New Architectures and Designs for Organic Photovoltaics

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DECLARATION

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

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DEDICATION

To everybody in the audience -

ACKNOWLEDGMENTS

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ABSTRACT

The field of organic photovoltaics has seen many significant findings over the last two decades. It is now a very active area of research generating thousands of publications, resulting in advancements in a multi-disciplinary setting. The research described in the body of this thesis aims to investigate the use of new materials and architectures in the fabrication of organic photovoltaics. An approach to incorporate carbon nanotube-Buckminster fullerene hybrid materials into the blended active layer of organic photovoltaic devices is introduced and the effects on devices are elucidated. It is found that the use of cut (barrel) single walled carbon nanotubes was the least detrimental to device performance. The use of alternative methods to fabricate or replace commonly used materials and inter-layers (PCBM, ITO, PEDOT:PSS) in the device structure are presented. The use of thin metal films such as silver and gold is shown to be viable and interesting alternatives to ITO. Layer-by-layer assembly of PEDOT:PSS and electrochemically deposited alternatives are found to have similar performance to standard devices. The fabrication and characterization of a new vertically orientated organic photovoltaic device architecture, the stack device, is presented with a proposed optical model to describe the experimental findings. In particular, the optical mechanism responsible for the operation of the stack device is determined to be frustrated total internal reflection. The new architecture is applied to the fabrication of devices using the standard P3HT:PCBM active layer resulting in an increase in performance.

CHAPTER 1.

Introduction

1.1 Motivation for developing renewable energy alternatives

The unsustainable rise in energy demand across the globe is one of the greatest problems facing society. Figure 1.1 is an example of the drastic projected rise in oil consumption faced by developing economies such as China over the next quarter of a century. As of June 2011, the world consumption of oil approached 90 million barrels per day [1] — the projection for 2035 from the Earth Policy Institute (EPI) [2] predict that China will almost match 2010 world consumption levels (Figure 1.2) in 25 years. This staggering projection is based on China's energy demand reaching the same per capita levels as developed nations.



Source: EPI from BP, UNPop, IMF

Figure 1.1 Oil consumption in the United States and China in 2010 and the projected consumption level for both countries in 2035 from the Earth Policy Institute [2].



Figure 1.2 World oil consumption from 1965 to 2010 [1].

As a result of the world's reliance on fossil fuels, pollution and climate change are becoming a dominant driving force influencing the world's populations to highlight the need to bring about change sooner rather than later. In 1997 the Kyoto Protocol to the United Nations Framework Convention on Climate Change was adopted and subsequently was entered into force from 2005. It was initially heralded as a unified solution signed by 37 industrialized countries and the European community to stabilizing or reducing greenhouse gas emissions and averting the catastrophic consequences predicted with allowing emission levels to rise unchecked [3,4]. The world use of energy per capita (tons of oil equivalent) is shown in Figure 1.3 [1]. It is clear that once consumption per capita of lesser developed nations begins to mirror that of the industrialized nations, the demand for energy will approach unprecedented and completely unsustainable levels.



Figure 1.3 2010 Equivalent (tons of oil) energy consumption per capita. [1]

The difficulties associated with the effectiveness of the Kyoto Protocol have been evident from its inception, especially seeing that one of the largest contributors to climate change such as the US has no intention of ratifying the protocol but rather at best, pledging to bring about change in their emissions. As a result of the global economic downturn, countries that have signed up to the protocol are considering leaving; recently Canada formally announced their withdrawal from the Kyoto Protocol. 2012 marks the end of the first commitment period of the Kyoto Protocol, unfortunately a new international framework has yet to be fully negotiated — it is clear that one of the only ways to further the important goals of reducing greenhouse gas emissions is by working to realize new inexpensive technologies than can compete economically with fossil fuels.

Until recently the topic of energy security was relatively muted in the main-stream media. It has been overshadowed by the international military campaigns led by the US and UK since 2001 which some may debate are one and the same thing. The issue of energy security is now coming to the fore as a result of the volatility and unpredictability of the world's major energy suppliers based in the Middle East and Russia — it has been evident that when political pressure is to be exerted it may easily be done by restricting flow or even turning off a gas pipeline.

With such a grave outlook on energy security for the future, the major energy companies are investing heavily and stepping up their exploration efforts in more stable but traditionally expensive regions. Countries are now seeking any means possible to reduce their dependence on foreign energy markets by developing their own national resources in an effort to reduce their dependence on foreign energy sources. In many countries this has led to the massive surge in renewable energy over the last decade. The EPI recently published data on world energy generation detailing the promising growth from 2000 - 2009 in renewable and more environmentally sustainable energy sources shown in Table 1.1.

Energy Source	Average Annual Growth Rate	Compound Annual Growth Rate
	(%)	(%)
Wind Power	27.9	31.8
Solar Photovoltaics	35.2	36.1
Geothermal Power (2000 - 2010)	3.0	3.0
Geothermal Heat	19.1	16.5
Hydroelectric	2.3	2.4
Oil	1.1	1.1
Natural Gas	2.4	2.2
Nuclear Power	0.7	0.5
Coal	3.9	3.8
Biodiesel	38.6	40.0
Fuel Ethanol	15.1	17.5

Table 1.1 World energy growth rates by source (2000-2009) [2].

1.2 The Potential of Renewable Energy

The potential of renewable energy to be a large contributor to solving the world's problems associated with energy supply and demand is unique. In terms of land usage, the return on investment for developing a wind farm to generate and sell energy compared to a standard agricultural enterprise (crops, animals) is in general more economically productive. In the US there are a number of states with great potential for wind energy as illustrated by the US wind map (Figure 1.4) where areas with an annual average wind speed of ~6.5 m/s at a height of 80 m height are considered viable for wind development [5]. Texas, historically the leading oil producing state has now become the largest producer of wind energy (~10,000 MW in 2011 according to the American Wind Energy Association) and as a result of the large number of projects

under construction it will soon be a net exporter of wind generated energy as a planned total of 50,000 MW comes online in the future [2].



Figure 1.4 The U.S. wind map shows the predicted mean annual wind speeds at an 80-meter height (at a spatial resolution of 2.5 kilometers that is interpolated to a finer scale) [5].

There are vast areas of land across the globe scorched by the sun, typically there is little or no opportunity for irrigation to sustain crops or animals but encouragingly these areas are ideal for large-scale photovoltaic installations. The growth of the installed world capacity of solar energy from 1996 to 2010 is close to exponential in Figure 1.5. It is currently being led by Europe (in 2010 Germany ~ 17000 MW), however the solar energy potential map shown in Figure 1.6 displays that the US with only ~1600 MW in 2010 has huge potential to become a dominant contributor to solar energy production.

Almost one quarter of the world's population do not have access to domestic electricity and 80 % of these people live in rural areas and on the periphery of urban zones of developing countries [6]. For developing nations the challenge of providing electricity to remote areas by means of installing transmission lines and constructing a modern electrical grid is the prohibitive cost. Solar and other renewable energy sources are now being viewed as a much more cost-effective means of supplying energy to these currently under-developed regions. The initial capital outlay required to setup renewable energy power plants and small scale production to support micro-grids in remote and poorer regions is being covered by loans from the World Bank and grants from the Global Environment Facility in an effort to raise the standard of living in a sustainable an economically viable way [7]. These steps also aid in the reduction of local air pollution by reducing the reliance on diesel generators and fossil fuel based generation methods that are part of the standard environmental policy for most nations.



Figure 1.5 World installed solar capacity from 1996 to 2010.



Figure 1.6 The U.S. solar energy potential map [8].

1.3 Organic Electronics

Electronics based on organic materials are most notably associated with polymeric conductors and the so-called synthetic metals. It is the presence of π -conjugation, a system of alternating single and double bonds that allows for the electrical conduction based on a type of charge transport that is quite different from that defined in classical solid-state physics. Indeed the one similarity between organic and inorganic materials is that their respective electronic and optical properties are closely tied together.

The field of organic electronics has matured to a level where the commonplace inorganic-based devices and components may be replaced by organic-based alternatives. A very comprehensive and excellent review on the development of the field is given by Moliton *et al.* and the following introduction is aligned with the opinions expressed in their review article [9]. The foundations of modern-day organic electronics and optoelectronics are often cited to be grounded on the pioneering work of Brédas *et al.* in 1982 [10] concerning the doping of conjugated polymers and the comprehensive study on "solitons in conducting polymers" by Heeger *et al.* in 1988 [11].

The first breakthroughs in the field were most notably the development of organic light emitting diodes (OLEDs) in 1987 by Tang *et al.* based on small molecules, 8-

hydroxyquinoline aluminum (Alq3) [12] and in 1990 by Burroughs *et al.* using a polymeric material, poly(para-phenylene vinylene) (PPV) [13]. The rapid pace of the success of these electroluminescent devices was a major stimulus behind the development of devices operating based on a principle mirroring electroluminescence — organic photovoltaics (OPVs), where light is absorbed with the creation of mobile charge carriers. The use and application of organic semiconducting materials in photovoltaics started slowly seeing low power conversion efficiencies (PCEs) in Schotky-type photodiodes. The first OPV having appreciable PCE of ~1 % was a two layer device reported in 1986 by Tang [14]. Subsequently the pace of developments gathered momentum with the revelation of donor-acceptor based device structures exhibiting photo-induced electron transfer from the excited state of a conducting polymer onto buckminsterfullerene (C₆₀) in 1992 by Saricifciti *et al.* [15]. This ultimately led to the concept of the bulk-heterojunction [16], a donor-acceptor blended layer still heavily under study today.

The relatively high cost per watt and limited advancement of mainstream, traditional inorganic photovoltaics places the emerging technologies of OPVs as the next logical material of choice for solar energy generation. The huge advantage of working with organic materials to fabricate the so-called next generation 'plastic solar cells' is their ease and simplicity of manufacture compared to that of inorganics. Solution processable materials utilized to make OPVs by means of a continuous roll-to-roll method will no doubt become commonplace. With such advantages and the exponentially rising demand and implementation of renewable energy sources across the globe, the projected market for OPVs is \notin 600 million in 2015 and \notin 3.4 billion in 2020 [9].

1.4 Challenges associated with organic photovoltaic technologies

The potential to increase efficiency and significantly reduce the cost per watt for photovoltaics can be achieved by use of organic materials, provided that the method to retrieve the charge carriers is tailored to the materials. The work in developing OPVs since the 80's to the present day has focused on getting organic semiconductors to mimic their inorganic counterparts in terms of their device fabrication and architecture. However, this has by necessity resulted in devices that have so far not reached their potential.

The ability to precisely engineer each layer of the OPV device is of paramount importance to the success of this field. To date the most widely used and studied materials employed in the fabrication of OPVs are not an ideal combination. Each material is chosen such that the electronic and optical properties are as closely matched as possible to that of an idealized device: in reality a balance of the inherent deficiencies of the chosen materials has to be made. It is clear that the choice of a certain transparent electrode having a particular work function or an active layer whose absorption profile matches a certain portion of the solar spectrum ultimately limits the other material choices in the device.

The morphology of the active layer is defined by the arrangement (shape, size, location) of the donor and acceptor materials. The fabrication processes employed to deposit the active layer do not yield identical morphologies but rather on average tend to yield similar device performance given the same processing conditions (spin-speed, solvent annealing time, oven temperatures). The active layer may be considered as a disordered structure relying on the particular alignment of polymers and molecules separated into crystalline and amorphous domains in a nano-scale, ultra-thin film, typically less than 100 nm in thickness.

There is one particular restriction observed in OPVs that is related to the interdependency of charge carrier extraction by percolative pathways through the respective conducting donor and acceptor moieties and the limitations imposed on this process by an increasing active layer thickness to improve optical absorption. This

limitation is compounded by the dynamics of the localized excited state (exciton) generated upon absorption of a photon. In order to achieve free charge carriers, the exciton must be dissociated at a hetero-interface within a small diffusion distance or else the energy may be lost to decay processes.

It is clear that a high level of interdependence is present between the materials used in device fabrication and as a result it is of great interest to further study and develop these materials. This may be achieved either by the addition of new materials, modification of deposition techniques or the use of alternatives having similar electronic and optical properties to the standard device structure In this thesis, issues that are of significant interest in the development of OPVs are addressed by building OPV device architectures in a manner that suit the material rather than mimicking those developed for inorganic photovoltaics.

1.5 Thesis Structure

The subsequent chapters of this thesis are devoted to the exploration of the materials and architectural modifications of OPVs. The thesis is structured and summarized below:

Chapter 2: Experimental Techniques, Materials Preparation and Fabrication

This chapter is concerned with the experimental apparatus used in the characterization of the materials discussed in this thesis. The synthesis and special preparation steps necessary to prepare the materials used are described. The general fabrication methods employed to build the organic photovoltaics are detailed along with a full description of the processes involved. The experimental setup for testing the organic photovoltaics is detailed and illustrated.

Chapter 3: Theoretical Background

The focus of this chapter is to introduce the theory behind the materials used in the fabrication of OPVs and to detail the important processes required for their operation and characterization.

Chapter 4: Conductivity, Charge Transport, Organic Photovoltaic Devices and Optical Processes

This chapter describes the processes behind conductivity in organic materials with a focus on charge transport through percolative processes such as hopping. The standard OPV device architecture is introduced and their subsequent electrical and optical characterizations are detailed.

Chapter 5: Modification of the active layer

The modification of the active layer with hybrid additives SWCNT(B)-C60 is presented. The results of the various characterization techniques (UV-vis, RAMAN) used to investigate the properties of the materials are outlined and discussed. Finally the electrical characterization of the fabricated OPV devices is given at the end of this chapter.

Chapter 6: Modification of OPV device interlayers and materials

The common issues observed when dealing with ITO anodes and the PEDOT:PSS hole transport layer are presented. Methods and modifications to the standard OPV device structure are detailed in terms of replacing ITO with more flexible and less reactive metals. The replacement of PEDOT:PSS using two different electro-chemically deposited thin films is shown to be viable. Finally a study concerning the use of newly developed C_{60} adducts in the place of PCBM is outlined for an OPV device structure that does not use LiF or Ca as an interlayer before Al deposition.

Chapter 7: The Stack OPV device design, characterization and modeling

An introduction to the OPV device design used in the fabrication of the stack architecture devices is presented. The discussion is then focused on the experimental results observed and the description and analysis of an optical model used to determine the origin of the phenomena observed in the stack OPVs.

Chapter 8: Summary and Conclusions

This chapter gives a brief overview of the work presented in the thesis. It is followed by a number of directions for further work and improvement of OPV devices.

1.6 References

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CHAPTER 2.

Experimental techniques, materials preparation and fabrication

2.1 Introduction

This chapter outlines the various experimental techniques used in the characterization of materials and device structures implemented throughout this thesis. A description of the synthesis procedures carried out in addition to the as received materials is given in order to allow the reproduction of the experiments detailed. An overview of the equipment required in building the OPV devices and how they operate is supplied for reference. The fabrication processes used in the building of organic photovoltaic devices are discussed; including substrate properties, cleaning procedures, spin coating, physical vapor deposition and encapsulation. The electrical characterization setup used to test the performance of fabricated devices is outlined with reference to the inert storage environment (glovebox), light source, reference cell calibration, probe tips, sourcemeter, data collection and analysis software.

2.2 Spectroscopy

Spectroscopy is the generalized term given to the study of the interactions between matter and electromagnetic radiation. It is clear that the various spectroscopic instruments available today are highly important tools used to improve our understanding of many complex systems. The majority of the electromagnetic spectrum may be used to study matter, however for applications involving organic materials the spectrum is divided into a number of different portions that that yield the most information. These spectral ranges, their effect on the molecule and information obtained from analysis of the data are reproduced from references [1] and [2] in Table 2.1. The forms of spectroscopy used in this thesis involve the determination of the properties of materials by means of the analysis of its absorption and emission profiles.

Radiation absorbed	Effect on the molecule (information deduced from data analysis)
X-ray	techniques such as photoelectron spectroscopy probes the transitions
\bar{v} , 10 ⁶ - 10 ⁸ cm ⁻¹	between energy levels of inner electrons of atoms and molecules
Ultraviolet-visible	changes in electronic energy levels within the molecule (extent of $\pi-$
λ, 190 - 400 nm	electron systems, presence of conjugated unsaturation, and
& 400 - 800 nm	conjugation with nonbonding electrons)
Infra-red	changes in the vibrational and rotational movements of the molecule
λ, 2.5 - 25 μm	(detection of functional groups, which have specific vibration
$ar{v}$, 400 - 4000 cm ⁻¹	frequencies, e.g. C=O, NH ₂ , OH etc.
<i>Microwave</i> υ, 9.5 x 10 ⁹ Hz	electron spin resonance or electron paramagnetic resonance; induces
	changes in the magnetic properties of unpaired electrons (detection of
	free radicals and the interaction of the electron with, e.g. nearby
	protons)
<i>Radiowave</i> υ, 60 – 300 MHz	nuclear magnetic resonance; induces changes in the magnetic
	properties of certain atomic nuclei, notably that of hydrogen (hydrogen
	atoms in different environments can be detected and counted, etc.)

 Table 2.1 Summary of analytical techniques used to obtain spectroscopic information on various organic materials. Adapted from [1].

The following text describes the spectroscopic techniques utilized to investigate the properties of the organic materials used throughout this thesis.

2.2.1 Ultraviolet visible (UV-vis) absorption

Ultraviolet visible absorption spectroscopy is an analytical technique used to determine the degree of absorption of ultraviolet/visible radiation by a sample. When broadband electromagnetic radiation is passed through a transparent material, a fraction of it is absorbed. The remaining light may then be dispersed through a prism to observe the missing portions of the spectrum denoted as an absorption spectrum. The absorption of light by the material leads to electronic energy level transitions and indeed it is appropriate to more accurately label UV-vis spectroscopy as electronic spectroscopy.

In terms of this thesis, the study of conjugated polymers using UV-vis absorption spectroscopy is of paramount importance. It is a very useful tool to investigate the suitability of a material for a photovoltaic device. By comparing the absorption spectrum of a thin film of the material with that of the solar irradiation spectrum we can

estimate the amount of sunlight that will be harvested within that potential active layer. Indeed looking at the complex absorption spectra of the active layer blend, P3HT:PCBM which are electron donating and electron accepting materials respectively, we can deduce the approximate band-gap. Investigating these underlying electronic properties such as optical band-gap is crucial for determining the possible efficiency of devices — only light at energies above the band-gap (resonant light) will be absorbed and possibly converted into useable charge carriers.

UV-vis spectra may also be used to compare the effect of slight modifications to the active layer. It is clear that by using different processing conditions (detailed later on in this text), changes in the absorption spectra are observed especially for solid state samples spin-coated onto glass substrates. There is evidence of links between active layer crystallinity and absorption peak positions [3]. There are rather large limitations on the choice of solvent for these materials as aggregates formed in the solution lead to poorly performing devices once the blend is spin-coated on the substrate to form the active layer.



Figure 2.1 Diagram of the experimental setup for UV-vis absorption spectroscopy.

All UV-vis absorption spectra presented in this thesis were obtained with an Ocean Optics HR2000+ high resolution spectrometer at room temperature using a Mikropack PH-2000-BAL deuterium-halogen light source. The experimental setup is shown in Figure 2.1. The data was recorded using the manufacturer supplied software package Spectra Suite. Samples were prepared for measurement as a solution or in the sold state. In solution, different solvents were selected for the material in order to ascertain their suitability for device fabrication. The sample was diluted in an appropriate solvent to a low enough concentration to obtain an unsaturated spectrum; a standard glass cuvette

was used. Solid state samples were spin-coated on a glass substrate using predefined parameters for comparison to the specific device structure of interest; a cleaned glass substrate was used for each measurement as a reference.

2.2.2 Photoluminescence (PL) emission

PL measurements were obtained using an Ocean Optics QE65000 spectrometer. The excitation source was a Stellar-PRO-Select 150 Argon ion laser with tunable output intensity. The 514 nm laser line was selected to obtain the maximum PL intensity for the samples. The experimental setup for PL measurements is illustrated in Figure 2.2. Excitation light from the laser source is directed at the sample which is placed in a mount at an angle relative to the laser beam path. This ensures that a large portion of the incident laser light intensity is reflected away from the detector allowing the lower intensity PL to be collected. An optical filter specific to the excitation laser wavelength is used to block any stray laser light from being detected. The PL is collected and collimated through the collimator and finally is focused onto an optical fiber coupled to a spectrometer for measurement and recording.



Figure 2.2 Diagram of the experimental setup for PL measurements.
2.2.3 Raman

Raman Spectroscopy is a very powerful analytical tool used to reveal the nature of vibrational / rotational transitions and low frequency modes in liquid, gaseous and solid samples such as molecules, crystals, powders, and biological media. Analysis of Raman spectra can yield information on the bonding, structure, symmetry and even electronic transitions between ground states and low lying excited energy states when working with resonance Raman spectroscopy [2,4].

In general, the spectra recorded for Raman spectroscopy are displayed as a shift from the incident beam frequency. Raman spectra were collected using a Horiba J-Yvon LabRam HR800 confocal Raman imaging microscope system. The source was a 660 nm semiconductor diode laser with maximum power of 50 mW at the sample. The Raman band of silicon (520.7 cm⁻¹) was used to calibrate the spectrometer, yielding a dispersion better than 1 cm⁻¹ using an 1800 lines/mm grating. Raman samples were prepared by spin-coating the material under investigation onto a clean silicon wafer.

2.3 Materials Synthesis and Preparation

The materials used to fabricate the various kinds of OPV devices are introduced in this section. Their chemical properties and structures are given for reference. The majority of materials were used as received; any additional treatment or modification is detailed.

2.3.1 Electrode Materials

Indium tin oxide (ITO)

In general the anode material used was indium tin oxide (ITO) used in the form of coated glass slides (Sigma-Aldrich) referred to as substrates. The ITO coating on the glass substrates is a transparent conductive oxide having a typical sheet resistance of 8 – 12 Ω /square and an optical transparency greater than 85% at 500 nm. Ideally, a lower sheet resistance results in a higher performance device as resistive losses impeding charge collection at the anode are minimized.

Silver (Ag) / Gold (Au)

A simple physical vapor deposition process was developed using the evaporator system for Ag and Au resulting semi-transparent (25 – 40% at 500nm) thin films with sheet resistances as low as 2 Ω /square. The use of these thin metallic films for anodes is advantageous because they are far more flexible than ITO.

Aluminium (Al)

Al is typically used as the cathode material for OPV devices due to its moderately low work function. Although it is sensitive to air and moisture it is still the most widely used cathode material for the stand layout OPVs. Most commonly it is physically deposited by thermal evaporation onto the active layer at a low pressure ($\sim 10^{-6}$ mbar). Aluminium was used exclusively throughout this work as the cathode material deposited by thermal evaporation. There are other choices available for the cathode such as Ca and Mg alloys, however these materials are very reactive adding more mechanisms for device degradation and failure.

2.3.2 Hole Transport Layer (HTL)

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

The hole transport layer (HTL) used for the standard devices referred to in this thesis is poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) which is sourced from Heraeus under the product name "Clevios PH 1000". This material is in an aqueous solution which has advantages in terms of ease of processability. In general it may be spin-coated or printed onto a rigid or flexible substrate.



Figure 2.3 Structure of PEDOT:PSS

Poly(N-vinyl-carbazole) (PVK) [5]

Materials. All chemicals were purchased from Aldrich and were used without further purification unless otherwise indicated. Tetrahydrofuran (THF) and toluene used in the synthesis and polymerization reactions, respectively, were distilled from sodium/benzophenone ketyl.

Synthesis of Cbz-CTA. The synthesis of 3,5-bis(4-(9H-carbazol-9-yl)butoxy)benzyl 4cyano-4-(phenylcarbonothioylthio)pentanoate (Cbz-CTA) was prepared as previously reported by Patton et al [6]. Electro-deposition of the CTA on ITO or Au surface. Electrochemical deposition of Cbz-CTA was performed using a Parstat 2263 (Princeton Applied Research) instrument equipped with PowerSuite software. All experiments were carried out using a three electrode set-up where the ITO or Au substrate was used as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. A solution of the CTA (0.5)mM) and the supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAH) (0.1 M) in THF was used for preparing the electrogenerated CTA film. A constant potential of 1.2 V was applied on the surface for 3 minutes to deposit the CTA on the surface.

Surface-initiated RAFT polymerization of vinyl carbazole. A solution of the 9vinylcarbazole (VK), azobisisobutyronitrile (AIBN) (VK:AIBN = 2500:1), and dry toluene was degassed in a Schlenck tube by bubbling with N₂ for 30-45 minutes. The degassed solution was transferred to another Schlenck tube backfilled with N₂ containing the CTA-modified ITO or Au through a cannula. The tube was placed in a preheated oil bath at 90°C for 24 hours. The modified slides were then subjected to Soxhlet extraction overnight to remove any unbound polymers.



Figure 2.4 Process for deposition of PVK onto an ITO substrate

2.3.3 Active layer materials

P-type polymers

Poly(3-hexylthiophene-2,5-diyl), (P3HT), 98% regioregular, average M \sim 87,000. Sigma-Aldrich used as received.



Figure 2.5 Structure of P3HT

Poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4- phenylene vinylene), (MDMO-PPV), was sourced from Sigma-Aldrich and used as received.



Figure 2.6 Structure of MDMO-PPV

N-type materials

Fullerene- C_{60} (98%) was sourced from Sigma-Aldrich and used as received.



Figure 2.7 Structure of C₆₀

1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]- methanofullerene, (PCBM), (> 99%), was sourced from Sigma-Aldrich and used as received.



Figure 2.8 Structure of PCBM

C₆₀ mono and bis-adducts

Indene-C₆₀ adduct

Materials. All chemicals used for the synthesis of the indene- C_{60} adducts were sourced from Sigma-Aldrich and used as received.

Synthesis. The synthesis procedure follows that of Zhao et al [7].



Figure 2.9 Diagram depicting synthesis of Indene-C₆₀ adducts.

2.3.4 SWNT(B)-C₆₀ hybrid additives

Syntheses and preparation of SWNT(B)

SWNT Fluorination. SWNTs were cut using a previously published method [8]. Initially SWNTs (produced by the HiPCO process) were fluorinated in a custom built fluorination reactor, using a flow gas of 10% F_2 in N_2 at 125 °C. The flow rate was set to 15 sccm. Additionally a flow of 2% H_2 in N_2 was introduced into the reactor at a rate of 10 sccm. After 3 hours the reaction was complete, the F_2 and H_2 were turned off and the reactor was then purged with Ar at 1000 sccm for a period of 15 minutes. Vacuum was then pulled on the system for 15 minutes. Ar was then flowed back into the reactor and the reactor is opened and the sample was removed.

Cutting of fluorinated SWNTs to form SWNT(B). After fluorination, cutting of the CNTs was achieved via pyrolysis. The SWNTs were placed in a ceramic crucible and heated to a temperature of 1000 °C resulting in etch-cut barrel-SWNTs (SWNT(B)). The barrel-SWNTs were further purified by sonication with 36% HCl for 30 minutes to remove any remaining catalyst or impurity. The average length of the resulting barrel-SWNTs is ~ 60 nm, which was estimated by AFM.

Syntheses of SWNT- C_{60} hybrids

Long or barrel-SWNTs (SWNT or SWNT(B)) were used to fabricate the hybrids following a published method [9].

Amination of SWNTs. SWNTs (200 mg) and polyethylenimine (2 g) were mixed in 20 mL of DMF. Sonication for 20 minutes and stirring at 100 °C for 5 days formed the product, SWNT-PEI 10,000. The resulting suspension was filtered through a 0.20 μ m nylon membrane and the precipitate was washed with 1M HCl, 1M NaOH, water and methanol to remove any excess PEI. After drying, 293 mg of the product was obtained.

Functionalization with C_{60} . SWNT-PEI 10,000 (100 mg), fullerene-C₆₀ (50 mg) and triethylamine (0.5 mL) were mixed in 10 mL of chlorobenzene. Sonication for 1 minute and stirring at 100 °C for 6 days formed the product, SWNT-C₆₀ hybrids. The resulting suspension was filtered through a 0.20 µm nylon membrane and the precipitate was washed with chlorobenzene and chloroform to remove any excess C₆₀ and triethylamine. After drying, 118 mg of the product was obtained.

2.4 Fabrication Equipment

2.4.1 Sputtering

A "Denton Desk V" DC sputtering unit, illustrated in Figure 2.10 was used to deposit all Au contacts and interconnects referred to in this thesis. Sputtering is a plasma-assisted, low temperature, physical vapor deposition technique that relies on an ionized gas environment containing active electrodes that take part in the deposition process.



Figure 2.10 Diagram of the DC sputtering apparatus.

In the case of DC (diode or cathodic) sputtering, a target material is positioned in the vacuum chamber and connected as a cathode. A DC voltage, typically several kV, is applied to a cathode that is directly above the sample or substrate to be coated at the anode which is grounded. The vacuum chamber is pumped down to the sputtering set point $\sim 30 - 50$ mTorr and Ar gas is introduced into the vacuum chamber to act as a medium for the initiation and maintenance of an electrical discharge. Provided the vacuum chamber is kept near the sputtering set point, a glow discharge is visible and a current flows between the electrodes indicating that the cathode material is being deposited on the substrate. This process occurs because the positive Ar ions (Ar⁺

plasma) generated across the electrodes physically interact with the Au target. The Au atoms are ejected or sputtered through momentum transfer. The Au atoms enter the glow discharge area and travel to the anode resulting in the deposition of the target material and growth of a thin film [10].

2.4.2 Thermal Evaporation System

Thermal evaporation is a physical vapor deposition technique which is capable of depositing thin films ranging in thickness from a few nanometers up to several microns. Typically a thermal evaporator is housed in a high vacuum chamber and the system comprises a heated source material from which atoms are transferred to a substrate where a thin film is grown over time. This process is achieved by heating the source material to a high enough temperature so that it evaporates.



Figure 2.11 Custom built thermal evaporator system bell jar configuration diagram.

Throughout this work electrode deposition was carried out using a custom built thermal evaporation system. The bell jar section of the thermal evaporator is drawn in Figure 2.11. It consists of a glass bell jar which is sealed using a rubber gasket to a stainless steel face-plate. The face plate was custom designed and fabricated by Kurt J. Lesker. It has a number of feedthroughs including: a 0.25" NPT for venting the sample chamber with N₂ gas; four ceramically isolated electrical wires used to operate the electrical shutter and resistance monitor; two copper evaporation feedthrough posts; and a fiberoptic SMA cable adapter accessory. The thermal evaporation feedthrough posts are modified to hold a tungsten wire evaporation basket (EVB2040W - Kurt J. Lesker) which is resistively heated by a high current source (ZUP20-40 - TDK lambda). The evaporation basket holds the source material usually consisting of highly pure pellets or ingots. The evaporation basket can reach temperatures as high as 1800°C under vacuum at an applied current of 36 A. An electrically powered motor was incorporated into the sample stand in order to actuate a metal shutter mechanism which shields the samples from the initial oxidized and contaminated metals during the early stages of evaporation. A double-pull-double-throw (DPDT) switch attached to a 12 V power supply is used to move the shutter in two directions allowing for accurate movement and positioning. The sample stand is also used to position a sample holder having a conical geometry designed to position each device substrate at an equal distance from the point source. This ensures that the deposited film is uniform across the entire substrate area.

Figure 2.12 displays the configuration of the evaporation system below the bell jar. The face-plate is connected to the vacuum system by means of CF flange terminated piping utilizing knife-edge seals which physically deform copper gaskets to maintain a high-vacuum. A manually actuated, bellows sealed gate-valve (Kurt J. Lesker) is used to isolate the sample chamber from the pumping station. Two compact full range gauges (PKR 251 - Pfeiffer Vacuum) are placed above and below the gate-valve so that the pressure in the system may be monitored when the gate-valve is open or closed. The two full range gauges are connected to a dual-channel measurement and control unit which the displays the system pressure on an LCD screen.



Figure 2.12 Diagram of the evaporation system components below the bell jar.

The gate-valve opens to a combined turbo-molecular and roughing pump system (HiCube 80 Eco – Pfeiffer Vacuum) which is capable of pumping down the system to a final pressure of 1×10^{-6} mbar. This is higher than the rated pressure (1×10^{-7} mbar) for the pumping station due leaking at the various seals and degassing of the internal surfaces of the system.

Our custom setup does not have a crystal thickness monitor installed to precisely control the thickness of the thermally evaporated films, however, the deposition of Al for the cathode does not require an extremely accurate control for thickness. The resistance of the thick Al layer is more important and as such, a resistance monitor was developed and incorporated into the thermal evaporation system. The resistance monitor consists of a cleaned glass slide attached to two electrodes connected to two of the electrical feedthroughs across which the resistance could be measured externally by a multimeter.

