the packing of the nanoparticles. Since the effective density of the ZnO layer (due to some level of porosity) has not been determined, the RBS thickness is calculated based on fully dense ZnO, with the potential for the true thickness of the porous ZnO layer being up to twice the values listed, based on the normal packing density of spheres.

Based on the similarity of the AFM images, it can reasonably be assumed that the porosity will be similar for all samples.

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The difference in the ZnO layer thickness, ranging from 17 nm to 28 nm by RBS (assuming full density) correlates with the observation of increasing planarization from sample A to C that was observed in the AFM results.



Figure 6.3: RB spectra of ZnO thin film acquired from sample A.

The ZnO layer is produced by the well-known in-situ oxidation of zinc acetate between 150 °C and 300 °C<sup>[28, 29]</sup> with the spontaneous formation of nanoparticles.<sup>[29]</sup> However, zinc acetate is electrically insulating and any remaining acetate (due to incomplete conversion) on the uppermost surface of the ZnO will significantly impact the device performance due to modification to the workfunction and act as a resistive layer, and is especially important for charge injection.

The role of the solvent is critical in both the maximum concentration of the solution that can be obtained as well as the spin coating characteristics. Conventionally, for synthesizing thin ZnO buffer layers for OPV applications, a high boiling solvent such as methoxyethanol (boiling point is 124.6 °C) is used as the precursor solvent<sup>[17]</sup> but in this work, ethanol was explored (boiling point of 78.4 °C) in order to separate solvent evaporation from oxidation of zinc acetate. As can be seen in the inset in Figure 6.4 ethanol is completely removed at 100 °C, which shows an initial 94 % mass loss at 85 °C, leaving only the coating of zinc acetate.

Table	<i>6.2</i> :	Summary	of the	e number	of	` monolayer	and	thickness	of	ZnO	buffer	layer	in
variou	s san	nples, assu	ming	the X-ray	dei	nsity of ZnO	laye	rs.					

RBS thickness [10 <sup>-7</sup> mol cm <sup>-2</sup> ]	RBS Thickness [nm]
$1.4 \pm 0.3$	17 ± 4
$1.7 \pm 0.3$	$20 \pm 4$
$2.0 \pm 0.3$	$28 \pm 4$
	<b>RBS thickness [10<sup>-7</sup>mol cm</b> <sup>-2</sup> ] $1.4 \pm 0.3$ $1.7 \pm 0.3$ $2.0 \pm 0.3$

The quality of ZnO films spin coated using ethanol were highly reproducible and homogeneous over large areas, which can be attributed to rapid drying of spin coated films due to the low boiling point of ethanol.



*Figure 6.4*: Mass loss observed on conversion of zinc acetate to zinc oxide using ethanol as the precursor solvent. Inset shows a full-scale image of the same.

The oxidation of zinc acetate to ZnO can be seen in a second weight loss, occurring between 100 °C and 250 °C and resulting in a total mass loss from 5.90 % to 2.23 %. This weight loss corresponds to 99  $\pm$  1 % conversion of zinc acetate to ZnO. A further slight mass reduction to 2.13 % was observed when heated up to 400 °C, with no further significant weight loss observed upon heating to 600 °C. An isothermal hold at 300 °C as shown in Figure 6.5 indicated that the weight loss ceased and the reaction is complete after 10 minutes of exposure to 300 °C.



*Figure 6.5:* Mass loss observed on conversion of zinc acetate to zinc oxide with an isothermal hold at 300 °C.

Samples prepared for UPS were first examined by X-ray photoelectron spectroscopy (XPS) in the same instrument to ensure that the surface to be measured (and ultimately the surface in contact with the bulk hetero-junction) was well characterised and understood. The expected peaks for zinc, oxygen and carbon were observed in the XPS survey spectrum. The high resolution peak of C 1s was found to be symmetric with a single component that has been attributed to adventitious carbon. There is no evidence of carbonyl groups which would be indicative of unreacted zinc acetate.

Also, the Zn 2p  $_{3/2}$  peak, as shown in Figure 6.6, was found to be symmetric with a single component at binding energy of 1022.3 eV which agrees well with the literature value for ZnO.<sup>[30]</sup> This confirms that the chemical nature of the nanoparticles formed on the surface as seen in the AFM images (Figure 6.2) is ZnO. Importantly, there is no component in the Zn spectrum around 1021.5 eV which would indicate the presence of metallic zinc.<sup>[31]</sup> Thus it can be concluded that all Zn is in the oxidation state of Zn<sup>2+</sup> in the ZnO<sub>1-x</sub> matrix<sup>[30]</sup> and the near surface region of the sample is completely oxidized.

The O 1s spectrum was found to be asymmetric and needs to be fitted with two components at binding energies of 530.9 eV and 532.45 eV respectively. The major component at a lower binding energy of 530.9 eV corresponds to the oxygen in the ZnO matrix<sup>[32]</sup> whereas the second component at higher binding energy can be attributed to chemisorbed oxygen.<sup>[31]</sup> The ratio between the low binding energy O atoms present in the

ZnO matrix and the chemisorbed oxygen was found to be 3:1. From the high resolution spectra (Figure 6.6), the ratio of the atomic concentration of zinc and oxygen was found to be 1:1.1  $\pm$  0.2. The above XPS results agrees well with the TGA results and confirms complete conversion of zinc acetate to ZnO at 300 °C in 10 minutes. Interestingly, the ratio of the lower binding energy peak in the O 1s spectrum has been reported to be 2:1<sup>[17]</sup> when the sample was only heated to 200 °C, but the significance of this observation is not clear.



Figure 6.6: High resolution spectra of Zn 2p and O1s recorded from sample C.

The UP spectra of ZnO layers synthesized at various spin speeds are shown in Figure 6.7 with the secondary electron cut-off region shown in the inset. In order to accurately determine the change in workfunction due to the deposition of the ZnO, the secondary electron cut-off needs to be corrected for the energy resolution of the method. For this purpose, the UPS measurements for all ZnO samples (A, B and C) were performed at pass energies of 2 eV and 10 eV and the secondary electron cut-off was fitted with a step function which was convoluted with a Gaussian function. The position of the onset of the step function was plotted as function of the pass energy and extrapolated to zero pass energy. The value at zero pass energy is taken as the workfunction and is shown in Table 6.3 for all of the samples.

A small shift in the secondary electron cut-off for various samples was observed (as seen in the inset of Figure 6.7), but is not significant considering the uncertainties involved.

The workfunction of sample B and C was found to be  $4.32 \pm 0.05$  eV, which is close to the values reported in the literature.<sup>[16]</sup> In the case of sample A, a slightly lower workfunction

of 4.28  $\pm$  0.05 eV was measured, but is within the experimental uncertainty of samples B and C.



*Figure 6.7*: UP spectra of ZnO layers in sample A, B and C. The inset picture shows a closer look at the secondary electron cut-off.

Also, the energy features of the spectra, which correspond to the density of states, were found to be similar for all samples, irrespective of the resultant layer thickness and the ZnO coverage on the surface and are similar to results in the literature.<sup>[33]</sup>

**Table 6.3:** Workfunction values of ITO and ZnO layers with various thickness and morphologies.

Sample No.	Workfunction [eV]
ITO	4.7
А	$4.28\pm0.05$
В	$4.32\pm0.05$
С	$4.32\pm0.05$

Despite similarity in the workfunction and electronic properties of the ZnO layers

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produced, the photovoltaic properties of devices produced by lamination from Samples A to C (Table 6.1) are quite different, as can be seen in Figure 6.8.



**Figure 6.8:** J-V characteristics of laminated devices with zinc oxide buffer layers of different thickness and morphologies. Device X: without zinc oxide buffer layer, device A, B and C were fabricated using ZnO buffer layers similar to samples A, B and C, as summarised in Table 6.1.

Among all the air processed laminated devices, the best efficiency of  $1.7 \pm 0.2$  % was recorded from device C, which also had the highest short circuit current density of 6.84 mA cm<sup>-2</sup> and a fill factor of 49.7 %. Device B, which had a thinner ZnO buffer layer than device C, had an efficiency of  $1.0 \pm 0.2$  % with a significantly reduced fill factor and also lower short circuit current. Device A had the least efficiency of only  $0.6 \pm 0.2$  % and an open circuit voltage of 422 mV. Device parameters recorded for all of the laminated devices, fabricated identically apart from variation in the ZnO thickness, are summarized in Table 6.4. These values compare with an efficiency of approximately 2.7 % for a recently reported optimised laminated inverted cell.<sup>[34]</sup> Differences such as a thinner active layer (200 nm in this work compared with 320 nm in reference [34]) and active area may contribute to the differences. Importantly, the results presented here are self-consistent, with the fabrication processes and structure identical for all devices, apart from ZnO thickness.

Device	η	V <sub>oc</sub>	<b>I</b> <sub>sc</sub>	FF	R <sub>s</sub>	<b>R</b> <sub>sh</sub>
	[%]	[mV]	[mA cm <sup>-2</sup> ]	[%]	$[\Omega \text{ cm}^2]$	$[\Omega \ \mathrm{cm}^2]$
X	$0.2 \pm 0.2$	189	3.70	27.7	39.5	61
Α	$0.6\pm0.2$	422	4.64	30	65	213
В	$1.0 \pm 0.2$	513	5.10	37.4	37.5	218
С	$1.7\pm0.2$	509	6.84	49.7	17	337

**Table 6.4**: Summary of various device parameters obtained from different devices. Device X corresponds to device fabricated without a ZnO buffer layer. Device A, B and C corresponds to devices prepared using ZnO recipes of samples A, B and C.

The difference observed in the device performance can be related to the equivalent circuit for these devices and analysed by the variation in the series and shunt resistances, calculated from the inverse slope of the J-V curves at  $V = V_{oc}$  (J = 0) and  $J = J_{sc}$  (V = 0) respectively.<sup>[35, 36]</sup> The series resistance in device C was 17  $\Omega$  cm<sup>2</sup> which increased fourfold to 65  $\Omega$  cm<sup>2</sup> in case of device A, despite device A having the thinnest ZnO layer which was expected to have the lowest resistance.

The shunt resistance showed a more predictable increase with ZnO thickness, however, the value was similar for devices A and B (213  $\Omega$  cm<sup>2</sup> and 218  $\Omega$  cm<sup>2</sup> respectively) and increased very strongly for device C (337  $\Omega$  cm<sup>2</sup>) as the ZnO thickness increased, which can be seen in Figure 6.9. Relatively low fill factors can be attributed to non-zero series resistance and relatively low and finite shunt resistance. In agreement with that, an increase in shunt resistance for devices A to C was found to result in increased fill factor. Atomic layer deposition (ALD) of ZnO has demonstrated a similar sudden increase in efficiency and fill factor at a ZnO layer thickness of 10 nm.<sup>[27]</sup> However, ALD typically produces high density conformal coatings and so the structure of the film is quite different to in-situ or sol-gel formed ZnO.

The chemistry and workfunction are identical for all of the samples with only relatively minor differences in surface morphology / roughness due to the second level of structure arising from the ITO. The relatively minor difference in morphology and total surface area (roughness) between device B and C cannot explain the significant difference observed in

the performance or the variation in series and shunt resistance if the interface between the BHJ and the ZnO is relatively sharp as in the idealised structure shown in Figure 6.1.



*Figure 6.9*: Variation of series and shunt resistance with increase in the ZnO thickness. A, B and C corresponds to the resistance values of device A, B and C respectively.

A model in which the BHJ penetrates into the effectively porous ZnO layer to form a mixed phase region can explain the variation observed in the device performance. In order to determine the impact of direct contact between the BHJ and ITO, a control device (device X) was fabricated with no zinc oxide buffer layer. The increasing trend in  $V_{oc}$  from device X (with no ZnO) to device A and devices B and C as well as the increase in shunt resistance with thickness of ZnO is consistent with P3HT/PCBM penetrating into the porous ZnO in some regions and making direct contact with the ITO electrode in device A. As the transport of holes from the BHJ to the ITO decreases, the shunt resistance will increase.

This interpenetrating structure has further implications on performance as the P3HT / ZnO can itself act as a hetero-junction, providing a complex second charge source and may explain the highest series resistance seen in device A, despite evidence of direct contact. The increased surface area between ZnO and BHJ in such a mixed phase model will also result in improved charge injection and decreased series resistance, but the impact of the mixed phase structure on the BHJ is unclear.

