

Recombination dynamics in polythiophene:fullerene solar cells

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Abstract of Thesis

Organic devices based on polymer:fullerene blend films are attracting extensive interest as low cost solar cells, with power conversion efficiencies over 5%. Improvements in performance are dependent on developing a better understanding of the pertinent loss processes. This in turn requires the ability to reliably determine charge densities (n) and carrier lifetimes (τ_n) in real devices under standard operating conditions. In this thesis, we address the recombination dynamics in organic solar cells based on blends of poly(3-hexylthiophene) (P3HT) and methanofullerene [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM), P3HT:PCBM devices, one of the best devices to date, using both experimental and modelling studies.

Initially, a drift-diffusion model was used to study the basic principles of solar cell operation, with particular focus on investigating the ‘corrected photocurrent’, where the effects of dark injection are removed. We then have employed a series of experimental techniques – including transient photovoltage and photocurrent, transient absorption spectroscopy and charge extraction – to determine the carrier lifetimes and charge densities in standard annealed P3HT:PCBM devices under operation. The results of our studies for a device under open-circuit conditions show that the open-circuit voltage (V_{oc}) is primarily governed by a trap dependent bimolecular recombination process. By applying charge extraction studies on devices under forward bias in the dark, we show that the dark current is also governed by the same trap dependent bimolecular recombination mechanism which determines V_{oc} .

Based on the understanding of charge carrier dynamics at V_{oc} and the forward bias dark current, a simple model has been developed to simulate ‘light’ current-voltage (J - V) curves. Despite the simplicity of this model, remarkably good agreement was observed with experimental J - V data.

Table of contents

Abstract of Thesis	3
Table of contents	4
Table of Figures	8
List of Publications	14
List of Abbreviations and Constants	15
Chapter 1 Introduction	17
1.1 Background & Development of Solar Cells	19
1.1.1 Inorganic solar cells	19
1.1.2 Dye sensitized solar cells	19
1.1.3 Organic solar cells	20
1.1.3.1 Small molecule OPV bi-layer devices	21
1.1.3.2 Polymer based donor: acceptor bulk heterojunction devices	22
1.2 Photogeneration	23
1.3 Device structure	26
1.4 Band Diagrams	26
1.5 Charge transport, charge collection at the wrong electrodes and bimolecular recombination	27
1.6 Capacitance and charge storage	29
1.7 Device operation	30
1.7.1 Device characterisation	30
1.7.1.1 Short-circuit	31
1.7.1.2 Open-circuit	32
1.7.2 Efficiency	33
1.8 Design rules for efficient solar cells	34
1.9 The equivalent circuit of a solar cell	36
1.9.1 Shockley diode equation	38
1.10 P3HT:PCBM BHJ devices	40
1.11 Project objectives	43
1.11.1 Numerical modelling	43
1.11.2 Experimental studies	44

Chapter 2 Modelling bulk heterojunction solar cells using a drift-diffusion model

	45
2.1 Background	47
2.2 Model	48
2.2.1 Generation	50
2.2.2 Recombination	51
2.2.3 Solving the equations	52
2.2.4 Boundary conditions	53
2.2.5 Simulation details	54
2.2.6 Description of parameters used	55
2.3 Results	56
2.3.1 Solar cell properties in the dark with no recombination	57
2.3.1.1 Testing the model	57
2.3.1.2 Discussion of distributions	58
2.3.2 Study into the effects of incident light on the solar cell while recombination is absent	60
2.3.2.1 ‘Corrected Photocurrent’	64
2.3.2.2 Light intensity dependence of V_{oc}	66
2.3.2.3 Origin for $QE_{sc} < 100\%$	66
2.3.2.4 Light intensity dependence of fill factor	67
2.3.3 Solar cell studies under dark conditions with recombination	68
2.3.4 Effects of recombination on the solar cells in the light	70
2.3.5 Studying the effects of carrier mobility on the properties of a solar cell	74
2.3.6 Comparison of numerical and with experimental studies of the ‘Corrected Photocurrent’	75
2.3.7 Future work	79
Chapter 3 Experimental Methods	81
3.1 Device details	81
3.2 Transient photovoltage (TPV)	85
3.2.1 Experimental requirements: Ensuring open-circuit conditions	86
3.2.2 Temperature effects on measurements	90
3.3 Transient photocurrent (TPC)	90
3.4 Transient absorption spectroscopy (TAS)	92
3.5 Charge extraction (CE)	94
Chapter 4 Experimental determination of the rate law for charge carrier decay in a polythiophene : Fullerene solar cell	98
4.1 Introduction	99

4.2 Determining whether transient photovoltage can be used as a direct measure of carrier lifetime	100
4.3 Verifying that by employing a small perturbation regime the transient photovoltage decays should take the form of single exponentials	101
4.4 TPV studies as a function of light bias	103
4.5 Differential Charging	106
4.5.1 Obtaining an estimate for ΔQ	106
4.5.2 Determining the appropriate value for ΔV_0 to use	107
4.5.3 Determining the charge density present in the photoactive layer of the device	108
4.6 Derivation of the rate law for carrier decay dynamics at the open-circuit voltage	111
4.7 Conclusion	115
Chapter 5 Bimolecular recombination losses in polythiophene: fullerene solar cells	116
5.1 Introduction	117
5.2 Comparison of thin film and device TAS data	119
5.3 Applied electrical bias TAS studies of electric field assisted charge generation	120
5.4 Converting the TAS $\Delta OD(t)$ data into charge carrier density	122
5.4.1 Determination of the effective P3HT ⁺ polaron molar extinction coefficient	122
5.5 Relating large perturbation TAS data with small perturbation TPV data	124
5.6 Bimolecular recombination coefficient k	126
5.6.1 Calculating k using TAS and TPV data	126
5.6.2 Discussion concerning this carrier dependent bimolecular rate constant	128
5.7 Calculating the loss in photocurrent at open-circuit due to bimolecular recombination	130
5.8 Future Work: Alternative explanation for the origin for the third order charge carrier decay dynamics	132
Chapter 6 Charge extraction studies of charge density	136
6.1 Introduction	137
6.1.1 Diagnostic test for the charge extraction technique	140
6.2 Charge extraction measure of the charge density stored in the device at V_{oc}	140
6.2.1 Evaluation of the incurred charge losses	141

6.2.2 Correction of electrodes	145
6.2.3 Comparison of differential charging and charge extraction to measure the charge densities in the device at V_{oc}	146
6.3 Self-consistency test to check the validity of the analysis	148
6.3.1 Determination of the small perturbation factor δ	150
6.3.2 Comparison of $J_{losses}(V_{oc})$ with $J_{GEN}(V_{oc})$	152
6.3.3 Potential limitations to our empirical results	154
6.3.4 General conclusions for $J_{losses}(V_{oc})$	155
6.4 Mapping the J-V curve for a device in the dark in terms of charge density, measured using charge extraction	156
6.4.1 Introduction	156
6.4.2 Charge extraction study of the forward bias current in the dark	157
6.4.3 Further Analysis:	163
6.5 General applicability of CE study to different organic solar cells systems	167
6.6 Summary	168
Chapter 7 Future Studies: Recreating the J-V curve for a device under illumination using charge extraction studies	169
7.1 Introduction	170
7.2 Mapping the J - V curve for a device under illumination in terms of charge density using charge extraction	172
7.3 Simulating the device ‘light’ J - V curve under 1 sun incident light conditions	174
7.4 Modifying the Shockley diode equation for the simulation of ‘light’ J - V curve data	175
7.5 Future charge extraction studies	179
Chapter 8 Final conclusions	181
References	184