2.4.3 Substrate cleaning and ultrasonication

Cleaning substrates is extremely important especially considering the ultra-thin device layers involved. The removal of possible contaminants and particulates from the substrates is necessary to ensure the layers and interfaces created are clean and of the highest quality.

Ultra-sonication in various treatment baths can be used as a reliable technique to remove organic contaminants such as oils and salts. Particulates such as dust or lint collected from the air which statically adhere to the substrate surface are particularly troublesome when fabrication is done outside of a clean room environment. The presence of these particles on the substrate lead to pin-hole defects in the spin-coated layers and consequently electrical shorts across the device created during electrode evaporation.

2.4.4 UV / O₃ treatment

The UV / O_3 treatment apparatus (Novascan PSD) utilizes a strong UV light source (185 and 254 nm) to remove organic contaminates. The strong UV light ionizes the oxygen in the ambient air creating a significant amount of O_3 . The O_3 reacts with almost any surface it comes into contact with. In the case of ITO substrates, it causes the surface to activate and become more hydrophilic.



Figure 2.13 Diagram of the Novascan PSD ozone treatment system

2.4.5 Spin Coating

Spin-coating is used to deposit solution-processable materials onto a variety of substrates. It is widely used to deposit photo-resist onto Si wafers in the semiconductor industry. More recently it has become very popular as a thin film deposition technique used in the fabrication of OPVs. It is possible to attain highly reproducible thin film layers provided adequate monitoring and control of the processing conditions are maintained.

The spin-coating process involves a number steps in the formation of a uniform thin film. A small volume of the material (depending on viscosity and substrate size) to be spin-coated is deposited onto either a stationary substrate (static deposition) or a rotating substrate (dynamically deposited). The technique employed in this thesis is static deposition. Once the material is applied to the substrate, a program controlling spin-coating process steps such as time intervals, acceleration and spin speeds is activated. The most simple spin-coating process programs typically consists of an acceleration step (~ 500 RPMs⁻²), followed by an interval at a high spin speed (500 – 4000 RPM) and then a deceleration to rest at the end of the program. As the spin-coater accelerates the rotation of the substrate to the high spin speed step, the majority of the applied solution is removed due to the rotational motion. Once at the high spin speed, the layer becomes thinner and smoothens out over time until it is almost completely dry as the solvent evaporates. The thickness of the resulting spin-coated thin film is determined by the high spin speed step.



Figure 2.14 Diagram of a spin-processing unit

All spin-coating procedures were carried out using a Laurell WS-400B-6NPP-Lite spin processor.

2.4.6 Polycarbonate glovebox system

A glovebox is necessary in order to protect the sensitive Al layer from degrading in the presence of oxygen and moisture. A polycarbonate glovebox (Terra Universal) was modified to allow for additional recycling of the inert gas atmosphere (Figure 2.15).



Figure 2.15 Diagram of the glovebox system

A small laboratory vacuum pump was used to pull gas from the glovebox system and push it through three molecular sieve drying columns before it re-entered the glovebox. A low flow of inert gas (1 standard cubic cm per minute [sccm]) is applied to the system to maintain positive pressure. The gas recycling and drying system allowed the glovebox system to reach a relative humidity (RH) of ~7% which greatly improves the device environment compared to ambient conditions ranging from 50 – 70 % RH.

2.5 Fabricating Organic Photovoltaic Devices

The processing steps followed to fabricate an organic photovoltaic device are relatively straight-forward, however, each step must be carried out meticulously to achieve a working device and reproducible results. The following sections are dedicated to the description of each step of the fabrication process

2.5.1 Substrate Preparation

The choice of substrate for the OPV device is not trivial and indeed there are many available to choose from. The most important properties for the substrate are optical transparency, smoothness and in the case of uncoated substrates for the custom deposition of electrode materials they must allow the chosen electrode to be deposited with good adhesion. In the work carried out in this thesis ITO-glass substrates (measuring $25.4 \times 25.4 \times 1.22 \text{ mm}$) with a sheet resistance of 12 Ohms/square were selected as the standard. Thinner ITO-coated coverslips (measuring $22 \times 22 \times 0.16 \text{ mm}$) were used for experiments requiring thinner glass substrates. For 'flexible' applications, ITO-PET (0.16 - 0.2 mm) thick films (cut to the desired length and width) were used. In the case of Ag electrodes glass slides were cleaned prior to deposition using the procedure outlined for the ITO-glass substrates below.

ITO-glass substrates

The substrates were etched using an aqueous HCL solution with the addition of a zinc powder catalyst to assist in the removal of any unwanted ITO. Depending on the exact device layout required for the experiment, the substrate was masked using adhesive tape leaving the ITO areas to be removed exposed. The ITO is removed when put in contact with the etching solution for approximately 10 - 20s. Once the etching is carried out the substrates are rinsed with water, the adhesive tape is removed and any excess adhesive is removed using isopropanol.

The cleaning process, carried out after etching is to ensure the adhesion of the subsequent layers onto the ITO. The substrates must be thoroughly cleaned to remove any contaminants such as oils, dirt and particulates. The substrates are immersed sequentially (ITO side facing up to prevent scratching the surface) in a series of covered glass containers placed in a heated bath under sonication for 15 mins. After each intermediate cleaning step, the substrates are rinsed with water. The first glass container is filled with a cleaning detergent, the second and third containers are filled with water, and the final container is filled with isopropanol. Immediately following the isopropanol procedure the substrates are removed from the container and allowed to dry in a dust free environment.

Plastic substrates

In the case of the plastic based substrates, the electrode patterning and etching processes are the same as for glass-based substrates. The cleaning step differs slightly as the sonication step is omitted to ensure the more weakly adhering electrode is not damaged or removed.

2.5.2 Formation of Au contacts and interconnects

A DC sputtering process is used to deposit gold contacts and electrode interconnects for flat and stack architecture OPV devices. A sample holder was designed to make the fabrication of the deposited contacts repeatable and uniform. The sample holder supports the substrates which are placed at an angle such that the sputtering of an Au strip with a predetermined width is achieved on the topside and edge of the substrate simultaneously. The substrates are positioned in the holder with the electrode side facing up to allow the sputtered Au to make contact with appropriate part of the electrode. One side of each substrate is sputtered first followed by the removal and repositioning of the substrates back in the sample holder to then sputter the opposite side.

2.5.3 Deposition of solution processable materials

Once the substrates are cleaned, they are ready for the deposition of the PEDOT:PSS layer. The substrates are typically UV / O_3 treated for period of time to make surface more hydrophilic to ensure the aqueous PEDOT:PSS solution adheres well. Spin-coating must be carried out immediately after the UV /O3 treatment to ensure that recontamination of the surface is minimized. The PEDOT:PSS solution is removed from the refrigerator and allowed to warm up to room temperature before being filtered through a 0.45µm filter (Corning). A 0.3 ml volume of the filtered solution is statically deposited onto the substrate using a syringe and a very thin layer (~50 nm) is formed by spin-coating at a predefined spin speed for 2 mins. The substrate is dried in an 80 °C oven for 1 hr prior to deposited using a micro-pipette onto the PEDOT:PSS covered substrate and consequently the active layer is formed by spin-coating. The substrate is then solvent-annealed at room temperature for 30 minutes in an environment saturated with chlorobenzene vapor and dried in an 80 °C oven for 1 hr prior to deposition of the active layer is formed by spin-coating. The substrate is then solvent-annealed at room temperature for 30 minutes in an environment saturated with chlorobenzene vapor and dried in an 80 °C oven for 1 hr prior to deposition of the active layer is not be priore by spin-coating.

2.5.4 Thermal evaporation, electrode deposition procedures

The substrates are aligned with a custom made shadow mask to define the electrode areas and are then loaded into the sample holder and placed on the sample stand. The bell jar is cleaned using 9% HCL, water and isopropanol to remove contamination and allow for a faster pump down time. The rubber gasket is placed on the bell jar and is coated with a thin film of vacuum grease to ensure a good vacuum is achieved in the chamber. Once the bell jar is aligned correctly on the face-plate, the gas inlet valve is closed, the gate valve is opened and the pumping station is turned on. Depending on the cleanliness of the vacuum chamber, the sample materials used and the placement of the bell jar, the system takes up to 12 hours to pump down to an adequate pressure for evaporation (typically below 1 x 10^{-5} mbar).

In the case where ITO was not used as an anode material, Ag was thermally deposited using the same thermal evaporator deposition system. A large degree of calibration was required in this instance as the film thickness needed to be controlled more stringently to maintain a sufficient degree of optical transparency in tandem with achieving a highly conductive film. The process parameters for a typical Al and Ag deposition are given in Table 2.2 and Table 2.3, respectively.

Step Time	Current	Voltage	Pressure	Commonte
(mins)	(A)	(V)	(mbar)	Comments
4	4	0	8.3 x 10 ⁻⁶	12 hrs after loading
4	8	0.1	8.3 x 10 ⁻⁶	
4	12	0.3	8.4 x 10 ⁻⁶	
2	16	0.7	8.7 x 10 ⁻⁶	
2	18	0.8	8.9 x 10 ⁻⁶	
2	20	0.9	9.1 x 10 ⁻⁶	
2	22	1	9.8 x 10 ⁻⁶	
1	24	1.2	9.8 x 10 ⁻⁶	
1	24	1.2	1.0 x 10 ⁻⁵	
1	24	1.2	1.1 x 10 ⁻⁵	Shutter Opened
2	24	1.2	9.1 x 10 ⁻⁶	
3	26	1.3	8.5 x 10 ⁻⁶	
3	28	1.5	8.4 x 10 ⁻⁶	
3	29	1.6	8.3 x 10 ⁻⁶	
3	20	1.8	8.4 x 10 ⁻⁶	
3	32	1.9	8.3 x 10 ⁻⁶	Shutter Closed

Table 2.2 Process parameters for an Al deposition.

Step Time	Current	Voltage	Pressure	Comments
(mins)	(A)	(V)	(mbar)	
3	4	0	8.6 x 10 ⁻⁶	12 hrs after loading
3	8	0.2	8.6 x 10 ⁻⁶	
3	10	0.2	8.7 x 10 ⁻⁶	
3	12	0.3	9.0 x 10 ⁻⁶	
3	14	0.5	1.0 x 10 ⁻⁵	
3	16	0.7	1.1 x 10 ⁻⁵	
3	18	0.9	1.2 x 10 ⁻⁵	
1	20	1.1	1.3 x 10 ⁻⁵	
15	20	1.1	1.4 x 10 ⁻⁵	Shutter Opened
5	21	1.1	1.5 x 10 ⁻⁵	
5	22	1.2	1.7 x 10 ⁻⁵	
2	22	1.2	1.9 x 10 ⁻⁵	Shutter Closed

Table 2.3 Process parameters for an Ag deposition.

2.5.5 Encapsulation of organic photovoltaic devices

Once the substrates have received the final layer in the fabrication process, the Al cathode; they are transferred to a N_2 filled glovebox for encapsulation. Encapsulation is achieved in the inert environment of the glovebox by adhering a glass encapsulation slide to the device electrode area. This is done by applying a UV – curable adhesive (Norland Products), positioning the glass over the electrode area and permanently fixing the glass in place by curing the glue under a UV lamp. Great care is taken during this process to ensure the Al electrode is not damaged by scratching, if the electrode is scratched or too much pressure places on it, an electrical short will most likely be formed between the anode and cathode through the active layer which destroys the entire device. The quality of the encapsulation is dependent on the initial environmental conditions that the device has been exposed to. It is therefore essential that as little oxygen and moisture as possible be introduced to the devices.

2.6 Characterization of Organic Photovoltaic Devices

The characterization of organic photovoltaic devices is carried out by a series of testing procedures. They are outlined and explained below.

2.6.1 Measurement of device areas

In order to ascertain the efficiency of the OPV device, its area is measured using either a Leitz Ergolux microscope with a micrometer scale in 0.05 mm divisions or a calibrated CCD microscope camera using "CaptureX" software.

2.6.2 Solar simulation, light source and calibration

An Abet LS 150 xenon arc lamp source coupled with an AM 1.5G filter was used as the illumination source for all OPV characterization measurements. The AM 1.5G filter is used to more closely approximate the solar spectrum having passed through by the earth's atmosphere. Figure 2.17 shows the basic layout of the Abet LS 150 xenon arc lamp source. The light source may be adjusted in a number of ways to obtain the desired output beam. The focus adjustment translates the lamp and reflector position with respect to the condenser lens allowing an output focus from beyond infinity to a point less than 150 mm in front of the light source housing. Lateral adjustment is used to accurately center the output beam on the optical axis of the experimental setup. The

optical output may be adjusted by changing the amount of radiation collected by the rear reflector from the arc lamp

The light source was calibrated before every set of measurements using an Oriel 91150V Solar Reference Si Cell certified by NREL. The light calibration setup has an incorporated thermocouple to allow for correction due to temperature changes in the reference cell.



Figure 2.16 Diagram of the Abet LS 150 Xe arc lamp light source used as a solar simulator.



Figure 2.17 Digital image of the Abet LS 150 xenon arc lamp source

The light source was adjusted to illuminate the OPV devices under test with an intensity equal to one sun (100 mW/cm^2). The light source is adjusted and recalibrated after each change in setting for intensity dependent measurements.

2.6.3 Measurement of I-V characteristics

All measurements were performed in a nitrogen filled glovebox (~10% relative humidity) for the standard flat panel devices. In the case of the angular dependency measurements for the stack devices, I-V traces were recorded under ambient conditions at room temperature outside the glovebox.

The characterization setup is mounted on a small optical bench situated inside the glovebox. The OPV device is placed on a glass testing stage above an angled mirror which is illuminated by the light source. The mirror is positioned so that the light is normally incident on the OPV device. Two gold-plated, probe tips were fabricated connected to coaxial cables terminated using BNC connectors. The tips are spring-loaded to reduce damage to the OPV device contacts over consecutive measurements.



Figure 2.18 OPV I-V characterization setup

Current-voltage (I-V) characteristics were determined using a 'Keithley 2400 SourceMeter'. Data is recorded using the manufacturer supplied "Labtracer" software and exported to '.txt' files for analysis using a Matlab program. The Matlab program enables the fast analysis of numerous data files, it only requires the input of the device area and then it extracts parameters from the data including open circuit voltage (Voc), short circuit current density (Jsc), fill factor (FF), and PCE.

Spectral mismatch was not accounted for in calculating the efficiency of the devices, however, the calibration of the light source to one sun using a Si reference cell with a quartz window will normally result in a slight underestimation of device efficiency.

2.6.4 Angular dependence of light entry into stack architecture devices

The experimental setup used to investigate the angular dependence of incident light on the efficiency of the stack OPV is illustrated in Figure 2.19. The solar simulator is aligned and calibrated on an optical bench. A custom-made sample holder is mounted on a rotating stage which allows the stack OPV to be rotated around the center point of the illuminated side of the device.



Figure 2.19 Experimental setup to determine angular dependency of incident light on the stack OPV efficiency

2.7 Conclusion

This chapter detailed the experimental techniques used in the characterization of the materials used in the fabrication of OPV devices. It is critical to combine these different methodologies to develop an understanding of the various materials and processes employed in the fabrication of OPVs. The handling, synthesis and preparation of the materials were outlined. The fabrication equipment used in the preparation and construction of OPV devices were presented and their operation and relevant parameters described. The specific processing steps and equipment parameters involved in fabricating standard OPV devices were given along with the setup and procedures for their electrical an optical characterization.

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CHAPTER 3.

Theoretical Background

3.1 Introduction

The underlying theories associated with organic materials are often compared and contrasted with analogies to those for inorganics. In some sense this can be an erroneous task as often the general principle of operation and the processes described are very different. The use of both physics and chemistry terminologies in terms of understanding atomic orbitals, band structures and their relation to ordered and disordered materials is problematic. In the beginning of this chapter, organic materials and their properties are discussed. This is followed by organic photovoltaics where their operation and characterization is detailed. The chapter is completed by a discussion of the relevant theory describing optical processes occurring in these materials and devices.

3.1.1 A brief overview of electronic orbitals

Atomic orbitals

An atomic orbital is the theoretical region around the nucleus with a high probability of finding an electron. They may be described by mathematical functions derived using quantum mechanics based on the wave behavior of electrons in an atom. The various atomic orbitals of an atom are at a fixed energy level and their shape, size, and geometry define the fixed spatial distribution of the electron cloud. Atomic orbitals are specifically defined by three quantum numbers corresponding to properties of the electron: energy level - n (size), angular momentum - l (shape) and angular momentum vector - m_l (orientation). Each atomic orbital is named (s-, p-, d-, f-) based on their angular momentum quantum number l (0, 1, 2, 3), respectively.

Molecular orbitals

Molecular orbital (MO) theory is a method used in the study of the electronic structure of molecules and their properties. MOs represent the motion of electrons in molecules in

regions encompassing more than one nucleus and in similarity to an atomic orbital; they are the theoretical regions in a molecule with a high probability of finding an electron. MOs are formed by the overlap of two atomic orbitals and as such the electronic wavefunctions associated with MOs can be considered as a linear combination of atomic orbitals (LCAO) — closely related to the tight-binding approximation. In the case of a covalent bond involving the sharing of electrons, a bonding MO (lower energy) and an anti-bonding MO (higher energy) is typically formed (Figure 3.1). MOs are occupied by electrons beginning with the lowest energy levels and can only be occupied by two spin-paired electrons. The most basic example of the combination of two atomic orbitals is the covalent σ -bond created between two hydrogen atoms in the formation of the MOs for molecular hydrogen (H₂).



Figure 3.1 The formation of a covalent σ -bond between two hydrogen atoms detailing the corresponding molecular orbitals and energy levels.

3.1.2 The band theory of solids and terminology

As the basis for understanding the principles of operation of organic materials, a brief discussion of the band-theory of solids is useful to introduce the foundation of the subject. In general crystallographic terminology, used in the classification of solids there are seven basic crystalline systems / forms: Cubic (Isometric) [P, I, F], Tetragonal [P, I], Orthorhombic [P, I, F, C], Hexagonal [P], Trigonal [P], Monoclinic [P, C] and

Triclinic [P]. When there is no apparent crystal structure the system is said to be amorphous. The seven crystalline classifications may then be further defined by the type of unit cell previously listed in: primitive [P], body-centered [I], face-centered [F] and side-centered [C] yielding the 14 Bravais Lattices (Figure 3.2) used in the unique description of the crystalline structure of solids [1].



Figure 3.2 The seven 3-D crystal structures and the 14 associated 3-D Bravais lattices. The side lengths are indicated by a, b and c. The angle between them is α [2].

In the case of inorganic, 3D crystalline structures (e.g. Si) the individual valence and conduction energy levels are narrowly separated such that they form continuous bands called the valence band and conduction band, respectively. This leads to the terminology of a band-structure for crystalline solids. Furthermore, the energy-

momentum dispersion (E-k) relationship for charge carriers in a periodic crystalline lattice may be examined viewing the first Brillouin Zone of the reciprocal lattice where E is plotted as a function of the wave vector. It is typically calculated using the one electron approximation (electron in an ideal free electron gas) for the Schrödinger wave equation applying the Bloch theorem (electrons moving in a periodic potential). The Bloch theorem states that if a potential energy V(r) is periodic with the lattice periodicity, then the solutions $\psi_k(\mathbf{r})$ of the Schrödinger wave equation

$$\left[-\frac{\hbar^2}{2m^*}\nabla^2 + V(\mathbf{r})\right]\psi_k(\mathbf{r}) = E_k\psi_k(\mathbf{r})$$
(3.1)

are of the form of the Bloch function

$$\psi_{k}(\mathbf{r}) = e^{jk\Box \mathbf{r}} U_{b}(\mathbf{r}, \mathbf{k})$$
(3.2)

Where there is a plane wave e^{jkT} , modulated by $U_b(k,r)$ which is periodic in r with the periodicity of the direct lattice and b is the index of the band [3].



Figure 3.3 Band energy diagrams for an insulator, semiconductor and a metal

The energy band diagrams for an insulator, metal and intrinsic semiconductor in the absence of an external potential are shown in Figure 3.3. In thermal equilibrium, the electron system of an intrinsic semiconductor material is defined by a completely filled

valence band at a temperature of 0 K. The gap in energy from the valence band to the conduction band is known as the bandgap (Eg) which ranges from ~1eV to 3eV for a semiconductor; Si has an $E_g \sim 1.1$ eV at 300 K (insulators have a larger separation between the valence band and conduction band, E_g is ≥ 5 eV). The Fermi level (E_F) is a hypothetical energy level used to describe the highest energy electrons can take at 0 K. At 0 K, the Fermi level lies practically halfway between the valence band and conduction band (assuming the electron and hole mass is equivalent), the electrons populate the lowest energy levels (as per the Pauli exclusion principle) and fill up to a maximum energy level, the Fermi level. As temperature is significantly increased, the electrons are thermally excited above the Fermi level and eventually into the conduction band where they are mobile; this is the basis for an increasing electrical conductivity with temperature. The Fermi-Dirac distribution function is used to calculate the energy distribution of identical indistinguishable particles with half integer spin which obey the Pauli exclusion principle (fermions). Electrons are fermions, and as such the probability of an electron occupying an available energy level (E) at a given temperature (T) is calculated by

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1}$$
(3.3)

where k_BT is the thermal energy. An important result from this distribution function is that $f(E_F) = 0.5$ and at normal operating temperatures for solid state devices ~ 300 K, the majority of energy levels are filled up to the Fermi level. Even though there is a probability for electrons to occupy states just above the Fermi level at 300 K, there are no available states to occupy i.e. the density of states (DOS) is zero. The DOS of a system is a general term used in the description of the number of available states per energy interval for each energy level to be occupied. In energy (k) space, the DOS, N(E) is the number of available energy states per unit volume for an energy range [E, E + δ E]. Taking the assumption that the bands are parabolic in shape, the DOS can be expressed in the free electron forms as

$$N(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{E}$$
(3.4)

where V is volume and m is the carrier mass. Thus, the DOS function may be considered as a statistical weighting and it is the multiplication of the electronic DOS and f(E) which yields the number of electrons at a particular level. The number of electrons in the CB can be summed up over an energy range from the bottom of the CB to infinity $[E_C, \infty]$ (at higher energies f(E) tends to zero so infinity may be used as the top of the conduction band) [1].

$$n = \sum_{E_{c}}^{\infty} N(E) f(E)$$
(3.5)

and similarly the concentration of holes (p) in the valence band may also be calculated using the fact that a hole is the absence of an electron.

$$n = \sum_{-\infty}^{0} N(E)[1 - f(E)]$$
(3.6)

In the case of a non-degenerate semiconductor where the Fermi level lies several k_BT below the conduction band energy (E_C), Boltzmann statistics apply and an effective DOS for the valence band (N_V) and conduction band (N_C) may be used. The concentration of electrons in the conduction band can then be expressed as

$$n = N_{c} \exp\left(-\frac{E_{c} - E_{F}}{k_{B}T}\right)$$
(3.7)

and the concentration of holes in the valence band is

$$p = N_{v} \exp\left(-\frac{E_{F} - E_{v}}{k_{B}T}\right)$$
(3.8)

where E_V is the valence band energy. The carrier density in an intrinsic semiconductor at a certain temperature, n_i is defined by the dynamics of a number thermally excited electrons (n) entering the conduction band leaving an equal number of holes (p) in the valence band; thus $n_i = n = p$ which then yields

$$n_{i} = \left(\sqrt{N_{C}N_{V}}\right)e^{E_{V}-E_{C}/2k_{B}T} = \left(\sqrt{N_{C}N_{V}}\right)e^{-E_{g}/2k_{B}T}$$
(3.9)

Whenever the thermal equilibrium of the charge carrier densities is distributed such that $pn \neq n_i^2$, equilibrium is regained again by electron-hole recombination; i.e. the thermal carrier generation rate is equal to the recombination rate.

Extrinsic semiconductors

If the semiconductor is modified to become extrinsic, typically by doping with a concentration of donor (N_D) or acceptor (N_A) impurities, shallow donor and acceptor states with energies E_D and E_A are introduced within the energy gap near the conduction band and valence band, respectively. An acceptor level is negative if it is occupied by an electron and neutral when empty. A donor level is neutral if it is occupied by an electron and positive when empty. Generally a semiconductor with a larger donor concentration is n-type, electrons are the majority carriers and holes are the minority carriers. Conversely, a semiconductor with a larger acceptor concentration is p-type, holes are the majority carriers and electrons are the minority carriers. Upon doping, to preserve charge neutrality, the Fermi level shifts either towards the valence band or conduction band as depicted in Figure 3.4 which details the energy band diagrams of intrinsic, n- and p-type semiconductors, their respective DOS, E_F , and carrier concentration plotted as a function of energy. Assuming that the majority of donors/acceptors are ionized at elevated temperatures, the Fermi level for an n-type semiconductor is given by

$$E_{\rm F} = E_{\rm C} - k_{\rm B} T \ln\left(\frac{N_{\rm C}}{N_{\rm D}}\right)$$
(3.10)

and similarly for a p-type semiconductor

$$E_{F} = E_{V} + k_{B}T \ln\left(\frac{N_{V}}{N_{A}}\right)$$
(3.11)

The generation of additional charge carriers by means of injection using an externally applied bias or photo-excitation due to incident light has the effect of bringing the system out of its equilibrium state. Upon absorption of incident photons electrons are promoted from the valence band to the conduction band leaving a corresponding hole in the valence band. The charge carrier densities are changed from equilibrium and as a consequence the Fermi level used to describe their populations is now inaccurate. This leads to the definition of imrefs or quasi-Fermi levels denoted by the subscripts F_n for electrons and F_p for holes. The quasi-Fermi levels may be evaluated using a reference energy level E_i which is the Fermi level for the intrinsic semiconductor such that

$$E_{Fn} = E_i + k_B T \ln\left(\frac{n}{n_i}\right)$$
(3.12)

and

$$E_{Fp} = E_i - k_B T \ln\left(\frac{p}{n_i}\right)$$
(3.13)



Figure 3.4 Energy band diagrams of intrinsic, n- and p-type semiconductors. Their respective density of states – N(E), Fermi distribution – f(E) and carrier concentration are plotted as a function of energy. Diagram redrawn and adapted from [3].

Charge carrier collection / injection are critical processes for OPVs and LEDs. The theory behind the creation of electronic junctions between materials is reflected in the energy band diagrams where the respective Fermi levels of the materials in intimate contact creating a junction align under equilibrium conditions — this in turn, has an effect on the shape and orientation of the valence band and conduction band.

The p-n junction diode

The p-n junction is the basis for the understanding of a large number of modern electronic devices. The foundation for the theory describing the p-n junction diode was first detailed by William Shockley who shared the Nobel Prize in Physics 1956 for his research on semiconductors leading to the discovery of the transistor. It is a two-terminal device consisting of a piece of n-type semiconductor which typically is modified by the introduction of p-dopants resulting in the formation of a heterojunction. A basic diode is formed as a result of having a p-type and n-type semiconductor in intimate contact where current may only flow readily in one direction — under forward bias.

As detailed in Figure 3.4, there are a number of additional electrons or holes in the nand p-type semiconductors, respectively. The Fermi levels of a p-type and n-type semiconductor are shifted with respect to an intrinsic one. The Fermi level of the p-type material is lower; upon formation of the heterojunction the Fermi levels must align under equilibrium conditions, the built-in potential is the difference between the two Fermi levels of the n- and p-type semiconductors, $qV_0 = E_{F(N)} - E_{F(P)}$. Electrons from the n-type material diffuse across the junction and fill holes in the p- type material, this forms negative ions resulting in a negative charge building up in the p-type semiconductor (conversely positive ions are formed in the n-type material and a positive charge is built up). An electric field is created due to the electron diffusion and once it is large enough, it balances the diffusion current, stopping the flow of electrons. Due to the recombination of electrons and holes near the junction, there are no free charge carriers, this area is acted on by the electric field and it is known as the depletion or space charge region.

The Shockley equation for current (I) flowing through a p-n diode (Figure 3.5) is given by

$$I = I_{s} (e^{qV_{D}/nk_{B}T} - 1)$$
(3.14)

where I_s is the reverse bias saturation current, q is the electron charge, V_D is the potential difference across the diode, n is the diode ideality factor – 1 for an ideal diode, and k_BT is the thermal energy.


Figure 3.5 Band structure diagram of a p-n junction.

Metal-semiconductor junctions

Metal-semiconductor junctions can behave as either a Schotky barrier or as an ohmic contact depending on the workfunctions of the metal (Φ_M) and semiconductor (Φ_S). The Fermi levels of two materials in contact must be aligned when they are in thermal equilibrium. Once a metal and semiconductor of different workfunctions are in contact, electrons flow from the one with the lower workfunction to the higher until the Fermi levels are aligned.

An ideal Schotky barrier diode (rectifying junction) is illustrated in Figure 3.6, it is formed when a metal is in contact with an n-type semiconductor such that $\Phi_M > \Phi_S$. Electrons from the conduction band of the semiconductor lower their energy by diffusing across the junction into the metal until equilibrium is reached and the Fermi levels coincide. This process leaves a negatively charged region at the metal side of the junction. The separation of charges forms a field inhibiting additional charge flow which is shown as the bending of the bands on the semiconductor side of the junction. The difference between the two Fermi levels, $qV_0 = \Phi_M - \Phi_S$ is called the contact or built-in potential. The potential barrier to electrons in the metal reentering the semiconductor is given by $\Phi_B = \Phi_M - \chi_S$, where χ_S (electron affinity) is the energy required to promote an electron from the conduction band of the semiconductor to the vacuum level.



Figure 3.6 Band structure at the interface of a p-type semiconductor and a metal with a smaller workfunction.

The application of an external bias removes the system from equilibrium; it has the effect of changing the potential drop across the semiconductor. In forward bias, a positive bias is applied to the metal, E_{FS} is raisewd with respect to E_{FM} and the potential drop across the semiconductor is decreased ($qV_0 - V_{APPLIED}$). This results in more electrons diffusing towards the metal than the number that drift into the semiconductor leading to a large positive current through the junction. In reverse bias, a negative bias is applied to the metal, E_{FS} is lowered with respect to E_{FM} and the potential across the semiconductor is increased ($qV_0 + V_{APPLIED}$). In this case, the depletion region is broadened restricting any current flow across the junction and as such the rectifying behavior of the device is evident.

An ohmic (non-rectifying) contact is characterized as having a voltage independent resistance. Illustrated in Figure 3.7, it is formed when a metal is in contact with an n-type semiconductor such that $\Phi_M < \Phi_S$. Electrons diffuse from the metal into the conduction band of the semiconductor until the Fermi levels are aligned leaving a negatively charged region at the semiconductor interface. The Schotky barrier height is either zero or negative and the field formed due to the separation of charges results in the bending of the semiconductor bands allowing electrons to freely flow into the conduction band of semiconductor with minimal resistance.



Figure 3.7 Band structure at the interface of a p-type semiconductor and a metal with a larger workfunction.

3.2 Organic materials and properties

The term 'organic' used in conjunction with the description of matter is predominantly describing a chemical structure based on carbon. In order to better understand the formation of organic molecules, crystals and polymers a brief overview of the formation of bonds based on the overlap of atomic and molecular orbitals is given.

3.2.1 The Carbon atom, hybrid orbitals and their role in common organic molecules

Carbon, the sixth element in the periodic table has a ground state electron configuration of $1s^22s^22p^2$ — that is it has six electrons which occupy the $1s^2$, $2s^2$, and $2p^2$ atomic orbitals. The $1s^2$ orbital contains two strongly bound, core electrons and the remaining four valence electrons that are more weakly bound occupy the $2s^22p^2$ orbitals. A carbon atom may have an alternate, less stable electron configuration which is a result of atomic orbital hybridization. The hybridization of an atomic orbital is the mixing of a number of different orbitals at the same energy level of an atom creating a corresponding number of hybrid orbitals. The hybrid atomic orbitals formed by this process are at the same energy level as each other and have identical properties. Hybridization of orbitals consisting of the lower 2s level and the higher 2p levels may create three different sets of equivalent degenerate (spⁿ) orbitals: sp³, sp² and sp. Each of these hybrid atomic orbitals is named based on the number of s-orbitals interacting with p-orbitals (n = 1, 2, 3...).

An sp³ hybrid orbital is formed when a carbon atom is bonded with another atom resulting in a 2s-orbital electron being promoted to a vacant 2p-orbital. Four degenerate sp³ hybrid orbitals are formed from the superposition of a 1s-orbital with the three 2p-orbitals. The outer valence shell, sp³ configuration of orbitals (s, p_x , p_y , p_z) gives rise to a tetrahedral bonding structure that is best exemplified in carbon compounds such as methane (CH₄). Four sp³ hybrid orbitals (having a single unpaired electron) are overlapped by the hydrogen 1s orbital resulting in four σ -bonds being made from the central carbon atom to the corners of the tetrahedral structure.