These results and the proposed mixed phase interface model is a better explanation of the

dependence on performance than previous papers in which performance differences are attributed solely to surface topography (and therefore overall roughness)<sup>[37]</sup> rather than BHJ penetration to the ITO electrode.

## 6.5. Conclusions

The chemical composition, morphology, workfunction and performance in laminated inverted OPV structures have been systematically determined for the modification of ITO with ZnO via a zinc acetate precursor. Zinc acetate layer was found to be fully oxidised to ZnO after heating in air for 10 minutes at 300 °C, with no remaining zinc acetate in the film by thermogravimetric analysis and XPS. The oxidation appeared to start at approx. 150 °C and in all cases, the ZnO layer was comprised of approximately 5 nm particles in what appeared to be a porous film. The thinnest ZnO layer clearly showed secondary topography consistent with the underlying ITO, however, this second level of topography disappeared in the thickest ZnO layer at approximately 28 nm, due to planarisation.

The workfunction of the ZnO layer over ITO was found to be at 4.3 eV in all cases, indicating it is independent of the topology and ZnO thickness. This compares with ITO at approx. 4.7 eV and suggests that a minimum of complete coverage will provide the required workfunction modification.

The device performance was found to be strongly dependent on the thickness and morphology of the zinc oxide buffer layer. An efficiency of 1.7 % was obtained from a device with the thickest ZnO buffer layer while the thinnest ZnO layer had an efficiency of 0.6 % with series resistances varying from 17  $\Omega$  cm<sup>2</sup> to 65  $\Omega$  cm<sup>2</sup> and shunt resistances from 337  $\Omega$  cm<sup>2</sup> to 213  $\Omega$  cm<sup>2</sup>.

The trend in the results can be explained by a mixed phase interface model, in which the BHJ penetrates into the porous ZnO layer. If the ZnO layer is not sufficiently thick (greater than 20 nm in this study), direct contact between the BHJ and the ITO electrode can result. This proposed structure is counter to the prevailing literature which attributes variable performance results with spin speed (and therefore thickness) as due to surface roughness.

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# Effect of Annealing Temperature of ZnO on the Energy Level Alignment in Inverted OPV's

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# 7.1. Abstract

The annealing temperature of ZnO layers was found to have a significant impact on the efficiency of inverted devices. Device efficiencies were found to increase significantly from 2.5 % to 3.6 % with increase in the post deposition annealing temperature of ZnO. A systematic study of the density of states shows that the workfunction varies from 3.2 eV to 3.9 eV with annealing temperature and the offset between the conduction band of ZnO and the LUMO of the PCBM reduces from 0.5 eV (250 °C annealing) to 0 eV (150 °C annealing) resulting in inefficient charge transport across the BHJ to the ITO electrode. The dependence of the electronic properties on the annealing temperature has been attributed to a deficiency of electrons corresponding to the non-bonding (lone pair) oxygen orbitals in the ZnO matrix and the presence of precursor impurities.

# 7.2. Introduction

Organic photovoltaic technology (OPV's) is rapidly maturing and devices with promising efficiencies are being reported,<sup>[1]</sup> however many challenges remain before they are commercially viable. The promise of high speed roll-to-roll processing has the potential to significantly reduce the cost of production and enable large-scale production using various methods,<sup>[2-6]</sup> however, processing temperatures and interlayer stability remain significant challenges.

OPV's based on the inverted structure indium tin oxide (ITO)/ zinc oxide particle layer (ZnO) / poly (3-hexylthiophene) (P3HT): [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/MoO<sub>3</sub>/Ag (as shown in Figure 7.1) have the potential to overcome interfacial instability at the PEDOT-PSS / ITO interface<sup>[7-8]</sup> which could otherwise lead to device degradation and shorter lifetimes in conventional OPV's.<sup>[9]</sup> Zinc oxide (ZnO) has been widely explored as a cathodic material in inverted devices and various processing methods compatible with flexible substrates are being explored.<sup>[10-12]</sup> Most commonly, ZnO is synthesised in- situ which involve high processing temperatures of over 300 °C.<sup>[13] [10]</sup>



Figure 7.1: Schematic of an inverted OPV incorporating ZnO particle layer.

Although these methods enable quick synthesis of ZnO buffer layers, they are incompatible with materials having low glass transition temperature such as polyethyleneterephthalate (PET) and polyethylenenaphthalate (PEN), which are the leading candidates for flexible substrates in roll-to-roll processing of OPV's.

In-order to use ZnO buffer layers on flexible substrates without the need for high temperature post deposition annealing ZnO nanoparticles have been deposited as thin films using roll-to-roll compatible methods such as spin-coating<sup>[10]</sup> and slot-die printing.<sup>[14]</sup> The particle layer must still be annealed post deposition not only to consolidate the particles, but also to promote adhesion to the substrate, remove the ligands<sup>[15-17]</sup> and any remaining organic fragments of the precursor which are present to aid dispersion and avoid aggregation. It has been shown that the annealing temperature can influence the chemical composition of in-situ produced ZnO derived using sol-gel for example.<sup>[12]</sup> Therefore, in the case of ZnO particle layers, it is equally important to optimise and understand the impact of the annealing temperature on device performance. A range of post-process conditions have been employed to ZnO particle films,<sup>[18]</sup> yet there has not been any systematic studies to determine the dependence of process conditions on the chemical and electrical properties of the ZnO layer and the resulting device properties.

In this paper, the effect of post-deposition annealing temperature on the chemical and electronic properties of ZnO particle layers in inverted OPV's is reported. X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) are used to study the surface chemistry and electronic properties of the ZnO particle layer. The measurement of energy level positions of ZnO (annealed at various temperatures) as determined using UPS was correlated to the I-V measurements and used to understand the difference observed in the device performance. The changes induced in the energy bands of ZnO as a result of various annealing temperatures is related to charge transport across the ZnO buffer layer from the BHJ to the cathode.

## 7.3. Experimental

## ZnO Particle Ink

The ZnO particles were synthesized by dissolving zinc acetate dehydrate (0.44 g) in ethanol (40 ml) at 60 °C for 30 minutes. This was followed by drop wise addition of tetramethylammonium hydroxide (2 ml) (20 % in MeOH) in ethanol (10 ml) to the solution over the period of 5 minutes. The ZnO nanoparticle solution was heated at 60 °C for 30 min to attain zinc oxide nanoparticles of ~ 5 nm in size. Detailed information about the synthesis can be found elsewhere.<sup>[19]</sup>

## Device Fabrication

ITO-coated glass substrates (7 ohms square<sup>-1)</sup> were cleaned using the standard recipe - the glass was cleaned in deconex PA neutral detergent (5 % solution supplied by Borer) at 90 °C for 20 minutes. The samples were then rinsed in deionized (DI) water followed by successive sonication for 10 minutes each in DI water, acetone and isopropanol. Subsequently UV-ozone cleaning of the ITO substrates was applied using a Novascan PDS-UVT UV/ozone cleaner with the lamp intensity being greater than 36 mWcm<sup>-2</sup> at a distance of 100 cm, giving ozone output greater than 50 ppm at ambient conditions.

The ZnO particle layer was spin coated at 3000 rpm followed by annealing on a preheated hot plate in air. Three different set of samples were prepared and were annealed at 150 °C, 200 °C and 250 °C. For device fabrication, all ZnO coated samples were transferred to the glove box, after annealing. Except the ZnO annealing temperatures, all devices were prepared similarly using the same batch of materials.

The hetero-junction blend was prepared by dissolving P3HT (45 mg, Merck) and PCBM (36 mg, purchased from nano C) in chlorobenzene (1.5 ml) each. Both solutions were dissolved separately in glove box at 80° C for an hour, followed by cooling down, filtering and stirring at room temperature. Hetero-junction layer of P3HT: PCBM was spin coated at 3000 rpm for 30 sec followed by annealing at 150 °C for 10 minutes.

20 nm thick molybdenum oxide was thermally evaporated as the anodic buffer layer, before evaporating 100 nm thick silver anode.

## Electron Spectroscopy

The investigations of the ZnO particle layer on ITO substrates with XPS were performed in an ultra-high vacuum (UHV) apparatus built by SPECS (Berlin, Germany) using a non-monochromatic X-ray source for Mg. The base pressure of the UHV chamber is a few 10<sup>-10</sup> mbar. High-resolution XP spectra were obtained to determine the chemical state of zinc and oxygen in the surface near region of the ZnO thin films. The XP spectra were referenced to the carbon 1s peak, which is due to the adventitious hydrocarbons absorbed on the ZnO surface. The carbon 1s peak was set to 285 eV.

The apparatus is further equipped with a ultraviolet photoelectron spectroscopy (UPS) with a two-stage cold cathode gas discharge from MFS (Clausthal-Zellerfeld, Germany) to generate simultaneously metastable helium atoms (He\*  ${}^{3}S_{1}$ ) and low intensity UV light

(He I line). The spectra of the electrons emitted from the samples were recorded at pass energy of 10 eV, with a hemispherical Phoibos 100 energy analyser from SPECS. At the pass energy of 10 eV the analyser has an energy resolution of 400 meV as evaluated from the Fermi edge of polycrystalline silver. The angle between the He\*/UV light irradiation and the analyser and the X-ray irradiation and the analyser are both 54°. The UP spectra were acquired by applying a bias of 10 V to the sample, in-order to clearly observe the secondary electron cut-off.

In a UPS experiment the sample is irradiated with UV photons leading to photoionization via the photoelectric effect. The energy of emitted electrons is given by

$$E_{kE} = E(h\vartheta) - E_{bin} - \phi_{spec}$$
 Eq. 7.1

where  $E_{kE}$  is the kinetic energy of the emitted electron,  $E(h\vartheta)$  the photon energy (21.22 eV for the He I line used here),  $E_{bin}$  the binding energy of the electron before excitation and  $\emptyset_{spec}$  the spectrometer workfunction. UP spectra can be used to determine the workfunction and the density of states in near surface region of a material. The workfunction of the samples is determined as the difference between the excitation energy and the length of the spectrum. The latter is given as the difference of the high binding energy cut-off and the cut-off of the spectrum at the lowest binding energy.

#### I-V characterisation

Inverted solar cells with an active area of  $0.1 \text{ cm}^2$  were fabricated, with device area being defined by the electrode geometry. The current-voltage (J-V) characteristics of the devices were measured inside the glove box, without encapsulation, under AM 1.5 G irradiation (100 mW cm<sup>-2</sup>). The devices were tested using Keithley 2400 source meter controlled by Labview software.

## 7.4. **Results and discussion**

Inverted OPV's were fabricated with three different post deposition annealing temperatures for the ZnO particle layer: Device A (annealed at 150 °C), device B (annealed at 200 °C) and device C (annealed at 250 °C). Figure 7.2 shows the resultant J-V characteristics. The photoconversion efficiency of device A was found to be 2.3 % while devices B and C were almost identical with an increased efficiency of 3.6 %. In both devices B and C, the

maximum open circuit voltage was 620 mV compared with 590 mV for device A and correspondingly higher short circuit current density as shown in Table 7.1. Also in case of device A, the variation observed in the short circuit current over multiple samples was large as compared to devices B and C.



*Figure 7.2: J-V* characteristics of best devices fabricated with ZnO particle layer annealed at various temperatures.

The improvement in series resistance with higher annealing temperature is reflected with an improved fill factor of 49 % (device B) and 48 % (device C) compared to 38 % in case of device A. The fill factor is driven by the series and shunt resistance in the devices, which were calculated from the inverse slope of the dark J-V curves at V = 1 V and V = 0 V respectively. The series resistance of device A was found to be 28  $\Omega$  cm<sup>2</sup>, an order of magnitude higher than that of device B and C whereas the shunt resistance was found to be 730  $\Omega$  cm<sup>2</sup>, almost half to that of device B and C. In order to investigate the origin of the observed differences in the J-V characteristics of Devices A, B and C, ultraviolet photoelectron spectroscopy (UPS) was used to determine any possible changes in the electronic structure of differently annealed ZnO. Following initial spectroscopic measurements, sample A was heated to 260 °C in the instrument (under vacuum) and is referred to as sample D.