Table of Figures

Fig. 1.1. Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell.¹⁴ Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of an oxide semiconductor film. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter-electrode by electrons passed through the load. Potentials are referred to the normal hydrogen electrode (NHE). The open circuit voltage of the solar cell corresponds to the difference between the redox potential of the mediator and the Fermi level of the nanocrystalline film indicated with a dashed line. The energy levels drawn for the sensitizer and the redox mediator match the redox potentials of the doubly deprotonated N_3 sensitizer ground state and the iodide/tri-iodide couple. _____ 20

Fig. 1.2. Polymeric solar cell heterojunctions.¹⁰ (a) Energy diagram of a heterojunction with an exciton in the polymer phase. The first heterojunction was a bi-layer (b), but this architecture is limited as the active layer must be thin in order to utilize all excitons. In order to have every exciton separated, a heterojunction must exist within an exciton diffusion length. This can be achieved in a bulk heterojunction (c) or in an ordered heterojunction (d). _____ 21

Fig. 1.3. Reported efficiencies of various polymer based BHJ technologies over recent years and the respective institutes from which they were reported.¹⁰ The abbreviations are: University of California, Santa Barbara (UCSB); University of California, Santa Cruz (UCSC); University of California, Berkeley (UC Berkeley); University of California, Los Angeles (UCLA); Technische Universiteit Eindhoven (TU/e). _____ 23

Fig. 1.4. Energy levels in an organic semiconductor and photoabsorption. The energy levels of the HOMO and LUMO in an organic semiconductor are given by the electron affinity (χ) and the ionisation potential (IP) respectively. Photon's absorbed from light with energy exceeding the optical bandgap, E_g , given by the difference between the IP and χ , causes an e^- to be promoted to the LUMO from the HOMO, leaving a h^+ in the HOMO. Due to strong coulombic binding energies, this ($e^- - h^+$) exists as neutrally bound exciton. _____ 24

Fig. 1.5. Formation of free charge carriers in a BHJ. The difference in LUMO levels between the donor and acceptor provides a driving force for charge dissociation to occur. The e^- passes from the donor to the acceptor (b). However, due to strong coulombic binding energies, it is possible that rather than directly form free charge carriers, an intermittent geminate bound electron hole pair is formed. c) These geminate pairs will either recombine or form charge carriers. d) A common approach in considering the behaviour of a BHJ, is to consider the blend in terms of a virtual semiconductor, which is given by the HOMO level of the donor and the LUMO level of the acceptor. _____ 25

Fig. 1.6. Schematics of the a) basic design of an organic solar cell and b) energy levels. a) A BHJ solar cell consists of an organic semi-conducting blend layer, typically 100nm thick, sandwiched between a transparent anode and a metallic cathode. b) The anode and cathode are chosen so there work functions approximately match the LUMO and HOMO of the active layer to ensure ohmic contacts. _____ 26

Fig. 1.7. Energy schematic of the solar cell when the fermi levels have equilibrated. When electrodes are connected to the active layer, electrons flow from the cathode to the anode to reduce their energy. Equilibrium is reached when the fermi levels of the two electrodes align. This leads to the presence of an internal electric field within the device. _____ 27

Fig. 1.8. Schematic of a BHJ solar cell, demonstrating the different possible current mechanisms. (A) In a solar cell electrons and hole charge carrier must travel to the cathode and anode respectively where they are extracted into the external circuit. However, if charge carriers reach the wrong collecting electrodes (B), i.e. electron charge carriers reach the anode and hole charge carrier reach the cathode, then they are also extracted resulting in a photocurrent which flows in the opposite direction to the net photocurrent, and hence, leads to a reduction in photocurrent output. An additional loss in current can result from the bimolecular recombination flux, which is generated when opposing charge carrier meet and recombine (C), which should predominantly occur at donor-acceptor interfaces. _____ 29

Fig. 1.9. Circuit diagram for the operation of a solar cell. A load resistance, R_L , is connected to the device which results in the production of power given by JV .	30
Fig. 1.10. J - V curves for a) a solar cell in the dark and b) under one sun illumination conditions.	31
Fig. 1.11. Band diagram for a device under illumination under short-circuit conditions.	31
Fig. 1.12. Band diagram for a device under illumination under open-circuit conditions.	32
Fig. 1.13. Band diagram depicting the energy levels for a BHJ device.	35
Fig. 1.14. Contour plot by Scharber <i>et al.</i> ³² showing the calculated energy-conversion efficiency (contour lines) versus the bandgap and the LUMO level of the donor polymer. If it was possible to make a BHJ device with a donor with optical bandgap of 1.5eV, it may be possible to reach efficiencies as high as 10% based on this simple form of analysis.	36
Fig. 1.15. Equivalent circuit for a solar cell. ³⁵ This replacement circuit consists of a current generator, which provides J_{GEN} , a diode and both parasitic shunt and series resistances.	37
Fig. 1.16. a) Chemical structure of P3HT and PCBM and b) the basic design of a P3HT:PCBM device. ² In a) light is absorbed by P3HT, which results in the formation of excitons. Due to the difference between the electron affinities between P3HT and PCBM, this results in the dissociation of excitons which diffuse to a P3HT:PCBM interface, where an electron transfers from the P3HT LUMO to the PCBM LUMO leaving a hole in the P3HT HOMO. When the P3HT:PCBM BHJ is sandwiched between two electrode, b) electron charge carriers travel to the cathode, whereas, hole charge carriers travel to the anode, through the interpenetrating networks of PCBM and P3HT respectively.	40
Fig. 1.17. Absorption spectrum for pristine P3HT, and for a 1:1 annealed (140°C, 20 min) P3HT:PCBM blend. P3HT has good absorption over the wavelength range 450 – 650 nm. However, its absorption is clearly limited into the red – infra-red range of the solar spectrum, which limits the current densities which are possible.	41
Fig. 1.18. J - V characteristics for an unannealed and an annealed (140°C for one hour) 1401:1 P3HT:PCBM BHJ device while under 50 mWcm ⁻² AM1.5 simulated light (bold) and in the dark (dashed). For the un-annealed device, $V_{oc} = 0.54V$, $J_{sc} = 3.9 \text{ mAcm}^{-2}$, $FF = 51\%$ and $PCE = 0.53\%$, whereas, for the annealed device, $V_{oc} = 0.5V$, $J_{sc} = 1.35 \text{ mAcm}^{-2}$, $FF = 39\%$ and $PCE = 2.13\%$.	42
Fig. 1.19. (a) Schematic of the design of the P3HT:PCBM device studied herein and (b) an energy level diagram detailing the relevant energy levels.	43
Fig. 2.1. The absorption profile of an incident light on a semiconductor.	50
Fig. 2.2. A plot showing the contributions to charge generation from both the transmitted light and the diffuse reflection at the opaque cathode.	51
Fig. 2.3. Comparison of the analytical (markers) and numerical (solid lines) solutions for the steady state carrier distributions and current densities for a device in the dark, for low injection and no recombination. a) The electric potential profiles, b) hole and c) electron distributions, and d) current densities are all shown for different applied biases.	57
Fig. 2.4. Steady state solutions for the carrier distributions and electric profiles in a device while under light with no recombination. The electric potential profiles are shown a) at a variety of (high) illumination levels (with an inset displaying the generation profile employed) and b) for a 1 sun light at different applied biases. c) Short-circuit hole and d) electron distributions evolving from dark to 1 sun incident light conditions, and e) hole and f) electron distributions for applied biases in the range 0 - 1.6V under 1 sun light level are also shown.	60
Fig. 2.5. J - V characteristics for a solar cell under illumination with no recombination for light intensities in the range 0.001 – 10 Suns. a) J - V curves b) FF , QE_{sc} , V_{oc} and leakage losses as a function	

of light intensity, plots of c) power (JV) d) QE_{ph} as a function of applied bias, e) hole and electron current densities and f) their corresponding drift and diffusion components are all shown. 63