A σ -bond structure, formed using carbon compounds consists of three sp² hybrid orbitals originating from the superposition of a 1s-orbital with two of the 2p-orbitals (p_x, p_y). The sp² orbitals are orientated in the same plane and separated by 120° (trigonal planar arrangement). Orthogonal to the sp² orbitals is a single remaining 2p-orbital (p_z) which has an electron available to form an additional orbital with other similar electrons. This is known as a π -orbital which is formed parallel to the σ -bond yielding a double bond. An example of this behavior can be observed in ethylene (C₂H₄). Two sp² hybrid orbitals are overlapped and each carbon atom has two covalent bonds with hydrogen.

An sp hybrid orbital is formed from the superposition of a 1s-orbital and a 2p-orbital. In this case the two formed sp orbitals are orientated at 180° to each other forming colinear σ -bonds. The two remaining p-orbital electrons are then free to form π -bonds perpendicular to the molecular axis. This type of hybridization is observable in acetylene (C₂H₂) where the chemical bonding consists of an overlap between the two ends of the hybrid sp orbitals; this forms a strong σ -bond between the two carbon atoms. The hydrogen atoms also attach by carbons and the remaining two, 2p-orbitals form a pair of weaker π -bonds. The combination of the carbon-carbon σ -bond and the weaker two π -bonds yields the triple bond in acetylene [4,5].

3.2.2 Organic molecules and crystals

Organic molecules are formed and held together by covalent bonds originating from the superposition of the atomic orbitals of the individual constituent atoms. Organic molecular crystals are comprised of these discrete molecules and are held together by a weak intermolecular bonding (van der Waals forces). An organic molecular crystal differs from its inorganic counterparts especially in terms of the bonding structure. This leads to a lower melting point and reduced hardness compared to the strong covalently bonded solids exemplified by inorganic crystalline structures comprised of atoms such as silicon. As a result of this dissimilarity in bonding regimes, the properties of an individual molecule are retained to a far greater extent in the solid state polymers formed by them which is in contrast to inorganics.

3.2.3 Polymers

Polymers can consist of organic, inorganic or hybrid components. Polymeric materials (macromolecules) exist in many different forms; they are abundant in the natural world (shellac, rubber, amber) and extend to complex biopolymers encompassing biochemical compounds such as proteins, peptides and DNA. The 'polymers' of interest for this thesis are synthetic organic compounds often referred to as industrial polymers. They are defined as having a long backbone structure with repeated molecular units (monomers) covalently bonded together forming a chain. The majority of the constituent atoms forming the backbone are carbon, however, they may also be present in combination with other atoms including nitrogen (polycarbazole), oxygen (polyester, polycarbonates) chlorine (polyvinylchloride), fluorine (polytetrafluoroethylene -Teflon), phosphorous, and sulphur (polythiophene). Each molecular chain can contain a large number of repeat units containing thousands of atoms. Polymers differ from smaller molecular weight materials in that they are only solution processable. This means that they must be dissolved by an appropriate solvent to form a solution which is then used in a wet processing deposition technique such as spin-coating. In solution the polymer chains are tangled and contort in a random orientation. The appearance of a polymer film changes with respect to the degree of organization and orientation of the polymer chains that form it — this is called crystallinity. The reorganization of the polymer chains during and / or after the deposition process can lead to crystallization

provided there is sufficient time. The degree of crystallization is dependent on numerous factors (processing conditions, solvent, temperature etc.) and clearly the type of polymer molecule used determines the amount of crystallization occurring based on its structure. In most cases the thin film formed is inhomogeneous and partially crystalline; it may consist of arranged molecular crystalline regions surrounded by amorphous polymer [6]. Even with the presence of crystalline regions, the overall response of the polymer is typically observed to resemble that of an amorphous solid allowing for similarities to be drawn to materials such as amorphous-Si.

3.2.4 Allotropes of carbon, structures and properties

Carbon is the only element in the periodic table known to have isomers with dimensionalities ranging from 0-D to 3-D. Table 3.1 shows the possible structures that carbon can form in the solid phase as a result of the hybridization of atomic orbitals. The dimensionality of these carbon-based molecules and indeed carbon-based compounds is dependent on the sp^n hybridization and as such we can take graphite as an example for the basis of the various isomers.

Dimension	0-D	1-D*	2-D	3-D
isomer	fullerene	nanotube	graphite/graphene	Diamond
hybridization	sp ²	sp² (sp)	sp ²	sp ³
electronic	semiconductor	metallic or	semi-metallic	insulator
properties	Eg = 1.9 eV	semiconductor		Eg = 5.47 eV

Table 3.1 Carbon isomers and their properties. Adapted from [5].

* Nanotubes have been considered as pseudo 1-D systems since their discovery but in the strictest sense they are a 3-D system but behave in a manner similar to that of a 1-D system such as trans-polyacetylene.

Carbon nanotubes

The sp² hybridization forms a planar structure which defines 2-D graphite or graphene. By taking this 2-D planar structure and rolling it up along a particular axis, a 1-D cylinder called a carbon nanotube (CNT) is formed. There are many forms of nanotubes; each one may exhibit different mechanical, electrical, optical and structural properties. Single-walled CNTs (SWNTs) defined by the cylindrical graphene sheet can be either metallic or semiconducting depending on the orientation of the six-membered carbon ring with respect to the nanotube cylindrical axis. The well-known honeycomb lattice structure may present itself at any arbitrary angle to this axis without deformation of the carbon ring (neglecting the curvature of the graphene sheet that comprises it). The nanotube structure can be generalized into two classes: achiral (armchair, zigzag) and chiral. A chiral nanotube exhibits a spiral conformation with axial symmetry whose mirror image cannot be superimposed on it. In contrast, achiral nanotubes have a mirror image structure which is identical to their original one. The names armchair and zigzag originate from the cross-sectional view of the cylindrical CNTs (Figure 3.8) which is observed as a ring.



Figure 3.8 Diagram illustrating the structure of achiral single-walled carbon nanotubes

The rolling-up of the graphene sheet to form the nanotube can be defined by assigning a vector which connects two crystallographically equivalent sites of the graphene sheet. It is called the chiral vector (C_h) and is expressed as a linear combination of the two hexagonal lattice vectors (a_1 , a_2) where,

$$\boldsymbol{C}_{h} = n\boldsymbol{a}_{1} + m\boldsymbol{a}_{2} \equiv (n,m), \quad (n,m \text{ are integers}, 0 \le |m| \le n). \tag{3.15}$$

Figure 3.9 depicts the formation of a nanotube from a graphene sheet. Wrapping the graphene sheet along C_h results in the connection of sites O to A and B to B' forming a nanotube defined by the unit cell rectangle OAB'B. The chiral angle (θ) is measured with respect to the hexagonal lattice vector a_1 . The translational vector (**T**) is defined by OB which is parallel to the cylindrical axis and the unit vector of the nanotube. **R** is the symmetry vector which is used to define the coordinates of the carbon atoms in the

nanotube with respect to **T** and C_h . Armchair nanotubes ($\theta = 30^\circ$) are metallic and defined by n = m yielding $C_h = (n, n)$. Zigzag nanotubes are for the mostpart semiconducting where $\theta = 0^\circ$, m = 0 and $C_h = (n, 0)$. Nanotubes defined by n and m values such that $\left(\frac{n-m}{3}\right)$ is a non-zero integer are also considered to be metallic.



Figure 3.9 Depiction of the formation of a nanotube from a graphene sheet. Wrapping the graphene sheet along OA (chiral vector - C_h) results in the connection of sites O to A and B to B' forming a nanotube defined by the unit cell rectangle OAB'B. T is the translational vector (OB) and R is the symmetry vector.

The electrical properties of pristine nanotubes are correlated to their chirality and diameter. The band gap of a semiconducting nanotube is inversely proportional to its diameter. In terms of metallic SWNTs, the long aspect ratio and 1-D nature allow it to realize very high mobilities for electron transport along the cylindrical axis. At low temperatures a SWNT may be considered as a quantum wire in which electrons can travel without being scattered. This special case is known as ballistic transport. A

quantum wire defined by width (W) and length (L) is characterized as having a resistance given by

$$R = \rho \frac{L}{W^2}$$
(3.16)

where ρ is the electrical resistivity [5]. Macroscopic conductors have resistivity values independent of dimensions or the applied bias which rely on the material properties. In the limiting case that the wire is small with respect to the characteristic lengths of electron motion quantum effects become apparent. The quantum regime implies that the wave-particle duality is considered and as such the electron may be considered as acting like a wave displaying interference effects. These effects, typical of mesoscopic systems, are sensitive to the boundary conditions and defects or impurities in the SWNTs.

In the more realistic case where SWNTs may be used at ambient temperatures in devices, scattering centers are present and serve to limit the ballistic conductivity through numerous elastic scattering events. Classical transport processes observed in macroscopic systems are often called diffusive transport and electrical resistance is governed by the effect of a large number of scattering centers yielding a series of microscopic resistances. As a result this is simply Ohm's law and the macroscopic resistance is proportional to L. The unique properties of CNTs in general are a driving force behind their use in composite materials. They are often functionalized to increase their solubility in common organic solvents to allow better processability and miscibility with polymers to form conducting composites.

The fullerene

A closed 0-D polyhedral structure defining a closed cage molecule known as a fullerene may be formed which also locally exhibits the planar structure from sp^2 hybridization. C_{60} is the roundest molecule found in nature and the most stable of the fullerenes (highest symmetry). The geometry of C_{60} (truncated icosahedron) is based on a closed polyhedron with 20 equilateral triangular sides (icosahedron). The icosahedron has 30 edges and 12 vertices, by cutting off each vertex (truncation), 12 regular pentagonal faces are generated leaving 20 remaining hexagonal faces.

3-dimensional allotropes

3-D structures, created due to the tetrahedral arrangement of σ -bonds in sp³ hybridization are exemplified by the diamond structure. Amorphous carbon systems (carbon black or soot) which are disordered typically have a combination of sp² and sp³ hybridizations present.

3.2.5 Polymers as insulators and conductors

In general, it is the nature of the chemical bonds which form the polymer that control their intrinsic electrical and optical properties — the chemical structure of the polymer directly influences whether the polymer is conducting or insulating. In general insulators have a sufficiently large band gap and as such they tend to be optically transparent in the visible (clear plastic bags such as polyethylene). Polymers formed from hydrocarbon molecules can have a chemical structure separated into two basic groups depending on which hydrocarbon family they are based upon. The difference between the two types of chemical structure is contrasted using the examples of saturated and unsaturated polymers, polyethylene and polyacetylene, respectively.



Figure 3.10 Structures of monomers (a, c) used to form saturated (b) and unsaturated (c) polymers

Saturated polymers

Alkanes consist of molecules which have carbon atoms connected only by single bonds. The maximum number of hydrogen atoms is present for the number of carbon atoms i.e. the structure is saturated containing the maximum number of atoms. In these saturated structures all available electrons are tied-up in strong covalent bonds formed from sp³ hybrid orbitals (σ – bonds). If we look at the simplest polymer structure shown in Figure 3.10b, polyethylene, the σ -bonds holding adjacent carbon atoms together are responsible for the zigzag polymer backbone pattern. The two remaining bonds are made with pendant hydrogen atoms. The electrons in this type of system are localized in the molecular structure and as a consequence, there are no free charges available to facilitate conduction. Polymers formed from these saturated compounds are insulators.

Unsaturated polymers

Alkenes and alkynes consist of molecules where double and triple bonds are present, respectively. In the case of a structure having double bonds, the classic example of polyacetylene may be used. Polyacetylene is a linear polymer with a 1-D backbone, where each carbon atom has σ -bonds with two neighboring carbons and a third one with a hydrogen side group. There is then one π -electron on every carbon atom. This is an important property of polyacetylene; if its structure consisted of equal length C-C bonds, its chemical formula would be that of pure trans (-CH)_n having one unpaired electron per repeat unit giving rise to a metallic state. In terms of band structure, it would be a quasi-one-dimensional metal a half-filled band. However, the situation where there is an unpaired electron is a rare occurrence; a result of the Peierls instability is that the actual structure of polyacetylene is dimerized (-CH=CH)_n as shown in Figure 3.10d i.e. having two carbons in the repeat unit and as such the carbon-carbon bond lengths are not equal. The carbon atoms are part of a conjugated system — they form a long backbone containing alternating double and single bonds forming a chain. Π – electrons are far more weakly bound; conjugated systems can be expected to conduct electrical charge but intrinsically it will not be metallic conduction as a result of the quasi-band gap (π - π * gap in polyacetylene ~1.7 eV) opened up due to the Peierls instability [7].

The Peierls Instability

The Peierls Instability is often referred to as a distortion and related to the Jahn Teller Effect. It is important to look at how the two molecular π bands originate. The Peierls instability is attributed to the instability of a quasi1-D metal to static lattice distortions. It predicts that a structure consisting of a linear array of N molecules (each containing only 1 valence electron) with a constant spacing (d) may display a wide variety of instabilities.



Figure 3.11 Illustration of two linear arrays of molecules

This system resembles that of the conjugated polymer backbone. Using the nearest neighbor tight binding approximation, the π band $-E(k) = E_0 + 2tCos(k \cdot d)$ is half filled due to the Pauli Exclusion Principle (it is a metal). (where at t < 0 is the interaction energy of the nearest neighbor and d is the unperturbed lattice spacing.) The Fermi-momentum $k_F = \pi/2d$ due to the band being filled $\forall |k| \le |k_F| = (\pi/2)|d|$ [8].



Figure 3.12 Illustration of the energy gap formed after the Peierls transition

Peierls predicted that this simplified description is inaccurate. The backbone dimerizes due to interactions with k_F phonons. This results in the linear array becoming an array of N/2 dimers i.e. an arrangement of longer single and shorter double bonds. Essentially this leads to unit cell that is doubled in size in real space. The corresponding unit cell in reciprocal space is therefore halved. This yields a lower total energy of the system and minimization of energy of the ground state because of the reduced symmetry. The total energy of the chain is lowered, reducing the Brillouin zone to half its original length. Electrons are localized due to the static lattice distortions forming an insulating state (Figure 3.12) with a periodicity across the lattice of 2d. In this dimer case, the Fermi momentum remains unchanged because the lattice dimension has doubled ($k_F = \pi/2d$) [9].

3.2.6 Models for polymeric systems

The complete theoretical description of a polymeric system is rather impractical and seems an almost insurmountable task without the use of specific techniques or broad assumptions. There are many degrees of freedom to consider including σ -bands, π -bands, lattice vibrations and particle-particle interactions and coupling. A system in which a large number of particles interact is treated as a many body problem. The solution to the many particle Schrödinger equation is non-trivial and as such other techniques must be implemented e.g. second quantization, quantum field theory, and

Green's functions [10]. An in-depth discussion of these techniques are outside the scope of this thesis but a brief description of the methodologies used in the description of π -electron systems is outlined below and also discussed in more detail in Ref [11].

The Hamiltonian operator (\hat{H}) may be defined as the energy operator and corresponds to the total energy of the system. The total Hamiltonian (\hat{H}_T) describes the electronic and nuclear degrees of freedom and takes on a rather complex form for a many body problem.

$$\hat{H}_{T} = H_{n-n}(\{Q\}) + H_{e-e}(\{r\}) + H_{e-n}(\{r\}, \{Q\})$$
(3.17)

where

$$\mathbf{H}_{\mathbf{n}-\mathbf{n}}(\{\mathbf{Q}\}) \tag{3.18}$$

describes the nuclei as classic particles having a kinetic energy and mutually interacting due to Columbic forces,

$$H_{e-e}(\{r\}) \tag{3.19}$$

Describes the kinetic energy of the electrons along with their mutual potential energy and

$$H_{e-n}({r}, {Q})$$
 (3.20)

describes the potential energy resulting from the columbic interactions between the nuclei and the electrons. $\{r\}$ and $\{Q\}$ represent the coordinates of the electrons and nuclei, respectively.

The Born-Oppenheimer approximation

The Born-Oppenheimer (B-O) approximation takes into account that the nuclear mass is far greater than that of the electron. Thus, the motion of the nuclei will appear to be slow with respect to the electrons allowing the consideration that the electrons respond instantaneously to change in the configuration of the nuclei. The B-O approximation is referred to as adiabatic; there are no transitions between the electronic states due to changes in the configuration of the nuclei. Thus the electronic states may be determined by a set of static nuclear coordinates $\{Q\}$, where the energy associated with the nuclear coordinate $\{Q\}$ can be drawn as an adiabatic potential energy surface i.e. the effective potential experienced by the nuclei.

A result of the various atomic orbital hybridizations discussed in Section 3.2.1, the higher energy σ electronic processes are decoupled from the π electronic processes allowing for the description of conjugated polymers using π -electron models.

П-electron models

The Hückel model assumes that the electrons are non-interacting and have a fixed geometry. This is the most drastic approximation where electron-electron interactions are ignored and the positions of the nuclei are fixed.

The SSH model introduced in 1970 by Su, Schreiffer and Heeger is used to describe the properties of polyacetylene [10]. The SSH Hamiltonian is defined as

$$\hat{H}_{SSH} = H_e + H_{n-n} + H_{e-n},$$
 (3.21)

This model builds on the B-O approximation, assuming non-interacting electrons with dynamic nuclei. It takes into account that electrons are strongly coupled to the lattice in organic materials i.e. electron-phonon coupling. The Pariser-Parr-Pople (P-P-P) model assumes interacting electrons with a fixed geometry.

3.3 Excitation and Emission Processes





Ground State



The state diagram in Figure 3.13 is often used to illustrate the electronic energy levels of a typical molecule. The electronic energy levels are drawn as horizontal lines arranged vertically depending on their respective energies. The levels are then grouped depending on their spin multiplicity singlet or triplet. The subscript i, for the singlet states (S) has an integer value in ascending order for increasing energy levels from 0 (ground state) to higher excited states. The subscript j, for the triplet states (T) also has an integer value in ascending order for increasing from 1. The relaxation of the

electron from various vibrational excited states is depicted. The wavy lines indicate a non-radiative transition. Charge transfer is another route for the excited state to relax which is not shown in the diagram above — it is discussed later concerning the competing processes to photoluminescence.

The UV-visible absorption spectrum

Following the absorption of an incident photon by a ground state molecule, an electron is promoted from the ground state molecular orbital, S₀ to a vibrational energy level of the first excited state molecular orbital, S_1 . It may also be promoted to an even higher electronic excited state such as S₂ or higher S_i. The quantization of the excitation process leads to an important result: the amount of absorbed energy ($\Delta E = hv$) is equal to the energy difference between the two states $(E_{n+1} - E_n)$. For an atom, one would expect to observe a UV absorption spectrum to consist of sharp well defined lines due to the quantized excitation process from one discrete energy level to another of higher energy. Molecules behave differently as they have many modes of vibrational and rotational excitation at room temperatures that do not disappear even if cooled to absolute zero. As a result, a group of molecules contains members which are in different states giving rise to the super-position of rotational and vibrational levels on the electronic structure, so that an envelope of transitions is formed. Generally the spectra are broadened to such a degree that the vibrational and especially the rotational information become totally obscured. In this case one observes a continuous broad-band absorption spectrum where the maximum normally corresponds to the main transition. This is often denoted as the UV band structure.

Typically the electronic structure of a molecule can be analogous to that of a crystalline solid when the number of atoms (N) in the molecule becomes very large. In this macromolecular case, as N tends to a large number the typical discrete energy levels become separated to a lesser degree eventually forming analogues to the valence and conduction bands. Often a transition which raises an electron from an occupied level in the conduction band to an unoccupied level in the valence band is denoted as an interband transition.

When observing electronic transitions associated with molecules, the most probable one takes place between the frontier orbitals. This occurs when an electron is promoted from the highest unoccupied molecular orbital (HOMO ~ valence band) to the lowest unoccupied molecular orbital (LUMO ~ conduction band). The symmetry relationship between the two orbitals is important as it defines whether the transition is allowed or forbidden (not all transitions between the HOMO and LUMO are allowed). The probability of a forbidden transition is low and therefore results in a low intensity of the absorption band associated with it. The degree of conjugation of a compound is directly related to the energy transition between its HOMO and LUMO. The larger the amount of conjugated bonds present the longer the wavelength of light the compound can absorb resulting in a smaller optical-bandgap ($E_{HOMO} - E_{LUMO}$).

For the large majority of molecules, σ -orbitals are the lowest energy occupied molecular orbitals which are linked to σ -bonds. At higher energy levels π -orbitals and subsequently non-bonding n-orbitals may be observed. Anti-bonding orbitals (π^* and σ^*) lie at the highest energy levels. Each of these energy levels and transitions are shown in Figure 3.14.



Figure 3.14 The excitation process, electronic transitions and energy levels observable for a conjugated polymer using UV-vis spectroscopy.

The photoluminescence spectrum

Photoluminescence (PL) occurs when a material absorbs an incident photon and subsequently re-radiates another photon of lesser energy. In a solution, the electron rapidly falls to the lowest vibrational sub-level of S_1 by internal conversion (vibrational relaxation) usually with the release of phonons (heat) but no change in spin. In order for the electron to relax back to the ground state ($S_1 \rightarrow S_0$) a radiative process can take place i.e. the release of a photon. This type of emitted radiation for singlet decay is typically at a lower energy than the absorbed photon (Stokes shift) and is called fluorescence; it has a lifetime of ~ 10⁻⁹ to 10⁻⁷ s.

The alternative to this is a process called intersystem crossing (ISC) where there is a loss in energy as the electron goes from the singlet state S_1 (containing spin-paired electrons) to the triplet state T_1 (containing spin-parallel electrons). The triplet states are more stable than singlet states resulting in increased photoluminescence lifetimes ($10^{-3} - 10^{-2}$ s) allowing for the emitted radiation for triplet decay, known as phosphorescence to be present after the excitation source is turned off.

There are several competing processes which may reduce the probability of photoluminescence. Energy transfer or charge transfer (CT) may also occur where the excited electron is transferred either to another nearby chromophore molecule (intermolecular) or along the polymer backbone (intramolecular). Non-radiative internal conversion (IC) may also occur from either the excited S or T states to S_0 .

Einstein coefficients for vibronic transitions, the Franck-Codon principle

In order to ascertain a more quantitative description of the aforementioned processes, Einstein defined three contributions to the transitions between different atomic and molecular states.

Stimulated absorption or induced absorption is caused by the interaction of incident electromagnetic radiation having an electric field oscillating at the transition frequency with an electron which results in a transition from a lower (l) to an upper (u) energy state. This process is typically associated with the excitation rate $B_{lm,un}$, where the

subscripts lm represent the mth vibrational level of the lth electronic state and un represents the nth vibrational level of the uth electronic state.

Spontaneous emission is a random process which is used to determine the radiative lifetime of the excited state, it is associated with the rate constant $A_{un,lm}$.

Stimulated emission, induced emission or decay is associated with the interaction of a photon of energy $(E_{un} - E_{lm})$ with an electron in the level *un*. The stimulated emission rate is defined as $B_{un,lm}$. If a suitable radiation field (such as black-body radiation) is present stimulated emission can occur at a rate similar to the absorption $(10^{-15}s)$ such that

$$\mathbf{B}_{\mathrm{lm,un}} = \mathbf{B}_{\mathrm{un,lm}},\tag{3.22}$$

which infers that the absorption and fluorescence spectra are almost mirror images of each other and Einstein's relationship is given by

$$\frac{A_{un,lm}}{B_{un,lm}} = \frac{8\pi h \upsilon^3 n_0^3}{c^3},$$
(3.23)

where v is the transition frequency, n_0 the refractive index of the medium and c is the speed of light.

By considering a unit cube containing chromophores under incident electromagnetic radiation we may apply the Einstein relationship to molecular system [8]. In this instance we have a unit cube containing a predefined number of chromophores and photons. For a certain frequency range dv the energy density is $\rho(v).dv$ which correspondingly leads to a photon density $\rho(v).dv/hv$. The density of chromophores in the lower energy state with m = 0 is N₁₀. Assuming the reaction is simply between the unexcited chromophores and the incident photons yields an expression for the excitation rate (ΔN_{10}) for photons having energy hv, per unit volume:

$$\Delta N_{10} = \frac{c}{n_0} \sigma(\upsilon) N_{10} \left(\frac{\rho(\upsilon) d\upsilon}{h\upsilon} \right).$$
(3.24)

where $\sigma(v)$ is the is the photon absorption cross-section for the unexcited chromophores, c/n_0 is the velocity of the photon in the medium with refractive index n_0 . Thus the excitation rate over the vibronic band from *l0* to *un* is

$$\Delta N_{10,un} = \frac{c}{hn_0} N_{10} \int_{10}^{un} \left(\frac{\sigma(\upsilon)\rho(\upsilon)d\upsilon}{\upsilon} \right); \qquad (3.25)$$

and already having the Einstein coefficient ($B_{10,un}$) defined for this transition ($l0 \rightarrow un$)

$$\therefore \Delta N_{10,un} = N_{10} B_{10,un} \rho(v_{10,un})$$
(3.26)

assuming a constant radiation density over the vibronic bandwidth yields

$$B_{10,un} = \frac{c}{hn_0} \int \left(\frac{\sigma(\upsilon) d\upsilon}{\upsilon} \right);$$
(3.27)

Relating the absorption cross section to the molar extinction coefficient (\in) of the absorbing medium, gives

$$B_{10,un} = \frac{2303c}{hn_0 N_0} \int \left(\frac{\epsilon(\upsilon)d\upsilon}{\upsilon}\right).$$
(3.28)

The probability for all vibronic transitions to the upper π electronic state u from the lower state l can be considered as the sum over the n vibronic levels such that

$$B_{lu} = \sum_{n} B_{l0,un} = \frac{2303c}{hn_0 N} \int \left(\frac{\epsilon(\upsilon)d\upsilon}{\upsilon}\right).$$
(3.29)

where the integration is taken over all vibronic levels in the upper state effectively summing up the area under the absorption spectrum curve $\in (v)$ vs. v, defined by the various vibronic transitions (m \rightarrow n). As per the Einstein relationship we can then write

$$B_{10,un} = B_{u0,lm}$$
 and $\frac{A_{u0,lm}}{B_{u0,lm}} = \frac{8\pi h \upsilon^3 n_0^3}{c^3}$, (3.30)

The energy level diagram in Figure 3.14 is redrawn to illustrate the respective Einstein coefficients and the labeling of electronic and vibrational levels (Figure 3.15).



Figure 3.15 Diagram illustrating the terminology for the Einstein coefficients combined with the simplified potentials of electronic energy states (I and m) and their associated vibrational levels (m and n).

In Figure 3.15, *a* corresponds to a vertical (Franck-Codon) transition. *b* is a zero-phonon transition (no energy is imparted to a phonon) and the wavy line again represents a non-radiative transition between vibrational states of the upper electron level u. c is a radiative transition such as fluorescence. ΔQ is the displacement of the nuclear coordinates between the upper and lower energy states. The Franck-Codon principle states that the nucleonic motion may be neglected because the mass of the electrons is

far greater. The Einstein A and B coefficients, oscillator strength and transition dipole moment are parameters used to quantify the strength of the transition.

3.3.2 Quasiparticles in organic semiconductors

There are many different quasi-particles that have been conceived to aid in the description of excitations and interactions occurring in crystal lattices, molecules and polymeric materials. They can be considered as a combination of a particle and the perturbation induced by the presence or absence of the particle on the surrounding environment. Table 3.2 lists the various types of these excitations and the common chemical term used in their description.

Excitation	Chemical term	Charge	Spin
positive polaron	radical cation	+e	1/2
negative polaron	radical anion	-е	1/2
positive bipolaron	dication	+2e	0
negative bipolaron	dianion	-2e	0
neutral soliton	neutral radical	0	1/2
positive soliton	cation	+e	0
negative soliton	anion	-е	0
singlet exciton (neutral bipolaron, exciton polaron)	S	0	0
Triplet exciton(neutral bipolaron, exciton polaron	Т	0	1

Table 3.2 List of the important quasi-particles observable in organic semiconductors [12].

The polaron and bipolaron

A polaron is a quasiparticle consisting of a charge and a phonon cloud. A polaron becomes apparent especially in organic polymer chains because it may be energetically favorable to localize charge that appears on the chain. In this case the polymer chain exhibits a deformation induced by the presence of the additional charge. The ability of a polaron to distort or deform its surroundings is a manifestation of strong electron (or hole)-phonon coupling. This process spurs the presence of localized electronic states in the gap where there is a local upward shift in the HOMO and downward shift in the LUMO (Figure 3.16) [13]. In the case of polaron formation the valence band remains

full and the conduction band is empty. The concept of a polaron is important as it is often used in the description of charge transport mechanisms in organic semiconductors (polaronic transport). The removal (addition) of electrons by oxidation (reduction), or in terms of 'p-type' ('n-type') doping, the introduction of electron acceptors (donors) results in the formation of a mobile hole (electron) on the polymer chain. The resulting potential-well serves to effectively trap the charge carrier along the chain. The polaron is positively (negatively) charged when an electron is lost (added) by means of an acceptor (donor). The resulting free radical may cause a break in the conjugation with the formation of the mobile deformation capable of transporting charge and spin — the polaron. They may be reasonably mobile along the chain (intrachain transfer) provided the chain segments are intact, however in order to realize macroscopic conduction the charge and deformation must travel from one chain to another (interchain transfer) [14]. This mechanism is typically described as a hopping process and is further discussed in Section 6.1.

A bipolaron (Figure 3.16c and d) may also be formed when an additional electron is removed from the polaron. The bipolaron is a pair of like charges which imposes a strong distortion and as a result the states appearing in between the valence and conduction bands are further away from the band edges than in the case of the polaron.



Figure 3.16 Band structure of a polymer chain containing polaronic levels (a) p⁺ (b) p⁻and bipolaronic levels (c) 2p⁺ (d) 2p⁻

The soliton



Figure 3.17 (a) Structure of cis-polacetylene (b) Structure of trans-polacetylene with undisturbed conjugation (c)The formation of a neutral soliton (• indicating an electron not involved in bonding) on trans-polacetylene and (d) a soliton domain wall extending over a number of carbon atoms [10].

The soliton is sometimes referred to as a structural kink, it is a quasi-particle which for polymeric materials may exist only if there is a degenerate ground state. The neutral soliton carries a spin $\frac{1}{2}$ like a single localized electron. Looking at polyacetylene which has a twofold degenerate ground state; it can be in either the cis (Figure 3.17a) or trans (Figure 3.17b) conformations each having two possible configurations. In the case where the trans-polyacetylene has an odd number of conjugated carbon atoms, there exists an unpaired π -electron or radical that is free to travel along the backbone. The soliton presents locally (several atoms along the chain) in the form of a distortion of conjugation (Figure 3.17c). It has been defined by Su, Schrieffer and Heeger as a bondalternation domain wall (Figure 3.17d) [10]. This infers that the soliton is situated at a point where one polymer domain ends and a new one begins i.e. two conjugated forms now coexist. The soliton may exist in a number of states: neutral and charged (positive or negative) [13]. The presence of a soliton yields a localized electronic level at the middle of the gap between the valence and conduction bands. The level is half-occupied in the case of a neutral soliton (Figure 3.18a). It is empty in the case of a positively charged soliton (Figure 3.18b) and doubly occupied for a negatively charged soliton (Figure 3.18c). A positively (negatively) charged soliton is formed when an electron is

removed (added) such that the system has zero spin (In the case of the negatively charged soliton, the additional electron results in the spins of the electron pair being opposed).



Figure 3.18 Band structure for a polyacetylene chain containing (a) a neutral [spin up or down](b) positively or (c) negatively charged soliton.

The exciton

The concept of the exciton first introduced by Frenkel in 1930 was based on the idea that for the electronic excitation of a solid, the first step of light absorption was not confined to an individual atom but widely spread out across numerous atoms in the form of excitation waves. In a manner analogous to phonons being quasi-particles and quanta of lattice vibrations, the exciton is used for an excitation wave. There are a few variations to what the term exciton can mean depending on the field of study. In quantum chemistry terminology for molecular physics, an exciton is any excitation above the ground state of a molecule. In solid state physics, an exciton may be referred to as a delocalized current conducting excitation consisting of an electron-hole pair in a bound state confined within an effective Bohr radius which defines the size of the exciton.

The excitons typically observed in molecular crystals and polymers are similar to those in amorphous inorganics. The difference between the situations in which an exciton may be observed in inorganic and organic materials is also noteworthy. In an inorganic crystal having a relatively high dielectric constant, the coulombic interaction between an electron carrying negative charge and a hole carrying positive charge is reduced due to screening but still results in a weakly bound electron hole pair known as a Wannier-Mott exciton which may be observed at low temperatures (\sim 50 K). The Wannier-Mott exciton has a low binding energy (\sim 10 meV) and as such its size (\sim 100 Å) is typically much larger than the lattice spacing (Figure 3.19). This shallow exciton is easily dissociated into a free electron and hole at higher temperatures and consequently is not observed e.g. Si at 300K.