UPS (Figure 7.3) shows that the workfunction increases from  $3.2 \pm 0.05$  eV (sample A) to  $3.87 \pm 0.05$  eV (sample C) with increased annealing temperatures due to the secondary

electron cut-off moving 0.7 eV towards lower binding energies for sample B and C relative to sample A. The value for the workfunction for sample A is significantly lower than the commonly reported value of workfunction for zinc oxide,<sup>[20]</sup> though workfunction close to 3 eV for ZnO nanoparticle layer has also been reported by Gutmann *et. al.*<sup>[21]</sup> In the spectrum, there were no visible signs of charging due to the photon flux of UV source used for UPS measurements and the measurements were reproducible across multiple samples. Additionally, spectra were highly reproducible and no changes were observed due to the low intensity UV radiation used for the UPS measurements, and the effect of storing samples under ultra-high vacuum, suggesting that the low workfunction value observed is not attributable to the loss of surface oxygen or due to UV exposure, as reported earlier.<sup>[21]</sup> Also, as all three samples A, B and C were annealed in air before transferring into the vacuum chamber, the exposure of all samples to hydrocarbons and/or moisture is similar. Therefore, presence of hydrocarbons and/or water on the surface cannot be the only reason for the low value of workfunction measured.

Devices	Annealing Temp.	Voc	<b>J</b> <sub>sc</sub>	FF	η	R <sub>sh</sub>	R <sub>s</sub>
	[°C]	[mV]	[mAcm <sup>-2</sup> ]	[%]	[%]	$[\Omega \text{ cm}^2]$	$[\Omega \text{ cm}^2]$
Device A	150	590	10.7	38	2.3	730	28
Device B	200	620	11.7	49	3.6	1490	1.5
Device C	250	620	11.8	48	3.6	1380	2.5

**Table 7.1:** Average of various device parameters after annealing ZnO particle layer at different temperatures.

The valence band maxima for sample A was found at 3.6 eV relative to the Fermi level and for samples annealed at higher temperatures were found to decrease to 3.5 eV for sample B and 3.4 eV for both samples C and D. The observed dependence of the valence band position on the annealing temperature is quite significant, as it influences the energy level alignment between the ZnO and PCBM, and thus the charge transport across the interface. The electron affinity for sample A was found to be  $3.5 \pm 0.05$  eV which increased significantly to  $3.9 \pm 0.05$  eV,  $4.0 \pm 0.05$  eV and  $3.9 \pm 0.05$  eV for samples B, C and D respectively.

In order to better understand the interfacial energetics in an inverted device structure such as the one reported here, we model the energy level alignment of ZnO with PCBM taking into account the interfacial dipole between the ZnO and PCBM, as reported elsewhere.<sup>[22]</sup> The energy band alignment of ZnO with the BHJ in two different scenarios (150 °C and 250 °C annealing temperatures of ZnO) is depicted in Figure 7.4, constructed using the workfunction and valence band maxima (VBM) values of ZnO as measured from the UPS. It is assumed that the band alignment in case of bulk hetero-junction devices would be same as that in case of an inverted bilayer structure resulting in Fermi level alignment between the ZnO and PCBM.<sup>[22]</sup>



Figure 7.3: UP spectra of ZnO nanoparticle layers annealed at various temperatures.

The offset between the conduction band of ZnO and the LUMO of PCBM for device C, was found to be 0.5 eV, facilitating efficient electron transfer across the BHJ-ZnO interface. However, in case of device A, there was no offset found between the conduction band of ZnO and the LUMO of the PCBM. This could result in poor charge separation and transport across BHJ-ITO electrode, which is evident from the relatively lower short circuit current density  $J_{sc}$  observed from the I-V characterisation of device A compared to device B and C.

The dipole at the interface used to construct Figure 7.4 is based on the assumption that it is the same as in Davis *et al.*<sup>[22]</sup> This assumption might be incorrect because the ZnO used in

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literature<sup>[22]</sup> might be slightly different than the ZnO used in the present study and this could also potentially be affected by different annealing temperatures of 150 °C and 250 °C. However, what is important for the correlation of Figure 7.4 with the J-V characteristics is not the exact values of the offset between the conduction band of ZnO and the LUMO of the PCBM but the fact that the offset is more positive for the 250 °C annealed ZnO sample than the 150 °C annealed ZnO sample. Even for the case that our assumption about the dipole at the interface is incorrect, this difference will be affected only to a minor degree.



**Figure 7.4**: Energy level alignment of ZnO nanoparticle layer with the acceptor (PCBM) in the BHJ in inverted OPV. Energy offset the ZnO-PCBM interface is showed in red (in case of 150 °C annealing) and green (in case of 250 °C annealing). The value for the dipole used to construct the energy diagram is based on an assumption. The implications of this assumption are discussed in the main body of the work.

X-ray photoelectron spectroscopy (XPS) was used to determine if there are chemical differences induced in the ZnO layer due to the annealing conditions which may have contributed in different electronic properties, as found with UPS. Figure 7.5 and Figure 7.6 shows the core level XP spectra of Zn 2p3/2 and O 1s respectively, for each of the annealing conditions.

The Zn 2p3/2 peak was found to be symmetric for all samples A, B, C and D and undergoes a shift of about 0.4 eV from 1021.66 eV to 1022 eV with the increase in annealing temperature, as shown in Figure 7.5.

This shift towards relatively higher binding energy has previously been attributed to increased oxidation of zinc and hence a more electronegative environment.<sup>[20]</sup> The atomic percentage of Zn was found to increase from 33 % at 150 °C annealing to 44 % and 45 % for treatments at 200 °C and 250 °C, respectively at the expense of total oxygen in the system. The ratio of total oxygen relative to zinc and carbon decreases from 37 % to 29 % with higher annealing temperatures.



Figure 7.5: Core level XPS of Zn 2p 3/2.

The oxygen peaks in all samples were found to be asymmetric with two components at approximately 530 eV and 532 eV, as shown in Figure 7.6 and both of the components of oxygen were found to shift slightly towards the higher binding energy when treated from  $150 \,^{\circ}$ C up to 260  $^{\circ}$ C.

The lower binding energy component corresponds to the oxygen in the zinc oxide matrix in stoichiometric composition,<sup>[23]</sup> whereas the higher binding energy component at 532 eV has earlier been reported to be due to chemisorbed oxygen,<sup>[24]</sup> zinc hydroxide<sup>[25]</sup> or due to the presence of remaining fragments of the zinc acetate precursor.<sup>[26]</sup> Based on the UP spectra, we will show below that the peak at 532 eV could partially be attributed to O in ZnO as well.



## Figure 7.6: Core level XPS of O 1s.

The peak ratios of the two components of the oxygen peak were found to be close to 1:1 for sample A, with only 51 % of the total oxygen corresponding to the zinc oxide matrix. However, as the annealing temperature increased, the relative peak area of the higher binding energy component of oxygen decreases compared to the lower binding energy component (corresponding to the ZnO matrix) becoming 68 % and 73 % of the total oxygen present in the system for samples C and D respectively.

The observed increase in the proportion of oxygen in the ZnO matrix (the lower binding energy component) upon thermal annealing can be attributed to either the removal of chemisorbed oxygen species (eg water) or the decomposition of remaining traces of the acetate precursor in the ZnO particle layer

From the ultraviolet photoelectron spectroscopy (UPS) of samples A, B and C, three characteristic emission peaks at around 11.5 eV, 8.2 eV and 5.2 eV were found, as seen in Figure 7.7. These peaks have previously been attributed to Zn 3d band, bonding of the Zn 4s and 4p with the O 2p and to the O 2p non-bonding electrons, respectively.<sup>[27]</sup> [28]

The Zn 3d peak at 11.5 eV for samples B and C was found to be more pronounced than

that of sample A. No peak at 8.2 eV was found for sample A, however for samples B and C, this feature also becomes more prominent. This is consistent with the XPS results, which showed increased zinc-oxygen interaction for sample B and C. For all samples A, B, C and D, no significant peak shift was observed.



*Figure 7.7:* UP spectra from samples A, B, C and D depicting the three characteristic peak emissions.

For sample A (annealed at 150 °C), the O 2p peak was almost absent initially, but with further heat treatment (up to 260 °C), both the Zn 3d and O 2p features became more prominent as seen from sample D. This suggests that 150 °C annealing treatment results in ZnO deficit in non-bonding oxygen orbital (lone pair), which could also have implications on its electronic properties and thus on the device performance.

Physisorbed water on the surface shows an oxygen feature at about 10 eV,<sup>[29-31]</sup> in the UPS. While intensity is seen in sample A in this region (a Gaussian function could be fitted after subtracting the background), it is not or to a much lower degree observed in samples B, C and D suggesting that the 532 eV peak seen from the XPS in all samples cannot be exclusively due to chemisorbed oxygen or absorbed water as there is no water found from UPS measurements in these samples. The oxygen component at 532 eV as seen in the core level XPS of oxygen (Figure 7.6) could therefore be due to the presence of the acetate in the ZnO particle layer, water and oxygen in ZnO.

All possibilities for the origin of the changes in the oxygen structure described above could

be the reason for the change in workfunction. Based on the information available through this study it cannot be decided which of the possibilities or which combination of possibilities are the reason for the change in workfunction upon heating. However, because the workfunction is a measure for the polarity of the interface it can be assumed, that the presence of acetate groups at the surface is the likely reason for the low workfunction of the sample annealed at 150 °C because of the compounds ZnO, H<sub>2</sub>O and acetate the latter is the least polar compound.

Further, the C 1s region of the ZnO particle layer for all samples, as shown in Figure 7.8, was found to have three components with the strongest peak at around 285 eV, and sub peaks at 287 eV and 289 eV, which has previously been attributed to the C-H or C-C bonds, C-O and C=O/COO<sup>-</sup> bonds respectively.<sup>[32]</sup>



## Figure 7.8: Core level XPS of C 1s.

Although there was only a slight difference of 1 % observed in the two carbon components at higher binding energy when the samples were heated from 150 °C (sample A) to 250 °C (sample B and sample C), the atomic concentration of the carbon component at 285 eV

was found to decrease from 22 % (sample A) to 15 % and 13 % for samples B and C, respectively. When sample A is subsequently heated at 260 °C under vacuum (to form sample D), the carbon component at 285 eV reduces from 22 % to only 17 %. The peak positions and atomic concentrations of Zn, O and C at different temperatures are summarized in Table 7.2.

The XPS results suggesting the presence of remaining acetate in the ZnO particle layer annealed at 150 °C, agrees well with the previous hypothesis established from the J-V characterisation of these devices that residual acetate or organic impurities could explain the high series resistance observed in devices that are annealed at sub-optimal temperatures. The relatively lower open circuit voltage of device A as compared to device B and device C can be attributed to reduced shunt resistance in device A.

**Table 7.2:** XPS peak positions and atomic concentration of oxygen, carbon and zinc in various samples treated at different temperatures.

Peak	Sample A		Samp	Sample B		ole C	Sample D	
	150 °C		200 °C		250	250 °C		vacuum)
	Position [eV]	[%]	Position [eV]	[%]	Position [eV]	[%]	Position [eV]	[%]
Zn 2p <sub>3/2</sub>	1021.7	$33 \pm 0.2$	1021.9	$44\pm0.2$	1021.9	$45\pm0.2$	1022	$50 \pm 0.2$
O 1s (Peak 1)	530.3	$19 \pm 0.5$	530.5	$23\pm0.5$	530.6	$24\pm0.5$	530.7	$21\pm0.5$
O 1s (Peak 2)	531.9	$18\pm0.5$	532.2	$12\pm0.5$	532.2	$11\pm0.5$	532.4	$8\pm0.5$
C 1s (Peak 1)	285	$22 \pm 1$	285	$15 \pm 1$	285	$13 \pm 1$	285	$17 \pm 1$
C 1s (Peak 2)	287	$4\pm0.5$	287.1	$3\pm0.5$	287	$3\pm0.5$	287	$2\pm0.5$
C 1s (Peak 3)	289.3	$4\pm0.5$	289.2	$3\pm0.5$	289	$3\pm0.5$	288.9	$2\pm0.5$

## 7.5. Conclusions

The annealing temperature of the ZnO particle layer deposited on the underlying ITO electrode in inverted OPV's is critical in order to achieve optimum device performance, with the efficiency was found to have a direct dependence on the annealing temperature of the ZnO buffer layer. An efficiency of 2.3 % was achieved from devices incorporating

ZnO particle layer annealed at 150 °C, which significantly increased to 3.6 % with an increase in the annealing temperatures of up to 250 °C, shown to be optimal for ZnO films from zinc acetate precursors.