Fig. 2.6. Device properties in the dark showing the a) electric potential profiles, b) hole and c) electron distributions, d) recombination densities with (lines) and without (dashed or markers) recombination for various applied biases, and e) a comparison between $J-V$ curves with and without recombination. 68

Fig. 2.7. Steady state distributions for a device in the light with recombination, showing a) the electric potential profile under high light intensities, b) short-circuit hole and electron distributions when $k_{pn}=0$, k_L and $10k_L$, and c) hole, d) electron and e) recombination distributions under various applied biases. 70

Fig. 2.8. $J-V$ characteristics for a solar cell under illumination in the presence of recombination ranging from dark to 1000 suns. a) $J-V$ curves b) FF , QE_{sc} , V_{oc} , diffusion losses and recombination losses for as a function of light intensity, c) a plot of $PP/V_{Bk}J_{max}$ against applied bias, d) QE_{ph} against applied bias and e) recombination rates at short-circuit conditions. 72

Fig. 2.9. Studying device behaviour for different matched charge carrier mobilities ranging from 10^{-6} - $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, when bimolecular recombination effects are included. In a) and b) the hole and electron carrier distributions are shown for different carrier mobilities (matched) respectively. c) and d) show the $J-V$ curves and the key features thereof respectively. In e) and f) plots of the power against applied bias and the $J_{ph}-V$ curves are shown for different carrier mobilities. 74

Fig. 2.10. Comparison of our numerical simulated $J_{ph}-V$ curves with experimental studies performed by Ooi on MDMO:PPV/PCBM and P3HT:PCBM blend devices. In a) and b) the numerically modelled corrected photocurrent are given for the single layer system modelled without and with the presence of bimolecular recombination effects respectively. c) and d) show the unnormalised and normalised (with light intensity) $J_{ph}-V$ curves as a function of light intensity for MDMO:PPV/PCBM devices. And e) and f) show the unnormalised and normalised $J_{ph}-V$ curves as a function of light intensity for P3HT:PCBM devices. 77

Fig. 3.1. $J-V$ characteristics for ‘standard’ annealed devices while under 100mWcm^{-2} AM1.5 simulated irradiation. For the $J-V$ curves shown, the values of importance were: d1: $J_{sc} = 6.2 \text{ mAcm}^{-2}$, $V_{oc} = 0.60\text{V}$, $FF = 51\%$ and $PCE = 1.9\%$. d2: $J_{sc} = 5.3 \text{ mAcm}^{-2}$, $V_{oc} = 0.60\text{V}$, $FF = 56\%$ and $PCE = 1.8\%$. d3: $J_{sc} = 7.0 \text{ mAcm}^{-2}$, $V_{oc} = 0.61\text{V}$, $FF = 47\%$ and $PCE = 2.0\%$. d4: $J_{sc} = 5.0 \text{ mAcm}^{-2}$, $V_{oc} = 0.61\text{V}$, $FF = 49\%$ and $PCE = 1.5\%$. 84

Fig. 3.2. (a) A basic schematic of the experimental setup used to measure transient photovoltage with (b) a typical TPV transient with a voltage amplitude ΔV and a baseline V_{oc} . The red line represents a single exponential fit of the TPV decay showing that in this small perturbation approach, the form of the TPV transient is well-describe by a single exponential, greatly simplifying data analysis. 85

Fig. 3.3. Comparison of the light intensity dependence of V_{oc} measured using an oscilloscope ($R_{osc} = 1 \text{ M}\Omega$) and a digital voltmeter ($R_{DVM} = 10 \text{ M}\Omega$). At relatively low light intensities, as the light intensity is reduced further, the voltage measured by the oscilloscope and the DVM deviates. This indicates in this regime, that the resistance of the oscilloscope is insufficient to provide open-circuit conditions in the device. 87

Fig. 3.4. (a) Light intensity dependence of the open-circuit voltage for a device with a relatively low shunt resistance $R_{SH} \sim 0.1 \text{ M}\Omega$. It is found to take the form of a biphasic curve is found with an observed transition occurring for a light intensity $\sim 2.5\%$ suns. (b) The corresponding $J-V$ curves are displayed for relatively low light intensities $\leq 5\%$ suns. It is apparent that for light intensities $< 2\%$ suns the $J-V$ curves are linear, which would be consistent with the effects of an electrical shunt limited dark current over the voltage range these low light intensity $J-V$ curves cover. 89

Fig. 3.5. a) Basic schematic of the transient photocurrent experimental setup. b) Transient photocurrent measured under at low light intensity (~ 0.01 suns) at approximately short-circuit conditions (50Ω) using the same intensity laser pulse as Fig. 3.2. (a). c) Time-integrated data ($Q_{sc}(t)$) derived from Fig. 3.5 (b) confirmed as a measure of charge through comparison with TAS performed under identical conditions. 92

Fig. 3.6. Schematic of the experimental TAS setup in reflective mode. _____ 94

Fig. 3.7 Typical charge extraction transients displaying the measured current transient for a device under approximately 1 sun (a) open-circuit and short-circuit conditions, and the time integrated form, which depicts plots of the corresponding (b) charge extraction ‘charge’ transients. _____ 95

Fig. 3.8 Basic experimental schematics are given for charge extraction studies at V_{oc} (a-b), and mapping of the J - V curves for a device whilst under illumination (c-d) and for dark conditions (e-f). (a) Initially the device is held at open-circuit conditions through the transistors internal resistance, under constant light bias conditions in the form of white LED’s. (b) Simultaneously these LED’s are switched off, whilst the device is shorted, which allows the charge density in the device to be collected by the device electrodes, and a voltage transient is measured by an oscilloscope. This voltage transient represents a current transient $I = V/R_L$. In the case of mapping the J - V curves in terms of charge density, (c) a variable resistor or (d) a voltage source is used to control the initial device voltage conditions. _____ 97

Fig. 4.1. The transient photovoltage (left, black) and transient absorption signals (right, grey) obtained in the small perturbation regime. Measurements were made under 1 sun illumination, $V_{oc} = 0.59V$, using a pump of wavelength 620 nm and a probe of 980 nm. _____ 101

Fig. 4.2. a) A plot demonstrating the typical TPV transients measured over a range of light biases. b) Comparison of TPV transients measured over a range of light intensities 0.1 – 1 suns, by plotting them using the same baseline for each. It is found that as the light bias is increased, both the TPV lifetime and the initial signal amplitude decrease. _____ 104

Fig. 4.3. The variation of the carrier lifetime τ_{An} with light intensity (bold, left) in the range 0.01 - 1 sun, which corresponds to an open-circuit voltage range 0.4 – 0.59 V (secondary axis). _____ 105

Fig. 4.4. Plots of carrier lifetime versus open-circuit voltage for several different devices. It is apparent that the results from the TPV studies are similar. _____ 105

Fig. 4.5. Comparison of time-integrated TPC data (Q_{sc}) with TAS performed under identical conditions. It indicates that Q_{sc} provides a direct measure of the loss in charge in the device. _____ 107

Fig. 4.6. Comparison of differential charging data, before and after making a correction for the electrode capacitance to take account of the charge which should be present on the device electrodes. _____ 109

Fig. 4.7. Plots of differential charging (bold, left) and carrier concentration (dashed, right) as a function of V_{oc} for light intensities ranging from 0.01 - 1 sun. Both follow the same exponential dependence with V_{oc} . _____ 110