Wannier-Mott Exciton



Figure 3.19 Diagram of a crystal lattice displaying a Wannier-Mott exciton having a size larger than the unit cell of the crystal. The Energy band diagram depicts the exciton energy level sitting within the gap of the semiconductor material.

In molecular crystals and polymeric materials, the electron – lattice coupling is much more pronounced, screening of the coulombic interaction is less due to lower dielectric constants and as a result, upon excitation a strongly bound Frenkel exciton is formed which is much smaller in size (~ 10 Å) practically localized to a single repeat unit of the polymer chain. The binding energy of the Frenkel exciton is typically much larger – values range from 0.1 to 1 eV depending on the material in question [8,15].





Figure 3.20 Diagram of a Frenkel exciton and its representation on an energy diagram labeled with the ground (S_0) , excited (singlet exciton) state (S_1) and excited (triplet exciton) state.

3.4 Raman Spectroscopy

Typically the monochromatic light source (such as an intense laser beam) used for Raman spectroscopy is in the UV-visible to near-IR portion of the EM spectrum. When this light is incident on a sample that is dust-free, optically transparent and in a gaseous, liquid or solid form, most of the light is transmitted unchanged. A portion of the incident electromagnetic radiation is observed to be scattered perpendicular to the direction of the laser beam. The scattering mechanism can either be an elastic process such as Rayleigh scattering or an inelastic scattering, defined as Raman scattering.

Rayleigh scattering is the most common scattering process observed; it is strong and causes no change in frequency for the scattered photon with respect to the incident photon. As it is an elastic process, the emitted photon is at the same energy as the absorbed incident photon. The atom is excited to what is said to be a virtual excited state by an incident photon of frequency (v_0), the atom relaxes back to the ground state whereby a scattered photon is emitted also having frequency v_0 as shown in Figure 3.21.





Figure 3.21 Diagram depicting Rayleigh scattering, where v is the vibrational energy level and the broken lines depict virtual energy levels.

In contrast, Raman scattering is extremely weak with an intensity $\sim 10^{-5}$ times that of the incident beam. Raman scattering is the interaction of the incident laser light with molecular vibrations, phonons or excitation in the system resulting in the laser light being altered. The Raman scattered photons are observed to have frequencies which are shifted either lower (Stokes) or higher (anti-Stokes) than the incident photons (v_0) by an amount v_m corresponding to the vibrational, rotational or electronic transitions of the molecule under investigation such that

Stokes:
$$v_{\text{scattered}} = v_0 - v_m$$

anti-Stokes: $v_{\text{scattered}} = v_0 + v_m$ (3.31)



Figure 3.22 Energy level diagram showing Stokes and anti-Stokes Raman scattering

In Figure 3.22 the vibrational energy levels v = 0 through v = 3 which belong to a single electronic energy state are shown. It can be seen from the energy level diagram that the Stokes and anti-Stokes lines as described in Equation 1.31 originate from the v = 0 state and the v = 1 states, respectively. The Stokes line is far more intense when compared to the Anti-Stokes line in the Raman spectrum because in general, the v = 0 state is populated to a far larger extent than that of the v = 1 state. This is expected from the Maxwell-Boltzmann distribution law: the ratio of the populations (P) at the v = 1 and v = 0 states is given by

$$\frac{P_{v=1}}{P_{v=0}} = e^{-\Delta E/k_{B}T}$$
(3.32)

where ΔE is the energy difference between the two states, k_B is Boltzmann's constant and T is the absolute temperature [16].



Figure 3.23 Illustration depicting the influence of an electric field on the electron cloud of an atom inducing a dipole moment.

A Raman signal or the observed scattering of incident light perpendicular to the direction of incidence is a result of the molecular polarizability (α) of a molecule. In order to observe a Raman signal, the vibrational mode or transition must be allowed (Raman-active) where the polarizability of a bond changes with the accompanying vibration. Polarizability is a measure of the ability of a bond to deform and is proportional to the electric field strength (E). This is related to the ease of displacement of the electrons in the bond which induces a temporary dipole. An intense Raman signal may be observed for the case that there is a large concentration of loosely held electrons in a bond i.e. the polarizability is large. Raman is especially useful in determining functional groups and spectroscopic fingerprints of organic molecules — Raman

vibrations are characteristic to a specific molecule due to the molecular vibrations as a whole encompassing interactions between multiple bonds.

3.4.1 Vibrations in diatomic and polyatomic molecules

In the case of a diatomic molecule only one kind of vibration occurs (stretching, denoted as v) where the two atoms are connected by a chemical bond. Raman scattering may be described by classical electromagnetic wave theory yielding a relatively simplistic mathematical description [16–19]. By considering the incident laser photons having frequency (v_0) and an electric field strength (E) that varies with time (t) given by

$$\mathbf{E} = \mathbf{E}_0 \cos 2\pi \mathbf{v}_0 \mathbf{t} \tag{3.33}$$

where E_0 is the amplitude of the vibration. Upon illumination of the molecule an electric dipole moment (P) is induced such that

$$P = \alpha E = \alpha E_0 \cos 2\pi v_0 t \tag{3.34}$$

where α , the polarizability of the molecule is a proportionality constant. The nuclear displacement (q) may be written as

$$q = q_0 \cos 2\pi v_m t \tag{3.35}$$

where q_0 is the vibrational amplitude and v_m is the molecular vibration frequency dependent on the atomic masses, the elastic forces between them and the force constants (bond strengths), and the geometry of the atomic positions). For small values of q_0 the polarizability may be expressed as a linear function of the nuclear displacement given by the Taylor series

$$f(x) = \sum_{n=0}^{\infty} \frac{f^{n}(a)}{n!} (x-a)$$
(3.36)

where $f^n(a)$ denotes the nth derivative of (f) evaluated at (a), and it is approximated to the first order about the equilibrium position for a harmonic oscillator.

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 + \dots$$
 (3.37)

In this expansion, α_0 is the polarizability at the equilibrium position and the second term is the rate of change of α with respect to q (derived polarizability), also evaluated at the equilibrium position. If an anharmonic oscillator was to be considered where the potential is typically approximated by the 'Morse' function similar to that illustrated in Figure 3.15, the Taylor series would have to be implemented allowing for cubic, quadratic and higher terms. This would also introduce overtones and combination bands in the Raman spectra.

The combination of Equations (3.33)-(3.35) along with the use of the trigonometric identity $\cos(x).\cos(y) = \frac{1}{2} {\cos(x+y) + \cos(x-y)}$ yields

$$P = \alpha E_0 \cos 2\pi v_0 t$$

$$= \alpha_0 E_0 \cos 2\pi v_0 t + \left(\frac{\partial \alpha}{\partial q}\right)_0 q E_0 \cos 2\pi v_0 t$$

$$= \alpha_0 E_0 \cos 2\pi v_0 t + \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \cos 2\pi v_0 t \cos 2\pi v_m t \qquad (3.38)$$

$$= \alpha_0 E_0 \cos 2\pi v_0 t$$

$$+ \frac{1}{2} \left(\frac{\partial \alpha}{\partial q}\right)_0 q_0 E_0 \left[\cos \left\{2\pi (v_0 + v_m)t\right\} + \cos \left\{2\pi (v_0 - v_m)t\right\}\right]$$

where the first term represents an oscillating dipole which emits photons having frequency (v_0) by Rayleigh scattering. Subsequent terms of the expansion which are omitted are where two phonons are involved: the transverse optical (TO) phonon and the longitudinal optical (LO) phonon. It is clear that for the case where the rate of

change of α with respect to q is zero, the vibration is not Raman-active. In reality this 1-D treatment which assumes that the dipole was created along molecular axis is a very specific case and it must be expanded to allow for the 3-D nature of vibrations where P and E are actually vectors quantities and must be expressed in terms of the x, y and z directions. This modification results in the introduction of a polarizability tensor which is often shown in the matrix format:

$$\begin{bmatrix} \mathbf{P}_{x} \\ \mathbf{P}_{y} \\ \mathbf{P}_{z} \end{bmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{bmatrix} \mathbf{E}_{x} \\ \mathbf{E}_{y} \\ \mathbf{E}_{z} \end{bmatrix}$$
(3.39)

For normal Raman scattering, the polarizability tensor is symmetric such that $\alpha_{xy} = \alpha_{yz}$, $\alpha_{xz} = \alpha_{zx}$ and $\alpha_{yz} = \alpha_{zy}$. With the introduction of this tensor form of the polarizability, in order for a vibration to be Raman-active at least one of the tensor quantities must be non-zero. In order to account for this modification the first order Taylor expansion given in Equation (3.35) may now be modified to include each component of the polarizability tensor such that

$$\alpha_{ij} = \left(\alpha_{ij}\right)_0 + \left(\frac{\partial \alpha_{ij}}{\partial q}\right)_0 q_0 + \dots$$
(3.40)

where α_{ij} is a particular component of the polarizability tensor (i,j are integers referring to the index of α in the matrix), $(\alpha_{ij})_0$ is its value at the equilibrium position and $\left(\frac{\partial \alpha_{ij}}{\partial q}\right)_0$ is called the derived polarizability tensor – often denoted as $(\alpha'_{ij})_0$

The vibrations occurring in a polyatomic system consisting of more than two atoms is far more complex due to each of the nuclei in the system having their own harmonic oscillation. The overall movement of the system can be considered as the superposition of a number of completely independent 'normal vibrational modes'. In the case considering more than one nuclear coordinate (q), the previous expression is modified to sum up over all q such that

$$\alpha_{ij} = \left(\alpha_{ij}\right)_0 + \sum_k \left(\frac{\partial \alpha_{ij}}{\partial q_k}\right)_0 q_k + \dots$$
(3.41)

where q_k are the normal coordinates of the normal vibration summed up over k different coordinates. The condition for a vibration to be Raman-active may now be satisfied provided that at least one component of the derived polarizability tensor with respect to any particular vibrational normal coordinate is non-zero.

This is a very simplified treatment of Raman scattering serving only as an introduction to the topic with reference to small linear molecules such as CO₂. When polyatomic molecules of greater complexity are considered, the vibrations involve compression and stretching of many bonds. Other motions may also be observed and are defined as deformation modes which may consist of bending (δ), wagging (ρ_{ω}), twisting / torsional (ρ_t), rocking (ρ_r) etc. In general once the system becomes more complex the determination of whether or not a vibration mode will be Raman-active relies on the combination of numerous polarizability tensor components arising from the increased number of individual nuclear displacements and the relative phases of the motions experienced by each bond [17].

In terms of quantum mechanics Raman scattering may only occur when a change in polarizability occurs when there is a transition from the ground (ψ_1) to an excited state (ψ_2). This can be represented by an integral over all space such that

$$\int \psi_1 \alpha \psi_2 d\tau \tag{3.42}$$

where α transforms like the functions x^2 , y^2 , z^2 , xy, xz etc. such that the Raman scattering is observed only when the wavefunction of the excited state belongs to the same irreducible representation as either x^2 , y^2 , z^2 , xy, xz etc. This infers that knowledge of the symmetry properties of the vibrational excited state of the molecule under investigation may predict whether or not it is Raman-active. This is commonly done with the aid of character tables having rows corresponding to irreducible group representations thus giving the transformation properties of the polarizability tensor.

3.4.2 The use of symmetry and group theory

Group theory is a very powerful mathematical tool used to aid the study of complex structured objects. It is the systematic mathematical approach to define symmetry. In order to simplify complex structures such as crystals and molecules, Group theory uses a set of operations associated with the symmetry elements (Table 3.3) of the molecule which then make up a mathematical set (Group). Mathematical theorems defined for these particular groups may in turn be used to rationalize and define certain symmetry operations which may be represented by a matrix which operates on a base set that is descriptive of the molecule.

	Symmetry element	Symmetry operation	Schönfliess notation	Hermann- Mauguin notation
1.	Identity	No operation carried out	E	1
2.	Centre of symmetry	Reflection through a point	i	ī
	(inversion center)	(Inversion)		
3.	Plane of symmetry	Reflection through a plane	() have a d	m
	(Mirror plane)		O n,v or a	
4.	Proper axis of symmetry	Rotation about an axis through	C.	n
		360°/n	Cn	
5.	Mirror plane			
6.	Improper axis of symmetry			
a)	Rotation reflection axis	Rotation about an axis through		
		360°/n followed by reflection		
		through a plane perpendicular to	Sn	n
		the axis		
			-	_ n
b)	Rotation inversion axis	Rotation about an axis through		
		360°/n followed by inversion		

Table 3.3 Symmetry elements, operations and their corresponding notations

A symmetry operation may be performed on an object only if it leaves it in a configuration that is indistinguishable from and superimposable on its original configuration. A symmetry element is defined as a point, line or plane to which a

particular symmetry operation is carried out. Combining the symmetry operations with the seven crystal systems yields 32 point groups and the consideration of the 14 Bravais lattices with all the possible symmetry elements and translations yields 230 space groups. In addition to the 32 crystallographic point groups, there are an infinite additional number of non-crystallographic groups. The icosahedral group (I) is of most interest and is related to C_{60} and some of the boranes. The concepts introduced for crystalline point groups and symmetry may be applied to molecules in the context of site symmetry or pseudo-symmetry. It is important to note that molecules in a crystalline structure may not necessarily have a correlation between the symmetry of their unit cell compared to that of the crystal; in general these concepts are useful in the prediction of possible bands for Raman studies.

The two most commonly used standards for the designation of Space Groups are the Hermann-Mauguin (spectroscopy) and Schönfliess (crystallography) notations. The 32 Point Groups are presented along with their various notations with reference to their crystal system in Table 3.5 [20]. The Hermann-Mauguin system is also called the International system for point groups. In Table 3.5 'n' denotes the presence of an n-fold axis and 'm' is used to denote a mirror plane. The diagonal line '/' is used when the mirror plane is perpendicular to the symmetry axis. The different classes of symmetry elements are also given where 'v' is vertical, 'h' is horizontal and 'd' is the diagonal / dihedral. A bar over a number represents an inversion [21].

All the matrix representations of a particular symmetry operation have the same character and may be further reduced to a block / diagonal matrix. Once the matrix is reduced to a point where no further reduction is possible it is called the irreducible representation. It is the characters (1 symmetric, -1 anti-symmetric) of each row of the character table that define the irreducible representation of a particular point group. The character table for the C_{2v} point group is shown in Table 3.4. The column headings are symmetry operation classes for the group and the basis functions having the symmetry properties of a given irreducible representation are on the right. R_x , R_y , R_z are rotations about the specific axes. The Mulliken Labels are detailed in the leftmost column [20].
C2v	E	C ₂	σ _v (xz)	σ _v (yz)			
A ₁	1	1	1	1	Z	x^{2}, y^{2}, z^{2}	z^{3} , $z(x^{2}-3y^{2})$
A ₂	1	1	-1	-1	Rz	ху	xyz
B ₁	1	-1	1	-1	x, R _y	xz	xz^{2} , $x(x^{2}-3y^{2})$
B ₂	1	-1	-1	1	y, R _x	yz	yz ² , y(3x ² -y ²)
Γ _{x,y,z}	3	-1	1	-1		•	

Table 3.4 Character table for the C_{2v} point group.

The character table may then be used in conjunction with an analysis of the molecule in question to ascertain the modes of vibration. This is achieved by examining the reducible representation for the molecule and applying the reduction formula with the character table to resolve the number of each species labeled by the Mulliken notation. The translational modes (all atoms move in the same direction equivalent to the moving molecule) and rotational modes (atoms move to change the orientation of the molecule) are subtracted to leave only the vibrational modes of interest.

Numbor	Schönfliess	Hermann-Maguin	Crustal Sustam	
Number	symbol	symbol	Ciystai Systemi	
1	C ₁	1	Triclinic	
2	Ci	ī		
3	Cs	m		
4	C ₂	2	Monoclinic	
5	C_{2h}	2/m		
6	C _{2v}	mm		
7	D ₂	222	Orthorhombic	
8	D_{2h}	mmm		
9	C ₄	4		
10	S ₄	4		
11	C_{4h}	4/4		
12	C _{4v}	4mm	Tetragonal	
13	D_{2d}	42m		
14	D_4	422		
15	D_{4h}	4/mm		
16	C ₃	3		
17	S ₆	3		
18	C _{3v}	3m	Rhombohedral	
19	D ₃	32		
20	D _{3d}	- 3m		
21	C _{3h}	$\overline{6}$		
22	C ₆	6		
23	C _{6h}	6/m		
24	D _{3h}		Hexagonal	
25	C _{6v}	6mm		
26	D ₆	622		
27	D _{6h}	6/mm		
28	Т	23		
29	T _h	m3		
30	T _d	43m	Cubic	
31	0	432		
32	O _h	m3m		

Table 3.5 The 32 crystallographic point groups, their symbols and crystal system [20].

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CHAPTER 4.

Conductivity, Charge Transport, Organic Photovoltaic Devices and Optical Processes

4.1 Introduction

This chapter discusses the relevant mechanisms of conductivity and charge transport in organic materials. Organic photovoltaics devices are introduced, where their operation and characterization is detailed. This chapter is completed by a discussion of the relevant theory describing optical processes occurring in these materials and devices.

4.2 Fundamental mechanisms of conductivity in polymers

4.2.1 Percolation

Percolation was originally studied as a mathematical concept and has become a powerful tool in statistical physics. It is often referred to a probabilistic model that exhibits a phase transition. Broadbent and Hammersly introduced the term 'percolation process' in a paper entitled "Crystals and mazes" published in 1957 [1]. Hammersly chose the term percolation because fluid flowing into a maze resembled coffee flowing through the grounds in a percolator. They studied generalized systems where the random properties of a 'medium' influenced the percolation of a 'fluid' through it. The difference between diffusion and percolation is defined such that the randomness is ascribed to the fluid in the former and the medium in the latter. Percolation theory has a strong ability to describe the physical properties of heterogeneous materials. The random spreading of such a fluid through a medium may be analogous to charges travelling within a bicontinuous network of two different materials being either conducting or insulating. This can further be used to describe the motion of an electron across various atomic sites in a lattice structure. In a 2-D case, one may consider a random assortment of spherical conducting (black) and insulating (white) species within a specific area as illustrated in Figure 4.1.



Figure 4.1 Illustration of a blended system consisting of conductive (black) and insulating (white) species.

If a voltage is applied across two edges of this system, a current will only pass across it in the event that there is a continuous path connected by the black spheres from one side to the other. As the two species take up a random placement the description of this system relies on probability. The concentration of the conducting spheres (filler material) with respect to the insulating (host) is often called the loading and is represented by p. The aim here is to decide what is the minimum loading or value for p such that current may travel across system? The minimum loading or critical point is described as the percolation threshold (p_c). The behavior of the system changes dramatically for $p < p_c$ (Figure 4.2a) and for $p > p_c$ (Figure 4.2b). A sharp transition occurs where the current begins to flow; this is called a phase transition or critical phenomenon and the value at which point this transition occurs is called the critical value. In the scenario that p has reached the percolation threshold, the assortment of conducting spheres is referred to as a cluster (group of connected sites) extending across the system, thus allowing for the flow of charge under bias. When p has not reached the percolation threshold then no such cluster exists and charge does not flow under bias.

The determination of p_c is dependent on the distribution of the filler material in the matrix which is influenced by the geometric parameters: particle size, shape and orientation. In the case of the spherical particles, where the particle size of host medium is R_1 and the filler is denoted as R_2 , the Sher-Zallen invariant where $R_1/R_2 \rightarrow 1$ the value for $p_c \sim 0.16$. As $R_1/R_2 \gg 1$, the filler material is more inclined to fill the interstitial gaps between the larger host particles such that a more orderly arrangement is imposed on the filler material which in turn allows for a much lower value for p_c [2].



Figure 4.2 Illustration of a blended system consisting of conductive (black) and insulating (white) species where (a) $p < p_c$ and (b) $p > p_c$

The geometry of the filler material becomes even more important due to the percolation threshold being inversely proportional to the aspect ratio. Once the shape of the filler material is changed from spherical to one having a higher aspect ratio, the value for p_c drops significantly. This leads to the popularity of using CNTs as filler materials in the fabrication of low concentration (consequently requiring a low p_c) but high conductivity percolative composites [3]. Typically a polymer is used as the host material which introduces a number of additional characteristics that affect the percolation threshold. These include surface tension, wettability, viscosity, crystallization and solubility of the filler material which all impact the uniformity of the filler distribution in the matrix and as such can alter the value of p_c significantly.

The mathematical description of the electrical conductivity of a composite material (σ_c) near percolation can be expressed if the electrical conductivity of the filler (σ_1) and host (σ_2) materials are very different. The following three cases are detailed by Nan *et al.* in [2]:

1. When $p > p_c$, the filler material forms a continuous percolating path throughout the composite matrix such that σ_c is determined by σ_1

$$\sigma_{\rm c} \propto \sigma_2 \left(p - p_{\rm c} \right)^{\rm t} \tag{4.1}$$

where t, the critical exponent for electrical conductivity is dependent on the dimensionality. t = 1.1 - 1.3 for 2D and t = 1.6 - 2.0 for 3D.

2. When $p < p_c$, the filler material is isolated in the matrix which prevents any continuous percolating path throughout the composite matrix such that σ_c is determined by the narrow gaps between neighboring fillers. This case may be exemplified by charge transport processes dominated by hopping. As p increases to approach p_c , σ_c may then be described by

$$\sigma_{\rm c} \propto \sigma_2 \left(p_{\rm c} - p \right)^{-\rm s} \tag{4.2}$$

where the critical exponent s is 1.1 - 1.3 for 2D and 0.7 - -1.0 for 3D.

3. When $|p - p_c| \rightarrow 0$, defined by the crossover of the two previous scenarios, σ_c is determined by

$$\sigma_{\rm c} \propto \sigma_2^{\rm u} \sigma_1^{\rm l-u} \tag{4.3}$$

where u = t/(t + s). These three laws have been verified empirically for numerous composite materials near percolation.

Conductive particles such as metals or suitable carbon allotropes may be blended with a non-conducting polymer host material at a concentration high enough to result in a percolative conducting network of charge pathways. Depending on the interaction of the polymer host with the additive in the blended structure, the percolation threshold is reached for a certain additive concentration above which significant conductivity values may be obtained.

4.2.2 Ionic conduction

The polymer may contain ions from impurities due to remaining catalyst materials from the polymerization process, the ionization of groups along the chain or it may deliberately be complexed with salts forming electrolytes. Modification of a polymeric material can comprise of chemical doping where either an oxidizing or reducing agent is introduced or electrochemical doping where electrons may be added or removed from the system by means of an external electrode. Cation-rich polymers are labeled as pdoped and anion-rich polymers are labeled as n-doped in analogy with the nomenclature used for extrinsic semiconductors such as silicon. The introduction of even the smallest concentrations of dopant atoms (less than 10⁻⁷%) to Si can alter conductivity by up to several orders of magnitude. Each impurity which is introduced into Si alters the valence energy states of the neighboring atoms in the lattice structure. In terms of polymer chains, there is no covalent type bonding between neighboring chains, so altering one chain may not have the same 'knock-on' effect as if it was done to a lattice structure. It may also be noted that the dopant carrier concentrations in inorganic semiconductors are directly proportional to the conductance. This is not the case for organics as impurities introduced act in a different way. In general polymers can be doped using iodine or bromine leading to p-type materials containing negatively charged counter-ions. The use of alkali-metals yields n-type polymers containing positively charged counter-ions. Acids have also been used to modify the conductivity of polymers by means of protonation which can introduce positively charged sites along the polymer backbone resulting in an oxidized state of the polymer — conversely deprotonation can be used with the application of a base.

4.2.3 Electronic conduction

The electronic conductivity of polymeric materials covers a very large range encompassing values representing insulators ($<10^{-12}\Omega^{-1}m^{-1}$) to semiconductors (10^{-12} to ~ $10^{-1} \Omega^{-1}m^{-1}$), metals (>10 $\Omega^{-1}m^{-1}$) and in some rare cases, superconductors based on ionic salts. Recalling the polymers previously discussed; polyethylene is one of the best known insulating materials and polyacetylene can display a higher conductivity per unit mass than that of copper [4]. Customarily the band-theory of conduction is used as the starting point for a discussion of electronic conduction in polymeric materials. A caveat must be issued to emphasize that band-theory is in many ways an insufficient model. Band-theory is correctly used to explain three-dimensional lattices consisting of inorganic atoms or compounds that are strongly bound together. It may be used to describe highly purified molecular crystals and it is accepted as a starting point when used to describe perfect, infinitely long polymer chains. It cannot however, accurately describe the behavior of a realistic, solid state, semiconducting polymer material held together by softer bonds which tend to deform in the presence of additional charges. Here, electronic conduction is governed by charge transport associated with the interactions of mobile localized excitations consisting of quasi-particles such as excitons, polarons, bipolarons and solitons. The discrepancies of the often used analogy comparing highly ordered materials to disordered polymers is highlighted later on in the discussion of charge transport mechanisms.

Unfortunately there is no complete and accurate model describing conductivity in polymers today. The exact conduction processes occurring in intrinsic and doped polymeric materials is still under intense scrutiny. In general there are three principle mechanisms: charge transport along the individual chain (intramolecular), charge transport between neighboring chains (intermolecular / hopping) and to a lesser degree tunneling between conductive regions separated by less conductive regions. There are many factors which can potentially influence these processes. The structure of the individual molecular unit, how it is arranged once polymerized into long chains and subsequently the morphological arrangements these chains form when processed into a thin solid film will ultimately define the polymer conductivity. It must be noted that whatever the precise conduction mechanism is, the bulk conductivity observed can vary greatly from samples prepared under similar conditions. This is reflected in the differing morphologies of the polymer films due to the processing conditions which directly affect the intra- and inter-chain charge transport. When considering the use of certain polymers for applications in organic electronics such as photovoltaics, sheet resistance and bulk resistivity are two properties that are especially of interest. Both of these properties rely on the directional dependence of charge transport through the material.

4.3 Charge carrier transport

As an introduction to this topic we can look at the different types of motion charge carriers can perform in a solid. Band-theory encompasses the collective nature of the conduction states. In a typical inorganic semiconductor material such as germanium, the holes move across the crystal lattice in the form of a delocalized plane wave within a broad carrier-band. If the crystal is free from defects and impurities no scattering of the charge carrier will take place. In reality, irregularities in the atomic structure in the form

of vacancies, point defects and dislocations or crystal grain boundaries have the effect of scattering the charge carrier into a different momentum state. Temperature effects resulting in the distortion of the crystal lattice also causes carrier scattering and is referred to as a thermal vibration (quantized as a phonon). In contrast, looking at a highly localized charge carrier exemplified by that associated with a molecule, the carrier moves from site to site and is scattered at almost every transition.

The motion of the charge carriers is characterized by a temperature dependent mobility. In the most basic form, the electrical mobility for charge carriers (μ_c) is a measure of the velocity at which a charge carrier travels through a medium per unit electric field and customarily it is presented in units of cm²V⁻¹s⁻¹. More specifically mobility may also be defined for each carrier separately; μ_e for electrons and μ_h for holes. The temperature dependence of the mobility is characteristic of the material being observed and as such is a useful metric in the determination of the mechanism dominating the charge transport processes. A characteristic feature of band transport is the inverse power law dependence for the mobility as a function of temperature [5].

$$\mu \propto T^{-n}$$
 with $n = 1...3$ (4.4)

4.3.1 Hopping

When imaged on a microscopic scale, a thin polymer film appears to be mostly amorphous. Polymer films exhibit this disorder due to irregular molecular packing; the presence of kinks, twists, defects; and vibrational or rotational movement of side groups attached along the back bone. These irregularities result in a vastly different situation for electronic conduction compared to ordered crystalline lattices or small molecular crystals. The π -conjugated system, consisting of π orbitals is divided into different electronic states which are localized over a few molecular units rather than along entire backbone or across a large crystalline domain. As a direct result of this localizing of electronic states to certain sites, charge transport must occur via an activated process moving them from site to site rather than via a band-like conduction process. Charge transport by phonon-assisted tunneling of electrons or holes between localized states with varying energies, randomly distributed in space is customarily called hopping. The hopping transition rate is unrelated to an averaged value for hopping but rather it is correlated to the number of the most difficult but relevant hops which may occur [6].

The incoherent hopping process may be described by a number of theoretical frameworks, the basis of which was proposed in 1956 by Conwell and Mott to explain impurity-band conduction in semiconductors [7,8]. Miller and Abrahams later proposed their own formalism building on the works of Conwell and Motts for low concentration impurities [9]. The classical Miller-Abrahams formalism describes the motion of the carrier to an adjacent inter- or intra-chain site with the assistance of a single phonon. Charges preferably hop to sites at lower energies but there is also a balance between the distance they travel and how favorable the energy level of the specific site is. The hopping transition rate for a charge carrier from an occupied site *i*, at energy ε_i to an empty site *j* at energy ε_i is given by

$$w_{ij} = v_0 \exp\left[-2\alpha\Delta r_{ij} - \left(\frac{\Delta\varepsilon_{ij}}{k_B T}\right)\right], \text{ for } \varepsilon_j > \varepsilon_i,$$

$$w_{ij} = v_0 \exp\left[-2\alpha\Delta r_{ij}\right], \text{ for } \varepsilon_j < \varepsilon_i,$$
(4.5)

where v_0 is the frequency of attempted hops related to electron-phonon coupling and the phonon frequency; α is the inverse of the wavefunctions (π -electron delocalization length); Δr_{ij} is a distance factor related to the wavefunction overlap between sites *i* and *j*; k_B is Boltzmann's constant; and T is the temperature in Kelvin.

Mott further introduced variable range hopping (VRH) in 1969 inspired by the Miller-Abrahams formalism using a constant density of states [10]. It was used to describe resistivity in strongly disordered systems with localized states at low temperatures. VRH owes its name to the random arrangement of atoms in an amorphous system leading to a varied hopping distance. Essentially hopping may be considered as a mechanism analogous to percolation and as such theoretical descriptions of hopping transport based on percolation theory were first proposed in the early 1970s [11,12]. Marcus theory was originally developed in 1956 to aid in the description of electron transfer from a donor to an acceptor [13]. It has since been applied as a semi-classical description of non-adiabatic small polaron hopping transport in semiconducting polymers useful in accounting for polarization and geometrical reorganization effects. The transition rate for polarons differs from the Miller-Abrahams formalism as it does not depend on whether the hop is to a higher or lower energy site. It is given by

$$w_{ij} = \frac{2\pi}{\hbar^2} t^2 \sqrt{\frac{1}{4\lambda\pi k_B T}} \exp\left[\frac{-\left(\Delta G^0 + \lambda\right)^2}{4\lambda\pi k_B T}\right]$$
(4.6)

where t is the transfer integral, λ is the reorganization energy related to electron phonon coupling, ΔG^0 is the difference in the Gibbs free energy from the initial to the final state, h is Planck's constant, k_B is Boltzmann's constant and T is the temperature in Kelvin.

These methods for estimating the hopping transition rates have been widely used in conjunction with the assumption that the DOS is a Gaussian profile for disordered organic systems. This assumption is based on observation of the shape of the excitonic absorption band and recognizing that the polarization energy is described by a large number of internal positions with small randomized variations [14]. This is in contrast to the exponential profile of the DOS generally accepted for their inorganic counterparts. It also relies on the energetic disorder of the system related to the variation of conjugation lengths of the polymer chain and is strongly affected by the electric field. The Gaussian distribution for the DOS is given by

$$N(E) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left(-\frac{E^2}{2\sigma^2}\right),$$
(4.7)

where σ is the distribution energy scale mirroring disorder, ε is the energy and N is the concentration of states. A far more in-depth and complete management of the description of the theory of charge transport in organic semiconductors is carried out by Coropceanu et al [15].

4.3.2 Traps, recombination sites and space charge limited current

A trap is defined in energy space as a potential-well which has the ability to confine or capture an electron or hole. The trapped charge carrier may be subsequently released or re-emitted after a period of time. Traps can be considered as either shallow or deep depending upon where they lie within the band-gap.