The workfunction of the ZnO particle layer treated at 150 °C was found to be 3.2 eV, significantly less than reported values, but it increased to 3.9 eV when the ZnO was annealed at temperatures of up to 250 °C. More importantly, the electron affinity of ZnO particle layer annealed at 150 °C was found to be 3.5 eV compared to 4.0 eV for a ZnO particle layer annealed at 250 °C. The significantly lower electron affinity for low temperature annealing leads to zero energy offset between the conduction band of ZnO and the LUMO of PCBM resulting in poor charge transport across the BHJ and the ITO electrode, and this is the proposed mechanism for the poor performance for devices in which the ZnO layer was annealed at lower temperatures. The change in electron affinity can be attributed to differences in the surface chemistry in the ZnO layer at different annealing temperatures. The nature of the oxygen in ZnO changes with annealing temperature of the Zn – oxygen bond itself, however, it cannot be due to changes in physisorbed water. Heating the partially converted zinc acetate in vacuum to 260 °C leads to ZnO, which shows deficiencies of the non-bonding oxygen orbital.

Though ZnO particle ink can be used for flexible OPV's as a low temperature alternative to the sol-gel method, this study suggests that temperatures lower than 200 °C are insufficient for achieving ZnO that is optimal for device performance.

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# The Influence of ZnO Thickness and Stoichiometry on Device Performance of Inverted OPV's

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Anirudh Sharma: Designed & performed experiments, data analysis & interpretation, prepared the first draft of manuscript.

Dr. Joseph Franklin: Deposited ZnO using PLD method; contributed to revision of manuscript.

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## 8.1. Abstract

Photoconversion efficiency of inverted polymer solar cells incorporating pulsed laser deposited ZnO electron transport layer have been found to significantly increase from 0.8 % to up to 3.3 % as the film thickness increased from 4 nm - 100 nm. While the ZnO film thickness was found to have little influence on the morphology of the resultant ZnO films, the band structure of ZnO was found to evolve only for films of thickness 25 nm or more and this was accompanied by a significant reduction of 0.4 eV in the workfunction. The films became more oxygen deficient with increased thickness, as found from X-ray photoelectron spectroscopy (XPS) and valence band XPS (VBXPS). We attribute the strong dependence of device performance to the zinc to oxygen stoichiometry within the ZnO layers, leading to improvement in the band structure of ZnO with increased thickness.

### 8.2. Introduction

Organic photovoltaic (OPV) technologies have attracted a lot of attention due to their potential to be a cheap source of clean energy. The activity has resulted in substantial progress in the power conversion efficiency (PCE) of OPVs<sup>[1]</sup> from 2.5 %<sup>[2]</sup> in 2001 with Heliatek more recently reporting to have achieved a record PCE of 12 %.<sup>[3]</sup> Though remarkable progress has been made in terms of device performance, the stability of devices; which is an essential prerequisite for commercializing this technology, still remains an area which needs further research advancements.

Inverted device structures incorporating transparent oxides such as ZnO as a replacement of low workfunction metals have been shown to improve the stability of devices.<sup>[4]</sup> Inverted device architecture such as ITO/ZnO/P3HT:PCBM/MoO<sub>3</sub>/Ag, also have the potential to overcome the interfacial instability at the poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/ITO interface in conventional devices,<sup>[5]</sup> which could otherwise lead to degradation of OPVs.<sup>[6]</sup>

ZnO has been demonstrated as a promising electron acceptor material in hybrid OPVs or an electron selective layer in inverted OPVs<sup>[7-9]</sup> and it continues to attract significant research focus as an electron transport material due to its excellent electronic properties, transparency and ability to be synthesised using various methods.<sup>[10-15]</sup> Though ZnO buffer layers with a range of different morphologies such as nanoparticles and nanorods have been used,<sup>[16, 17]</sup> the dependence of device performance on the morphology of the ZnO film is controversial with some reports suggesting a significant dependence of device performance on the ZnO film thickness,<sup>[18]</sup> while other reports attributed the performance changes to the morphology of these thin films.<sup>[19, 20]</sup> For sol-gel processed ZnO, Sharma et al. recently proposed a model where ZnO layer is porous due to the spherical particle morphology, resulting in some inter-diffusion at the ZnO-P3HT:PCBM interface and hence the thickness of the ZnO layer plays a crucial role.<sup>[21]</sup> However, it must be emphasised that the validity of such a model depends on the morphology and the porosity of the resultant ZnO films, which can be strongly dependent on the deposition method used. Consequently the optimal thickness of ZnO buffer layer for a device would also depend on the deposition methods and this has not been systematically investigated, resulting in a range of ZnO buffer layer thicknesses being reported in the literature.<sup>[18, 22]</sup>

Pulsed laser deposition (PLD) of ZnO films has been reported<sup>[23]</sup> to produce high quality oxide closed layers with controllable and scalable thickness whilst maintaining low surface roughness.<sup>[23]</sup> Such a morphology provides an opportunity to compare the role of film thickness with sol-gel produced ZnO films. In this paper, we investigate the role of layer thickness on the chemical and electronic properties of the film and the impact on device efficiency without the added complication of increasing roughness and porosity (which typically scale with thickness) for ZnO thin films deposited by other methods such as solgel. We employ X-ray photoelectron spectroscopy (XPS), valence band XPS (VBXPS) and ultraviolet photoelectron spectroscopy (UPS) for chemical properties such as the Zn:O ratios and electronic characterisation of the deposited ZnO films including workfunction and valence band structure.

## 8.3. Experimental

#### Device Fabrication

Patterned ITO-coated glass substrates (10  $\Omega/\Box$ , Xin Yan Technology LTD) were cleaned in pyroneg (5 % solution) at 90 °C for 20 minutes. The samples were then rinsed in deionized (DI) water followed by successive sonication for 10 minutes each in DI water, acetone and isopropanol. Subsequently UV-ozone cleaning of the ITO substrates was applied for 10 minutes.

The ZnO films of thicknesses varying from 4 nm up to 100 nm were deposited by PLD at 150 °C at an oxygen pressure of 75 mTorr, with thickness controlled by the number of pulses (100 - 2500). The PLD set up and conditions used for ZnO deposition is described in more detail elsewhere,<sup>[23]</sup> briefly; a KrF laser was used with a pulse duration of 25 ns and laser energy density of 1.5 Jcm<sup>-2</sup>. For device fabrication, all ZnO coated samples were transferred to the glove box prior to further fabrication of devices.

The hetero-junction blend was prepared by dissolving P3HT (45 mg, purchased from Merck) and PCBM (36 mg, purchased from nano C) in di-chlorobenzene (1.5 ml) each. Both solutions were dissolved separately in glove box at 80 °C for an hour, followed by cooling down, filtering and stirring at room temperature. Hetero-junction layer of P3HT: PCBM was spin coated at 3000 rpm for 30 seconds followed by annealing at 150 °C for 10 minutes. An anodic buffer layer of molybdenum oxide (20 nm) was thermally evaporated, before evaporating 100 nm thick silver anode.

#### Electron Spectroscopy

The investigations of laser deposited ZnO on ITO substrates with XPS were performed in an ultra-high vacuum (UHV) apparatus built by SPECS (Berlin, Germany) using a nonmonochromatic X-ray source for Mg. The valence band XPS (VBXPS) was performed using an Al anode. The base pressure of the UHV chamber is a few 10<sup>-10</sup> mbar. All highresolution XPS and VBXPS measurements were performed at 200 W using the medium magnification lens mode and the XP spectra were referenced to the carbon 1s peak, resulting from adventitious hydrocarbons absorbed on the ZnO surface. The carbon 1s peak was set to 285 eV.

Ultraviolet photoelectron spectroscopy (UPS) measurements were performed using a low intensity UV light (He I line). The spectra of the electrons emitted from the samples were recorded at pass energy of 10 eV, with a hemispherical Phoibos 100 energy analyser from SPECS. At this pass energy, the analyser has an energy resolution of 400 meV as evaluated from the Fermi edge of polycrystalline silver. The angle between the He\*/UV light irradiation and the analyser and the X-ray irradiation and the analyser are both 54°. The UP spectra were acquired by applying a bias of 10 V to the sample to clearly observe the secondary electron cut-off.

The workfunction of the samples was determined from the secondary electron cut-off of the UP spectra. Due to sensitivity of workfunction measurements to surface contaminants, the UPS measurements presented in this study were acquired from samples cleaned by being vacuum annealed at 300 °C for 10 minutes to remove hydrocarbons and any other adsorbed species from the surface.<sup>[37]</sup> As ZnO was deposited on patterned ITO substrates for device fabrication, all XPS, VBXPS and UPS measurements were performed by collecting the signals from a small area of ~ 0.5 mm on the substrate which partially constitute the electrode in the active area of the device; leading to relatively low intensity of the signal.

#### J-V characterisation

The J-V characteristics of the inverted devices were measured in an inert atmosphere with a computer-controlled Keithley 2400 Source Measure Unit. A 150 W Xenon lamp (Newport) coupled with an AM 1.5G solar spectrum filter was used as the light source. Light was illuminated through a quartz window of the glove box and intensity was calibrated and monitored using a secondary reference cell (Hamamatsu S1133, with KG-5

filter, 2.8 x 2.4 mm of photosensitive area) which was calibrated by a certified reference cell (PVMeasurements, certified by NREL) under 1000  $Wm^{-2}$  AM 1.5G illumination from an Oriel AAA solar simulator fitted with a 1000 W Xe lamp. Devices were measured at the same position as the secondary reference cell. The calibrated intensity was also regularly confirmed using encapsulated devices under the AAA solar simulator.

#### 8.4. **Results and Discussion**

Inverted OPVs fabricated with pulsed laser deposited ZnO buffer layers resulted in a significant enhancement in the device performance as thickness increased from 4 nm to 100 nm. The photoconversion efficiencies increased from 2.1 % (device A, 4 nm ZnO) and 0.8 % (device B, 12 nm ZnO) up to 3.3 % (device D, 100 nm ZnO). Table 8.1 summarises the best values of various photovoltaic parameters as a function of ZnO thickness.

Devices incorporating 4 nm and 12 nm thick ZnO films were found to have a s-shaped kink in the J-V curves as shown in Figure 8.1, which has also been previously attributed to low conductivity of ZnO, dipole formation, ionic migration or charge imbalance at devices interfaces.<sup>[6, 24-26]</sup>



*Figure 8.1:* J-V characteristics of devices fabricated using ZnO buffer layer of different thicknesses.

The s-shaped kink resulted in significantly reduced fill factors of 38 % (device A) and 25 % (device B) as compared to 55 % (device D) for the device incorporating a 100 nm thick ZnO. For devices with ZnO thickness of 25 nm and above, the s-shaped kink was found to disappear, consequently increasing the fill factor and PCE of these devices.

Interestingly, 4 nm ZnO device appeared out of sequence with the other devices with the open circuit voltage ( $V_{oc}$ ) decreasing as the ZnO thickness increased from 4 nm to 12 nm and the s-shaped curve becoming less pronounced.

Bare ITO showed the typical flaky morphology in the AFM, with a root mean square (rms) roughness of  $4.7 \pm 0.2$  nm, as shown in Figure 8.2. Since the PLD process is a line-of-sight technique, a 4 nm film is likely to be insufficient to provide closed coverage of the ITO, hence it can be expected that some ITO will be in direct contact with the bulk heterojunction (BHJ) which may be the cause of the s-shaped curve. As the ZnO layer increases, it can be expected that a fully closed layer will form and the trends with higher ZnO thickness are more representative of the impact of thickness of the ZnO layer.



*Figure 8.2:* Surface morphology (2 x 2  $\mu$ m scans) of ITO and ZnO modified ITO substrates with various thicknesses of ZnO.

The film thickness of PLD ZnO showed little effect on the surface morphology and grain size as can be seen in Figure 8.2. The rms surface roughness of the 4 nm ZnO layer was similar to that of bare ITO at  $4.7 \pm 0.2$  nm and the roughness decreased only slightly to

 $4.3 \pm 0.2$  nm as the ZnO thickness increased to 100 nm (Table 8.1) which is consistent with a line of sight deposition technique. However, the significant changes in device behaviour cannot be attributed entirely to these small changes in the surface roughness (Table 8.1) as proposed in earlier studies,<sup>[19]</sup> suggesting other mechanisms are likely to be limiting the device performance. The change in the J-V characteristics with thickness, in particular of the 12 nm to 100 nm films, indicates that the chemical and electronic properties of the ZnO film are varying with thickness on the ITO substrate.