Fig. 4.8. Several examples of differential charging data as a function of light bias, V_{oc} , for a range of different P3HT:PCBM devices. _____ 111

Fig. 4.9. Small perturbation carrier lifetime as a function of charge density for light intensities from 0.01 - 1 sun. (a) The carrier lifetime is found to follow an inverse square relationship with increasing charge density n . (b) Values for λ are found to typically be in the range 1.15 – 2.9. _____ 112

Fig. 5.1. Comparison of reflection-mode TAS film (left) and device data (right - brown dashes) using a 520nm pump and 980nm probe. In both cases, a power law decay $\Delta OD \propto t^{-\alpha}$ with $\alpha \sim 0.47$ is found at relatively high pump intensities/long timescales. _____ 119

Fig. 5.2. (a) Reflection-mode TAS data for a P3HT:PCBM device under different applied electrical bias. (b) Over the voltage range 0 – 0.6V (~ 1 sun V_{oc}), there is no significant variation in initial (~ 0.5 μ s) signal amplitude, indicating that geminate recombination losses do not strongly increase. _____ 122

Fig. 5.3. a) Plot of μ s-TAS device data at a relatively low pump intensity (6 μ Jcm⁻²) in which the initial signal amplitude is not saturated, and b) the corresponding short-circuit photocurrent (red, left) and total charge Q (blue, right) transients measured under the same excitation conditions. _____ 124

Fig. 5.4. Reflection-mode TAS device $n(t)$ data (left) compared to the simulated TAS data derived from TPV data (right - grey dashes). _____ 125

Fig. 5.5. Plots of bimolecular recombination coefficient, k , as a function of carrier concentration, n , calculated from measurements of TAS (bold) and TPV (dashed). _____ 127

Fig. 5.6. Several examples of plots of the charge density dependence of the bimolecular recombination coefficient in standard annealed P3HT:PCBM devices. _____ 128

Fig. 5.7. Microscopic model of a bimolecular recombination process incorporating an intra-band exponential density of trapped states ρ in P3HT. (a) At low light/excitation intensity, a low number of these trapped states are filled, and thus, this leads to slow de-trapping times, and therefore, the holes spend less time at the mobility edge. As a result, this will lead to slower recombination dynamics and lower charge carrier mobility. (b) At high light/excitation intensity, much more of these trapped states are filled. Therefore, the de-trapping times become much faster, which leads to faster bimolecular recombination dynamics, and a higher charge carrier mobility. _____ 129

Fig. 5.8. Comparison of the calculated bimolecular recombination flux at open-circuit J_{BI} (crosses) with the corresponding short-circuit photocurrent, J_{sc} (open squares). _____ 131

Fig. 6.1. Schematic of the charge extraction measurement. Initially the device is positioned at a fixed point on either the 'light' J - V curve J_{light} , or the dark J - V curve J_{dark} . The device is then shorted whilst being placed under dark conditions, which allows the charge density in the device to be extracted in the form of a current transient. _____ 138

Fig. 6.2. A typical charge extraction current transient for a device under approximately 1 sun open-circuit conditions, with inset displaying the corresponding time integrated form. _____ 140

Fig. 6.3. Initial charge extraction data on a typical P3HT:PCBM solar cell, before making corrections for the incurred carrier losses and for the charge which would be present on the device electrodes. _ 141

Fig. 6.4. The main plots involved in the iterative procedure used to evaluate the incurred carrier losses during the charge extraction transients. (a) A typical initial CE plot is shown for a device under initial 1 sun V_{oc} conditions. Based on the initially measured charge extraction transient, we obtain an initial estimate of the amount of charge present in the device n_{device} as a function of time. (b) TPV determined carrier lifetimes as a function of V_{oc} , $\tau_{\Delta n} = \tau_{\Delta n0} \exp(-\beta V_{oc})$ with $\beta = 14.53$. (c) By using the derived expression for the carrier decay dynamics dn/dt , an initial mapping of the incurred carrier losses n_{losses} was made. The charge extraction transient is then corrected for these losses and the same procedure repeated. In (d), a plot is given which shows that the additional incurred losses $n_{losses}[j] - n_{losses}[j-1]$ between iteration $j-1$ and j converges to zero after several iterations (left axis), and therefore, by summing these losses, the total losses incurred during the charge transient based on the expression of dn/dt converges to a fixed value (right axis). This procedure was repeated for each of the light biases studied, with each of the initial CE determined charge densities then corrected for these incurred carrier losses. The expression dn/dt was then modified to take into account for this correction for the charge density and the same method was then repeated for several iterations. In (e) plots of the determined values for λ and n_0 are shown as function of iteration, showing that after several iterations, these values converge to a fixed value, resulting in a fixed expression for dn/dt . _____ 143

Fig. 6.5. Comparison of the charge densities determined in the device by charge extraction before and after correcting for the evaluated carrier losses, n_{ext} and n_{total} respectively. _____ 145

Fig. 6.6. Comparison of the charge densities n determined by the charge extraction technique in the device as a function of light bias V_{oc} before and after correcting for the charge which will be present on the device electrodes given by n_{device} and n_{active} respectively. _____ 146

Fig. 6.7. Comparison of the charge densities determined in the active layer of the device using charge extraction (red) and differential charging measurements (blue). All data have been corrected for the charge resident on the electrodes. _____ 148

Fig. 6.8. A J - V curve depicting the loss in photocurrent at V_{oc} . In the absence of an electric field assisted charge generation then this loss in photocurrent will equal the photocurrent.	148
Fig. 6.9. A plot of light intensity versus open-circuit voltage. The open-circuit voltage is found to follow an inverse exponential voltage with incident light intensity.	151
Fig. 6.10. Comparison of the photo-generated current (estimated by using the current density in reverse bias at -2V) with the calculated loss in current at open-circuit, over a range of light intensities 0.02 – 2 suns. This comparison is made on both (a) a linear – linear scale and (b) a log – log scale.	153
Fig. 6.11. Comparison of transient photovoltage (left, black) and transient absorption signals (right, red) obtained in the small perturbation regime. Measurements were made for an open-circuit voltage 0.6V (~ 1 sun), using a pump of wavelength 620 nm and a probe of 980 nm.	155
Fig. 6.12. Typical J - V curve for a device in the dark. It consists of a (1) ohmic shunt limited current at low applied voltages, an (2) exponential regime and a ohmic at high applied voltages where the current is limited by the internal serial resistance R_s (this behaviour is amplified in the inset displaying its linear behaviour from which we determine a value for R_s which is required for our studies (below)).	156
Fig. 6.13. Charge extraction determined values for the charge densities in the active layer of the device as a function of the applied voltage and the cell voltage while under dark conditions.	158
Fig. 6.14. Comparison of the charge density present in the device as function of applied electrical and applied light biases. As the applied voltage is reduced, these two curves converge as expected, due to the reduction in light bias indicating that the device is approaching dark conditions.	159
Fig. 6.15. Comparison of the current density as a function of charge density for the forward bias current density in the dark and the loss in current at V_{oc} , given by $J_{GEN}(-2V)$. The vertical axis corresponds to the effective cell voltage for $J_{FW,dark}$.	160
Fig. 6.16. Plot of the forward bias current density in the dark against n_{dark} , for an extended range of charge densities. It is found that at lower charge densities, the exponent for the observed power law relationship relating $J_{FW,dark}$ with n_{dark} increases from 2.64 to 3.47.	162
Fig. 6.17. Modelling the dark current using a Shockley diode equation with $m = 1.6$.	166
Fig. 7.1. Basic description of a ‘light’ J - V curve in terms of a constant photocurrent J_{GEN} and a loss in current J_{losses} .	170
Fig. 7.2. Charge extraction measurements of the charge density present in an annealed P3HT:PCBM device under approximately 1 sun incident light intensity. It shows plots of the CE initial data (red), the charge densities after correcting for the incurred carrier losses and the electrode capacitance (black, open circles), and after correcting these charge densities for the influence of the series resistance on the applied voltage (blue), $V_{int} = V - IR_s$.	173
Fig. 7.3. Simulation of the J - V curve for a solar cell under approximately 1 sun conditions, based on the forward bias current in the dark as a function of charge density in the device for 1 sun conditions, found from charge extraction measurements.	175
Fig. 7.4. The relationship of fill factor with the effective ideality factor m' found under light conditions for a $V_{oc} = 0.6V$.	179