Space charge limited current

When there are a significant number of trapping sites present in a semiconducting polymer device, a high charge density may build up at the electrode due to the injection of low mobility carriers. The built-up charge density is called space charge and it acts on the applied field resulting in reduced current flow across the semiconducting polymer. This process is called space charge limited current (SCLC) and is for the most part observable when the material is subjected to a considerable bias at room temperature. In the case of insulating or wide band-gap semiconductors, a very small number of thermally generated carriers are present and as such the presence of charge carriers in the material is either due to injection at the electrode or photogeneration. Taking this example neglecting diffusion currents Child's Law gives the relationship between current and voltage in an insulator

$$I = \frac{9}{8}\mu\varepsilon\varepsilon_0\Theta\frac{V^2}{d^3}$$
(4.8)

where Θ , V, d, μ , and ε are the ratio of free to total carrier concentration, the applied voltage, distance between the electrodes, permeability and permittivity of the material. In general a log-log plot of current vs. voltage would yield a slope m = 2 (current proportional to the square of the voltage) for the trap free case (Θ =1). In practice, real materials contain deep traps and as such Θ is a function of voltage and m ≥ 2 .

4.4 Organic Photovoltaics

4.4.1 Basis of OPV device operation

The principle of operation for an organic photovoltaic (OPV) device is based on the conversion of incident electromagnetic radiation to electrical charges which may then be extracted at the electrodes. There are a number of processes which occur in order to achieve this and the OPV architecture is an ensemble of planar layers engineered to

carry out these processes as efficiently as possible. Essentially the OPV device layered structure is tailored to accommodate the so-called active layer which typically comprises of one or more semiconductor materials which are either made up of organic materials that are solution processed or small molecular systems, which may be physically deposited by vapor deposition.

In summary the operation of an OPV may be listed as follows:

- Light is absorbed in the active layer creating an exciton
- The exciton diffuses to a dissociation site
- The exciton dissociates to a free electron and corresponding hole
- The free charge carriers are transported to the appropriate electron for extraction

Throughout these steps there are competing processes which reduce the power conversion efficiency (PCE or η) of the OPV. The external quantum efficiency (EQE) of the OPV device describes the likelihood of an incident photon giving rise to an electron available to an external circuit; it includes the losses due to the competing processes and can be written as

$$\eta_{EQE} = \eta_A \eta_{IQE} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$$
(4.9)

It may be considered as the product of the internal quantum efficiency (IQE) and the absorption efficiency η_A accounting for the absorption cross-section of the active layer and losses due to reflection. IQE is the ratio of absorbed photons to charge carriers extracted at the electrode and as such is the product of the following efficiency terms: exciton dissociation efficiency η_{ED} - related to the number of excitons successfully dissociated at an interface accounting for recombination losses; charge transport efficiency η_{CT} - defining the number of charges successfully transported to the electrode accounting for scattering losses, traps etc.; and charge collection efficiency η_{CC} - linked to the suitability of the electrodes in collecting the available charges.

4.4.2 Photovoltaic Characterization

The current – voltage (I-V) or the area normalized current density – voltage (J-V) characteristic curve is a graphical representation of the parameters reflecting the performance of an OPV device. The comparison of J-V curves for a device in the dark and under illumination yield the majority of the parameters required to determine the PCE of an OPV device under test. An example of a typical J-V curve for an OPV device with a bulk-heterojunction active later is shown in Figure 4.3. The critical parameters of the device are marked, namely the open circuit voltage (V_{OC}), short circuit current density (J_{SC}) and the maximum power point (MPP) with its corresponding values for J_{MPP} and V_{MPP} . The fill factor (FF) is a ratio which is used to gauge the quality of the OPV device and is given by

$$FF = \frac{J_{MPP}V_{MPP}}{J_{SC}V_{OC}}$$
(4.10)

The power conversion efficiency of an OPV is defined as the ratio between power incident on the device active area from the sun to the maximum power extracted at the electrodes

$$\eta_{PCE} = \frac{P_{MAX}}{P_{IN}} = \frac{J_{MPP}V_{MPP}}{P_{IN}} = \left(\frac{J_{SC}V_{OC}}{P_{IN}}\right) \times FF$$
(4.11)

The device shown in Figure 4.3 has an active area of 2.34 mm², $V_{OC} = 0.52$ V, $J_{SC} = 5.94$ mAcm⁻² and a FF = 0.53. These values yield a PCE = 1.66 % as per Eqn. (1.29) for an illumination intensity of 1 sun (100 mWcm⁻²).



Figure 4.3 J-V characteristic curve of an OPV device displaying J_{SC}, J_{MPP}, V_{OC} and V_{MPP}.

Similarly, a J-V curve may be presented in another form where the y-axis is displayed using a logarithmic scale as shown in Figure 4.4. This semi-logarithmic J-V curve is used to more clearly show the characteristics of a device tested in the dark which in turn yields more information concerning the parasitic resistances inherent in real photovoltaic devices. The series resistance (R_S) observed occurs as a result of the contact resistance of the electrodes and factors reducing the net charge reaching the electrodes such as trapping sites and carrier mobility in the active layer. The shunt resistance (R_{SH}) is influenced by the leakage current in the device – that is any current paths that circumvent the diode in the ECD.



Figure 4.4 Semi-log plot of J-V characteristic curve of an OPV device displaying J_{sc} and $\,\,V_{oc}$

In order or maximize the FF to unity, the values for R_S and R_{SH} must tend to zero and infinity, respectively. The series and shunt resistance may be estimated from the slope of the I-V or J-V curves around V = 0 and V = V_{OC}, respectively. The effect of changing the values for R_S and R_{SH} on an illuminated photovoltaic device is demonstrated in the J-V curve shown in Figure 4.5.



Figure 4.5 The effect of changing the values for R_s and R_{sH} on an illuminated photovoltaic device

4.4.3 Equivalent circuit diagrams (ECDs) and diode models for photovoltaics

In general, the I-V curve of an ideal photovoltaic device (series and shunt resistance are ignored) in the dark may be modeled as a standard diode. In particular the following section is an overview of the analytical models used to describe an inorganic photovoltaic based on the p-n junction. In the case of OPVs a complete analytical description has not yet been realized due to the complexity of the constituent layers that form the device. However, it is yet again, useful to examine the diode models used for the description of inorganic photovoltaics to give a basis for the discussion of OPVs. Under illumination, the photovoltaic device may be considered as a constant current source which is connected in parallel with a diode. In a real system however, the effects of parasitic resistances (series and shunt) must be accounted for in the one diode model. This is achieved by modifying the ECD to include two resistors in the circuit. The idealized equivalent circuit diagram (ECD) for an ideal photovoltaic device and one that is coupled with parasitic resistances is given in Figure 4.6.



Figure 4.6 Equivalent circuit diagrams for an ideal photovoltaic device and one that is coupled with inherent parasitic resistances.

4.4.4 Photogeneration of charges - the role of the exciton

The generation of charges through the interaction of the active layer with sunlight is a multifaceted process for organic semiconductors. Organic materials have huge potential due to their optical properties as they are able to convert practically all incident light they absorb into energy (photo-generation), i.e. they have a very high quantum efficiency approaching values close to 100 %.

When light is absorbed in an inorganic semiconductor such as Si or Ge, free charge carriers are created due to the low exciton binding energy characteristic of these materials which is less that the thermal energy $k_BT \sim 25$ meV, at room temperature.

Charge carriers are generated in the bulk of the material at any place where incident photons are absorbed. The p-n junction style inorganic photovoltaic has a built-in electric field due to band bending which does not allow the electron – hole pair to recombine easily. This subsequent carrier separation process induces a forward voltage because the carriers' electric field is in the opposite direction to the junction field.

In contrast to this scenario, upon absorption of a photon by the organic semiconductor an exciton is formed with a much higher binding energy. Generally this is referred to as the generation of a Frenkel exciton. As this type of exciton has a binding energy that is far larger than the available thermal energy another mechanism is required to dissociate the exciton into the desired free electron and hole. A dissociation site is required to facilitate the separation of the exciton into free charge carriers and in the case of OPV devices there have been a number of different active layer designs conceived to allow this process to take place more efficiently.

In particular the average distance an exciton can travel before decay, known as the exciton diffusion length (L_{ED}) is an important parameter. Typically, L_{ED} for conjugated polymers is measured to be of the order of 5 – 20 nm) [16]. There are a number of methods employed to carry out the measurement of this key parameter of organic materials including: photoluminescence quenching [17,18], exciton-exciton annihilation [19], flash-photolysis time-resolved microwave conductivity [20,21] and photocurrent modeling techniques utilizing electro-optic models [22]. Upon dissociation occurring at a heterojunction, there is a free hole in one chemical phase and a free electron in the other.

4.4.5 The active layer

The active layer of the simplest inorganic photovoltaic is doped with p and n type impurity atoms to attain the p-n junction structure. It is more accurate to describe the most common type of doping carried out with organic based active layers as a physical doping where nanowires, nanotubes, fullerenes (C_{60}) or their derivatives are used in conjunction with a p-type polymer. By combining organic materials in this way the efficiency of OPVs has significantly increased compared to that of the first single or bilayer heterojunction devices.

Single and bilayer OPV devices

The earliest OPVs were based upon the single layer structure consisting of a thermally evaporated molecular layer (p-type) sandwiched between two electrodes of differing workfunctions. This arrangement facilitates the transport of charge carriers by the difference in the anode and cathode electrode workfunctions. A Schotky barrier is formed between active layer and the lower workfunction electrode. The molecular layer serves to absorb incident light and facilitates the creation of excitons. The excitons must diffuse to the interface between the active layer and the electrode in order to dissociate. As a result of the long distance the exciton must travel before dissociation, there is a high probability that they will decay. This yields a very low efficiency device $\sim 0.1\%$. Rectification in single layer architectures is a close analogy to that in metal-insulatormetal (MIM) devices [23].

The bilayer structure is more efficient as it consists of a planar heterojunction interface. The two separate layers; an electron donor and an electron acceptor material favor exciton dissociation. Compared to the single layer device, the bilayer structure lowers exciton diffusion distance before dissociation which reduces exciton decay. The layers are sandwiched between two appropriate electrodes to form the device. The electrodes are chosen so that their workfunction closely matches the donor HOMO and acceptor LUMO. Exciton dissociation is still limited due to the large distance the exciton must travel to a dissociation site at the planar heterojunction in the center of the active layer. An advantage of this system is that the competing charge recombination is reduced because upon exciton dissociation the electron and holes travel solely in the appropriate polymer material phase. Thus, the charge carriers are effectively separated within their corresponding layer. This architecture was first introduced in 1986 by Tang reporting a device operating at approximately 1% efficiency using a derivative of pthalocyanine as the donor layer material and a perylene tetracarboxylic derivative as the acceptor [24].

The bulk-heterojunction

The bulk-heterojunction active layer is often called a blend structure where two organic materials are mixed together in solution before deposition onto the device substrate.

Typically the blend consists of an electron donor (p-type) and an electron acceptor (n-type) material.



Figure 4.7 Bulk-heterojunction OPV architecture

The most widely used solution processed active layer structure is the bulkheterojunction consisting of P3HT:PCBM. PCBM is known to be an excellent electron acceptor and as such it is an efficient PL quencher when blended with P3HT suggesting exciton dissociation is being achieved [25]. The devices fabricated for the purpose of this work are based upon this OPV active layer architecture.

In a bulk-heterojunction, the active layer comprises of a complex diffusive structure of interfaces between the two materials in the form of a bicontinuous interpenetrating network. In essence, this method attempts to maximize the available interface surface area allowing higher exciton dissociation efficiencies to be achieved. This process is complicated due to the low exciton diffusion lengths associated with the photo-active organic material which absorbs the available sunlight. This restriction imposed on the active layer blend morphology such that the two material phases (donor and acceptor) must be arranged such that an interface is available within L_{ED} is crucial to device engineering. In the case of P3HT:PCBM, there is a random or quasi-random distribution of the two phases. It has been observed that there is a quasi-periodic characteristic to the morphology of the P3HT:PCBM (dimensions of the P3HT phases) which especially in more efficient devices seems to coincide with the estimated value for L_{ED} within the dominant chromophore in the active layer [26].

4.4.6 Interfaces in bulk-heterojunction OPVs

The bulk-heterojunction active layer of an OPV device may be broken down into a number of important interfaces: ITO-PEDOT:PSS, PEDOT:PSS-P3HT, P3HT-PCBM and PCBM-AL. It is clear that an understanding of organic on metal and metal on organic interfaces is of great interest in this device structure.

4.4.7 Additional device layers and band alignment

The extraction of charges at the electrodes requires a delicate balance between the energy levels of the material layers. In the case of a P3HT:PCBM OPV, the structure consists of the anode, hole conducting layer, active layer and the cathode denoted by the following materials: ITO/PEDOT:PSS/P3HT:PCBM/A1. PEDOT:PSS serves as an interfacial layer facilitating hole transport to the cathode.

Device optimization through materials engineering

The decision for what materials to use as the donor and acceptor components of a BHJ is dependent upon maximizing the amount of charge generated and ensuring the efficient transfer of the carriers the electrodes. In 2007, Bundgaard et al. discussed the need for optimum band level alignment between the donor and acceptor species as shown in Figure 4.8 [27]. Using lower bandgap materials allows more photons to be absorbed from the incident solar irradiation leading to higher current densities. The open circuit voltage (V_{oc}) is traditionally defined as the difference between the donor HOMO and the acceptor LUMO (The minimum acceptable value for V_{oc} defined as β in Figure 4.8). The difference between the donor LUMO and the acceptor LUMO is also critical as it defines the efficiency of electron transfer (shown as α in Figure 4.8).



Figure 4.8 Band level alignment in OPV bulk-heterojunction devices

In order to optimize the OPV, it is not as trivial as maximizing any one quantity but rather a complex balance between them and thus it often relies on an appropriate choice of the available materials. The effect of the electrodes must also be considered as the V_{oc} and electron transfer efficiency are limited by their respective workfunctions. Assuming appropriate electrodes are used; the range (ΔE) for which the HOMO of the donor may vary can be given by $\Delta E = E_G - \alpha - \beta$, where E_G is the difference between the HOMO and the LUMO of the donor.

4.5 Reflection and Transmission of Light at a Boundary

4.5.1 Oblique Incidence

When an electromagnetic wave is incident upon an interface between two media with non-equal refractive indices, a portion of the incident light will be reflected from the interface and the remainder will be transmitted into the second medium. In this scenario, the angle that the incident light makes with respect to the normal of the interface is defined as the incident angle θ_i . From the Law of Reflection, it is clear that the reflected light at the interface will propagate at an angle of reflection θ_r which is equal to θ_i . Light transmitted through the boundary will be refracted either towards are away from the normal to the interface. The angle of reflection is determined by the angle of incidence and the relative fraction of the refractive indices of the two media. This relationship determining the angle of the transmitted light through the interface θ_t is known as Snell's law or the Law of Refraction

$$\mathbf{n}_1 \sin \theta_i = \mathbf{n}_2 \sin \theta_t \tag{4.12}$$

where n_1 and n_2 are the refractive indices of the first and second medium respectively. When the first medium has a refractive index (n_1) that is less than the second (n_2) , total internal reflection (TIR) may occur over a defined angular range. The smallest angle at which TIR occurs is known as the critical angle (θ_c) . TIR occurs when the angle of refraction is at the critical angle or greater yielding the expression

$$\sin \theta_{c} = \left(\frac{n_{1}}{n_{2}}\right) \sin \left(90\right) = \left(\frac{n_{1}}{n_{2}}\right) \therefore \theta_{c} = \sin^{-1}\left(\frac{n_{1}}{n_{2}}\right)$$
(4.13)

Incident light waves of any polarization may be considered as a linear combination of the two basic polarization states. These states arise when either the electric field vector **E** is parallel or perpendicular to the interfacial plane (taken to be in the XY directions). The two modes of propagation are called the transverse electric (TE) and the transverse magnetic (TM) as shown in Figure 4.9 and Figure 4.10 respectively.

The TE mode occurs when the three light waves of interest have electric field vectors parallel to the interfacial plane and have magnetic field vectors lying on the plane of incidence (taken to be in the XZ directions).



Figure 4.9 Diagram illustrating the incident, reflected, and transmitted waves for the TE mode.

The TM mode occurs when the three light waves of interest have magnetic field vectors parallel to the interfacial plane and have electric field vectors lying on the plane of incidence.



Figure 4.10 Diagram illustrating the incident, reflected, and transmitted waves for the TM mode.

To investigate the intensities of the reflected and transmitted light it is assumed that each one of the light waves is uniform and single frequency with a harmonic time dependence (sinusoidal). Plane harmonic waves can be written with their electric vector (\vec{E}) and magnetic vector (\vec{B}) in the phasor form. In general, for the TE or TM modes an incident wave defined by

$$\vec{E}_{i}(\vec{r},t) = E_{0i}e^{j(k_{i}\cdot r - \omega_{i}t)}, \quad \vec{B}_{i}(\vec{r},t) = \frac{1}{\nu_{1}}\left(\hat{k}_{i} \times \vec{E}_{i}\right)$$
(4.14)

travels through the first medium until it reaches the interface with the second medium and gives rise to a reflected wave propagating back into the first medium,

$$\vec{E}_{r}(\vec{r},t) = E_{0r}e^{j(k_{r}\cdot r - \omega_{r}t)}, \quad \vec{B}_{r}(\vec{r},t) = \frac{1}{\nu_{1}}(\hat{k}_{r} \times \vec{E}_{r})$$
(4.15)

and a transmitted wave propagating through the second medium,

$$\vec{E}_{t}(\vec{r},t) = E_{0t}e^{j(k_{t}\cdot r - \omega_{t}t)}, \quad \vec{B}_{t}(\vec{r},t) = \frac{1}{\nu_{2}}\left(\hat{k}_{t} \times \vec{E}_{t}\right)$$
(4.16)

where E_{0i} is the magnitude of the vector \vec{E}_i and the exponential term contains information concerning phase $(k_i \cdot r)$ and frequency (ω_i) and similarly for the reflected and transmitted waves [28,29]. The boundary conditions for Maxwell's equations are applied to derive the Fresnel equations for the two distinct polarization states TE and TM:

Boundary conditions, reflection and transmission coefficients (TE wave)

The electric field vector is tangential to the interface (parallel to the boundary plane separating the first and second medium) and thus must be continuous across it yielding

$$\mathbf{E}_{i} + \mathbf{E}_{r} = \mathbf{E}_{t} \tag{4.17}$$

The parallel components of the associated magnetic fields must also be continuous and their amplitudes are related by

$$B_{i}\cos\theta_{i} - B_{r}\cos\theta_{r} = B_{t}\cos\theta_{t}$$
(4.18)

Using the Law of Reflection - $\theta_r = \theta_i$ and the relationship between electric and magnetic field vectors in Equations (4.14) to (4.16) yields

$$\mathbf{n}_{1}\mathbf{E}_{i}\cos(\theta_{i}) - \mathbf{n}_{1}\mathbf{E}_{r}\cos(\theta_{i}) = \mathbf{n}_{2}\mathbf{E}_{t}\cos(\theta_{t})$$

$$(4.19)$$

By substituting in Eqn. (4.16) and rearranging the terms to get a ratio of the reflected wave to that of the incident wave $\frac{E_r}{E_i} = r_{TE}$, the reflection coefficient for TE modes is given by

$$r_{\text{TE}} = \frac{n_1 \cos(\theta_i) - n_2 \cos(\theta_t)}{n_1 \cos(\theta_i) + n_2 \cos(\theta_t)}$$
(4.20)

Snell's Law is then used in order to write the expression for r_{TE} in terms of only the incident angle with the help of the trigonometric identity

$$\cos(\theta_t) = \sqrt{1 - \sin^2(\theta_t)}$$
(4.21)

which then gives the Fresnel Equation:

$$r_{\text{TE}} = \frac{\cos(\theta_i) - \sqrt{\left(\frac{n_2}{n_1}\right)^2 - \sin^2(\theta_i)}}{\cos(\theta_i) + \sqrt{\left(\frac{n_2}{n_1}\right)^2 - \sin^2(\theta_i)}}$$
(4.22)

which may be further simplified by using a relative refractive index $n = \frac{n_2}{n_1}$ such that

$$r_{TE} = \frac{\cos(\theta_i) - \sqrt{n^2 - \sin^2(\theta_i)}}{\cos(\theta_i) + \sqrt{n^2 - \sin^2(\theta_i)}}$$

$$(4.23)$$

Boundary conditions, reflection and transmission coefficients (TM wave)

The magnetic field vector is tangential to the interface and thus must be continuous across it such that

$$-\mathbf{B}_{i} + \mathbf{B}_{r} = -\mathbf{B}_{t} \tag{4.24}$$

Using the Law of Reflection - $\theta_r = \theta_i$ and the relationship between electric and magnetic field vectors in Equations (4.14) to (4.16) yields

$$-n_{1}E_{i} + n_{1}E_{r} = -n_{2}E_{t}$$
(4.25)

and

$$E_{i}\cos(\theta_{i}) + E_{r}\cos(\theta_{i}) = E_{t}\cos(\theta_{t})$$
(4.26)

By substituting in Eqn. (4.17) and rearranging the terms to get a ratio of the reflected wave to that of the incident wave $\frac{E_r}{E_i} = r_{TM}$, the reflection coefficient for TM modes is given by

$$\mathbf{r}_{\mathrm{TM}} = \frac{\mathbf{n}_{1} \cos(\theta_{\mathrm{t}}) - \mathbf{n}_{2} \cos(\theta_{\mathrm{i}})}{\mathbf{n}_{1} \cos(\theta_{\mathrm{t}}) + \mathbf{n}_{2} \cos(\theta_{\mathrm{i}})}$$
(4.27)

Snell's Law is then used in order to write the expression for r_{TE} in terms of only the incident angle with the help of the trigonometric identity given in Eqn. (4.21) in order to write the reflection coefficient in terms of the incident angle giving the Fresnel Equation:

$$r_{\rm TM} = \left[\frac{-\left(\frac{n_2}{n_1}\right)^2 \cos \theta_i + \sqrt{\left(\frac{n_2}{n_1}\right)^2 - \sin^2 \theta_i}}{\left(\frac{n_2}{n_1}\right)^2 \cos \theta_i + \sqrt{\left(\frac{n_2}{n_1}\right)^2 - \sin^2 \theta_i}} \right]^2$$
(4.28)

which may be further simplified by using a relative refractive index $n = \frac{n_2}{n_1}$ such that

$$\mathbf{r}_{\mathrm{TM}} = \left[\frac{-n^2 \cos \theta_{\mathrm{i}} + \sqrt{n^2 - \sin^2 \theta_{\mathrm{i}}}}{n^2 \cos \theta_{\mathrm{i}} + \sqrt{n^2 - \sin^2 \theta_{\mathrm{i}}}}\right]^2 \tag{4.29}$$

A similar treatment may be carried out in order to calculate the transmittance, however a more simplistic method is to use the fact at the boundary, energy is conserved yielding R+T=1 and as such T=1-R.

For both the TE and TM modes, the power (P_r) of the reflected light is the square of the respective reflection coefficient (r_{TE} or r_{TM}). It follows that the Reflectance R is given by

$$R = \frac{P_r}{P_i} = \left(\frac{E_r}{E_i}\right)^2$$
(4.30)

and similarly Transmittance T is given by

$$T = \frac{P_t}{P_i} = \left(\frac{E_t}{E_i}\right)^2$$
(4.31)

In the case of a broadband unpolarised light source such as the sun it is assumed that there is an equal amount of each distinct mode and as a result the average the TE and TM modes is used

$$R_{AVG} = \frac{\left(r_{TE}^{2} + r_{TM}^{2}\right)}{2}$$
(4.32)

4.6 Evanescent waves and frustrated total internal reflection

Evanescent waves are generated when an incident wave impinges a boundary between two media such that total internal reflection (TIR) occurs. This phenomenon may happen when incident light travelling in the first medium, having a refractive index (n_1), is propagating at an angle (θ_i) with respect to the normal at the interface between the two media that is greater than the critical angle θ_c for transmission into the second medium (n_2). This may be expressed by the following relationship

$$\theta_{\rm c} = \sin^{-1} \left(\frac{\mathbf{n}_2}{\mathbf{n}_1} \right) \forall \mathbf{n}_1 > \mathbf{n}_2 \tag{4.33}$$

Evanescent waves are described as near-field standing waves which are transmitted through the interface but their amplitude exponentially decays with distance inside the second medium. In the scenario that there is no suitable additional medium to couple the evanescent wave, the energy of the evanescent wave returns to the first medium.



Figure 4.11 Diagram illustrating frustrated TIR.

In the case that a suitable third medium (n_3) is introduced in close proximity to the first medium and the thickness of the second medium is considerably less than the wavelength of the incident light an optical phenomenon called frustrated TIR may occur. It may be observed under conditions that satisfy

$$\sin^{-1}\left(\frac{\mathbf{n}_2}{\mathbf{n}_1}\right) < \theta_i < \sin^{-1}\left(\frac{\mathbf{n}_3}{\mathbf{n}_1}\right)$$
(4.34)

an evanescent wave is generated as described by TIR in the second medium. It is then converted to a propagating wave in the third medium, at the interface between the second and third medium [30].

4.7 References

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CHAPTER 5.

Modification of the active layer

5.1 Introduction

In this chapter, the aim was to investigate how fullerenes may be used in OPVs and to determine whether there is a form of charge transfer process that successfully enhances the prospects. The effect of incorporating carbon nanotubes (CNTs) in a polymer-fullerene blend host is investigated and discussed. Single walled carbon nanotube (SWNT)- C_{60} hybrids are introduced, a study on how such functionalization can aid OPV device PCE and finally how shortened SWNT barrels linked with C_{60} , SWNT(B)- C_{60} , may be used as an additive to P3HT:PCBM. The purpose of such a system is to detail the use of CNTs as a carrier host for the fullerenes as they are one of the best organic based charge carriers available. The final goal of this investigation was to determine whether there is a form of charge transfer process that successfully enhances the prospects of using these larger molecules as charge delivery systems within the semiconductor host.

5.1.1 Background

In the drive to build new organic based electronics and in particular photovoltaics (OPVs) using a variety of organic materials, Fullerenes have played a significant part in the success of making them more attractive [1]. From the initial work incorporating Buckminsterfullerene (C_{60}) in a polymer host, such as a polyphenylenevinylene (PPV) derivative or the more advanced polythiophenes; poly-3-octylthiophene (P3OT) or poly-3-hexylthiophene (P3HT), certainly the desire in classic semiconductor phraseology to use an n-type material to form a heterojunction with p-type polymers has been pursued vigorously [2–4]. However, after many years of research into C_{60} and the higher molecular weight Fullerenes, it is clear that dispersion, miscibility, charge transport and in particular carrier mobility is a challenge — even using a functionalized version in the form of [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) has limitations.

In general, the conjugated polymer such as P3HT is the dominant absorber of incident sunlight having a band-gap $\sim 1.9 - 2.1$ eV (PCBM also absorbs but to a far lesser extent) [5]. Upon absorption of a photon, a localized excited state (exciton) is generated which either can diffuse to a nearby P3HT:PCBM interface or relax, which most probably occurs as a radiative process resulting in photoluminescence (PL) and loss in overall device performance. The extent to which this loss occurs is determined by the ratio of the constituent materials and the size and distribution of each material phase in the blended active layer structure. PCBM is known to be an excellent PL quencher when blended with P3HT which suggests efficient exciton dissociation [6]. A more rigorous discussion regarding the complex processes involved in the photogeneration and extraction of energy from OPVs may be found in a recent review [7].

5.1.2 Challenges associated with semiconducting polymer active layers

The challenge with organic semiconducting materials is that they famously possess low mobility charge carriers when compared to their inorganic counterparts [8]. This imposes restrictions on device architecture which includes the thickness of the semiconductor layer, the blending process in formation of the heterojunction and the use of specific transparent electrode contacts. Poor exciton dissociation efficiency, related to small exciton diffusion lengths in conjugated polymers (5-20 nm) [9] leads to the requirement for an ultra-thin active layer film, adding to the complexity of OPV device fabrication. In spite of the limitations of P3HT:PCBM based devices, power conversion efficiencies (PCEs) of around 5% have been achieved [10–12]. The success seen in PCE improvement for devices blended with Fullerenes is encouraging and investigating the role of Fullerenes in these systems to see how else we can modify them to improve PCE is of particular interest.

5.1.3 The use of Fullerenes in organic electronic devices

Carbon nanotubes (CNTs), the largest and most complex in the Fullerene family, possess an equally interesting but complex array of properties and have been studied exhaustively in terms of spectroscopic properties and electronic characteristics [13–15]. While there is also a whole host of mechanical studies available on CNTs, the

compelling drive to use them in a more practical manner has seen little success as carbon fibers have always been the cheaper and more effective material of choice. However, the electronic properties of CNTs cannot be understated and in fact the individual conductance of a pristine CNT can mirror and exceed those of metals. Using CNTs as electrodes in OPVs to replace ITO fails to impress due to the requirement for high conductivity and optical transparency [16] for electrical contacts. This issue is not trivial, there are even more complex problems in using carbon nanotubes which includes that the electrode has a low sheet resistance for the best devices (less than 10 Ω/\Box) and a more controlled interface between the electrode and next layer as morphology is intricately linked with device efficiency. In dealing with the electrode in a typical CNT/P3HT:PCBM/Al device for example, is that the open circuit voltage (V_{oc}) generated will always be low. The workfunction of the CNTs is just too low for this use and consequently their use here will always be flawed.

Over a decade ago the first organic light emitting diode (OLED) made using a conjugated polymer and CNTs was fabricated in a similar manner to what was seen in OPVs [17]. The logic behind this approach was to use the larger 'Fullerene' as a carrier in a polymer host, this provided some interesting new phenomena aside from transport effects such as polymer wrapping, oxygen scavenging, lower turn on voltage for OLED devices and longer device lifetimes in air. However, simply using CNTs in their raw state was only a starting point to how these molecules could be used and we have seen even more exotic devices fabricated from molecular functionalization [18], quantum dots [19], self-assembly [20] and eventually their use in OPVs as an attempt to get the largest of the Fullerenes involved in energy harvesting.

However, this has been achieved with limited success, in part because the use of pure CNTs causes shorting of devices due to their physical length, the active layer for an OPV is typically less than 200 nm while CNTs in general are considerably longer (~10 μ m). In looking to functionalize CNTs, it is also clear that having a molecule which enhances light harvesting is critical as CNTs in themselves have such a low bandgap [21] and poor absorption coefficient. However, it is not clear how beneficial the use of CNTs in OPVs will be and a critical examination of their performance is needed. Numerous groups are attempting to improve optoelectronic devices with the addition of
CNTs in various forms — reviews of progress made in this area are referenced here [22,23].

5.2 Fabrication of devices

All devices were fabricated on ITO coated substrates. The pristine ITO substrates were dusted with Zinc powder and etched under an 18% HCl_(aq) solution for 10 seconds to form the anode layout. The substrates were cleaned in a heated ultrasonic bath with 1.5 % Micro 90 (15 minutes), deionized water (15 min x 2 cycles) and isopropanol (15 minutes). Ozone plasma treatment was carried out for ten minutes immediately followed by the deposition of a PEDOT:PSS layer spin-coated at 3000 rpm for two minutes to form a thin (50-80 nm), hole transport layer. The substrates were dried in an 80 °C oven for 1 hour before deposition of the different types of active layer. The active layers deposited in this study were spin-coated on top of the PEDOT:PSS layer at 1500 rpm for 2 minutes. Once the active layer was deposited, the substrates were solvent annealed in a chlorobenzene vapor rich environment for 30 minutes followed by curing in an 80 °C oven for 1 hour before thermal evaporation of the Al cathode. The thermal evaporation was carried out as described in Chapter 2, Section 5.4. The patterned Al electrodes deposited on top of photoactive layer define the device area and their geometry is defined by a custom made shadow mask. All devices were encapsulated with glass slides using epoxy resin in an inert nitrogen atmosphere (~10% relative humidity) before characterization.

5.3 Results and discussion

5.3.1 UV-Vis absorption

There are four notable peaks in the UV-Vis absorption spectra of the P3HT, P3HT-PCBM and P3HT-PCBM:SWNT(B)-C₆₀ composites shown in Figure 5.1. The features observed in the UV portion of the spectrum are dominated by the Fullerene, the peak at 330 nm (3.75 eV) is attributed to the weakly dipole-allowed HOMO ${}^{1}A_{g}$ (S₀) \rightarrow LUMO ${}^{1}T_{1u}$ (S₁) transition of C₆₀ [24], while the features in the visible region are in the main polymeric attributed where the segments of the polymer chain take on the role of the chromophore. The UV-Vis spectrum of P3HT in a dilute (0.02 g/l) solution using chlorobenzene as a solvent has an absorption maximum at ~460 nm (2.7 eV) attributed to the intra-molecular π - π^* delocalized (HOMO –LUMO) transitions, low level molecular ordering due to aggregates is visible in the subsequent shoulders (#1, #2 & #3).



Figure 5.1 UV - Vis absorption spectra of spin coated thin films on glass consisting of P3HT, P3HT-PCBM and P3HT:PCBM:SWNT(B)-C₆₀ composites. SWNT(B)-C₆₀ loadings range from 1 to 20 wt.% with respect to P3HT. Inset (A) is a magnified view depicting peaks #1 and #2. Inset (B) is a magnified view of peak #3.