The workfunction of 4 nm and 12 nm thick ZnO was  $4.3 \pm 0.05$  eV and  $4.2 \pm 0.05$  eV respectively and was found to decrease to  $3.9 \pm 0.05$  eV for both the 25 nm and 100 nm thick ZnO films deposited on ITO (Table 8.1). Closer examination of the UP spectra (Figure 8.3 a), indicates that the 4 nm ZnO film have a significantly different secondary electron cut-off profile compared with the 12, 25 and 100 nm ZnO films, with a shallow onset of the secondary electron cut-off as well as a different slope. This profile is consistent with a broad distribution of workfunction over the surface indicating a heterogeneous surface (as demonstrated in Chapter 9)<sup>[27]</sup> – either chemically or electronically.

**Table 8.1:** Characteristics of PLD ZnO films with different thicknesses and the device performance parameters of inverted devices fabricated using the PLD ZnO as an electron transport layer.

Parameters	Device A	Device B	Device C	Device D
ZnO Thickness [nm]	$4\pm0.6$	$12 \pm 0.6$	$25\pm5$	100 ± 5
Workfunction [eV]	$4.3\pm0.05$	$4.2\pm0.05$	$3.9\pm0.05$	$3.9\pm0.05$
Roughness [nm]	$4.7\pm0.2$	$4.4\pm0.2$	$4.4\pm0.2$	$4.3\pm0.2$
$J_{sc}$ [mA cm <sup>-2</sup> ]	$9.5\pm0.2$	$7.1\pm0.4$	$8.7\pm0.3$	$10.7\pm0.4$
V <sub>oc</sub> [mV]	$560\pm10$	$430\pm10$	530 ± 10	$550\pm10$
FF [%]	$36 \pm 3$	$21\pm 4$	53 ± 1	$54\pm3$
PCE [%] (Average over 10 devices)	$1.9\pm0.2$	$0.7\pm0.2$	$2.4\pm0.1$	$3.1 \pm 0.3$
PCE [%] (Best Device)	2.1	0.8	2.5	3.3



*Figure 8.3:* Normalised (a) secondary electron cut-off (b) valence band region of the UP spectra of ZnO modified ITO substrates.

Importantly, the band structure of ZnO was found to continuously evolve with increased ZnO thickness until 100 nm, as seen from the developing characteristic peak emissions for Zn 3d and O 2p peaks at 11 eV and ~ 5 eV respectively (Figure 8.3 b). As the thickness of ZnO was increased, the Zn4s/4p-O2p hybridisation emission at 8 eV was also found to develop. Although the position of the valence band maxima (VBM) for ZnO did not change with thickness, the intensity of the low binding energy region corresponding the O 2p orbital, was found to be smaller in the case of the 4 nm and 12 nm ZnO films as compared to the 25 nm and 100 nm films. This is important as the 2p orbital originating from oxygen forms the valence band<sup>[28]</sup> which can significantly influence the charge transport and conductivity of ZnO. Cheun *et al.*<sup>[18]</sup> has previously proposed that atomic layer deposited (ALD) ZnO films of thicknesses less than 10 nm have poor conductivity due to high surface to bulk ratio resulting in more defects at the grain boundaries.

Elemental compositions studies of ZnO surfaces were performed using XPS in order to obtain atomic ratios of zinc and oxygen. While the Zn 2p3/2 peak was found to be symmetric (Figure 8.4) for all samples (4 nm – 100 nm ZnO) and no significant chemical shift was observed, the oxygen peak for all ZnO thicknesses was found to be asymmetric with two components at around 530 eV and 532 eV.

The lower binding energy component is attributed to  $O^{2-}$  ions in the ZnO matrix,<sup>[29]</sup> whereas the higher energy component is believed to be due to chemisorbed oxygen,<sup>[30]</sup>

hydroxyl groups attached to the Zn<sup>[31]</sup> or singly bonded oxygen radicals.



Figure 8.4: Core level XP spectra of Zn 2p<sub>3/2</sub> (left) and O 1s (right)

For 4 nm ZnO, the ratio of two oxygen peaks was ~ 1:1, with the high binding energy component of oxygen decreasing with increasing ZnO thickness. In the case of the 4 nm ZnO film, indium and tin was also found in the XP spectra, while no indium or tin was detected for films of thickness 12 nm and more. The significantly higher amount of the high binding energy component of oxygen (which has previously also been attributed to  $In_2O_3^{[32]}$ ) in case of 4 nm ZnO combined with the presence of indium and tin, supports the hypothesis that the higher binding energy oxygen could be from the underlying ITO due to incomplete coverage of the ZnO.

After correcting the XP spectra for the transmission function of the analyser and using the Scofield crosssections,<sup>[33]</sup> the atomic ratio of oxygen (low binding energy component corresponding to the ZnO matrix) to zinc was  $1.05 \pm 0.03$  for the 12 nm film, which decreased to  $0.92 \pm 0.02$  for the 100 nm thick ZnO film showing an increased oxygen deficiency for thicker ZnO films (Table 8.2).

The decrease in the oxygen content in ZnO films with increased film thickness was also confirmed from valence band XPS (VBXPS), which can probe the valence band region of the surface much deeper ( $\sim 8 - 10$  nm) than UPS ( $\sim 2 - 3$  nm) due to higher electron mean free path.

Figure 8.5 shows the VBXP spectra of ZnO films of various thicknesses deposited on ITO. No shift in the valence band cut-off was found in the VBXP spectra, however the results



Figure 8.5: Normalised VBXP spectra of ZnO coated ITO substrates.

show more prominent O 2p and Zn 3d feature with increased ZnO film thickness, and agree with the UPS results. In case of 12 nm thick ZnO layer, while UPS showed an unevolved band structure on the surface (Figure 8.3 b), from the VBXPS it was found that the bulk (deeper than top ~ 8- 10 nm of surface) of 12 nm thick ZnO had band features similar to that of 25 nm thick ZnO layer, as seen from the Zn 3d band intensity (Figure 8.5). This could be due to a different composition of ZnO surface than that of the bulk.

Figure 8.6 shows O:Zn ratios measured from XPS and the quantitative estimation of O:Zn ratios from the peak heights of the Zn-3d and O-2p peaks of the VBXP spectra, plotted against the ZnO thickness.

The n-type doping/semiconducting behaviour of ZnO is known to be due to the native defects which form in oxygen deficient conditions.<sup>[34]</sup> Thus, the improved performance of devices C and D incorporating 25 nm and 100 nm thick ZnO can be attributed to a fully evolved band structure of ZnO and improved conductivity due to oxygen deficiency. Also, increased ZnO thickness has been shown to result in improved crystallinity<sup>[35, 36]</sup> resulting in higher conductivity,<sup>[35]</sup> which could explain further enhancement of the photocurrent when ZnO thickness increases from 25 nm to 100 nm.



**Figure 8.6:** Plot depicting the O:Zn ratios (measured from XPS and VBXPS) plotted against the ZnO film thickness. The ratios calculated from VBXPS are only a quantitative estimation from the Zn 3d and O 2p peak heights from VBXP spectra and do not represent the atomic ratios of Zn and O in ZnO.

**Table 8.2:** Oxygen to zinc ratio in ZnO films of various thicknesses, as measured from XPS.

Samples	$O_{530}^{:}O_{532}$	O <sub>530</sub> :Zn	O <sub>total</sub> :Zn	
ZnO 4 nm	1	$1.07 \pm 0.05$	$2.15 \pm 0.06$	
ZnO 12 nm	2.3	$1.05\pm0.03$	$1.51\pm0.03$	
ZnO 25 nm	2.6	$0.94\pm0.02$	$1.30\pm0.02$	
ZnO 100 nm	3	$0.92\pm0.02$	$1.22\pm0.02$	

## 8.5. Summary and Conclusions

Inverted OPVs fabricated using pulsed laser deposited (PLD) ZnO films between 4 nm and 100 nm showed a strong increase in photo-conversion efficiencies with thickness. Since PLD is known to result in non-porous closed layers, the interpenetration of the BHJ layer

into the ZnO layer as proposed for the thickness dependence of sol-gel prepared ZnO,<sup>[21]</sup> can be eliminated, provided complete coverage of the ITO can be achieved.

Incomplete coverage was confirmed by the presence of indium and tin in the XPS for very thin (4 nm) ZnO layers, in which the ZnO thickness was less than the roughness of the ITO substrate (4.7 nm). Devices produced from these incompletely closed layer samples behaved significantly differently from those with thicker ZnO layers and showed a strong s-shaped feature in the J-V curves, but a surprisingly high average photo-conversion efficiency of 1.9 %, due largely to a high  $V_{oc}$  at 560 mV.

Thicker ZnO layers from 12 nm to 100 nm were completely closed as confirmed by the lack of indium or tin in the XPS. The ZnO morphology did not appear to change with film thickness, while the root mean square surface roughness decreased from 4.7 nm to 4.3 nm as the layer thickness increased from 4 nm to 100 nm, consistent with the line-of sight deposition mechanism. Devices fabricated from these layers showed an increase in average efficiency from 0.8 % to 3.1 % as thickness increased from 12 nm to 100 nm. The 12 nm device displayed an s-shaped J-V curve and a significantly decreased V<sub>oc</sub> of 430 mV compared with the 25 and 100 nm layers at 530 mV and 550 mV respectively. Surface morphology and roughness cannot therefore solely account for the dependence of device performance on ZnO layer thickness, as has been proposed in previous studies.

Importantly, the stoichiometry of the ZnO layer showed a strong dependence with layer thickness, with the oxygen to zinc ratio decreasing from 1.05 for the 12 nm layer to 0.92 for the 100 nm. This change in the chemistry of the ZnO layer was accompanied by the developing electronic properties of the ZnO with thickness, including the ZnO band structure and the workfunction and is thought to be the primary mechanism for the observed dependence. The band structure observed in UPS continued to evolve as the thickness of the ZnO layer increased, with a minimum thickness of 25 nm necessary to achieve ZnO with a band structure showing fully evolved O 2p orbitals for optimum charge transport. Similarly, the workfunction of the ZnO decreased from  $4.2 \pm 0.05$  to  $3.9 \pm 0.05$  as the film thickness increased from 12 nm to 100 nm.

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# **Invisible High Workfunction Materials on Heterogeneous Interfaces**

This chapter is a reformatted version of the manuscript submitted to Applied Surface Science.

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Anirudh Sharma: Designed & performed experiments, data analysis & interpretation, prepared the first draft of manuscript.

Dr. Rudiger Berger: Facilitated sample preparation; contributed to revision of manuscript.

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## 9.1. Abstract

We demonstrate that the determination of workfunction of heterogeneous surfaces by electron spectroscopy measurements is complex due to enhanced secondary electron emission from the lower workfunction material. This can lead to misunderstanding the electronic properties of interfaces in electronic devices and have significant influence on the design and performance of the interfaces therein. Ultraviolet photoelectron spectroscopy (UPS) measurements on a range of artificially created ITO-Au heterogeneous surfaces demonstrate that contributions to the secondary electron cut-off are not proportional to the compound coverage on the surface and that the lower workfunction material dominates the secondary electron cut-off.

## 9.2. Introduction

The latest electronic gadgets such as smart phones, touch screen tablet computers, curved television displays and flexible solar cells are no longer science fiction and are just some of the latest examples of the latest generation of electronics in our day to day lives. Such tremendous progress in semiconductor technology has largely been possible due to the evolution of thin film organic devices such as diodes and transistors. Structurally, thin film devices are a sandwich of various energetically favourable semiconducting materials between two conducting electrodes.<sup>[1-3]</sup> To design devices, the electronic structure of the various layers must be carefully matched to maximise electron and hole transport through the structure to avoid charge traps and internal resistance at interfaces. One of the important material properties determining the charge transport across material interfaces is the workfunction.<sup>[4]</sup>

Workfunction is an intrinsic surface property of a material that describes the potential barrier for an electron to be emitted from the material and can be determined through a number of techniques including ultraviolet photoelectron spectroscopy (UPS) and Kelvin probe measurements.<sup>[5]</sup>

In a UPS experiment, excited electrons are generated following the absorption of a UV photon. These electrons then generate a large number of low energy electrons (secondary electrons) which subsequently lose energy on their path through the material. Workfunction is determined from the lowest kinetic energy of electrons that can escape from the sample, i.e. electrons which have just enough kinetic energy to overcome the potential barrier at the surface. Electrons with a lower kinetic energy than the workfunction of the material cannot escape and remain within the sample. Materials are often quoted as having a specific workfunction, however, only single crystals have a unique workfunction and these are specific to the crystal face. All other materials, including polycrystalline and amorphous materials, have a degree of heterogeneity resulting in a distribution of values for workfunction. Typically, this distribution of workfunctions across a surface is relatively narrow and is ignored. The impact of significant heterogeneity of an interface on workfunction is not normally considered.