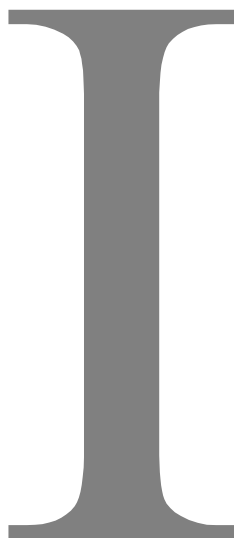
List of Publications

- 1) C. G. Shuttle, A. Maurano, R. Hamilton, B. O'Regan a, J. de Mello, and J. R. Durrant. '*Charge extraction analysis of charge carrier densities in a polythiophene / fullerene solar cell: Analysis of the origin of the device dark current*', Appl. Phys. Lett., **93**, 183501 (2008).
- 2) C. G. Shuttle, B. O'Regan, A. M. Ballantyne, J. Nelson, D. D. C. Bradley, and J. R. Durrant. '*Bimolecular recombination losses in polythiophene: Fullerene solar cells*', Phys. Rev. B., **78**, 113201 (2008)
- 3) C. G. Shuttle, B. O'Regan, A. M. Ballantyne, J. Nelson, D. D. C. Bradley, J. de Mello, and J. R. Durrant. '*Experimental determination of the rate law for charge carrier decay in a polythiophene: Fullerene solar cell*', Appl. Phys. Lett., **92**, 093311 (2008).

List of Abbreviations and Constants

PCE	Power conversion efficiency
P3HT	Poly(3-hexylthiophene)
PCBM	Methanofullerene [6,6]-phenyl C ₆₁ -butyric acid methyl ester
MDMO:PPV	Poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene]
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
e ⁻	Electron
h ⁺	Hole
BHJ	Bulk Heterojunction
DONOR	Electron donating material
ACCEPTOR	Electron accepting material
ETM	Electron transporting material
HTM	Hole transporting material
V_{BI}	Built-in potential
E	Electric field
d	Device thickness
J	Current density
V	Applied voltage
V_{int}	Cell voltage
PP	Peak power
V_{oc}	Open-circuit voltage
J_{sc}	Short-circuit current density
FF	Fill factor
IQE	Internal quantum efficiency
EQE	External quantum efficiency
QE	Quantum efficiency
R_s	Series resistance
R_{SH}	Shunt resistance
m	Ideality factor
A	Device area
μ	Mobility

ITO	Indium tin oxide
Al	Aluminum
G	Generation
R	Recombination
J_{ph}	Corrected photocurrent
J_{dark}	Dark current
J_{light}	Light current
J_{ph} - V curve	Internal quantum efficiency corrected photocurrent J - V curve
k	Bimolecular recombination coefficient
k_L	Langevin bimolecular recombination coefficient
TPV	Transient photovoltage
TPC	Transient photocurrent
TAS	Transient absorption spectroscopy
CE	Charge extraction
CELIV	Charge extraction with a linearly increasing voltage
DOI	Double injection currents
TOF	Time of flight
$J_{losses}(V_{oc})$	Loss in photocurrent at V_{oc}
J_{GEN}	Photogenerated current
$J_{GEN}(V_{oc})$	Loss in photocurrent at V_{oc} determined from the reverse bias light current
$J_{BI}(V_{oc})$	Loss in photocurrent at V_{oc} due to bimolecular recombination
$J_{FW,dark}$	Forward bias current in the dark
n	Total charge density (cm ⁻³)
$\tau_{\Delta n}$	Small perturbation carrier lifetime
τ	Total charge density carrier lifetime
ΔOD	Change in optical density
$e = 1.602 \times 10^{-19} C$	Electronic charge
$k_B = 1.38 \times 10^{-23} m^2 kgs^{-2} K^{-1}$	Boltzmann's constant
$\epsilon = 8.85 \times 10^{-12} Fm^{-1}$	Permittivity of free space
$N_A = 6.02 \times 10^{23} mol^{-1}$	Advogrado's constant



Chapter 1 Introduction

As the global energy requirements of the world continue to increase and our fossil fuel reserves continue to deplete there is increasing pressure to find alternative energy sources. However, if it was possible to access effectively the most plentiful energy source available to us, energy from the sun, this energy crisis we are facing would be resolved.

Extensive time and effort has been spent on developing high efficiency inorganic solar cells, based on inorganic semiconductors such as silicon. This has led to power conversion efficiencies (PCE's) in excess of 20%.¹ However, due to high production costs, at present they are not economically competitive with fossil fuels. Therefore, for solar cells to be able to compete with fossil fuels, it is essential that cheaper alternative materials are found.

Organic materials pose as a potential alternative to silicon due to their lower production costs.^{2,3} They also have other additional advantages such as ease of fabrication, the potential to be used to produce flexible devices. They also have extremely high absorption coefficients, typically 10^5 cm^{-1} , which allows devices to be considerably thinner, typically 100 – 500nm, compared to crystalline silicon devices, which require a thickness of 100 μm to absorb effectively the incident light.⁴ One of the most promising types of organic solar cells is based upon a blend of a conjugated polymer with fullerene (C_{60}). In particular, devices with blends of regioregular poly(3-hexylthiophene) (P3HT) with methanofullerene [6,6]-phenyl C_{61} -butyric acid methyl ester (PCBM), a soluble derivative of C_{60} , have had reported PCE's exceeding 4%.⁵⁻⁷ If it was possible to improve this efficiency up to 10% and achieve sufficiently long device lifetimes, then their low production costs would result in organic solar cells being economically competitive with fossil fuels. For this to be possible, it is important that the understanding of the fundamental science involved with these organic based solar cells is advanced, thereby allowing us to understand what presently limits the device performance and thus achieve advances in power conversion efficiencies towards 10%.

This thesis focuses on the investigation of the charge carrier loss processes which limit the efficiencies obtainable in standard annealed P3HT:PCBM blend devices. This is done by first considering a simple drift-diffusion model to obtain a basic understanding of the fundamental processes involved with device function, and then performing a wide range of experimental studies. The basic concepts of polymer:fullerene blend solar cells will now be introduced.

1.1 Background & Development of Solar Cells

Since the 1950's when the first crystalline silicon solar cell was developed at Bell Laboratories⁸ which had an efficiency of 6%, photovoltaic devices have been extensively studied. A wide range of different types of solar cells now exist and are currently being developed. These include inorganic solar cells which are presently the best PV devices to date with efficiencies above 24% for devices based on crystalline silicon,¹ dye sensitized solar cells with efficiencies up to 11%,¹ small molecule bi-layer structured OPV devices with efficiencies above 4%⁹ and polymer based solar cells with efficiencies now exceeding 5%.^{1,10}

1.1.1 Inorganic solar cells

Practically all conventional inorganic solar cells incorporate a semiconductor that is doped to form a p-n junction across which the photovoltage is generated. The p side contains an excess of the positive charges (holes), and the n side contains an excess of the negative charges (electrons). In the region near the junction, an electric field is formed and the electrons and holes, which are generated by light absorption in the bulk inorganic semiconductor, diffuse to this junction where they are directed by the electric field towards the proper electrode. See Section 1.9.1 for more details on the p-n junction.¹¹

To date the efficiency for crystalline silicon solar cells has reached 24%,¹ which is already close to the theoretical predicted upper limit of given by the detailed balanced limit of 30 %.¹² Devices based on III-V materials have had reported efficiencies of 25.1% for crystalline gallium arsenide (GaAs) and 21.9% for crystalline indium phosphide (InP).¹ The efficiency of inorganic devices is highly dependent of how crystalline the materials are, which when reduced leads to lower efficiencies.