Solvent evaporation during the formation of a thin spin cast film enables the P3HT to self-organize and form polycrystalline domains consisting of long 1-D polymer chains orientated in lamellar (2-D sheet) structures, this is often called intrachain or π - π stacking [25]. It is this assembly with longer conjugation that induces a bathochromic shift in the P3HT absorption spectrum (intrinsic π - π * transitions) toward 520 nm (2.38 eV). The bands at 550 and 600 nm (2.25 and 2.07 eV) are often attributed to the 0 - 1 and 0 - 0 transitions respectively, however their assignment is under debate [26–30]. No apparent chromic shift is observed for the solid film compared to the aggregate peaks observed in solution, their increased absorption intensity is indicative that the majority of the polymer self organizes forming aggregates in the solid state. Only the intensity of the spectral feature at 600 nm (#3) is dependent on the regioregularity of the polymer (increasing with less variation of conjugation lengths) and thus it is changes in the local

ordering of the packing structure and aggregation that can be observed here which is in agreement with the observation made by Brown *et al.* (28).

The introduction of PCBM forming a composite blend with P3HT lowers the degree of local order. It is especially evident that the 20 wt. % loading of SWNT(B)-C₆₀ has a significant effect on the local order of the P3HT chains compared to that of the 1, 5 and 10 wt. % loadings which are almost identical to that of the regioregular P3HT, as shown in the inset B of Figure 5.1 (31). However, an increase in absorption in a large section of the π - π^* region of the spectrum (400 – 560 nm) is observed for the lower SWNT(B)- C_{60} (1, 5 wt. %) loadings — a possible explanation for this phenomenon is that at higher CNT loadings polymeric absorption is hindered due to increased levels of CNT aggregation. The most notable changes occur are the slight chromic shifts in peak #1. For P3HT peak #1 is at 520 nm, with the addition of PCBM a hypsochromic shift to 515 nm is observed. A hypsochromic shift would implies that here is an interruption in the ordered polymer backbone i.e. a reduction of the P3HT conjugation lengths due to the additional forces exerted on the P3HT chains with the introduction of PCBM molecules into the thin film blend structure. It is interesting that upon the addition of the SWNT(B)-C₆₀, peak #1 is shifted to a lesser degree to 518 nm for 10 and 20 wt. % loadings whilst the presence of the 1 and 5 wt. % loadings increase the hypsochromic shift to 513 nm. This is attributed to the increased aggregation of the SWNT(B)-C₆₀ at the higher concentrations altering the effect of PCBM in the system in tandem with the reduced PCBM concentration in the composite.

The relative intensities of the absorption peaks were calculated in order to further investigate the effects of changing the composition of the blends by incorporating different SWNT(B)-C₆₀ loadings. The intensity of peak #1 is less than #2 in the case of the pure P3HT composite where the ratio of intensity #1 : #2 is 0.98. However, this ratio reverts to being above unity for all the other composites having a value ranging from \sim 1.03 - 1.10. There is a similar trend observed for all the peak intensity ratios (#1 : #2, #1 : #3 and #2 : #3) which centers around that for the P3HT:PCBM composite. For higher loadings (10 and 20 wt. %), they are at a reduced intensity ratio for #1 : #3 for P3HT is 1.40, the other composites range from 1.52 – 1.70. The intensity ratio for #2 : #3 for P3HT is 1.43, the other composites range from 1.50 – 1.55.

5.3.2 Photoluminescence spectra

There are at least two major emission bands visible in the photoluminescence (PL) spectra of the P3HT, P3HT:PCBM and P3HT:PCBM:SWNT(B)- C_{60} composites. Looking at the spectral features for each of the composites it is clear that the P3HT PL is dominant at the excitation wavelength of 514 nm (2.41 eV) as is expected from the absorption spectra in Figure 5.1.

The maximum emission intensity at 712 nm (1.74 eV) and a second resolved peak occurring at ~ 655 nm (1.89 eV) correspond to the 0 - 1 and 0 - 0 emissions, respectively. The spacing between the two discernible emission peaks (0 - 0 and 0 - 1) was calculated by means of fitting a Gaussian line-shape to the PL spectra and was determined to be ~ 0.15 - 0.18 eV suggesting that interchain exciton emission coupled to the $C_{\alpha}=C_{\beta}$ symmetric stretching of the thiophene ring (~1442 cm⁻¹) is observed.



Figure 5.2 PL spectra of spin coated thin films on glass consisting of P3HT, P3HT:PCBM, P3HT:PCBM:SWNT(B) and P3HT:PCBM:SWNT(B)-C₆₀ SWNT(B)-C₆₀ loadings range from 1 to 20 wt.% with respect to P3HT.

The intensity of the 0 - 1 emission is greater than that of the 0 - 0 emission, this supports that a single species of weakly coupled H-aggregates is the emissive element in

regioregular P3HT [30]. This behavior is typical for conjugated polymers and coincides well with the Raman data shown in Figure 5.4 — these phenomena are also discussed in other works [28,32,33]. It is also noted that the separation of the two emission peaks is reflected in the UV-Vis absorption spectra where the two spectral features (#2 and #3) labeled in Figure 5.1 are separated by ~ 0.18 eV.

The PL spectra clearly demonstrate the effect of PL quenching by the PCBM in the polymer films. The higher loadings (10 and 20 wt. %) of SWNT(B)-C₆₀ coincide with lower amounts of PCBM present in the films. The lower loading samples (1 and 5 wt. %) of SWNT(B)-C₆₀ contain the same ratio of PCBM, this demonstrated that quenching was more prevalent as the loading decreased implying that the addition of the SWNT(B)-C₆₀ is detrimental to PL quenching.

5.3.3 Optical limiting properties of CNT-C₆₀ hybrids

CNT-C₆₀ hybrids based on double – walled CNTs [34], were synthesized in a similar manner by covalently linking CNTs and C₆₀ by an amination reaction with polyethylenimine. The optical limiting performance of CNT-C₆₀ hybrids was found to be superior to those of C₆₀ and SWNTs at the same level (~80%) of transmission. This unusual finding suggested that charge transfer between the CNTs and C₆₀ moieties plays an important role in optical limiting. It is known that CNTs can form charge transfer species by electrochemical doping with redox dopants. The intrinsic phonon line shapes of CNTs are very sensitive to doping [35–37], for example, the G⁺ feature is associated with C–C vibrations along the CNT axis and is vibronically sensitive to charge transfer from dopants, such as functionalization of SWNTs with C₆₀ (upshifts in G⁺ for acceptors) [38]. As a result of these previous findings, RAMAN spectroscopy was used to further investigate the properties of the newly formed composite materials.

5.3.4 Raman spectroscopy

Raman Spectroscopy of graphite and carbon nanotubes

A characteristic Raman band of crystalline graphite called the 'G-band' is located around 1580 cm⁻¹ and is ascribed to the tangential displacements of the carbon atoms. It

is also related to quantum confinement and electron-phonon coupling. Additionally there is a second order G' band at 2700 cm⁻¹ sensitive to small changes in the electronic and vibrational structure. The 1580 cm⁻¹ feature is the only first-order peak (where only one scattering event has taken place) that is observable. A peak at around 1350 cm⁻¹ (D-band) is typically observed having a low intensity in graphite and is a result of the presence of defects or the reduced symmetry of a non-infinite sample. The D band is induced by disorder and as such can yield information on local disorder. This D band is proportional to the amount of crystallite boundaries and as such the ratio of the intensities of the D and G bands is linearly proportional to the crystallite size giving

$$\frac{I_{\rm D}}{I_{\rm G}} = \frac{A}{L_{\alpha}} \tag{4.1}$$

Where A is a constant and L_{α} is the crystallite size [38,39].

Raman spectroscopy of CNTs is a very powerful tool as it relates the excitation caused by an incident photon to the phonon and electronic processes in the material. Group theory may be utilized to determine the Raman-active vibrational modes of CNTs by specifying the particular lattice and symmetry structure of the CNT: achiral CNTs have vertical and horizontal mirror symmetry operations. Armchair CNTs belong to the D_{nd} group, zigzag CNTs belong to the D_{nh} group and chiral CNTs belong to a special "Abelian" group C_n as they have no mirror plane [39].

In CNTs, unlike graphite, the G-band spectra are split into two dominant components around 1580 cm⁻¹ — the G⁺ and G⁻ bands appear due to the vibration of carbon atoms along (longitudinal optical [LO] phonon mode) and perpendicular (transverse optical [TO] phonon mode) to the CNT axis, respectively, shown on the RHS of Figure 5.3. This occurs due to the fact that a CNT takes the form of a rolled up graphene sheet introducing a degree of curvature. As the diameter of the nanotube is increased (reduced curvature) the G-band of the CNT approaches what is observed in graphite.



Figure 5.3 Diagram illustrating the RBM and G-band observed in the Raman spectra of SWNTs [40].

The G^+ band is sensitive to dopants and functionalization effects, its frequency up-shifts for acceptors and downshifts for donors. The particular lineshape of the G^- band may yield information on the electrical properties of the SWNT: a narrow symmetric lineshape (Lorentzian) may be assigned to a semiconducting species whilst a broader asymmetric lineshape (Breit-Wigner-Fano) may be ascribed to metallic SWNTs [40].

In particular for SWNTs, another first-order feature at a lower frequency called the radial breathing mode (RBM) is observed. The G-band and the RBM are typically the most intense bands. The RBM originates from the bond-stretching out-of-place phonon mode having A_{1g} symmetry. It is characterized by all the carbon atoms moving in a coherent fashion in the radial directions as shown on the LHS of Figure 5.3. SWNTs having a diameter d ~ 2 nm possess an RBM with a reasonably strong intensity and its frequency ω_{RBM} scales inversely with diameter.

$$\omega_{\text{RBM}} = \frac{C_1}{d} + C_2 \tag{4.2}$$

where C_1 ranges from 220 – 230 cm⁻¹ and C_2 typically ranging from 10 - 20 cm⁻¹. C_2 is characteristic of the SWNT interaction with either the supporting substrate or other SWNTs in a bundle [35].

Resonance Raman was found to be a very useful technique in the advancement of the understanding of CNT structures [38]. Resonance Raman spectroscopy (RRS) uses an excitation source having a frequency that is close to that of the electronic absorption of the molecule under investigation. Under these conditions resonance occurs allowing the molecule to be excited near one of its electronic transitions rather than excitation to a virtual energy state. This serves to enhance the intensities of observed Raman lines by a factor as high as several orders of magnitude. The enhanced intensity is especially apparent for lines corresponding to Raman-active vibrations of a chromophore that are totally symmetric (in phase) [41].

Raman spectroscopy of P3HT and the hybrid composites

Poly(3-hexylthiophene-2,5-diyl) abbreviated to P3HT, is a polymeric material originating from thiophene. Thiophene is a heterocyclic compound consisting of a five flat membered ring. In order to increase processability and solubility an alkyl group is introduced in the 3 position and takes the form of a hexyl radical $[CH_2(CH_2)_4CH_3]$. The repeat units for P3HT are attached at the 2,5 positions such that two H atoms are substituted by two single bonds (2,5-diyl) forming the polymer chain.

Regioregular P3HT has various Raman modes between $600 - 1600 \text{ cm}^{-1}$; the main in plane skeleton modes at ~ 1445 cm⁻¹ (symmetric C=C stretch mode), the intra-ring C-C stretch mode at ~1380 cm⁻¹, the inter-ring C-C stretch mode at 1208 cm⁻¹, the C-H bending mode with the C-C inter-ring stretch mode at 1180 cm⁻¹ and the C-S-C deformation mode at ~726 cm⁻¹. The two main in-plane skeletal modes at ~1445 cm⁻¹ and 1381 cm⁻¹ are said to be the most sensitive to changes in the P3HT chain conjugation length [42].



Figure 5.4 Raman spectra of P3HT:PCBM, SWNT(B)- C_{60} and P3HT:PCBM:SWNT(B)- C_{60} composites. Inset is a magnified view depicting the peak-shifts for the SWNT(B)- C_{60} and P3HT:PCBM:SWNT(B)- C_{60} composites. Intensities of all spectra are offset for clarity.

The formation of charge transfer species between P3HT:PCBM and CNT- C_{60} hybrids is of particular interest. Raman spectroscopy has proven to be an excellent tool to probe complex interactions in the numerous forms of carbon nanostructures such as Fullerenes, CNTs and graphene [13–15,20,38,43–45].

Raman signals were acquired for the P3HT:PCBM, SWNT(B)-C₆₀ and P3HT:PCBM:SWNT(B)-C₆₀ composites, respectively (Figure 5.4). Notable features observed in the Raman spectrum of the P3HT:PCBM composite include peaks due to stretching in the aromatic thiophene ring: $C_{\alpha}=C_{\beta}$ (symmetric) at 1442 cm⁻¹, $C_{\alpha}=C_{\beta}$ (anti-symmetric) at 1512 cm⁻¹, C_{β} -C_{β} at 1378 cm⁻¹ and C_{α} -S-C_{α} ring deformation observed at 726 cm⁻¹ (shown in Figure 5.5). It is clear that the 1442 cm⁻¹ phonon feature observed in the Raman spectrum is attenuated due to the presence of the SWNT(B)-C₆₀ indicating increased disorder in the blended system.



Figure 5.5 Raman spectrum of P3HT:PCBM showing the Si substrate peak at 520 cm⁻¹ and a peak due to C_{α} -S- C_{α} ring deformation at 726 cm⁻¹

Broadening is observed in the D-band defect peak of the CNTs in the P3HT:PCBM:SWNT(B)-C₆₀ sample. This is attributed to the overlap of two vibrational modes originating from the P3HT:PCBM and SWNT(B)-C₆₀ materials. When comparing the G-bands of CNTs from the P3HT:PCBM:SWNT(B)-C₆₀ with that of SWNT(B)-C₆₀, the most intense peak at the higher frequency (G^+) shows an upshift of 8.6 cm⁻¹ (from 1581.0 to 1589.6 cm⁻¹) and the peak of G⁻ shows an upshift of 7.8 cm⁻¹ (from 1545.6 to 1553.4 cm⁻¹).

While there are no shifts of signals from P3HT in the P3HT:PCBM:SWNT(B)- C_{60} composite, the upshifts of G band spectra suggest charge transfer of the CNTs to either the C_{60} moieties or the PCBM (or both). Similar upshifts in G band spectra have been observed in the interaction of electron-donating and electron-withdrawing groups with SWNTs [46].

5.3.5 Rationale for functionalizing and shortening the SWNTs

In order to successfully incorporate SWNTs into the active layer composite their solubility/miscibility with the solvent used for the host active layer was studied. For the case of P3HT:PCBM composite OPV devices; chlorobenzene is a popular solvent.

Pristine SWNTs do not dissolve readily in chlorobenzene, they tend to bundle together and form very large sized aggregates. The addition of a functional group to the SWNTs allows them to disperse more readily improving their compatibility with the OPV layer. Coating the SWNTs with a linker (amination) allows the subsequent attachment of C_{60} molecules resulting in much improved solubility in chlorobenzene.



Figure 5.6 Schematic depicting various situations for the CNTs in the OPV device active layer. CNTs are drawn approximately to scale with respect to the active layer. (a) P3HT:PCBM:SWNT. (b) P3HT:PCBM:SWNT(B)-C₆₀ at high concentration. (c) P3HT:PCBM:SWNT(B)-C₆₀ at low concentration.

The typical length of CNTs and indeed SWNTs is problematic in thin film device structures as it is an order of magnitude longer than the active layer thickness. Conceptually, it can be preferable to furnish an idealized and unrealistic picture depicting a precise and most preferred placement of CNTs within the device structure; in particular the extremely high aspect ratio of CNTs is ignored [47,48]. It is very unlikely that numerous CNTs which are more than 1 μ m long could sit within a layer ~100 nm thick without protruding through either side and inevitably form a short-circuit as seen in Figure 5.6a resulting in an ohmic device characteristic (blue I-V trace shown in Figure 5.8). Consequently, making organic electronics by simply dispersing long CNTs to change the transport properties invites failure more often than not.



Figure 5.7 AFM image of SWNT(B) spin coated on a mica substrate. Scale 2 µm x 2 µm.

The most direct way to rectify such problems is to either use extremely low concentrations of SWNTs (of the order of 0.1 - 1 % wt.) in the blend or to carry out a process which shortens them considerably. Fluorination was used in order to attain SWNTs with an average length of ~60nm — the SWNT(B) are imaged by an AFM (Figure 5.7). Others have used complex alignment techniques such as applying an alternating current with a high frequency requiring a thick active layer [49]. Even using extremely small concentrations of CNTs will either destroy the device by means of shorting or with some luck have little or no effect in real terms for improving the device [50]. Incorporating a higher loading of shortened CNTs may have a positive effect but this is open to some debate, in particular with significantly higher loadings. It is well known that CNTs and in particular SWNTs will inevitably aggregate Figure 5.6b). Shortened SWNTs functionalized with linked C₆₀ molecules clearly are more successful forming a P3HT:PCBM:SWNT(B)-C₆₀ hybrid composite, having better miscibility, film homogeneity and aiding charge collection at the electrodes, this is illustrated in Figure 5.6c. When shortened, SWNTs inevitably lose some special features attributed to CNTs such as extreme conductivity and ballistic transport. However, we know that

having metallic states, while changing the overall conductivity of the composite through a percolation effect does not aid in producing a better semiconducting, charge carrying material. By creating smaller nanotubes and then functionalizing them, we alter the nanotubes in two ways. First of all, there is no chance of ballistic transport and therefore no risk of metallic SWNTs short-circuiting the devices. Secondly, functionalizing nanotubes is a classic way of altering the C-C bond lengths. The shortened and functionalized SWNT(B)-C₆₀ do not possess the same electronic transport properties as pristine uncut SWNTs. Even if they aggregate and form a network between the electrodes they cannot serve to directly short the device. Ballistic transport is observed in pristine CNTs which have a long undisturbed structure, this is not the case for the SWNT(B)-C₆₀ as each covalent bond made to the sidewalls acts as a scattering site for charges travelling along them and they become pseudo-semiconductors. The reduction in their length by means of fluorination also introduces defects. In terms of OPVs the addition of the SWNT(B)-C₆₀ may introduce new exciton dissociation sites enhancing the bulk-heterojunction.

5.4 Characterization of devices fabricated using the P3HT:PCBM:CNT-Fullerene hybrids

5.4.1 Electrical characterization

Current Density – Voltage (J-V) characteristics of the P3HT:PCBM:CNT-Fullerene hybrids are shown in Figure 5.8 and Figure 5.9, the important device parameters are detailed in Table 5.1. While the P3HT:PCBM:SWNT blend showed ohmic behavior because of the long conductive SWNTs shorting the device, functionalization of the long SWNTs with C_{60} changed their electric characteristics dramatically displaying a more diode-like behavior but no photocurrent was generated. It is obvious that SWNTs (up to 10 µm long) can cross easily through the photoactive layer (~100 nm) making an electrical contact with both the cathode (AI) and the anode (ITO).



Figure 5.8 J-V characteristics of OPVs using P3HT:PCBM:CNT-Fullerene hybrids as the photoactive layer. SWNT: pristine long SWNT up to 10 μ m in length; SWNT-C₆₀: long SWNT functionalized with C₆₀; SWNT(B)-C₆₀: SWNT barrels with ~ 60 nm in length, functionalized with C₆₀.

A fluorination procedure followed by thermal treatment successfully shortened the SWNTs to ~60 nm. The resulting SWNT(B)-C₆₀ showed an improved solubility in chlorobenzene yielding a more homogeneous mixture with the P3HT:PCBM blend. The fabrication of OPVs using P3HT:PCBM:SWNT(B)-C₆₀ blend as the photoactive material showed encouraging results as seen in Figure 5.8. The J-V characteristics of OPVs made with P3HT:PCBM:SWNT(B)-C₆₀ [1:0.5:0.1] (by weight) showed a V_{oc}, J_{sc}, FF and η of 0.43 V, 6.30 mA/cm², 0.41 and 1.14%, respectively. The control P3HT:PCBM cell for comparison had a V_{oc}, J_{sc}, FF and η of 0.51 V, 7.30 mA/cm², 0.48 and 1.81 %, respectively. The series resistance of both device types is similar but the shunt resistance was reduced compared to the control indicating the 10 wt. % loading may be marginally too high.



Figure 5.9 J-V characteristics of OPVs using P3HT:PCBM:SWNT(B)-C₆₀ as the photoactive layer with different mixing ratios.

Optimization of the OPV performance by changing the ratios of the P3HT:PCBM:SWNT(B)-C₆₀ blend is shown in Figure 5.9. Generally, a trend of increasing J_{sc} (Figure 5.10a) and V_{oc} (Figure 5.10b) was observed with decreasing SWNT(B)-C₆₀ loadings. The changes in efficiency and FF are also shown in Figure 5.10a and Figure 5.10b, respectively. It is encouraging that the J_{sc} of the OPV made with P3HT:PCBM:SWNT(B)-C₆₀ [1:0.6:0.05] is approaching that of the standard P3HT:PCBM blend control devices. The J-V characteristics of OPVs made with P3HT:PCBM:SWNT(B)-C₆₀ [1:0.5:0.02] showed a V_{oc} , J_{sc} , FF and η of 0.55 V, 8.83 mA/cm², 0.37 and 1.81%, respectively. The control P3HT:PCBM cell for comparison had a V_{oc} , J_{sc} , FF and η of 0.60 V, 8.70 mA/cm², 0.41 and 2.17 %, respectively. In this case both the series and shunt resistances are almost equal for the control devices and those fabricated from the P3HT:PCBM:SWNT(B)-C₆₀ [1:0.5:0.02] blend.



Figure 5.10 (a) A plot of efficiency and J_{sc} vs. SWNT(B)-C₆₀ loading (b) A plot of V_{oc} and FF vs. SWNT(B)-C₆₀ loading.

In order to ascertain the possible role of C_{60} in an OPV device, C_{60} was used as the sole n-type material in a blended cell structure. The P3HT: C_{60} device is shown in Figure 5.11 and a comparison is made with the standard P3HT:PCBM reference device. It is clear that the P3HT: C_{60} device operates at a significantly lower efficiency due to poor exciton dissociation resulting in reduced open circuit current. The miscibility of C_{60} in chlorobenzene is not as good as that for PCBM leading to a different interpenetrating network morphology in the active layer which does not readily allow for excitons to dissociate.



Figure 5.11 J-V characteristics of OPVs using P3HT:PCBM and P3HT:C₆₀ AS blends in the active layer.

	Conc. wt. %	J_{sc} (mA/cm^2)	V _{oc} (V)	η (%)	FF
P3HT:PCBM	[1:0.66]	7.30	0.51	1.81	0.48
P3HT:PCBM:SWNT(B)-C60	[1:0.5:0.1]	6.27	0.43	1.14	0.43
P3HT:PCBM	[1:0.66]	8.72	0.60	2.17	0.41
P3HT:PCBM:SWNT(B)-C60	[1:0.6:0.01]	7.41	0.58	1.67	0.39
	[1:0.6:0.02]	8.83	0.55	1.81	0.37
	[1:0.6:0.03]	6.50	0.56	1.50	0.42
	[1:0.6:0.05]	4.58	0.34	0.42	0.27
P3HT:C ₆₀	[1:0.4]	2.45	0.35	0.30	0.35

Table 5.1: Characteristics of OPV devices.

5.5 Conclusion

It is clear that the incorporation of CNT materials into OPVs is quite often problematic and detrimental to overall device performance. Ideally only semiconducting CNTs should be incorporated into OPV active layers to avoid the issues of electrical shorting by metallic or pseudo-metallic CNTs. Until CNTs can be sorted in large quantities based on their conductivity it is not practical to use them in OPVs, whether as some functionalized active layer or even as electrodes.

The variation of device performance from batch to batch of devices can be substantial as the fabrication process is rather complex. It may not be uncommon to observe a change in V_{oc} of 0.1 V and J_{sc} of more than 10-20% based upon the unique conditions of each fabrication batch. For each of the J-V characterizations shown in Figures 6 and 7, the included curves for a standard reference P3HT:PCBM active layer device serves as a direct comparison for the unique fabrication conditions of that batch of devices. Although it is preferred to show an improvement in device operation, the assertion of an improvement must be based upon a result that can be traced back to the change made rather than it being compared to a poor performance device. In conclusion, until a largescale source for pure semiconducting CNTs is available at a reasonable price, CNTs are not suitable for incorporation in OPVs in terms of practicality, film homogeneity and processability. The findings of this chapter have been published in *Thin Synthetic Metals* [51].

5.6 References

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CHAPTER 6.

Modification of OPV device interlayers and materials

6.1 Introduction

This chapter deals with the development and alteration of the standard glass substrate ITO/PEDOT:PSS/P3HT:PCBM/Al OPV device structure. The beginning of this chapter introduces transparent conducting oxides focusing on the most common OPV anode material, ITO. The discussion is expanded with respect to the notable drawbacks of ITO and the presentation of methods to either replace the ITO or the factors which are responsible for these issues which are detrimental to device stability, reproducibility and efficiencies. The most common hole transport layer, PEDOT:PSS is discussed in terms of its inherent challenges when used in conjunction with ITO. Two new hole transport layers, namely PVK and PPy-PSS are demonstrated in working OPV devices realizing that there are alternatives to PEDOT:PSS which may be inspired by the advancements and work carried out in the older field of OLEDs.

6.2 Transparent Conducting Oxides

The development of transparent conducting oxides (TCOs) has been active since 1907 when K. Bädecker first reported on the properties of Cd sputter deposited in a glow discharge chamber which upon thermal oxidation became optically transparent whilst retaining electrical conductivity [1]. Since that time a vast number of different materials consisting of non-stoichiometric and doped oxides of tin, indium, cadmium, zinc and various alloys have been developed for electronic, and optoelectronic devices [2]. These materials have been demonstrated to maintain near metallic conductivity whilst possessing high optical transparency in the visible and high reflectance in the IR. The most widely used and studied of these materials is ITO (In_2O_3 :Sn) which has boasted

sheet resistances as low as two ohms per square and optical transparencies in the visible of up to 90% since the 1980s [3]. ITO has become a significant electrode material in the OPV field. Although ITO has impressive optical transparency and near metallic conductivity, there are some undesirable properties associated with it that are now leading to attempts to either modify or replace it.

6.2.1 Issues and future concerns associated with ITO

The values reported for excellent optical transmittance and low sheet resistance for ITO thin-films are dependent on the fabrication method. Once the method has been optimized by means of changing various deposition parameters comparable results are observed from the different methods. Comparing laboratory manufactured ITO electrodes to high throughput batches that are commercially available, it is clear that in order to obtain the desired properties which are possible when fabricated in the lab, the commercial cost is rather prohibitive. Currently the cost of purchasing ITO coated substrates is high (~ US\$10 for a 25 x 25 mm glass substrate having a sheet resistance of 10 - 12 ohms per square) and worldwide demand for Indium is continuously rising due to the ever increasing presence of touch-screen devices, it is evident that costs will rise even more.

The use of ITO is problematic in OPVs due to a number of material drawbacks. ITO is brittle and does not resist bending stresses that it is subjected to when deposited onto flexible substrates such as PEN or PET instead of glass. As a result of this the sheet resistance of ITO deposited on PET tends to be higher (~20 - 30 ohms per square). This increased sheet resistance leads to much lower performance OPV devices fabricated on 'flexible' ITO substrates especially for larger area devices. Table 6.1 summarizes the typical OPV device parameters observed for OPV devices (~54 mm²) fabricated on ITO coated PET substrates

Ag Anode Devices Data	I _{sc}	J _{sc}	V _{oc}	η	FF
	(<i>mA</i>)	(mA/cm^2)	(V)	(%)	
	1.98	3.67	0.53	0.69	0.35
	2.04	3.78	0.54	0.71	0.35
	1.92	3.56	0.53	0.67	0.36
	1.91	3.54	0.55	0.67	0.35
	1.93	3.57	0.53	0.61	0.32
	1.94	3.59	0.53	0.61	0.32
	1.86	3.44	0.52	0.58	0.32
	2.10	3.88	0.54	0.77	0.37
	2.12	3.93	0.54	0.71	0.33
	2.14	3.96	0.54	0.73	0.34
	1.99	3.69	0.53	0.68	0.35
	2.04	3.77	0.52	0.69	0.35
	1.90	3.51	0.52	0.59	0.32
	1.87	3.47	0.51	0.56	0.31
	1.79	3.32	0.51	0.57	0.33
	2.11	3.91	0.52	0.74	0.36
	2.18	4.04	0.52	0.75	0.35
	2.11	3.90	0.52	0.74	0.37
	2.26	4.18	0.53	0.76	0.34
	1.81	3.36	0.53	0.60	0.34
	1.89	3.50	0.53	0.65	0.35
	1.87	3.46	0.53	0.60	0.33

 Table 6.1 Characteristics of OPV devices fabricated on ITO coated PET substrates.

The numerous issues associated with ITO have been addressed by our research group at the Institute for NanoEnergy in the University of Houston by replacing the ITO with Ag (S. Yambem *et al.*) [4] or Au (A. Haldar *et al.*) [5].

In the standard OPV materials structure, an inter-layer (PEDOT:PSS) used for hole transport or electron blocking is deposited on top of the ITO. The chemical stability of ITO in the presence of acidic materials such as PEDOT:PSS is a concern with the detrimental effects on device performance due to ITO etching and migration in the presence of PSS. It can be demonstrated that these effects are far less severe when ITO is replaced with a thin Ag film [4]. Both of these solutions to the drawbacks of ITO are discussed in the next sections of this chapter.

6.3 Replacing ITO

In order to remove the heavy reliance on ITO, replacement materials have been sought. The use of thin metallic films with a reasonable optical transmittance in the visible is an option. The work functions of both Ag (5.0 eV - oxidized) [6] and Au (~5.1 eV) [7] are well suited to the electronic structure of the typical active layer P3HT:PCBM composite. The thin metal films are deposited on the substrate to a thickness where they have a sheet resistance similar to that of ITO whilst still allowing light to enter that active layer.

6.3.1 Silver Anode OPVs

In the case of Ag anode OPVs, the Ag thin film was thermally evaporated onto glass substrates using process parameters described in Chapter 2, Section 5.4. After thermal evaporation, the optical transmission of the Ag films was characterized using UV-vis spectroscopy and the average film sheet resistance was determined using a two-point probe method. The first attempt to deposit a very thin Ag film on glass yielded colored films comprising of Ag nanoparticles with a varying particle size. This results from the resonant oscillations of confined electrons in the film. The colors observed are indicative of the nanoparticle size (Figure 6.1). The optical and electrical properties of Ag films may be correlated with the variation of the film structure as a function of growth. As the film is deposited, silver islands are formed on the substrate and these individual islands eventually link up forming clusters. Ultimately a transition to a continuous film occurs and the optical properties of the films rely on the size, shape and separation of the islands [8].



Figure 6.1 UV-vis transmission of thermally evaporated Ag films on glass.

The dominance of nano-sized particle domains in the film is undesirable as the conductivity of a film comprised of such a structure is limited; the challenge is to get a film that is thin whilst reaching conductivities that resemble the bulk properties of Ag. An Ag film ~ 20 nm thick with a slightly silvered appearance was determined to have an appropriate sheet resistance (\sim five to ten ohms per square) whilst still maintaining reasonable optical transmittance ($\sim 40 - 50$ % at 500 nm) in the visible (Figure 6.2).

Issues with the adhesion of the Ag film on the glass substrate were discovered during subsequent fabrication steps. The Ag film deposited on the substrate has varying degrees of adhesion correlated to the cleanliness of the substrate before deposition by thermal evaporation. Even for the cleanest substrates used, the Ag film simply rubbed away under very little force and completely desorbed when washed with water. This was due to the evaporated Ag films formed from fractal structures of small Ag particles tended to float on top of the substrate. In order to merge the discontinuous Ag film together and allow better adhesion to the glass substrate, the films were sintered in an N₂ filled oven at 120°C for 20 mins. The effect of sintering was immediately evident upon characterizing the Ag films using UV-vis spectroscopy.



Figure 6.2 UV-vis transmission of thermally evaporated Ag films on glass before and after sintering

A small change was noted in the conductivity of the Ag films after sintering, however this change corresponded to an improvement of less than one ohm per square on average. Ag anode OPVs were fabricated using the standard procedure for OPV fabrication as outlined in Chapter 2, Section 1.5. The UV treatment time for the Ag films before PEDOT:PSS deposition was reduced to 2 mins to protect the Ag film from losing adhesion to the glass substrate. The batch of Ag anode OPV devices fabricated were characterized and their performance parameters are shown in Table 6.2. It is clear that the repeatability in the fabrication of Ag anodes is sufficient such that an anode comprising of a thin film of Ag is a viable contender to replace ITO.