In this paper, we show that for a heterogeneous surface of Au and ITO, which have distinctly different workfunction, the lower workfunction material dominates the part of the UP spectrum from which the workfunction is derived. Values derived from the UP spectrum with current procedures could lead to errors in the order of a few tenths of an eV which can be significant, resulting in erroneous conclusions being drawn when determining the workfunction of heterogeneous surfaces with UPS. It should be noted that even for pristine materials similar in chemical nature and crystal structure, a range of workfunction values are reported.<sup>[6, 7]</sup> The implication of this observation is that the presence and impact of high workfunction regions in electronic devices (LEDs and OPVs) can be overlooked and in particular their contribution to the charge transport in electronic devices in which the effective interfacial area for charge transport is reduced due to mismatch in workfunction across the interface.

## 9.3. Results and Discussion

UV excitation leads to the generation of a large number of low kinetic energy electrons which originate from secondary processes initiated by photogenerated electrons. The possible processes are shown schematically in Figure 9.1, in which electrons "A" and "D" have high kinetic energy and are emitted from the near surface region immediately following photoexcitation resulting in counts in the high kinetic energy region, i.e. kinetic energy > 12 eV range. For the structure shown in Figure 9.1, provided the thickness of Au on ITO (30 nm in this case) is much larger than the electron mean free path of the high energy photoelectrons (less than 1 nm) the contribution of processes "A" and "D" is proportional to the coverage of the surface of the respective material. Secondary electrons occur through processes indicated with "B", "C", "E" and "F" (Figure 9.1) and have relatively low energy. Such low energy electrons have a large mean free path and can reach much farther than those originating from the processes "A" and "D". Electron "C" is shown to migrate from one component of a heterogeneous sample to another before escaping, while other secondary electrons are lost within the material and never escape to be detected. The processes indicated with "B", "C", "E" and "F" are those which lead to the secondary electron cut-off in the UP spectra from which the workfunction is determined.

In a UPS experiment the sample is irradiated with UV photons leading to photoionization via the photoelectric effect. The energy of emitted electrons is given by

 $\frac{E_{kE} = E(h\vartheta) - E_{bin} - \phi_{spec}}{Page \ 168}$ 



**Figure 9.1:** A schematic depicting potential photoemission processes during a UPS experiment and the labels indicate their contributions to an experimental spectrum for an Au-ITO heterogeneous surface prepared using TEM grid of mesh size 300.

where  $E_{kE}$  is the kinetic energy of the emitted electron,  $E(h\vartheta)$  the photon energy (21.22 eV for the He I line used here),  $E_{bin}$  the binding energy of the electron before excitation and  $\emptyset_{spec}$  the spectrometer workfunction. The workfunction of a sample is given by the lowest kinetic energy of electrons emitted from a sample.<sup>[4, 8]</sup> Therefore, the workfunction measurements using UPS relies on accurate determination of the minimum kinetic energy in the spectrum, which is also referred to as the secondary electron cut-off as this part of the spectrum is mainly comprised of the low energy secondary electrons.

For the present study, heterogeneous surfaces were prepared by thermally evaporating 30 nm gold (Au) on indium tin oxide (ITO) substrates (Figure 9.2) through a transmission electron microscopy (TEM) grid as an evaporation mask to create a patterned structure on the surface. Four samples were prepared: three grid patterns (Figure 9.2) prepared by evaporation through TEM grids (mesh size 100, 300 and 400 corresponding to 100, 300 and 400 bars per inch respectively), and one uniform sample, prepared without a grid mask

– note that the samples were held tightly against the grid to minimise migration under the mask. All of the samples were sputtered with Ar with a dose of  $3 \times 10^{14}$  ions cm<sup>-2</sup> before the UPS measurements to remove adventitious hydrocarbons adsorbed from the atmosphere which can affect the measurement. For the UPS measurements, signal was collected from a spot with a diameter of ~ 0.5 mm either at the centre of the samples or scanned across the centre of the samples.



*Figure 9.2:* Optical image (on the left) of the grid pattern created on an ITO substrate by thermally evaporating Au using a TEM grid of mesh 300 as a mask. On the right side is a SEM image showing a blown out grid to scale.

Figure 9.3 shows a spectrum of a sample prepared using a TEM grid of mesh 300. Unlike a typical UP spectrum of a homogeneous surface, the secondary electron cut-off in the UP spectrum of the patterned surface was found to show two cut-offs, similar to the one shown in Figure 9.1. Appearance of double secondary cut-offs for these artificially created heterogeneous surfaces were reproducible for all grid samples. Such an observation was recently reported by Helander *et. al.* and was attributed to contamination producing a "patchy surface".<sup>[9]</sup>

Spectra were recorded at various positions across the diameter of the grid changing the fraction of the surface covered with Au in spot analysed. When changing the analysis position over the sample the height of the secondary electron cut-off attributed to ITO and Au changed as well as the intensity of the Au 5d features. As the Au 5d feature in the UP spectra stem from the top few nanometres, no signal from the underlying ITO is recorded, because the Au layer is much thicker than the mean free path of the high kinetic energy

electrons. Further, ITO does not show features in a UP spectrum at this kinetic energy. Thus the peak height of the Au 5d peak is a measure for the fraction of the coverage of the sample with Au.

The secondary electron cut-offs were found at  $4.2 \pm 0.05$  eV and  $4.8 \pm 0.05$  eV corresponding to ITO and Au respectively (Figure 9.3). Literature values for the workfunction of ITO vary from 4.2 eV TO 4.7 eV <sup>[10-14]</sup> possibly due to surface treatment which results in a range of metal (In and Sn) to oxygen ratios. The experimental value determined here is consistent with reported values, but more importantly, all samples were from the same batch and treated identically in this work to ensure that the workfunction for ITO is self-consistent in this paper and allow separating the ITO and Au secondary electron cut-offs.



**Figure 9.3:** The normalised secondary electron cut-off and the valence band region of the UP spectra acquired from samples for all three meshes. The determination of the height of the secondary electron cut-offs for ITO and Au is exemplified for the 100 mesh samples. The expanded region between 12 eV and 22 eV shows the Au 5d band used to determine Au coverage.

For the sample completely coated with Au, the workfunction was calculated after extrapolating the main cut-off and was found to be 4.9 eV, which is comparable to reported values.<sup>[15]</sup> The corresponding workfunction of ITO and Au in various samples is summarized in Table 9.1. Measurements with samples prepared with the other grid sizes were performed at the centre of the samples and are shown in Figure 9.3. The contribution

of Au to the secondary electron cut-off was calculated from the height of the second cutoff in secondary electron cut-off as marked by a double-sided arrow in Figure 9.3. The contribution of the Au to the secondary electron cut-off as a function of fraction of the Au surface coverage is plotted for all measurements in Figure 9.4.

In Figure 9.4 it can be seen that the contribution of Au to the secondary electron cut-off was found not to be directly proportional to the overall Au coverage on the surface. The data points can be fitted approximately with a straight line. Interestingly, when this plot is extrapolated, there is no identifiable contribution of Au in the secondary electron cut-off below Au coverage of less than approximately. 60 %. Thus there is no evidence for the presence of the higher workfunction material below these levels despite clear evidence for the presence of Au on the sample.



Fraction of the surface covered with gold

*Figure 9.4:* Plot showing the Au contribution in the secondary electron cut-off vs the intensity of the Au 5d signal.

In addition, the slope of the plot in Figure 9.4 indicates that the number of secondary electrons emitted from the high workfunction material is lower than contributed by the lower workfunction material. This is also reflected visually in the relative heights of the peaks in Figure 9.3 and can be explained based on the mechanism of the emission of photoelectrons and secondary electrons.

The contribution of the processes "A" and "D" in Figure 9.1 is proportional to the coverage of the surface with the respective material. Secondary electrons are occurring through processes indicated as "B", "C", "E" and "F" (Figure 9.1). The energy loss converting photoelectrons into secondary electrons is caused by scattering and excitation mechanism with the latter mechanism creating even more secondary electrons.<sup>[16]</sup> Due to the nature of these secondary processes the number of secondary electrons in a material under UV irradiation increases with decreasing energy of the secondary electrons can have a very large range because the electron mean free path for electrons with a kinetic energy < 10 eV increases rapidly.<sup>[18]</sup> They can be involved in many secondary processes. Though in this process, some secondary electron from Au or ITO might still retain their identity (processes "B" and "E" in Figure 9.1) while others might constitute a "random flood of secondary electrons" in the sample (process "C" and "F" in Figure 9.1); the material in which the first electron in the cascade of secondary processes has been generated cannot be identified anymore.

Because the number of secondary electrons increases with decreasing kinetic energy, the fraction of electrons with sufficient energy to pass through the lower workfunction ITO surface is greater than the fraction of electrons with sufficient energy to pass through the higher workfunction Au surface For this reason the secondary electron cut-off is dominated by the electrons emitted from a surface area with low workfunction. Consequently, the height of the secondary electron cut-off is not proportional to the coverage of the surface with a given material as shown by Figure 9.4.

In the case of a binary heterogeneous surface with materials having very different workfunction, such as Au and ITO, the effect described can be easily identified as seen in Figure 9.3. However, when a surface consists of materials with a distribution of workfunction or where the workfunctions are closer together, the phenomenon described is much more difficult to identify as they will not lead to distinct separable secondary electron cut-offs. Instead, the slope of the secondary electron cut-off will be influenced with the lowest workfunction material dominating the measured outcome, regardless of the surface coverage, leading to a misunderstanding of the surface properties.

Sample	Au % (S.E. cut-off intensity)	Workfunction ± 0.05 eV		5d Intensity
Au	90.7	4.8		94.6
400	10.2	4.2	4.8	85
300	44	4.2	4.8	80
100	36.5	4.2	4.8	68

**Table 9.1**: Amount of Au present on the sample surface and the corresponding positions of the secondary electron cut-offs.

Due to the nature of the usual procedure to determine the workfunction from the secondary electron cut-off, a broadening of the cut-off due to the existence of a distribution in the workfunction can easily be overlooked. In order to demonstrate the case of a continuous distribution in workfunction, UPS measurements on a polycrystalline surface such as that of sol-gel prepared ZnO have been performed. For such a surface the processes leading to electron emission as sketched in Figure 9.1 apply.

The slope of the secondary electron cut-off is a function of both the resolution of the electrostatic energy analyser as well as the distribution in workfunction. The resolution of the analyser can be separated from the distribution of workfunction by taking measurements over a range of analyser pass energies (2 eV, 4 eV, 6 eV, 8eV and 10 eV) and fitting a step function, which was convoluted by a Gaussian function to the secondary electron cut-off. The full-width-half-maximum (FWHM) of the Gaussian distribution for the ZnO sample is plotted as a function of pass energy in Figure 9.5 and extrapolated to zero pass energy. If the surface is homogeneous in its workfunction, the extrapolation of the FWHM to 0 eV pass energy should intersect the y-axis (FWHM) at the origin (0 eV). The non-zero value of the intercept in Figure 9.5 shows that the sol-gel prepared ZnO is inhomogeneous in its workfunction. The y-intercept value of 0.16 eV is an approximate measure for the distribution in workfunction of the ZnO surface.

In order to separate the distribution of workfunction and the energy resolution of the analyser, the energy resolution of the analyser was determined by fitting a convolution of a Fermi function and a Gaussian function to the Fermi edge in the UP spectra of an Au surface measured across the same range of pass energies. The FWHM of the Gaussian

distribution used to fit the secondary electron cut-off was then corrected for the resolution of the analyser resulting in a horizontal line in Figure 9.5, intersecting the y-axis at 0.2 eV and also representing another estimation for the distribution in workfunction of the ZnO.



Figure 9.5: Plot showing the FWHM of the Gaussian function as a function of pass energy.