1.1.2 Dye sensitized solar cells

Dye sensitized solar cells (DSSC's) consist of two conducting glass electrodes, one coated with a compact but highly porous film of Titanium dioxide (TiO₂) on which was adsorbed generally ruthenium based dyes and the other platinised separated by a

solution containing a high concentration of the iodide/tri-iodide redox couple in an organic solvent. In the pivotal work by O'Regan and Grätzel in 1991 an efficiency of 7.1% was reported for simulated sunlight.¹³ Since then laboratory efficiencies have now reached 11%.¹

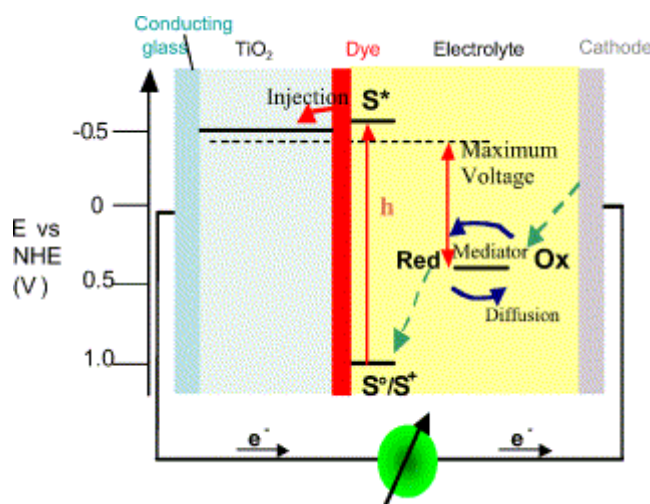


Fig. 1.1. Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell.¹⁴ Photoexcitation of the sensitizer (S) is followed by electron injection into the conduction band of an oxide semiconductor film. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter-electrode by electrons passed through the load. Potentials are referred to the normal hydrogen electrode (NHE). The open circuit voltage of the solar cell corresponds to the difference between the redox potential of the mediator and the Fermi level of the nanocrystalline film indicated with a dashed line. The energy levels drawn for the sensitizer and the redox mediator match the redox potentials of the doubly deprotonated N_3 sensitizer ground state and the iodide/tri-iodide couple.

1.1.3 Organic solar cells

Organic solar cells show considerable promise for the future. Advantages of organic solar cells are they are mechanically flexible, lightweight, and disposable with little environmental impact. The constituents can be made soluble so they are low-cost, low-temperature solution processing methods which should be easily scalable up. However, due to their relatively low efficiencies to date OPV has some way to go before becoming a commercial reality.

Molecular photovoltaic devices consist of a thin film of continuous phases of donor and acceptor materials, sandwiched between two electrodes. Devices differ principally in the structure of the interface between the two materials and the way in which they are put together. Fig. 1.2 shows three different device structures; b) a bi-layer device, c) a random bulk heterojunction and d) an idealised ordered structure bulk heterojunction device.¹⁰

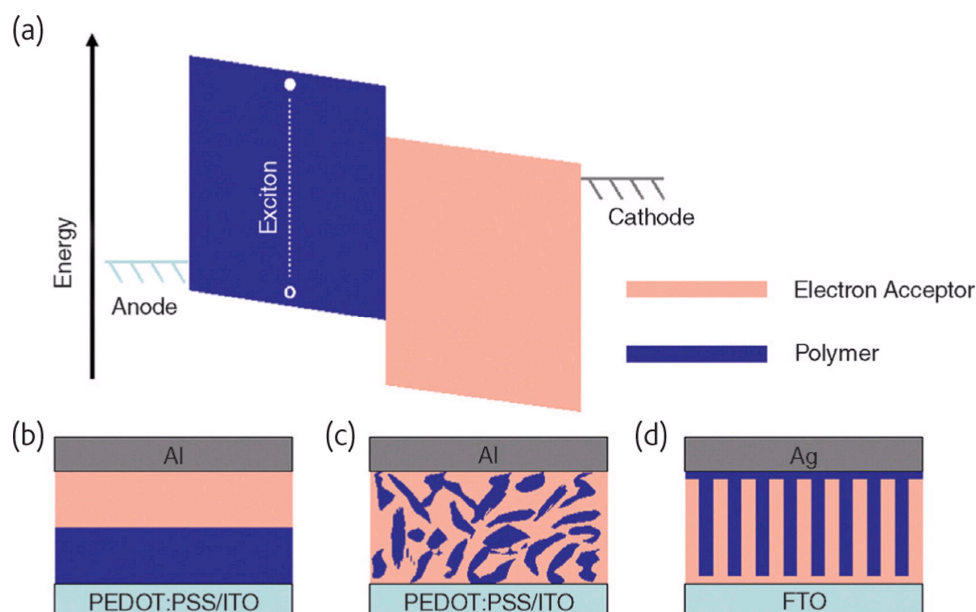


Fig. 1.2. Polymeric solar cell heterojunctions.¹⁰ (a) Energy diagram of a heterojunction with an exciton in the polymer phase. The first heterojunction was a bi-layer (b), but this architecture is limited as the active layer must be thin in order to utilize all excitons. In order to have every exciton separated, a heterojunction must exist within an exciton diffusion length. This can be achieved in a bulk heterojunction (c) or in an ordered heterojunction (d).

1.1.3.1 Small molecule OPV bi-layer devices

Bi-layer OPV devices, as the name suggests consist of two layers which form a planar junction (see Fig. 1.2(b)) at which light generated excitons dissociate into spatially separated charge carriers preventing direct recombination and allowing the transport of electrons to one electrode and the holes to the other electrode mainly via diffusion (see Section 1.5). The efficiency of bi-layer devices is limited due to the exciton diffusion length (see Section 1.2) of the electron donating material which limits the thickness of the photo-absorbing material. This limits the amount of photons that may

be absorbed and thus, limits the efficiencies which are possible. This bi-layer structure has been developed in particular for vacuum-evaporated small-molecular devices.