Figure 6.3 J-V characteristic plot of the best Ag anode device fabricated on a glass substrate

The J-V characteristic plot of the highest efficiency Ag anode OPV device shown in Figure 6.3 is comparable to those taken for previously fabricated ITO based devices. The best Ag anode device has a Jsc, Voc, PCE and FF of 8.34 mAcm⁻², 0.55 V, 1.88 % and 0.41, respectively. The Jsc obtained from this device is indicative that the standard flat panel architecture in its current form is not optimized for the active layer thickness. As a result, the transparency of the anode may not need to be as high as that for ITO in order to get an OPV device with a reasonable efficiency. It is evident that with further optimization of the deposition process of the thin Ag anode it should be possible to further improve OPV device performance. The ability to heat and rotate the substrate whilst depositing the Ag anode may yield improved optical transparency whilst maintaining the low sheet resistances observed.

Ag Anode Devices Data	Area	$\mathbf{J}_{\mathbf{sc}}$	V _{oc}	η	FF
	(mm)	(mA/cm^2)	(V)	(%)	
	1.00	6.55	0.57	1.58	0.43
	1.20	6.08	0.57	1.48	0.43
	1.10	6.17	0.55	1.58	0.47
	0.70	6.74	0.57	1.78	0.47
	0.50	7.40	0.55	1.81	0.44
	0.60	7.00	0.55	1.73	0.45
	0.60	6.29	0.54	1.53	0.45
	0.70	6.97	0.56	1.81	0.46
	0.70	6.94	0.55	1.76	0.46
	0.70	6.34	0.55	1.61	0.46
	1.10	6.83	0.55	1.74	0.47
	1.20	5.72	0.55	1.43	0.46
	1.30	5.50	0.54	1.32	0.45
	2.00	5.59	0.54	1.46	0.48
	1.80	5.58	0.55	1.50	0.49
	2.00	5.66	0.54	1.39	0.46
	1.80	5.53	0.47	0.91	0.35
	0.80	7.10	0.55	1.63	0.41
	0.85	7.12	0.55	1.68	0.43
	0.65	8.34	0.55	1.88	0.41
	0.60	8.24	0.55	1.80	0.40
	1.80	5.35	0.55	1.35	0.46
	1.60	6.08	0.55	1.54	0.46
	1.60	6.67	0.56	1.72	0.46
	2.00	5.39	0.55	1.39	0.47
	1.60	4.81	0.57	1.32	0.48
	1.44	5.92	0.57	1.59	0.47
	1.68	6.41	0.58	1.79	0.49
	1.44	6.89	0.57	1.86	0.47

Table 6.2: Characteristics of fabricated Ag anode OPV devices.

6.3.2 Gold Anode OPVs

Gold is particularly suited for use as an anode material in OPV devices due the matching of its workfunction to that of the HOMO of P3HT, the donor polymer in the active layer yielding an efficient layer for charge collection. Au has previously been used as an interlayer in the formation of OLED devices [7]. It was deposited as 5, 10 or 15 nm thick film on top of ITO (20 ohms per square) to enhance hole injection efficiency and a lower turn on voltage for the OLED was observed (4 - 1.6 V).

Various groups have also utilized ultra-thin Au layer to enhance the operation of their organic electronic devices, however the use of Au exclusively as an anode is rare [9,10], the thermally evaporated Au anode OPV structure described in this section is another step taken by our group in the realization of replacing ITO. The new OPV device structure consists of the following layers: Glass/Cr/Au/PEDOT:PSS/ P3HT:PCBM/Al. In order to assure adhesion of the thermally evaporated gold layer to the glass substrate a thin (~20 nm) adhesion layer of Cr is deposited first.



Figure 6.4 UV-vis transmission spectrum of a typical Cr/Au thin anode film on glass [5].

The Ag anode characterized by UV-vis shown in Figure 6.4 has and optical transmission over 50 % at 500 nm and a sheet resistance (5.19 ohms per square) which is almost half that of the commercially available ITO ($\sim 10 - 12$ ohms per square).



Figure 6.5 J-V characteristic plots of a typical Cr/Au anode OPV device, a standard ITO OPV device and both devices without the PEDOT:PSS hole transport layer. [5]

The J-V characteristics of the gold anode OPV devices (Figure 6.5) are comparable to that of the standard ITO devices fabricated. The parameters of the best fabricated Cr-Au anode OPV device are given in Table 6.3. It is encouraging to see that the Cr-Au OPV devices are almost as efficient as the standard ITO anode OPV devices having very similar fill factors despite the very large difference in optical transmission. This result opens up a promising new anode to replace ITO for use in OPV devices.

	Area	\mathbf{J}_{sc}	V _{oc}	η	FF
Standard Device	(mm^2)	(mA/cm^2)	(V)	(%)	
	1.92	7.83	0.54	2.16	0.51
X/P3HT:PCBM/Al					
X=					
ITO/	2.70	4.98	0.41	0.76	0.37
Cr-Au/	1.08	1.97	0.32	0.24	0.38
Cr-Au/PEDOT:PSS/	1.13	7.01	0.55	1.90	0.49

Table 6.3: Characteristics of a standard OPV device compared to one without PEDOT:PSS.

6.4 Hole transport (electron blocking) layers

6.4.1 PEDOT:PSS

Poly(3,4-ethylenedioxithiophene) a derivative of polythiophene known as PEDOT, was first developed in the late 1980s by BAYER AG research laboratories in Germany [11,12]. It was found that PEDOT was an insoluble polymer but interestingly it possessed conductivities as high as ~ 300 Scm⁻¹ [13]. Poly(styrene sulfonate) (PSS), a water-soluble polyelectrolyte was added and used as a charge balancing dopant enabling the system to retain high conductivity, good solution processability and stability — typical commercially available PEDOT:PSS solutions have a typical shelf-life of six months. PEDOT:PSS was originally used as an antistatic coating for photographic films by AGFA [14], however it was soon realized that it may lend itself to a more important role in organic electronics.



Figure 6.6 J-V characteristic plots displaying the effect of adding a PEDOT:PSS hole transport layer

The use of PEDOT [15] and eventually PEDOT:PSS as hole injection layers in organic light emitting diodes lead to their integration as a hole transport layer in OPVs. At present PEDOT:PSS is the most common used material in the hole transport layer, however inverted structure OPVs which are gaining popularity due to improved lifetimes and stability often use MoO₃ and V₂O₅ [16]. The insertion of PEDOT:PSS

between the ITO anode and the active layer of the OPV device results in a dramatic improvement in V_{oc} and efficiency as shown in Figure 6.6 and Table 6.4. The rise in open circuit voltage is ascribed to charge transfer and alignment of the Fermi levels of ITO and PEDOT:PSS when they are in contact. The ITO work function (4.5-4.7 eV) is slightly lower than that of PEDOT:PSS (5.1-5.4 eV) and as a result, PEDOT:PSS is a closer match with the highest occupied molecular orbital (HOMO) ~5.1 eV for P3HT. PEDOT:PSS also serves as a buffer layer which planarizes the ITO surface reducing the frequency of short-circuits due to pinhole defects in the device structure which increases Jsc and FF, yielding improved device efficiency.

	Area	\mathbf{J}_{sc}	Voc	η	FF
Standard Device	(mm^2)	(mA/cm^2)	(V)	(%)	
1	2.00	6.19	0.54	1.73	0.51
2	1.80	7.61	0.54	2.10	0.51
3	2.20	7.56	0.54	2.13	0.52
4	1.92	7.83	0.54	2.17	0.51
5	2.60	6.43	0.54	1.75	0.50
6	2.50	6.35	0.54	1.73	0.51
7	2.40	6.83	0.54	1.84	0.50
8	2.00	7.44	0.53	1.87	0.47
Device with no PEDOT:PSS					
1	2.00	5.75	0.24	0.45	0.33
2	2.10	5.31	0.41	0.72	0.33
3	2.10	5.76	0.24	0.44	0.31
4	1.76	5.64	0.38	0.64	0.30
5	2.70	4.98	0.41	0.76	0.37
6	2.70	4.90	0.36	0.60	0.34
7	2.61	5.32	0.33	0.57	0.32
8	2.76	4.80	0.31	0.46	0.31

Table 6.4: Characteristics of a standard device compared to one without PEDOT:PSS.

Spin assisted layer-by-layer coating of PEDOT:PSS

Typically the PEDOT:PSS hole transport layer is spin-coated from an aqueous solution in one processing step yielding a hole transport layer approximately 40 - 80nm thick depending on the spin speed. In the case of layer-by-layer (LbL) assembly, polycations and polyanions are alternately adsorbed onto the substrate from their respective solutions forming a bilayer film where control of the layer thickness is more precise than single step spin-coating [17]. In order to fabricate a hole transport layer using the LbL process, alternating polycationic, poly(diallyldimethylammonium chloride) (PDDA) and polyanionic (PEDOT:PSS) species were used in the formation of the bilayers.



Figure 6.7 Spin-assisted LbL process steps to fabricate the hole transport layer

The spin-coating parameters and material deposition timings are shown in Figure 6.8 where the substrate is cleaned are per the standard procedure outlined in Chapter 2, Section 5.1 and activated under O_3 plasma treatment for 20 mins. The substrate is then coated with the polycations, washed, coated with the polyanions and washed again to form a single bilayer. The processing steps shown in Figure 6.7 may be repeated in order to deposit a number or bilayers. After the hole transport layer is deposited, the substrates were used to fabricate OPVs as per the standard procedure.



Figure 6.8 Spin speed parameters and timings for the spin-assisted LbL deposition of one bilayer coating for the hole transport layer. Each of the four steps required to form one bilayer are shown.

A preliminary study was carried out to determine the possibility of applying this process in the fabrication of the hole transport layer for OPVs. The J-V characteristic plots (Figure 6.9) for OPV devices employing 1, 5 and 10 bilayers are compared to the standard OPV device structure with and without a PEDOT:PSS layer.



Figure 6.9 J-V characteristic plots of the highest efficiency OPVs fabricated utilizing one step spincoating and spin-assisted LbL deposition of the hole transport layer.

The performance of the bilayer devices dropped with an increasing number of bilayers. A summary of the fabricated OPV devices is given in Table 6.5. The reduction of OPV device performance with increasing number of bilayers may be ascribed to the insulating nature of PDDA, where the increasing number of PDDA layers serves to raise resistance at the interface, impairing charge collection.



Figure 6.10 Plots of averaged OPV device parameters as a function of the number of bilayers (0 indicates the standard spin-coated PEDOT:PSS devices). The error-bars are calculated from the standard deviation of the measured data.

In all cases, the OPV parameters are negatively affected by the additional deposited bilayers. It is clear that the single-step spin-coating of PEDOT:PSS yields the best performing device but as a preliminary study, the LbL process has potential for generating repeatable thinner and more homogenous layers.
	Area	\mathbf{J}_{sc}	V _{oc}	η	FF
Standard Device	(mm^2)	(mA/cm^2)	(V)	(%)	
PEDOT:PSS	2.34	5.94	0.52	1.66	0.53
	2.70	6.82	0.53	1.95	0.54
	2.60	6.59	0.51	1.81	0.54
	1.43	6.84	0.51	1.71	0.49
	1.19	7.69	0.52	1.97	0.49
	1.43	7.41	0.52	1.90	0.49
	1.50	7.75	0.51	1.95	0.49
No PEDOT:PSS					
Best Device	2.70	4.98	0.41	0.76	0.37
1-BL PDDA-PEDOT:PSS					
	2.10	5.15	0.50	1.28	0.50
	1.80	5.30	0.51	1.31	0.49
	1.60	5.98	0.51	1.53	0.50
	1.90	4.63	0.50	1.17	0.50
	1.89	5.69	0.50	1.46	0.51
	2.40	5.08	0.50	1.27	0.50
	2.34	4.03	0.50	1.04	0.52
5-BL PDDA-PEDOT:PSS					
	2.30	5.52	0.44	0.95	0.39
	2.30	3.71	0.44	0.63	0.39
	2.00	3.91	0.43	0.66	0.39
	1.76	6.45	0.42	1.03	0.38
	2.65	4.88	0.45	0.89	0.40
	2.40	4.62	0.43	0.75	0.38
	1.92	4.86	0.42	0.77	0.38
10-BL PDDA-PEDOT:PSS					
	2.20	2.07	0.46	0.20	0.21
	2.20	1.79	0.44	0.13	0.17
	2.30	1.61	0.42	0.14	0.20
	2.19	1.24	0.43	0.11	0.20

 Table 6.5: Characteristics of OPV devices using LbL PDDA-PEDOT:PSS in the hole transport

 layer compared to the standard single-step process spin-coated layer.

Device degradation due to PEDOT:PSS

While PEDOT:PSS has been frequently used to improve the performance of both OLEDs and OPVs, it is the acidic and insulating nature of PSS which is found to pose the most issues in terms of device stability. The composition of the ITO/PEDOT:PSS interface was studied by means of Rutherford backscattering by De Jong *et al.* [18]. Samples consisting of glass/ITO/PEDOT:PSS were determined to have 0.02 atomic % indium in the PEDOT:PSS film immediately after fabrication by spin-coating. Degradation of the ITO/PEDOT:PSS interface was observed to much faster upon exposure to air at 8 °C for 10 days. The indium levels detected in the PEDOT:PSS ultimately reached a high of 1.2 atomic % highlighting the severity of the degradation. The acidic PSS present in the film structure etched the ITO resulting in the degradation of the interface. In Figure 6.11 the effects of exposing the standard ITO anode of OPV devices to PEDOT:PSS for different durations (0, 1, 3, 5 & 10 days) are displayed.



Figure 6.11 Plots of averaged OPV device parameters as a function of the amount of time the ITO is exposed to PEDOT:PSS. The error-bars are calculated from the standard deviation of the measured data.

The predominant degradation mechanism in OPV devices using PEDOT:PSS as the hole transport layer was also determined to be the increasing resistance of the PEDOT:PSS/active layer interface by Kawano *et al.* [19]. They attributed the rising number of insulating domains to be a result of a reaction between the acidic species in PSS and water. Detailed mapping of the electronic properties of PEDOT:PSS films using conductive atomic force microscopy shows that small conductive domains (~20 nm) surrounded by more insulating regions are present in all films studies by Pingree *et al.* [20]. The conductive domain density is observed to change dramatically based on the grade of PEDOT:PSS used as well as processing parameters. It is clear from the J-V plots shown in Figure 6.12 that the OPV device performance significantly deteriorates for exposure times greater than three days where a kink in the J-V curve is observed. This is indicative that the interface between the PEDOT:PSS and the active layer is dramatically changing, resulting in the formation of a very poor diode.



Figure 6.12 J-V characteristic plots of representative OPV devices containing ITO anodes exposed to PEDOT:PSS for 0, 3, 5 & 10 days.

	Area	\mathbf{J}_{sc}	V _{oc}	η	FF
Standard Device	(mm^2)	(mA/cm^2)	(V)	(%)	
0 Day	1.17	9.42	0.62	2.32	0.40
	1.40	8.72	0.60	2.17	0.41
	1.40	8.83	0.61	1.77	0.33
	1.40	6.62	0.60	1.39	0.35
	1.17	11.59	0.60	2.06	0.30
	1.17	10.64	0.61	2.06	0.32
3 Days					
	0.88	7.85	0.61	1.76	0.37
	1.00	7.50	0.60	1.65	0.37
	1.44	6.37	0.61	1.71	0.44
	1.70	7.62	0.60	1.79	0.39
5 Days					
	1.28	3.25	0.60	0.64	0.32
	1.52	3.90	0.61	0.42	0.18
	0.63	5.79	0.60	0.60	0.17
	0.81	5.77	0.60	0.67	0.19
	0.60	6.85	0.60	1.37	0.33
10 Days					
	1.60	2.10	0.60	0.19	0.15
	1.70	2.68	0.60	0.26	0.16
	1.10	2.35	0.59	0.27	0.20
	0.80	1.82	0.59	0.18	0.17
	0.90	2.93	0.58	0.36	0.21
	1.00	1.77	0.58	0.22	0.21

Table 6.6: Characteristics of OPV devices fabricated with different ITO exposure times toPEDOT:PSS.

6.5 Alternative materials to PEDOT:PSS

6.5.1 PVK

Poly(*N*-vinylcarbazole) (PVK) has become a material of interest in OLEDs and subsequently OPVS as a result of its electro-optical, charge-carrier and good hole-transport properties [21,22]. The use of crosslinked PVK brushes as the hole transport layer in place of PEDOT:PSS removes the issues that arise due to the acidic nature of PSS. The capability of the PVK to form a linkage at the 3,6-position of its carbazole pendant units leads to the formation of a conjugated species of oligomeric to polymeric carbazole units [23,24]. This important characteristic yields better electrical conductivity, good adhesion and optical properties (Figure 6.13). The work outlined in the following paragraphs was carried out as part of a collaboration with the Advincula Group in the University of Houston and published in the Journal of Materials Chemistry entitled "*Electrochemically crosslinked surface-grafted PVK polymer brushes as a hole transport layer for organic photovoltaics*" [25]. The research carried out was recognized and highlighted by the journal (shown on the next page).



Figure 6.13 UV-vis characterizations of the crosslinked grafted PVK hole transport layer (closed triangles) taken by the Advincula Group [25].



Highlighting research from the Advincula (Chemistry) and Curran (Physics) Groups at the University of Houston.

Title: Electrochemically crosslinked surface-grafted PVK polymer brushes as a hole transport layer for organic photovoltaics

Investigating novel thin films and polymer materials for improving efficiency and stability of solar cells by directly modifying indium tin oxide (ITO) surfaces. Electrochemically surface-grafted poly-N-viny/carbazole (PVK) brushes as hole-transport layers (HTL) on a photovoltaic device have been demonstrated using surfaceinitiated living free radical (SI-RAFT) polymerization. Comparable performance on P3HT#PCBM /PEDOT#PSS based devices was achieved. A main advantage is strong adhesion to ITO with possible long-term stability against acid dopants and oxygen.



See M. C. Tria et al., J. Mater. Chem, 2011, 21, 10261.

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In order to compare the OPV performance between devices using different hole transport layers, all P3HT:PCBM based OPV devices were fabricated under the same processing conditions as described in Chapter 2, Section 5.3 (sequential spin-coating of P3HT:PCBM on each substrate and thermal evaporation of Al). For devices with PVK as the hole transport layer, the ITO glass substrates were not UV plasma treated before the PVK layer was deposited by the methods described in Chapter 2, Section 3.2.



Figure 6.14 J-V characteristic plots comparing the best OPV devices using PEDOT:PSS and PVK as the hole transport layer

The J-V characteristic plots of the P3HT:PCBM OPVs using the crosslinked PVK brushes and PEDOT:PSS as the hole transport layer are shown in Figure 6.14. Devices fabricated using the crosslinked PVK brushes as the HTL showed comparable performance (PCE 2.3%) to the PEDOT:PSS devices (PCE 2.1%). A higher V_{oc} (0.55 V) suggested the workfunction of PVK hole transport layer is well aligned with the HOMO of P3HT, forming an Ohmic contact. A comparable J_{sc} (8.8 mA) and FF (0.47) suggested good hole transport properties compared to the standard devices using the most conductive grade of PEDOT:PSS (Clevios PH-1000) currently available. Because there is no insulating and acidic dopant such as PSS in the PVK hole transport layer, it is expected to be more robust under water and oxygen, the main factors reducing the lifetime of OPVs.

Standard Device	(mm^2)	(mA/cm^2)	(V)	(%)	
	2.20	7.56	0.54	2.13	0.52
Devices with PVK					
1	1.40	7.11	0.56	1.76	0.45
2	1.12	6.97	0.49	1.42	0.41
3	1.08	8.84	0.55	2.31	0.47
4	1.00	6.96	0.55	1.55	0.40

Table 6.7: Characteristics of OPV devices using PEDOT:PSS and PVK in the hole transport layer.

6.5.2 Polypyrrole-PSS

A novel method employing the electrochemical polymerization of pyrrole (Py) in the presence of PSS allows for the deposition of a hole transport layer of Polypyrrole (PPy)-PSS onto a conducting substrate (ITO). This work led by Dr. Enrico Andreoli at the Institute for NanoEnergy is built upon research forming part of his PhD thesis [26]. Electrochemical deposition allows for precise control of the growth of the hole transport layer which contrasts that of spin-coating. The optical transmission (Figure 6.15) of the electrochemically grown PPy-PSS layer is comparable or superior to that of the PEDOT:PSS typically spin-coated at 3000 rpm.



Figure 6.15 UV-vis characterizations showing the optical transmission of PEDOT:PSS and PPy-PSS films used to fabricate the hole transport layer.



Figure 6.16 J-V characteristic plots comparing the best OPV devices using PEDOT:PSS and PPy-PSS as the hole transport layer

The J-V characteristics of the most efficient devices fabricated using standard spincoating and electrochemical deposition are compared in Figure 6.16 and Table 6.8. The control device consisting of ITO/PEDOT:PSS/P3HT:PCBM/A1 displayed relatively good operating parameters with respect to previous fabrication batches. The performance of the OPV device using PPy-PSS was not as efficient, however attaining an efficiency over 2.5 % whilst replacing PEDOT:PSS is noteworthy.

	Area	\mathbf{J}_{sc}	Voc	η	FF
Standard Device	(mm^2)	(mA/cm^2)	(V)	(%)	
1	1.57	11.86	0.55	3.09	0.48
Devices with PPy-PSS					
1	1.03	9.25	0.56	2.51	0.48

Table 6.8: Characteristics of OPV devices using PEDOT:PSS and PPy-PSS as the hole transport layer.

6.6 Implementation of new acceptor materials

6.6.1 ICBA / ICMA Adducts of C60

In the search to improve OPV device efficiency new acceptor materials to improve upon PCBM have been elusive. The energy difference between the HOMO of P3HT and the LUMO of PCBM is considered to be relatively small which results in open circuit voltages being restricted to ~0.6 V. Derivatives of C_{60} are now emerging as viable contenders to use in the place of PCBM and novel indene-C60 adducts have first been reported by He *et al.* [27] and further optimized by Zhao *et al.* [28]. The success of these acceptor materials is due to the lowering of the acceptor LUMO allowing for an enhanced Voc and efficiency. The P3HT:ICBA active layer OPV device was fabricated using a donor : acceptor weight ratio of 1:1. It exhibited a maximum values for PCE of 6.48 %, V_{oc} of 0.84 V, J_{sc} of 10.61 mA/cm2, and FF of 0.727. The exceptional FF can in part be attributed to the Ca interlayer used in their OPV device structure (ITO/PEDOT:PSS/P3HT:ICBA/Ca/AI).

When used as an interlayer, Ca having a low workfunction ~ 2.9 eV is proposed to facilitate a better ohmic contact with the active layer (PCBM) and acts as a hole blocking layer. It typically was used as an electron injection material for OLEDs. The reactivity of Ca is also of interest as it may diffuse into the polymer active layer and combine with oxygen atoms forming Ca²⁺ ions yielding a thin metal oxide interface before deposition of Al. This process may allow for a more stable Al interface maintaining its desired properties [29]. It may also serve to protect the active layer during deposition of the cathode from degradation due to excessive heating.



Figure 6.17 J-V characteristic plots of OPVs using ICMA as the acceptor material in the BHJ blend

In order to ascertain OPV device performance using these new acceptor materials, the mono and bis-adducts (ICMA and ICBA) were synthesized at the Institute for NanoEnergy by Dr. Shawn Liao and were implemented as the acceptor material in the standard OPV device structure. Ca is not used as an interlayer due to its volatility in air — from a device stability standpoint it is unacceptable to add another even more unstable material to the device stricture.

The J-V characteristic plots for the most efficient device fabricated using ICMA are shown in Figure 6.17. Upon fabricating the device a significant improvement in performance was observed following thermal treatment on a hotplate at 150°C for 5 mins. This is attributed to an improvement in the active layer morphology allowing for much improved exciton dissociation and possible diffusion of species at the active layer cathode interface. Subsequent thermal treatment under the same conditions for an additional 5 mins yielded a slightly higher J_{sc} and V_{oc} yielding a small increase in efficiency suggesting the rearrangement of the active layer was stable under the processing conditions.



Figure 6.18 J-V characteristic plots of OPVs using ICBA as the acceptor material in the BHJ blend

The J-V characteristic plots for the most efficient device fabricated using ICBA are shown in Figure 6.18. Once again, after fabricating the device a significant improvement in performance was observed following thermal treatment on a hotplate at 150°C for 5 mins. In this case the Voc was increased but the Jsc was impaired resulting in small drop in efficiency.



Figure 6.19 J-V characteristic plots of the best ICMA and ICBA devices compared to the standard OPV using PCBM.

It is noted that the OPV devices using ICMA outperformed those using ICBA. The unexpected lower V_{oc} observed in the ICBA devices is possibly due to the presence of numerous different-adducts of C_{60} that serve to decrease device performance. This is a result of the difficulties encountered in the purification process of the materials during synthesis. It is important that a highly pure source of the acceptor material is used. In this case it is likely that too many different adducts of the synthesized acceptor are present yielding an inhomogeneous acceptor material system.

	Area	$\mathbf{J}_{\mathbf{sc}}$	V _{oc}	η	FF
Acceptor Material	(mm^2)	(mA/cm^2)	(V)	(%)	
PCBM (Standard)	48.75	7.53	0.48	1.74	0.48
ICMA (1.03 mm ²)	Anneal time (mins)				
	0	2.41	0.32	0.27	0.34
	5	6.48	0.64	1.55	0.37
	10	5.59	0.68	1.36	0.36
ICBA (1.20 mm²)					
	0	0.94	0.24	0.06	0.28
	5	2.55	0.43	0.30	0.27
	10	2.65	0.45	0.32	0.27

Table 6.9: Characteristics of OPV devices using PCBM, ICMA and ICBA as the electron acceptor material in the blended active layer.

6.7 Conclusions

In this chapter the drawbacks of using ITO were presented and the effects of the acidic nature of the hole transport layer PEDOT:PSS are evidenced. It was demonstrated that ITO may be replaced by thin thermally evaporated Ag or Au films. The issue of attaining a thin film that is as conductive as ITO whilst allowing light to enter the active layer was resolved by the lower sheet resistance of the metal films.

The hole transport layer, PEDOT:PSS was studied in terms of novel deposition technique, spin-assisted layer-by-layer deposition. The degradation of ITO in the presence of PEDOT:PSS was highlighted and demonstrated. In order to address this issue either the ITO must be replaced by Au or Ag or else a new material must be sought to replace PEDOT:PSS. PVK and PPy-PSS are demonstrated to work as effective hole transport layers when substituted for PEDOT:PSS in the standard OPV device structure yielding comparable OPV device parameters.

Initial studies on the development of acceptor materials in the BHJ blend resulted in the use of ICMA and ICBA. It was determined that more work is needed in attaining highly pure stocks of these materials in order to rival the low impurities observed in the commercially available PCBM.

6.8 References

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CHAPTER 7.

The Stack OPV device design, characterization and modeling

7.1 Introduction

In this chapter the stack OPV device architecture is introduced. The development of the stack OPV device architecture is outlined. Data pertaining to the performance of a standard flat panel used to fabricate a stack OPV device is presented. An optical model is compared to the experimental data and the results show that this new architecture has great potential in terms of increasing the efficacy of harvesting photons. By maintaining the ultra-thin nature of the films whilst ensuring the active layer material can gather in all resonant photons we can increase the current output addressing a familiar challenge in OPVs.

7.1.1 Background

Organic photovoltaics (OPVs) are often described as a disruptive technology that is now a significant topic of scientific and entrepreneurial study rather than a decade ago being a fringe field. Organic based electronics and OPVs in particular have been extensively studied by multidisciplinary research groups in the hope to form the critical blend of device architecture and ideal material base. A key parameter is the power conversion efficiency (PCE) and there have been many success stories based on new material structures such as a recent NREL certified OPV device having a PCE value of 8.3% for an active area of 0.1cm². Successes related to OPV modules include a 3.5% PCE for an illumination window area of 208.4 cm² (these results are published regularly in the solar cell efficiency tables) [1]. A large part of the current work on OPVs is highly focused on the materials science aspects of design and rarely has a new architecture been presented as an alternative to the common flat-panel structure which was originally conceived for the first silicon devices. Progress made in OPV research with respect to engineering of novel materials has yielded some interesting advancements. Fill factors achieved for OPV devices are now reaching values as high as 0.7, comparable to other thin film photovoltaics such as CdTe (0.7) and CIGS (0.79). Also the open circuit voltage (V_{oc}) in OPV devices is comparable to or has even surpassed CIGS (0.7) and CdTe (0.84) in champion cells [1]. The promise of organic materials for use in OPVs is that they possess a very high quantum efficiency meaning that almost 100 % of the absorbed photons are converted into excitons. The solution processability of these materials and their inherent flexibility are both important parameters that are yet to be fully realized in their inorganic counterparts. The short circuit current density (Jsc) has always been a major obstacle to the success of OPVs. Even with a trend of achieving higher currents over the past number of years, the changes are at best incremental. It is now becoming clear that another way to gather current from organic materials is required. Current OPV architectures can deliver significant exciton generation, but it is the manner in which the photo-generated charges are collected that is proving to be an impasse and as such it is the motivation for proposing a new architecture in this chapter.

7.1.2 The Queisser Shockley limit

In 1961 Shockley and Queisser published an article entitled "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells" where they detailed a theoretically justified upper limit on the efficiency of a standard p-n junction Si solar cell [2]. Their calculations took into account an ideal case where the only recombination mechanism was radiative and another case where it was a fraction of the total recombination with the remainder being non-radiative. The illumination form the sun was approximated by a blackbody at 6000 K and the solar cell was assumed to behave as one at 300 K. The active layer is assumed to be thick enough to absorb all incident solar radiation with energies higher than the band gap.

It was found that under perfect conditions where all absorbed light is converted to charge carriers and allowing for no losses due to contact or series resistance, a solar cell utilizing a material with a bandgap of 1.09 eV would have a maximum possible or 'ultimate efficiency' of 44 %. When considering some inherent limiting properties of Si, the detailed balance limit yields a reduced efficiency ~26 % and a maximum of ~30 %

for a material having a bandgap of ~1.2 eV. Shockley and Queisser state that the true physical limit is probably slightly less as a result of a certain rate of unavoidable non-radiative transitions and it should lie between a previously calculated empirical limit of 21.7% and that of the detailed balance limit of 26%. In terms of OPVs based on P3HT having a bandgap of ~1.85 eV the 'ultimate efficiency' would be ~34 % yielding a maximum possible J_{sc} f~ 19 mAcm⁻². In realistic devices, accounting for the lack of precisely tailored materials having ideal conductivity and optical transparency properties the actual maximum efficiency is far lower. Taking into account the external quantum efficiency a more realistic value for the Jsc is of the order of 10 – 12 mAcm⁻²[3].

7.1.3 New OPV architectures

Previously we reviewed the main aspects of OPV design [4] and detailed some interesting developments in architecture which included the inception of the fiber m-c cell [3]. This was a foundation for the redesign of OPVs in terms of how they harvest the incident light and we propose a vertically aligned, OPV stack device. The design accommodates the requirement that the active layer is relatively thin of the order of 30-100 nm in order to achieve optimal exciton dissociation and charge collection given the percolating nature of charge transport within bulk-heterojunction OPVs. The dichotomy associated with this scenario is evident in terms of light lost due to the inherent optical transparency of such a thin layer. The thickness of the active layer in the OPV stack architecture can be reduced to allow an improved exciton dissociation efficiency due to the active layer being a smaller multiple of the exciton diffusion length of 5-20 nm [6]. Thus, there is no need to compromise absorption over exciton dissociation and carrier mobility or vice versa in this new device architecture. The stack architecture is designed to maximize the absorption of incident light by means of increasing the effective optical pathlength through the active layer and to act as an optical cavity trapping the incident light until it is absorbed.

7.2 Development of stack OPV devices

The stack OPV was first conceived in our research group at the Institute for NanoEnergy in 2008 and a subsequently a US patent was filed. We found that the OPV stack device architecture was an efficient new means of harvesting light. The early stack

devices were developed using ITO coated glass slides (1.2 mm thick) as the substrates. The aluminium electrode geometry is based upon a number of small area OPV devices (pixels) connected in parallel that is called the "comb" electrode layout. This electrode layout is advantageous over much larger single device layouts as it limits the effects of electrical shorting due to pinholes in the spin-coated layers. The comb electrode layout is presented in an article published in *Thin Solid Films* entitled "Design and fabrication of linear pixel arrays for organic photovoltaic modules to achieve scalable power output" [7]. The I-V characteristic plots for five pixel devices in a comb electrode layout from the aforementioned publication are shown in Figure 7.1. A linear rise in photo-generated current is observed as the number of devices connected in parallel increases from one to five. The very closely matched open circuit voltages observed indicates that the spin-coated layers are homogenous and contain few defects such as pinholes.