Such precise observations usually go unnoticed when UPS measurements are performed only at single pass energy, which is often the case. From the data in Figure 9.5 it can be estimated that the FWHM of the distribution of workfunction in ZnO produced by a sol-gel procedure is about 0.15 to 0.2 eV. It is important to note, however, that even determining that a distribution of workfunctions exist for the sol-gel ZnO sample, the fraction of the surface coverage within this distribution cannot be quantified.

### 9.4. Conclusions

For an ITO-Au heterogeneous surface with a lateral variation in workfunction, the secondary electron cut-off was found to have two cut-offs corresponding to each of ITO and Au. Below certain coverage of the surface with the high workfunction material, its contribution cannot be resolved anymore and there appears to be no contribution to the experimentally determined workfunction. This observation has significant ramifications to

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the design of the interfaces in electronic devices. Finite presence of more than one compound on a heterogeneous surface was found to influence the position and slope of the secondary electron cut-off of the UP spectrum and hence the measured workfunctions.

We have for the first time quantified the contribution of two different workfunction materials to the two cut-offs observed in the secondary electron region of a UP spectrum. It is successfully demonstrated that the ratio of the height of the two cut-offs of Au and ITO is not proportional to the ratio of the Au and ITO coverage on the surface. The secondary electrons from the low workfunction material dominate the secondary electron cut-off relative to the contribution of the secondary electrons from the high workfunction material. A mechanism for this phenomenon has been proposed in which a higher fraction of secondary electrons are able to pass through the lower workfunction interface than for the higher workfunction interface.

While this study was performed on Au-ITO system, the fundamental understanding of the phenomenon where the signal from a high workfunction gets buried under the signal from a low workfunction material that has been demonstrated in this study is relevant to all studies which use UPS as a technique to measure absolute workfunction. The shape of the cut-off, in particular steps or variations in the slope, often found in the secondary electron region of UP spectra must not be ignored. In order to derive absolute workfunction values from UP spectra, we propose that multiple pass energies must be examined to separate the broadening of the secondary electron cut-off due to workfunction distribution and the analyser resolution.

Importantly, the fraction of the surface contributing to each workfunction cannot be quantified from the secondary electron cut-off, even when performing the analysis of the secondary electron cut-off, as the probability for the emission of a secondary electron depends on the workfunction itself, thus the lower workfunction area will dominate the distribution found. This result has critical implications on the design of electronic structures, such as o-LEDS and OPV's if even slightly heterogeneous surfaces and interfaces are present.

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# **Nanoscale Electronic Properties of ZnO Thin Films**

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## **10.1.** Abstract

The workfunction of sol-gel derived polycrystalline ZnO thin films was found to be significantly different for a planar and a rough surface. From UPS studies, the workfunction of planar ZnO was found to be 3.7 eV while ZnO with a rough morphology had a significantly lower workfunction of 3.4 eV with some indications of electronic heterogeneity across the surface. KPFM studies confirmed the workfunction dependence on the surface roughness of ZnO. While the workfunction of a nano-roughened ZnO surface measured from UPS was found to be more representative of the low workfunction regions on the surface, KPFM showed the presence of energetically dissimilar domains having lateral variation in workfunction across the surface. On a ZnO surface with a rough morphology, workfunction difference of over 0.1 eV was found to exist within a small area of 500 nm x 500 nm.

#### **10.2.** Introduction

Precise understanding of the electronic properties of semiconductor material is essential for tailoring the device properties. The new generation of electronic devices are based on thin film technology, which involves sandwiching of various energetically favourable semiconducting materials between conducting electrodes.<sup>[1-3]</sup> Therefore in order to achieve optimum device performance, efficient charge transport across various material interfaces is crucial and it is largely driven by the relative difference in workfunction of the materials used. With the advances in thin film semiconductor technologies, modern designs uses semiconducting films of thicknesses in the order of nano-meters comprised of nanoparticles or nanostructures. The crystal structure and lattice orientations in the resultant semiconducting film of materials similar in chemical nature can still be different depending on the deposition method and the synthesis conditions used. Considering the important role that workfunction of a material plays in the device physics and given that the workfunction is dependent on the lattice structure and orientation,<sup>[4]</sup> it is very important to study the electronic properties of materials on a nanoscale.

Zinc oxide (ZnO), due to its high electron mobility, transparency, and solution processability,<sup>[5-7]</sup> has been widely explored in recent times as a promising material in the field of organic electronics as a workfunction modification or an electron transport buffer layer<sup>[5, 8]</sup> and even as a transparent electrode.<sup>[9]</sup> Application of ZnO in inverted organic solar cells has been widely reported and ZnO film thickness and morphology has been shown to significantly influence the device performance.<sup>[10-12]</sup> ZnO-polymer interface with a quality contact between the polymer layer and a dense and homogenous ZnO surface is considered to be ideal for efficient charge transport and devices with increased interfacial area between the polymer and ZnO has been shown to have a better performance.<sup>[13]</sup> Yu and colleagues have shown that the distribution of surface conductivity of ZnO can also depend on the surface structure of the ZnO film.<sup>[14]</sup>

Recently, UPS studies have shown that the workfunction of sol-gel prepared polycrystalline thin films of ZnO ( $\phi \sim 4.3 \ eV$ ) is independent of the layer thickness when deposited on ITO ( $\phi \sim 4.7 \ eV$ ),<sup>[10]</sup> but it can be strongly influenced by the processing conditions of ZnO.<sup>[15]</sup>

UPS is commonly used to measure workfunction of electronic materials and absolute Page 181 workfunction is defined by the cut-off value, which represents the lowest energy electrons coming off the surface.<sup>[16]</sup> Therefore, in case of heterogeneous surfaces having a distribution of workfunction, the lowest workfunction dominates the UP spectrum and varying slope of the secondary electron cut-off due to the higher workfunction material is thus often overseen in the spectra, as demonstrated in Chapter 9.

The typical UV illuminated area in UPS is typically larger (~ 2 mm) than the perforation diameter (~ 5- 10 nm) in heterogeneous and porous surfaces, as in case of polycrystalline ZnO thin films composed of nanoparticles, providing an average value. Here Scanning Kelvin Probe Microscopy (SKPM) provides the means for analysis of such surfaces.<sup>[17]</sup> This way, SKPM compliments UPS measurements of ZnO surfaces and can reveal the distribution of workfunction across the ZnO surface composed of nanoparticles.

While the surface morphology of ZnO is known to influence the charge transport in devices,<sup>[13]</sup> no rigorous studies have been performed yet to investigate the possible mechanism behind the morphology driven changes in the electronic properties of ZnO, and hence its influence on devices.

It is therefore imperative to understand the correlation between the nanoscale electronic properties with the surface morphology. In this work, we have investigated the lateral variation of workfunction on ZnO surfaces composed on nanoparticles using UPS and Kelvin Probe Force Microscopy (KPFM).

### **10.3.** Experimental

#### Sample Preparation

The ITO coated glass substrates with a sheet resistance of  $15 \Omega \text{ sq}^{-1}$  (purchased from Kintec) were used. The ITO glass was cleaned by immersing it in a well-stirred solution of 2 % Hellmanex III (supplied by Osilla ) at 60 °C for 15 min. Samples were then rinsed in deionized (DI) water and were successively sonicated in DI water, acetone and isopropanol for 10 min each. Subsequently the substrates were then cleaned with mild oxygen plasma for 1 minute.

Zinc oxide sol-gel was prepared following the method reported in the literature.<sup>[18]</sup> ZnO buffer layers were synthesised as per the following method: Zinc acetate dihydrate

 $(Zn(C_2H_3O_2)_2 (H_2O)_2 (99.9 \% \text{ chemical purity, Sigma Aldrich, 1 gm) and ethanolamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, Sigma Aldrich, 99.5 %, 0.28 g) was vigorously dissolved overnight in 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH, Aldrich, 99.8 %, 10 mL). The prepared sol was then spin-coated on cleaned ITO substrates at 3000 rpm for 45 seconds followed by 10 minutes annealing on a pre-heated hotplate at 300 °C in order to get ZnO planar surface. In order to create ZnO ridge structures in the spin-coated films, ZnO coated ITO substrates were annealed by ramping the temperature from laboratory conditions (room temperature) up to 300 °C at a rate of ~ 40 °C per minute. This ramp annealing method has previously been shown to result in ridge patterns on ZnO surfaces.<sup>[19a]</sup> The spontaneous formation of nanoroughned surface or the so called ridge structure is believed to be due to the re-organisation of the sol-gel particles during the slow drying process.<sup>[19b]</sup> The samples were then stored under vacuum in a desiccator, till KPFM measurements were performed.$ 

An ITO-Ag grid sample with artificial roughness was prepared by thermally evaporating  $\sim 25$  nm of Ag on cleaned ITO using TEM grids as masks. After one cycle of metal deposition the mask was then removed and 25 nm of the same metal (Ag) was again deposited all over the surface. This results in a top surface composed of Ag with  $\sim 25$  nm high topographic grid features.

#### Kelvin Probe Force Microscopy (KPFM)

Due to the hydrophilic nature of ZnO, KPFM experiments were performed in a nitrogen atmosphere (by maintaining a constant flow of nitrogen in a chamber with less than 5 % RH) using a commercial SFM (Agilent 5500). All KPFM measurements were performed in frequency modulation mode simultaneously to the topography imaging <sup>[20]</sup> using the Pt/Ir coated cantilever (Nanosensors, PPP-EFM).

In KPFM, the contact potential difference (CPD) is measured which is defined as the difference in the workfunction between tip and sample. For the investigation of the workfunction of surfaces, the Pt/Ir coated SFM-tip was first calibrated on freshly cleaved, highly ordered pyrolytic graphite (HOPG). The measured CPD is defined as:

$$CPD = \frac{\Delta \Phi}{e} = \frac{(\Phi_{tip} - \Phi_{sample})}{e}$$
 Eq. 10.1

which is valid for the case that the AC potential is applied to the cantilever. Here, *e* is the elementary charge. HOPG has a workfunction of  $\phi_{HOPG} = 4.475 \pm 0.005 \, eV$ .<sup>[21]</sup> The

workfunction of the cantilever  $\phi_{tip}$  can then be calculated as

$$\phi_{tip} = eCPD_{HOPG} + \phi_{HOPG}$$
 Eq. 10.2

For example with  $eCPD_{HOPG} = -0.545 \pm 0.002 \text{ eV}$  we determined the workfunction of the SFM-tip to be  $\phi_{tip} = 3.929 \pm 0.005 \text{ eV}$ . Since each sample was measured using a fresh tip, different tip workfunction values are quoted in the results, corresponding to the workfunction of tip used for respective sample.

#### Ultraviolet photoelectron spectroscopy (UPS)

The investigations of the ZnO seed layer on ITO substrates with UPS were performed in an ultra-high vacuum (UHV) apparatus built by SPECS (Berlin, Germany). The spectra of the electrons emitted from the samples are recorded at pass energy of 10 eV (UV/ He I line) with a hemispherical Phoibos 100 energy analyser from SPECS. At the pass energy of 10 eV the analyser has an energy resolution of 400 meV as evaluated from the Fermi edge of polycrystalline silver. The workfunction of a sample is determined as the difference between the excitation energy and the length of the spectrum. The latter is given as the difference of the high binding energy cut-off and the cut-off of the spectrum at the lowest binding energy, as described elsewhere.<sup>[22]</sup>

#### **10.4.** Results and Discussion

Freshly prepared ZnO sample with a planar morphology was found to have a workfunction of  $3.7 \pm 0.05$  eV by UPS, which is in agreement with the literature value for as prepared ZnO.<sup>[23]</sup> However, ZnO with a rough morphology was found to have a lower workfunction of  $3.4 \pm 0.05$  eV.

Closer examination of the UP spectrum of the rough ZnO surface revealed an inflection point in the S.E. cut-off, as indicated with a pointed arrow in Figure 10.1, which did not exist for the planar ZnO sample. The position of this inflection in the second S.E. cut-off (Figure 10.1) in case of rough ZnO sample was found to correspond to a workfunction of  $3.7 \text{ eV} \pm 0.05 \text{ eV}$ , which is similar to that found for a planar ZnO.

From the findings reported in Chapter 9, these UPS results indicate that the ZnO sample with a rough morphology possesses a non-uniform workfunction, potentially due to a distribution of workfunction across the surface. In order to further investigate that, KPFM
studies were performed on ZnO modified ITO surfaces having both rough and planar morphologies.