The bi-layer copper phthalocyanine/perlene tetracarboxylic derivative (CuPc/PTC) cell developed by Tang in 1986 was the pioneer in this field, obtaining an efficiency of 0.95%.¹⁵ Currently the best bi-layer efficiencies are for devices consisting of a vacuum-deposited molecular layer of a metal phthalocyanine as the photo-absorbing electron donor and a fullerene (C₆₀) derivative as electron acceptor with bi-layer heterojunction structures using CuPc and C₆₀ with a maximum efficiency of 4.2%.⁹

1.1.3.2 Polymer based donor: acceptor bulk heterojunction devices

Three common materials used in photovoltaic devices are the conjugated polymers poly(3-hexylthiophene) (P3HT), poly[2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV), and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylenevinylene] (OC1C10-PPV). A major advantage of these materials is they contain side chains that make them soluble in common organic solvents. This allows these polymers to be cast from solution using wet-processing techniques such as spin casting, dip coating,¹⁶ ink jet printing,^{17,18} screen printing,¹⁹⁻²¹ and spray deposition. These techniques are required for the high-throughput roll-to-roll processing that will drive the cost of polymer-based PV down to a point where it can compete with current grid electricity.⁴

By blending a soluble conjugated polymer with a soluble acceptor this ensures an intermixing between the donor and acceptor resulting in a large interfacial area which promotes increased exciton dissociation resulting in an increased photo-generation of charge carriers. These charge carriers must then be transported to their respective electrodes to obtain photocurrent. However, a clear downside of this intermixed structure is that it also increases the probability of recombination. There are a wide range of different organic solar cells employing this device design. These are documented in Fig. 1.3 which shows the maximum reported efficiencies for polymer based solar cells over time.¹⁰ These include blends of the conjugated polymer P3HT as the donor with a fullerene derivative PCBM as the acceptor (~ 5%), blends of the conjugated polymer PPV as the donor with PCBM (~ 3%) and other low bandgap

polymers with PCBM ($> 5\%$), blends of polymer:polymer where one polymer is used as the donor and a different polymer is used as the acceptor ($\sim 2\%$), and hybrid based blend devices consisting of an organic semiconductor as the electron donor and an inorganic semiconductor such as a III-VI compound semiconductor or a metal oxide ($\sim 1.5\%$) or cadmium selenide (CdSe) nanocrystals as the electron acceptor ($\sim 2.5\%$).

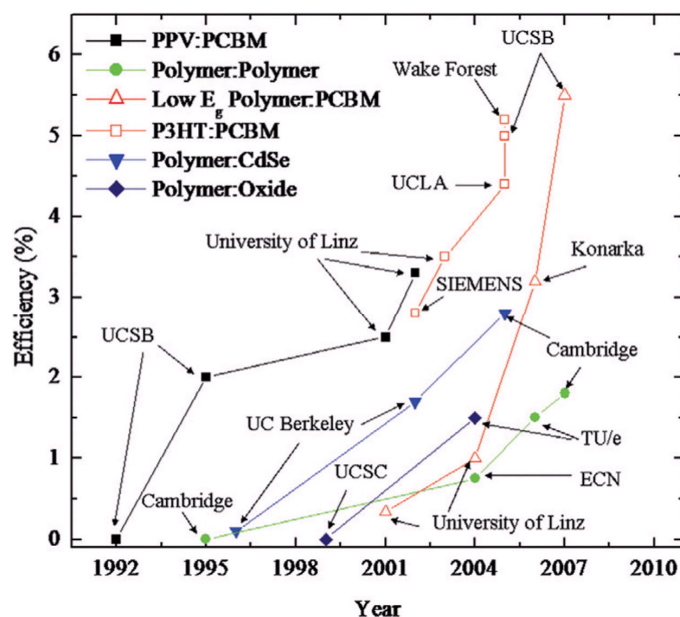


Fig. 1.3. Reported efficiencies of various polymer based BHJ technologies over recent years and the respective institutes from which they were reported.¹⁰ The abbreviations are: University of California, Santa Barbara (UCSB); University of California, Santa Cruz (UCSC); University of California, Berkeley (UC Berkeley); University of California, Los Angeles (UCLA); Technische Universiteit Eindhoven (TU/e).

1.2 Photogeneration

In organic semiconductors, absorption of a photon results in an electron (e^-) being promoted from its highest occupied molecular orbital (HOMO) into its lowest unoccupied molecular orbital (LUMO), leaving a vacancy, known as a hole (h^+), in the HOMO. Unlike inorganic semiconductors, this (e^-h^+) pair does not exist as free charge carriers, but instead, due to strong coulombic binding energies, exists as a neutral, bound state, known as an exciton (see Fig. 1.4). To liberate free charge carriers, the exciton must reach an interface within its diffusion length, typically 1-10nm in organic semiconductors,^{22,23} where it is energetically favourable for the

exciton to dissociate. Otherwise, the exciton will decay back to its ground state by electron recombination with the hole, and the sun's energy is lost. In single layer organic solar cells, where an organic semiconductor is sandwiched between two electrodes, dissociation will only occur at the organic semiconductor-electrode interface, therefore, the resulting dissociation yields are small, which leads to very low power conversion efficiencies (PCE's) ($<0.1\%$) being obtained.^{24,25}

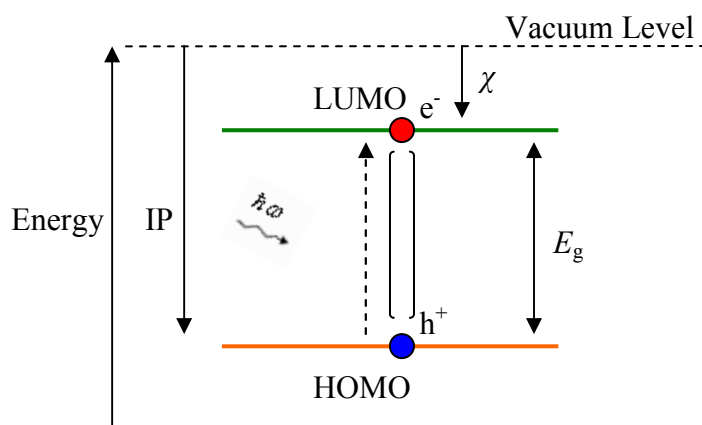


Fig. 1.4. Energy levels in an organic semiconductor and photoabsorption. The energy levels of the HOMO and LUMO in an organic semiconductor are given by the electron affinity (χ) and the ionisation potential (IP) respectively. Photon's absorbed from light with energy exceeding the optical bandgap, E_g , given by the difference between the IP and χ , causes an e^- to be promoted to the LUMO from the HOMO, leaving a h^+ in the HOMO. Due to strong coulombic binding energies, this (e^-h^+) exists as neutrally bound exciton.

In 1995 it was first realised that by mixing the light absorbing semiconductor with an additional species with a LUMO energy level which is lower, it was possible to increase the yield of exciton dissociation.^{26,27} More specifically, if the difference in electron affinities between the two materials exceeds the exciton binding energy, considered typically to be ~ 0.4 eV,¹¹ then this promotes the dissociation of these excitons (see Fig. 1.5). The light absorbing semiconductor behaves as the e^- donating material (donor) and the semiconductor with the lower LUMO behaves as the e^- accepting material (acceptor). Excitons which reach the donor-acceptor interface will dissociate, with an e^- moving from the LUMO of the donor to the LUMO of the acceptor, leaving the h^+ in the HOMO of the donor, Fig. 1.5(b). This charge transfer process in conjugated polymer- C_{60} blends can be ultrafast (~ 40 fs).^{28,29} However, rather than directly form free charge carriers, it is believed that the creation of free charge carriers follows a two step process where initially, formed electron - hole pairs

are bound at the interface as a result of the strong Coulombic binding energies between the two, see Fig 1.5(b).¹¹ These geminate charge pairs can then either separate into free charge carriers or recombine ('geminate recombination'). In the case of devices based on blends of P3HT:PCBM, as studied in this thesis, it has been found that it is possible to obtain photocurrent densities corresponding to near complete collection of all photogenerated charges formed,³⁰ and hence, this suggests, that geminate recombination is relatively unimportant in these devices.