Figure 7.1 I-V characteristics of a 5 pixel comb electrode layout device. (Published in [7])

Figure 7.2 is a comparison of the I-V trace of the five devices connected in parallel to that of the summation of the measured currents of the five individual pixels. It is clear that the two I-V characteristics shown are very similar suggesting that the comb electrode layout allows the efficient interconnection of pixel devices with very little loss of energy.



Figure 7.2 Comparison of I-V characteristics of five devices connected in parallel to the summation of the same devices when individually measured.

To further show that the comb electrode layout effectively connects the pixel devices together with minimal losses, a device with much smaller area pixels ($\sim 0.3 \text{ mm}^2$) was fabricated. The I-V characteristics for eight pixel devices in a comb electrode layout are shown in Figure 7.3. It is again clear that there is a linear rise in photo-generated current with an increasing number of connected devices. There is a small discrepancy in the contribution from pixel to pixel as a result of the slightly varying pixel size.



Figure 7.3 I-V characteristics of a 8 pixel comb electrode layout device

Figure 7.4 is a comparison of the I-V trace of the eight devices connected in parallel to that of the summation of the measured currents of the eight individual pixels. In this case the two I-V characteristics shown are again quite similar, it may also be noted that the comb electrode layout displays a slightly improved short circuit current. This is attributed to the amount of time that has elapsed between measuring the connected device to that of the individual pixels. A small degree of degradation may have resulted in slightly poorer performing individual pixels.



Figure 7.4 Comparison of I-V characteristics of eight devices connected in parallel to the summation of the same devices when individually measured

The I-V characteristics of the eight connected pixels show that a smaller amount of photocurrent is generated compared to the five pixel device. This is due to the overall total device area being 2.50 mm² compared to 22.42mm². Once the current densities are calculated and plotted in Figure 7.5, it is clear that smaller pixels contributing to the eight pixel device have a higher efficiency as detailed in Table 7.1.



Figure 7.5 Comparison of J-V characteristics of the five and eight pixel comb electrode devices

Fig. 7.1 Data [7]	I _{sc}	$\mathbf{J}_{\mathbf{sc}}$	V _{oc}	η	FF
# of devices in parallel	(m A)	(mA/cm^2)	(V)	(%)	
1	0.29	6.07	0.61	2.13	0.58
2	0.59	6.47	0.60	2.25	0.58
3	0.86	6.40	0.60	2.20	0.57
4	1.15	6.42	0.60	2.17	0.56
5	1.47	6.54	0.61	2.35	0.59
Fig. 7.3 Data					
# of devices in parallel					
1	0.3	14.70	0.61	3.73	0.42
2	0.63	15.21	0.61	3.96	0.43
3	0.93	13.52	0.61	3.51	0.43
4	1.23	13.33	0.61	3.43	0.42
5	1.53	12.64	0.61	3.22	0.42
6	1.73	13.54	0.61	3.42	0.42
7	2.08	14.06	0.61	3.62	0.42
8	2.5	14.03	0.61	3.69	0.43

Table 7.1: Characteristics of OPV devices.

7.2.1 Stack OPV device structures

Fabricating stack OPVs from ITO coated glass substrates

The first operable stack OPV devices fabricated used standard ITO coated glass substrates employing the comb electrode layout which may comprise a number of pixel cells (having an area ranging from $\sim 1 \text{ mm}^2$ to 4 mm^2) being electrically connected in parallel with each other. In the case of the device shown in Figure 7.6a, there are six pixel devices connected in parallel, yielding a total device active area of $\sim 24 \text{ mm}^2$.



Figure 7.6 (a) Digital image of a comb electrode layout device used in the making of the first operable stack OPVs. (b) Diagram of the stack OPV device (multi-layered, mirrors not shown for clarity)

A number of similar devices are fabricated and stacked together to form a multi-layered stack device. The devices that are used to form the multi-layered stack are selected such that their performances (J_{sc} , V_{oc} , and FF) are similar by means of prior electrical characterization. Each stack layer is fixed in place using a UV curable epoxy and subsequently each of the devices are then connected in parallel using silver paste on the side faces which are sputter-coated with gold (discussed in more detail in Chapter 2, Section 4.1). A mirror consisting of Al coated glass is placed on the outside of the stack OPV device to form the resonating cavity which traps incident light enhancing the amount of absorption in the active layer.

7.3 Characterization of stack OPV devices



7.3.1 Electrical characterization of one and three-layer stack devices

Figure 7.7 J-V characteristic plot of a standard comb electrode device illuminated in the standard flatpanel orientation..

In Figure 7.7 the J-V characteristic plot of a standard comb electrode device is displayed. It is characterized using the solar simulator and illuminated in the standard flat-panel orientation as described in Chapter 2, Section 6.3, before being used to fabricate a stack OPV device. The actual device parameters may vary in devices fabricated in the one batch due to minor differences in the active layer morphology, common defects in the spin-coated layers or issues with substrate condition due to contamination and roughness. The Al cathode is prone to oxidation and is typically the most volatile layer in the device structure. As a result of these issues it is preferable to fabricate and compare devices from a single fabrication attempt and subsequent thermal evaporation of the cathode which may then yield more comparable results. It is this constraint that makes the comparison of stack OPV devices more challenging and as such it was only possible to directly compare a one-layer and a three-layer device. Later on in this chapter, a five-layer device is characterized solely to demonstrate the effects of changing the angle of incidence of the illumination source (solar simulator) on the device performance.



Figure 7.8 J-V characteristic plot of three devices used to make a three-layer stack OPV

In Figure 7.8 the J-V characteristic plots of three devices used in the fabrication of the three-layer stack OPV device are presented. It is important to choose devices of similar performance when fabricating the stack OPV device. This ensures that when they are electrically connected in parallel the open circuit voltages are matched allowing for a balanced contribution from each individual layer of the final stack device. Comparing the devices chosen for the one and three-layer stack devices, it is clear that their performances are similar. This particular fabrication process yielded enough similar devices to fabricate the two different stack OPV devices for comparison.

Comparison of one to three-layer stack OPV



Figure 7.9 J-V characteristic plots of the one and three –layer stack OPV devices

In comparing the two different stack OPV devices, the J-V characteristic plots shown in Figure 7.9 show that the process of adding additional layers to stack device are not detrimental to overall device performance. This result indicates that the stack OPV device architecture is scalable and as such, given the correct environment and controls over the fabrication process and conditions, it is conceivable that there is not a limit for the number of interconnected devices.

To further illustrate this point, Figure 7.10 displays the I-V characteristic plots for the two different stack OPV devices. The maximum actual photo-current generated by the one stack device is close to one third of the three-stack device (0.65 mA / 0.26 mA = \sim 2.5). If the individual devices characterizations are compared we can see that the sum of the short circuit current of the three devices used in the fabrication of the three-layer stack is \sim 2.9 times that of the device used in the fabrication of the one-layer stack OPV device. This suggests that there is little additional loss in individual device performance caused by the additional handling and electrical connections made in the fabrication of the stack OPV device when scaled to a larger number of layers.



Figure 7.10 I-V characteristic plots of the one and three –layer stack OPV devices

The characteristics of the devices fabricated are shown in Table 7.2. The fill factors of the individual devices are less than that of the stack OPV devices. This indicates that the stack OPV architecture is utilizing the incident light more effectively allowing for an increased pathlength for absorption in the active layer. The efficiency value quoted for the stack devices is a modular efficiency, accounting for the actual area of the entire device whereas for the individual devices the efficiency is calculated based on the active area alone. In order to increase the modular efficiency of stack OPV devices the amount of area being wasted must be minimized and the active area maximized.

One-Laver Stack Data	I_{sc} (mA)	J_{sc} (mA/cm^2)	V _{oc} (V)	η (%)	FF
Device 1	1.05	7.51	0.53	1.82	0.46
	1.05	7.51	0.55	1.62	0.40
1-Stack (40°)	0.26	3.09	0.45	0.67	0.49
Three-Layer Stack Data					
Device 1	1.05	7.52	0.51	1.58	0.42
Device 2	1.06	7.58	0.51	1.54	0.39
Device 3	0.94	6.73	0.53	1.66	0.46
3-Stack (40°)	0.65	2.59	0.46	0.58	0.50

Table 7.2: Characteristics of the 1, 3-layer stack OPVs and the individual devices used in their fabrication.

7.3.2 Preliminary angle dependence study of a stack OPV device The five-layer stack OPV device



Figure 7.11 J-V characteristic plots of the devices used to fabricate the five-layer stack OPV

In Figure 7.11 the J-V characteristic plots of five devices used in the fabrication of the five-layer stack OPV device are presented. These devices were selected from the fabrication batch such that their open circuit voltages were matched as closely as possible (0.51 - 0.53 V).



Figure 7.12 J-V characteristic plots of the five-layer stack OPV for varying incident angles of illumination.

The performance of the stack OPV device was determined to be dependent on the angle of incidence of the illumination source. The five-layer stack OPV device was placed on a rotation stage and electrical characterization was carried out over a range of incident angles ($0^{\circ} - 50^{\circ}$). In this initial study of the angular dependence, a linear increase in device performance was not seen with increasing angle. In Figure 7.12 the J-V characteristic plots of the five-layer stack OPV for varying incident angles of illumination is shown. A large increase in performance is observed for angles greater than 30° with a maximum appearing at 40° .



Figure 7.13 The effect of incident angle of illumination on the five-layer stack OPV device parameters (FF, Jsc, PCE, Voc). Lines are added as a guide to the eye.

In Figure 7.13 the angular dependence of the five-layer OPV stack on four device parameters (fill factor, short circuit current density, power conversion efficiency and open circuit voltage) are shown. Each of the four parameters follow a similar trend and are maximized at 40° .

Table 7.3 is a summary of all the devices used in the fabrication of the five-layer stack OPV device. The short circuit current generated by the five-layer stack OPV device is superior to that of the previous one and three-layer devices. This is attributed to the additional number of devices and the variable factors of a different fabrication batch.

	I _{sc}	\mathbf{J}_{sc}	$\mathbf{V}_{\mathbf{oc}}$	η	FF
Five-Layer Stack Data		(mA/cm^2)	(V)	(%)	
Device 1	1.95	8.14	0.52	1.88	0.44
Device 2	1.70	7.08	0.53	1.68	0.44
Device 3	1.86	7.75	0.52	1.77	0.44
Device 4	1.72	7.17	0.51	1.46	0.39
Device 5	2.18	9.08	0.53	2.18	0.45
5-Stack Device (Angle)					
0°	0.40	0.40	0.37	0.06	0.39
10°	0.50	0.49	0.37	0.07	0.40
20°	0.75	0.73	0.39	0.12	0.42
30°	1.81	1.77	0.44	0.36	0.46
40°	2.05	2.01	0.44	0.42	0.47
50°	1.96	1.92	0.43	0.38	0.45

 Table 7.3: Characteristics of the individual devices used in the fabrication a five-layer stack OPV

 and the performance of the five-layer stack OPV for varying incident angles of illumination.

7.4 The single layer PET stack OPV device

In order to minimize the stack OPV device, a different ITO coated substrate is employed. The ITO glass substrates are too thick and are much more difficult to cut to an appropriate size in comparison to PET. PET being a plastic, is very easy to cut accurately leaving only the desired device area behind. The electrode area was effectively increased ($\sim 55 \text{ mm}^2$) but on a smaller overall substrate area. The electrode now consists of just one larger pixel device. Although this electrode design is problematic in terms of repeatability when fabricated outside of a clean room environment, the aim is to fabricate a larger number of devices. The best performing device is then used to fabricate a PET stack OPV which can operate at a higher efficiency than the device in the flat panel orientation.

7.4.1 Fabrication of the PET stack OPV device

ITO coated, polyethylene terephthalate (PET) substrates (Aldrich) were cleaned in a heated sonication bath under μ 90 detergent, deionized water and isopropanol. The hole transport layer and active layer were deposited as per the standard procedure detailed in Chapter 2, Section 4. Additionally, the edges and the underneath of the substrates were cleaned to remove any excess P3HT:PCBM.

Suitable individual devices were selectively cut away from the main substrate and used to fabricate PET stack OPV devices. The PET stack OPV device was fabricated using silver paste to connect the electrodes to the side of the PET substrate allowing the encapsulation of the cathode by means of UV curable glue. The glue was also used to fix aluminium coated PEN mirrors on each side of the PET substrate to form the optical cavity of the PET stack OPV device. The angular dependence of the stack OPV was determined using a custom made rotating sample holder aligned on an optical bench.

Figure 7.14 Digital image of a flat OPV segment (with cm scale) used to fabricate a PET stack OPV device. (b) A typical fabricated stack device including the aluminium coated PEN side mirror.

7.4.2 Optical modeling of a single layer, PET stack OPV device

In order to model the behavior of light within the stack OPV it is assumed that all layers and interfaces are flat and parallel to each other, the air-PET interface is perpendicular to each of the parallel interfaces and all media are linear and isotropic. We also define reflection and transmission to be the only optical phenomena occurring at the interfaces and absorption of the propagating light takes place within the medium. 500 nm was selected as the wavelength for the incident monochromatic light as it approximates the strongest absorption peak of P3HT:PCBM. The refractive indices for ITO (1.85), PEDOT:PSS (1.42) and P3HT:PCBM (1.87) were determined for 500 nm incident light from previously published values in literature [8]. We took the value for the refractive index of PET to be 1.656 [9].

Light incident on the stack OPV device is partially transmitted into the PET substrate whilst the remainder is back-reflected at the air-PET interface. It is essential that the initial reflection at this interface is minimized to ensure that the maximum external quantum efficiency is attained. The initial angle of incidence at the air-PET interface (θ_i) and the refractive index (n) of each medium determine the new angle of incidence at each subsequent interface in the stack. The refracted angle (θ) is evaluated using Snell's law.

$$n\sin(\theta_i) = n_i\sin(\theta) \tag{7.1}$$

Figure 7.15 Ray Diagram depicting the path incident light takes through a stack OPV device on one optical pass. I_0 is the initial incident ray at an angle θ_i , R and T denote the reflected and transmitted rays for each layer.

The degree of reflectance (R) or transmittance (T) at each interface is dependent on the angle of incidence and the refractive indices of the two media bounding the interface. T and R are calculated at each interface using the Fresnel equations [10,11]. Specifically, the equations are manipulated to calculate the propagation of light within the stack OPV layers depicted in Figure 7.15 for the transverse electric (TE) and transverse magnetic (TM) polarizations. The reflectance at the interface for each polarization (R_{TE} , R_{TM}) is given by

$$\mathbf{R}_{TE} = \left[\frac{\cos\theta_{I} - \sqrt{N^{2} - \sin^{2}\theta_{I}}}{\cos\theta_{I} + \sqrt{N^{2} - \sin^{2}\theta_{I}}}\right]^{2}$$
(7.2)

$$\mathbf{R}_{TM} = \left[\frac{N^2 \cos\theta_I - \sqrt{N^2 - \sin^2\theta_I}}{N^2 \cos\theta_I + \sqrt{N^2 - \sin^2\theta_I}}\right]^2$$
(7.3)

N is the relative refractive index (n_2/n_1) of the bounding media at the interface of first to the second medium and θ_I is the incident angle at the interface. The average value for each polarization is used to approximate an unpolarised light source.

$$\mathbf{R} = \left[\mathbf{R}_{TE} + \mathbf{R}_{TM}\right]/2 \tag{7.4}$$

Similarly the transmittance at the interface for each polarization (T_{TE} , T_{TM}) and the average value for T can be calculated using the corresponding reflectance values.

$$\mathbf{T}_{TE} = \mathbf{1} - \mathbf{R}_{TE} \tag{7.5}$$

$$\mathbf{T}_{TM} = \mathbf{1} - \mathbf{R}_{TM} \tag{7.6}$$

$$T = 1 - R = \left[\mathbf{R}_{TE} + \mathbf{R}_{TM} \right] / 2 \tag{7.7}$$

Total internal reflection (TIR) occurs when incident light from a first medium (n_1) is at an angle greater than the critical angle θ_c for transmission into a second medium (n_2) where

$$\theta_{\rm c} = \sin^{-1} \left(\frac{\mathbf{n}_2}{\mathbf{n}_1} \right) \forall \ \mathbf{n}_1 > \mathbf{n}_2 \tag{7.8}$$

Evanescent waves generated by TIR, under normal conditions are propagated parallel to the interface of the bounding media carrying zero net energy across the second medium. A special case of TIR arises when a third medium (n_3) is in close proximity to the first medium, where the thickness of the second medium is considerably less than the wavelength of the incident light. For $\sin^{-1}(n_2/n_1) < \theta_1 < \sin^{-1}(n_3/n_1)$ an evanescent wave is generated described by TIR in the second medium, it is then converted to a propagating wave in the third medium at the interface between the second and third medium. This special optical phenomenon is called frustrated TIR and has recently become more synonymous with the mechanism enabling multi-touch display technologies [12].

Figure 7.16 Ray diagram illustrating frustrated TIR within the stack OPV.

The PEDOT:PSS layer is of particular interest because it has a refractive index of 1.42 and is sandwiched between two media (ITO and P3HT: PCBM) with higher almost identical refractive indices at 500nm. Thus evanescent wave coupling associated with frustrated TIR illustrated in Figure 7.16 allows the transmission of energy from the ITO layer across PEDOT:PSS into the active layer because the thickness of the PEDOT:PSS (40nm) is far less than the wavelength of the incident light. The derivation of equations describing the mechanisms behind evanescent wave coupling in frustrated TIR are detailed by S. Zhu *et al.* [13]. We also use a common refractive index for ITO and P3HT:PCBM (1.86). The transmittance of light from ITO for incident angles greater than the critical angle at the ITO-PEDOT:PSS interface into the active layer due to frustrated TIR is approximated by

$$T = \left(\alpha \sinh^2 y + \beta\right)^{-1} \tag{7.9}$$

where $y = \frac{2\pi t}{\lambda} (n_1^2 \sin \theta_i - n_2^2)^{1/2}$ and t is the thickness of the PEDOT:PSS layer. α and β are dependent on the polarization of the light source such that
$$\alpha_{TM} = \left[\frac{\left(N^2 - 1\right)\left(n^2 N^2 - 1\right)}{4N^2 \cos \theta_i \left(N^2 \sin^2 \theta_i - 1\right)\left(n^2 - \sin^2 \theta_i\right)^{1/2}}\right]$$
(7.10)

$$\alpha_{TE} = \frac{\alpha_{TM}}{n^2} \Big[\left(N^2 + 1 \right) \sin^2 \theta_i - 1 \Big] \Big[\left(n^2 N^2 + 1 \right) \sin^2 \theta_i - n^2 \Big]$$
(7.11)

where $n = n_3/n_1$ and $N=n_1/n_2$. For the special case that $n_3 = n_1$ then n = 1 and equations (7.10) and (7.11) simplify to:

$$\alpha_{TM} = \left[\frac{N^2 - 1}{2N}\right]^2 \left[\frac{1}{\cos^2 \theta_i \left(N^2 \sin^2 \theta_i - 1\right)}\right]$$
(7.12)

$$\alpha_{TE} = \alpha_{TM} \left[\left(N^2 + 1 \right) \sin \theta_i - 1 \right]^2 \tag{7.13}$$

The β terms can be expressed as

$$\beta_{TM} = \beta_{TE} = 1 \tag{7.14}$$

where the simplification of the expressions for β are the same as in reference [13] and are omitted for brevity.

The optimum angle for incident light entering the stack is calculated based on the amount of light transmitted into the active layer ($T_{air-P3HT:PCBM}$) and the degree of absorption (A _{P3HT:PCBM}) due to the increased pathlength as a result of changing θ_i . A _{P3HT:PCBM} can be evaluated using a variant of the Beer Lambert law for absorption:

$$A_{P3HT:PCBM} \propto e^{-4\pi k l/\lambda}$$
 (7.15)

where k is the extinction coefficient for P3HT:PCBM (0.33) [8], 1 is the optical pathlength and λ is the wavelength of the incident light (500 nm).

7.5 Characterization of the single layer PET stack OPV device



7.5.1 Electrical characterization

Figure 7.17 J-V characteristics of the flat device used to fabricate the stack OPV device (o). The stack OPV device is orientated so that $\theta_i = 40^\circ$.

The J-V characteristic curves of the flat device before it was used to fabricate the PET stack OPV are shown in Figure 7.17. There is an increase in the fill factor from 35% to 44%; the J_{sc} from 3.95 mA/cm² to 4.79 mA/cm²; and the power conversion efficiency (PCE) from 0.73% to 0.93%. The lower V_{oc} from flat to stack (0.52V to 0.44V) is due to degradation of the OPV and excess handling to fabricate the PET stack OPV device. The increased fill factor and J_{sc} indicate that the OPV stack device architecture is acting as an optical cavity, trapping the incident light until it can be absorbed in the active layer.

	I _{sc}	J _{sc}	V _{oc}	η	FF
PET Stack Data	(<i>mA</i>)	(mA/cm^2)	(V)	(%)	
Flat Device	2.18	3.95	0.44	0.73	0.35
PET Stack					
0°	0.062	2.28	0.44	0.47	0.48
5°	0.062	2.31	0.43	0.46	0.46
10°	0.079	2.95	0.44	0.59	0.45
15°	0.097	3.72	0.45	0.79	0.47
20°	0.104	4.09	0.45	0.86	0.47
25°	0.107	4.37	0.45	0.90	0.46
30°	0.108	4.61	0.45	0.91	0.44
35°	0.106	4.79	0.45	0.92	0.43
40°	0.099	4.79	0.44	0.93	0.44
45°	0.089	4.67	0.44	0.89	0.43
50°	0.081	4.67	0.44	0.89	0.44
55°	0.069	4.46	0.43	0.78	0.40
60°	0.060	4.41	0.42	0.81	0.43

Table 7.4: Characteristics of the PET stack OPV and the individual device used in its fabrication.



Figure 7.18 Angular dependence of the OPV stack device short circuit current density as a function of the initial angle of incidence θ_i .

The angular dependency study of the stack device shows that the optimum angle for light entry is approximately 40° shown in Figure 7.18. The highest J_{sc} is measured at

this angle and this indicates that the evanescent wave coupling responsible for the transmission of light from ITO across PEDOT:PSS to the active layer is maximized.



Figure 7.19 The dependence of the angles of incidence at each layer boundary is a function of the θ_i . The plots denoted as θ_1 , θ_2 , and θ_3 correspond to the refracted angles that light travels within for the PET, ITO, and PEDOT:PSS layers, respectively. θ_4 is the refracted angle range within P3HT:PCBM. The broken line for θ_4 indicates the range of incident angles for which evanescent wave coupling is the dominant mechanism for light transmittance into the active layer.

After applying Snell's law over the complete possible angular range for incident light (0°-90°), the optical model of the stack OPV device predicts that TIR will occur at the ITO-PEDOT:PSS interface for the majority of incident angles ($\theta_i = 0^\circ-58^\circ$) as seen in Figure 7.19. θ_1 , θ_2 , θ_3 , and θ_4 correspond to the refracted angles for light traveling within the PET, ITO, PEDOT:PSS, and P3HT:PCBM layers respectively as a function of θ_i . Ordinarily the occurrence of TIR at the ITO:PEDOT:PSS interface would be a serious issue that almost completely diminishes the OPV device performance over this angular range. However, as discussed previously in the optical model, the specific layer structure in this system allows for the special case of frustrated TIR to occur. This results in very different optical behavior within the device as opposed to standard optical transmission.



Figure 7.20 The angular dependence of the light transmission from air to P3HT: PCBM by frustrated TIR and standard optical transmission is plotted as a function of the initial angle of incidence (θ_i).

Figure 7.20 illustrates the result of combining the transmission coefficients for all the interfaces as a function of θ_i , this yields an angular profile for light transmitted into the active layer from air. It shows that light transmitted into the active layer of the stack device is by evanescent wave coupling for $\theta_i < 58^\circ$ due to the respective refractive indices of the constituent layers. For larger angles the incident light enters the active layer through normal transmission allowed by standard geometrical optics.



Figure 7.21 The angular dependence of reflection at the air-PET interface is plotted as a function of θ_i .

It is clear that reflection at the air-PET interface is important as it determines the amount of the incident light that may enter the stack OPV device. Figure 7.21 shows that the amount of reflection is low for angles of incidence ranging from 0° to 60°, this may also be observed in the angular profile shown in Figure 7.20. Above this range, the degree of reflection increases substantially and thus further reduces the likelihood that standard transmission occurring for $\theta_i > 58^\circ$ is the optimum mechanism for efficient light harvesting.



Figure 7.22 The angular dependence of the light transmission from air to P3HT: PCBM is combined with the absorption within the active layer and plotted as a function of θ_i . This angular profile shows the optimum angle for θ_i in order to maximize light harvesting within the OPV stack device.

When we consider the contribution of evanescent wave coupling and standard optical transmission which are dependent on θ_i , we must also take into account the angularly dependent pathlength of light travelling within the active layer in order to ascertain the optimum angle for light harvesting. The product of the transmission of incident light into the P3HT:PCBM layer from air and the absorption within the layer as a function of θ_i is shown in Figure 7.22. The maximum of this profile denotes the optimum angle for θ_i (~ 42°) where light harvesting is maximized within the OPV stack device.



Figure 7.23 The measured short circuit current density and the calculated profile for light harvesting from the optical model are normalized and plotted as a function of θ_i .

The optical model is a good predictor for the optimum value of θ_i to ensure that the maximum amount of incident light is harvested and converted to electricity. Figure 7.23 shows that the experimentally measured angular profile for the J_{sc} of the OPV stack device is in very close agreement with the optical model confirming that evanescent wave coupling can be used to describe the behavior observed.

7.6 Conclusion

In this chapter, the fabrication, electrical and optical characterization, and comparison of the OPV stack architecture to conventional flat-panel devices is discussed. By using a vertical geometry as opposed to that of a planar one, an increase in the current output is observed simply by changing the cell orientation to allow for greater absorption of incident light. The behavior of light inside the single-layer PET OPV stack device was modeled for incident monochromatic light at 500nm. The light propagation into the active layer followed two different mechanisms depending on θ_i at the air-PET interface. Light propagates into the active layer by evanescent wave coupling for angles ($0^{\circ} < \theta_i < 58^{\circ}$) and by transmittance for larger angles. Experimentally the optimum angle for light entry into the stack device was found to be 40° which is in very close agreement with the optical model that predicts the maximum for light harvesting to be 42°. The OPV stack architecture collects and converts incident light more efficiently resulting in improved fill factor and short-circuit current density. The results pertaining to the single layer stack OPV device from this chapter have been published in the Journal of Applied Physics [14].

7.7 References

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CHAPTER 8. Conclusions and further work

This thesis aimed to investigate alterations to the standard P3HT:PCBM based flatpanel architecture OPVs. This was achieved in a number of ways: investigating the use of novel fullerene based additives to the active layer, replacing the various interlayers with alternatives possessing improved properties and finally the introduction of a new architecture for OPVs.

8.1 SWNT(B)-C₆₀ additives

The effects of incorporating carbon nanotubes (CNTs) in a polymer-fullerene blend host were investigated. Single walled carbon nanotube (SWNT)- C_{60} hybrids were studied by UV-vis and RAMAN spectroscopy in order to investigate how functionalized and shortened SWNT barrels linked with C_{60} , SWNT(B)- C_{60} , may be used as an additive to P3HT:PCBM. The purpose of this system was to use CNTs as a carrier host for the fullerenes and to attempt to ameliorate the charge transfer processes possibly enhancing OPV device performance. It became clear that the incorporation of CNT materials into OPVs is for the most part detrimental to overall device performance. Only semiconducting CNTs should be incorporated into OPV active layers to avoid electrical shorting by metallic or pseudo-metallic CNTs. Until CNTs can be sorted in large quantities based on their conductivity it is not practical to use them in OPVs, whether as some functionalized active layer or even as electrodes. Thus, until a large-scale source for pure semiconducting CNTs is available at a reasonable price, CNTs are still not feasible for incorporation in OPVs.

8.2 Replacement and modification of the anode, hole transport and acceptor materials

The development and alteration of the standard ITO/PEDOT:PSS/P3HT:PCBM/Al OPV device was carried out to address the issues which are detrimental to device

stability, reproducibility and efficiency. The drawbacks of using ITO were presented and it was demonstrated that ITO can be replaced by thin thermally evaporated Ag or Au films. The issue of attaining a thin film that is as conductive as ITO while allowing light to enter the active layer was resolved resulting in the characterization of Ag and Au substituted anodes.

The hole transport layer, PEDOT:PSS was studied in terms of novel deposition technique, spin-assisted layer-by-layer deposition, however the insulating nature of PDDA was detrimental to device performance with an increasing number of layers. PEDOT:PSS was shown to be a major contributor to device degradation due to the etching of ITO caused by the acidic species in PSS. As a result, two new hole transport layers, namely PVK and PPy-PSS were demonstrated as effective new hole transport layers yielding comparable results to devices made with PEDOT:PSS.

Initial studies on the development of acceptor materials in the BHJ blend resulted in the use of ICMA and ICBA. Unfortunately it was difficult to attain highly pure samples of these materials in order to rival the low impurities observed in the commercially available PCBM. Although it was not possible to improve upon PCBM under the laboratory conditions available, OPV devices were fabricate using these new acceptors without the use of LiF or Ca as inter- layers.

8.3 The fabrication, characterization and modeling of the Stack OPV device

The stack OPV device architecture is introduced with an introduction to its early development. A flat panel OPV device on a PET substrate was presented and used to fabricate a stack OPV device. The experimental data from this device demonstrated that this new architecture has great potential in terms of increasing the efficacy of harvesting photons. The device data was compared to an optical model for incident monochromatic light at 500 nm calculated using the Fresnel equations and the laws of refraction.

The use of vertical geometry as opposed to that of a planar one, yielded an increase in the current output modeled. The light propagation into the active layer was found to follow two different mechanisms depending on the initial angle of incidence at the airPET interface. Evanescent wave coupling due to frustrated total internal reflection was the dominant mechanism whilst transmittance only occurred for larger angles of incidence. The optimum angle for light entry into the stack device was found to be 40° that was in very close agreement with the optical model predicting 42°. The OPV stack architecture was also observed to collect and convert incident light more efficiently resulting in improved fill factor and short-circuit current density.

8.4 Further work and future directions

There is scope for many different projects arising from the work of this thesis and that of others often referred to in the previous chapters. The processing of nano-materials such as carbon nanotubes into more pure forms that are grouped by their electronic properties is currently underway. It is now possible to separate carbon nanotubes by their chirality, however until recently the yield of this processing was of the order of 1 x 10^{-9} grams by ultra-centrifugation [1]. It is hoped that soon larger scale samples will be available and according to the work carried out by Liu *et al.* their contribution may accelerate the use of single-walled carbon-nanotubes in practical applications [2].

The fabrication of hole transport layers by electrochemical deposition is a welcome step forward in the never-ending search for new materials that allow for more flexibility in the design of novel OPV architectures. The realization of crosslinked polymer brushes illustrated by the effectiveness of PVK may also be an inspiration. OPV device active layers may be completely fabricated using polymer brushes where the electrochemical growth of the active layer could contain a network of n-type and p-type materials. This may yield an active layer thickness and morphology that is more precisely controlled compared to the highly disordered films resulting from spin-coating processes encompassing thermal and solvent annealing steps. Preliminary studies are underway using co-deposition of organic layers to form OPV devices [3], although the efficiency is limited this new fabrication route has promise and is the beginning of a productive and vibrant direction for OPV research.

The further development of the stack OPV architecture is ideally suited to the use of additional active layer material combinations to allow for a greater spectral overlap of absorption with the solar spectrum. The advantage of this type of tandem OPV device is that there are almost no limitations on the materials that can be used provided they work

as OPVs. The issues of solvent compatibility when forming the standard spin-coated, tandem architecture OPV devices fabricated in a multilayer structure is very limiting due to the nature of typical organic materials being soluble in a range of common solvents such as chlorobenzene.

The use of polymer printing currently under investigation at the Institute for NanoEnergy led by Ms. Amrita Haldar [4], is another deposition method that may be explored in more detail allowing for more facile integration of serially connected devices utilizing different active layer materials. This subject is discussed in detail in her doctoral thesis work carried out at the University of Houston, which is expected to be concluded by mid-2012.

The combination of polymer batteries [5] into the stacked OPV architecture is currently being developed at the Institute for NanoEnergy in collaboration with Dr. Thomas Sutto at the Naval Research Laboratories may yield interesting compact hybridized electricity generation and storage devices.

8.5 References

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