Figure 10.1: UP spectra of the sol-gel prepared ZnO nanoparticle layer and nano-roughned ZnO layer (ridge structure). Inset shows the magnified version of the secondary electron cut-off depicting a second onset in the UP spectrum of the nano-roughned ZnO sample.

The topography of bare, cleaned ITO showed the known flaky morphology<sup>[10, 24]</sup> as shown in the AFM image in Figure 10.2 (a). The CPD as measured over the ITO surface was found to be uniform, suggesting that a uniform and stable workfunction distribution is dominant on the surface.



*Figure 10.2 KPFM image showing the simultaneously acquired (a) topography (b) CPD of a cleaned ITO surface.* 

The CPD mean value was measured to be - 0.654 V. Considering the KPFM-tip workfunction of ~  $3.929 \pm 0.005$  eV that was obtained for an SKPF tip calibrated on HOPG, the workfunction for cleaned ITO was calculated to be  $4.580 \pm 0.05$  eV, which is consistent with previous values.<sup>[25]</sup>

KPFM measurements were then performed on similar ITO substrates coated with ~ 25 nm thick layer of sol-gel prepared planar ZnO with particle size of ~ 5- 10 nm. The flaky ITO morphology was not visible anymore (Figure 10.3). However, the CPD of the planar ZnO surface was found to be different from that of ITO, and a mean value of -0.206 V was measured. Using a fresh SKPF-tip calibrated on HOPG (tip workfunction of  $3.875 \pm 0.005$  eV), the workfunction was calculated to be  $4.08 \pm 0.058$  eV for the planar ZnO surface.



*Figure 10.3 KPFM image showing the simultaneously acquired (a) topography (b) CPD of planar ZnO surface.* 

The difference observed in the absolute values of ZnO workfunction measured from KPFM and UPS can be explained as a result of the exposure of surface to different conditions, as UPS was performed in ultrahigh vacuum and KPFM measurements were

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performed in ambient nitrogen atmosphere. Also, workfunction values measured from KPFM are often found to be higher than the ones obtained from UPS,<sup>[26]</sup> as KPFM gives the average workfunction under the probe, while workfunction in UPS is defined by the lowest energy electron coming off the surface.

In case of ZnO with nano-roughened morphology (Figure 10.4), the ITO surface was found to have been covered with ZnO grains situated in parallel rows and forms a ridge like structure as reported earlier.<sup>[19]</sup> On such a rough ZnO surface, the CPD was found to be non-uniform with two CPD values with a difference of > 0.1 V observed across a small area of 500 nm x 500 nm on the surface (Figure 10.4).



*Figure 10.4 KPFM image showing the simultaneously acquired (a) topography (b) CPD of ZnO surface with nano-roughened morphology.* 

Although the absolute workfunction values obtained from KPFM and UPS were different, KPFM results showing changes in CPD across a rough ZnO surface supports UPS results which showed non-uniformity of workfunction in case of nano-roughened ZnO surface. Importantly, the CPD across the nano-roughned ZnO sample was not found to correlate with the grainy morphology, rather two different surface potentials can be attributed to areas A and B. For clarity, regions corresponding to different workfunction have been enclosed with a white line (Figure 10.4). Using the workfunction of the calibrated KPFM-tip ( $3.929 \pm 0.005 \text{ eV}$ ), the workfunction corresponding to region A was found to be  $3.89 \pm 0.05 \text{ eV}$  and that of region B was  $4.04 \pm 0.05 \text{ eV}$ . The line that enclosed the areas with higher workfunction was also outlined in the topography (Figure 10.4). It must be noted that the workfunction difference of over 0.1 eV is on a small area of 500 nm x 500 nm, and there could potentially be larger variations on a bigger surface area as analysed by UPS.

Though the potential distribution as marked by the white lines could not be correlated to any peculiarities in the topography image and the height of the topography is not correlated with the surface workfunction, an important conclusion that can be made from KPFM results is that rough ZnO surface is energetically heterogeneous with lateral variations in workfunction, unlike a planar ZnO nanoparticle layer.

In order to validate that the KPFM results on rough ZnO are not influenced by experimental factors and are inherent to the material properties, control experiment on an ITO-Ag grid sample with artificially created 25 nm high topographic features, was performed. While the topography image of control sample shows a 25 nm high step, the CPD was not found to be influenced by the high topographic features and a uniform CPD across the sharp step of 25 nm was found, as shown in Figure 10.5.



*Figure 10.5*: *KPFM image (5 X 5 micron) showing (a) topography (b) CPD of the ITO-Ag patterned surface.* 

This demonstrates the absence of any cross talk of signal while measuring CPD on rough surfaces with high topographic features. Thus, differences observed in CPD in case of rough ZnO can be entirely attributed to the inherent chemical and structural properties of the material.

## **10.5.** Conclusions

Workfunction measurements of sol-gel derived polycrystalline ZnO with a planar and rough morphology were performed using UPS and KPFM. From UPS studies, planar ZnO was found to have a workfunction of 3.7 eV, while a lower workfunction of 3.4 eV was measured in case of ZnO with a rough morphology. The UP spectra of nano-roughened ZnO had two onsets in the S.E. cut-off indicating electronic heterogeneity on the surface.

From KPFM studies, planar ZnO was found to have a uniform distribution of surface potential across the surface, whereas rough ZnO surface was found to have lateral variations in workfunction. Domains with a workfunction difference of ~ 0.1 eV were found across a small area of 500 nm x 500 nm, though the relation between the topographic features and the workfunction could not be established.

The significance of this study is twofold. Firstly, it is demonstrated that the workfunction of heterogeneous surfaces as measured from UPS is more representative of the species having the lowest workfunction in the heterogeneous system. Careful examination of the slope and shape of the UP spectra is thus critical in obtaining absolute workfunction values which are truly representative of the surface properties.

Secondly, in thin film devices, such heterogeneity in the electronic properties of materials could significantly influence the interfacial charge transport across materials and thus these findings could have strong implications on device design and understanding of device behaviour. While this study was limited to ZnO surfaces, the fundamental understanding of the morphology driven lateral variations of workfunction on a nanoscale would be useful for all thin film electronic devices.

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## **Chapter Eleven**

## Conclusions

This thesis presents the results of various studies performed on the electronic and chemical properties of interfaces and their influence on the overall device performance of OPVs. The device performance was found to be strongly dependent on the stability and electronic properties of interfaces in both conventional and inverted devices.

In conventional structured OPVs it was demonstrated that the indium and tin concentration profiles in PEDOT:PSS are not diffusion controlled but appear to be a result of etching by the PSS in PEDOT:PSS as they were found in ionic form. Humidity strongly enhanced the rate of migration, with up to 1 ion for every 4.7 monomer units in PEDOT:PSS present after 20 hours at 96 % RH. Devices incorporating PEDOT:PSS having controlled, predetermined indium and tin contamination showed a 65 - 75 % reduction in performance and displayed s-shaped J-V curves. These results now provide a basis for understanding the underlying cause for previous observations that moisture limited the device performance and lifetime.

The possible cause for the s-shaped J-V curves was identified as a change in the charge injection barrier at the ITO-PEDOT:PSS interface as a result of an increase in interfacial dipole formed by the indium and tin contaminations. Interestingly, exposure of ITO-PEDOT:PSS samples to humidity also reduced the electron density for the low binding energy states in PEDOT:PSS, which was proposed to be the second mechanism behind the reduced efficiency of devices on exposure to humidity.

As a result of these studies, it was observed that the role of water is so significant on device performance and presumably lifetime that conventional devices will struggle to be competitive and hence focus shifted to inverted devices.

The processing conditions and the layer thickness of ZnO as an electron transport layer between the bulk hetero-junction and the cathode in inverted OPVs were found to be crucial to achieve optimum device performance. Also, the surface topography of ZnO was found to have a significant influence on the local distribution of workfunction across the surface.

ZnO prepared via a range of methods such as sol-gel process, pulsed laser deposition and colloidal particles prepared in solution, was used as electron transport layer in inverted devices. In all cases, device performance improved as the thickness of the ZnO layer increased for thicknesses up to 100 nm. For laminated devices incorporating sol-gel prepared ZnO, device performance was found to increase significantly from 0.6 % to 1.7 % for ZnO layer thickness of 17 nm and 28 nm respectively. ZnO prepared via pulsed laser deposition was found to have a threshold thickness of 25 nm, and an improvement of over 75 % in the PCE was found when ZnO thickness was increased from 12 nm to 100 nm.

The mechanism postulated for the counter-intuitive performance improvement with thickness (up to 100 nm) was related to the nanostructure of the ZnO layers produced and their electronic properties.

The workfunction of the resultant sol-gel prepared ZnO layer was found to be independent of the layer thickness. A mixed phase interface model where the bulk hetero-junction penetrates the porous ZnO layer was proposed to explain the strong thickness dependence of device performance. Whereas in case of laser deposited ZnO, layers of up to 12 nm were not found to have a completely evolved band structure and the zinc oxygen stoichiometry was also found to be strongly dependent on the layer thickness resulting in oxygen deficiency in thick layers. Possible enhancement in conductivity as a result of oxygen deficiency and improved band structure were proposed to be the main cause for significant enhancement in device performance with increase in ZnO thickness.

Electronic properties of ZnO such as workfunction and electron affinity were shown to be strongly influenced by the changes in the surfaces chemistry, induced due to possible presence of any precursor impurities or changes in the Zn-O interaction. Device performance was found to be strongly influenced by post deposition annealing temperature of ZnO particle layer casted from a colloidal solution. Over 50 % improvement in the device efficiency was demonstrated by increasing the annealing temperature of ZnO from 150 °C to 250 °C. It was shown that annealing temperature of at least 200 °C was required to remove remaining fragments of precursor impurities and achieve ZnO with a favourable

workfunction and valence band maxima position. Relatively poor performance of devices in case of 150 °C annealed ZnO was mainly attributed to the significantly low electron affinity of resultant ZnO layers, which leads to zero energy offset between the conduction band of ZnO and the LUMO of PCBM.

It was shown that heterogeneous surfaces consisting of energetically different species could have different domains corresponding to multiple workfunction. Absolute workfunction value measured from such a surface using UPS was found to be dominated by the low workfunction material on the surface.

UP spectra from an artificially prepared surface made of ITO and Au with micron scale heterogeneity, was found to have distinct S.E. cut-offs corresponding to both ITO and Au, hence two distinct workfunctions. Though the slope and shape of the S.E. cut-off of the UP spectra was shown to be dependent on the surface coverage of Au on ITO, secondary emissions (and hence the workfunction) from low workfunction material; in this case ITO were always found to dominate the spectra while the Au contribution was found to be underestimated. A mechanism in which a higher fraction of secondary electrons are able to pass through the lower workfunction interface than from the higher workfunction interface, was proposed to explain this phenomenon

Identifying this phenomenon using UPS on a control binary system as that of ITO and Au, which are known to have distinct workfunction is relatively easy compared to polycrystalline materials with inherent distribution of workfunction on a nanoscale. It was shown that on careful examination of the slope and shape of S.E. cut-off of UP spectra, information about any possible local variations of workfunction in a polycrystalline material could be obtained.

For example, KPFM studies showed that ZnO surface with nano-roughened ripple morphology have significant lateral variations of as much as 0.1 eV in the workfunction across a small area of 500 x 500 nm. While such local variations were found to be quiet evident from KPFM, the results would not have been so obvious from UPS measurements without the understanding that was developed in this work from UPS studies on ITO/Au heterogeneous system.

While this PhD work was focussed on studying the interfacial properties of conventional and inverted OPVs, the fundamental understanding of the factors influencing the interfacial

energetics and charge injection barriers in a working device, which has been demonstrated in this research are relevant to a wide range of organic electronic devices incorporating similar materials in device structures.

Workfunction studies on heterogeneous surfaces also highlights the importance of correctly interpreting the shape and slope of the secondary electron cut-off in a UP spectrum in order to derive absolute workfunction values which are an actual reflection of the surface properties. For thin film devices, variations of surface potential of this magnitude, if go unnoticed, can potentially have critical implications on the interfacial energetics and charge transport. Thus, results of this study are not only very important for the surface science community where UPS is used as a method of choice for measuring workfunction of materials, but these findings could potentially be useful in better understanding the behaviour of thin film devices.

"The scientific man does not aim at an immediate result. He does not expect that his advanced ideas will be readily taken up. His work is like that of the planter — for the future. His duty is to lay the foundation for those who are to come, and point the way. He lives and labors and hopes."

- Nikola Tesla