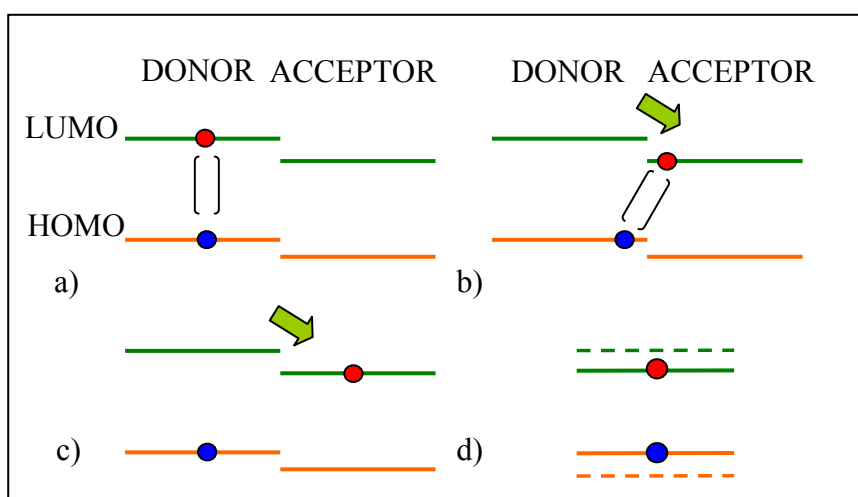


Fig. 1.5. Formation of free charge carriers in a BHJ. The difference in LUMO levels between the donor and acceptor provides a driving force for charge dissociation to occur. The e^- passes from the donor to the acceptor (b). However, due to strong coulombic binding energies, it is possible that rather than directly form free charge carriers, an intermittent geminate bound electron hole pair is formed. c) These geminate pairs will either recombine or form charge carriers. d) A common approach in considering the behaviour of a BHJ, is to consider the blend in terms of a virtual semiconductor, which is given by the HOMO level of the donor and the LUMO level of the acceptor.

A blend of the type described above is often referred to as a bulk heterojunction (BHJ). In a BHJ, the acceptor behaves as the e^- transporting material (ETM) and the donor behaves as the h^+ transporting material (HTM). It is common to consider the 'active layer' given by the blend of the ETM and HTM in terms of a 'virtual semiconductor', with the HOMO of the HTM and the LUMO of the ETM (see Fig. 1.5(d)).³¹

1.3 Device structure

To harvest the light's energy, the active layer is sandwiched between a transparent anode and a metallic cathode to form a BHJ solar cell (see Fig. 1.6(a)). The transparent anode allows the transmission of incident light into the active layer. The work functions of the anode and cathode, ϕ_a and ϕ_c respectively, are chosen to approximately align with the HOMO and LUMO levels of the virtual semiconductor respectively to ensure ohmic contacts, Fig. 1.6(b).

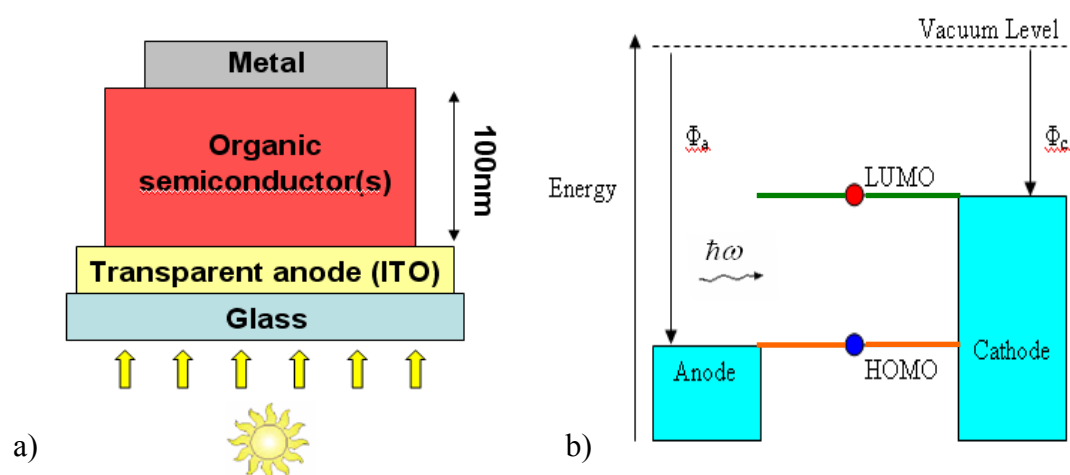


Fig. 1.6. Schematics of the a) basic design of an organic solar cell and b) energy levels. a) A BHJ solar cell consists of an organic semi-conducting blend layer, typically 100nm thick, sandwiched between a transparent anode and a metallic cathode. b) The anode and cathode are chosen so their work functions approximately match the LUMO and HOMO of the active layer to ensure ohmic contacts.

1.4 Band Diagrams

To understand how solar cells work, it is useful to consider their band diagrams. Initially, when contacts are made between the active layer and the electrodes in a BHJ device, the Fermi levels of the electrodes are misaligned (see Fig. 1.6(b)). Electrons in the cathode are higher in energy than those in the anode, so will travel to the anode in order to reduce their energy. This results in the raising of the Fermi level of the anode and the lowering of the Fermi level of the cathode. Equilibrium is reached when the Fermi levels of both electrodes equilibrate, which provides the Fermi energy level in the device, E_F . The cathode now is positively charged and the anode is negatively charged, which results in an electric potential gradient to be present within the active

layer of the device, as shown in Fig. 1.7, thereby, resulting in a built-in electric field (E_{BI}) given by

$$E_{BI} = \frac{V_{BI}}{d} = \frac{\phi_c - \phi_a}{d} \quad (1.1)$$

where $V_{BI} = (\phi_c - \phi_a)$ is the built-in electric potential and d is the thickness of the active layer in the device (which we refer to as device thickness herein).

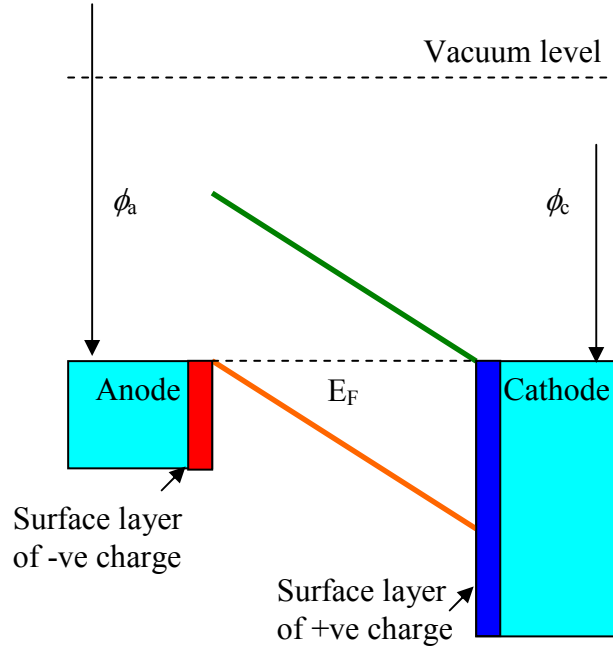


Fig. 1.7. Energy schematic of the solar cell when the fermi levels have equilibrated. When electrodes are connected to the active layer, electrons flow from the cathode to the anode to reduce their energy. Equilibrium is reached when the fermi levels of the two electrodes align. This leads to the presence of an internal electric field within the device.

1.5 Charge transport, charge collection at the wrong electrodes and bimolecular recombination

To obtain an efficient solar cell, when photogenerated charge carriers are formed, they must travel to their appropriate electrodes. Electrons charge carriers must travel to the cathode and hole charge carriers must travel to the anode, where they are extracted, providing a photocurrent. This can occur through two different charge transport processes; ‘drift’ and ‘diffusion’. In the presence of an electric field, free charge

carriers will ‘drift’ towards the electrodes, with the electrical polarity configured such that the electrons travel towards the cathode, whereas holes travel to the anode. Alternatively, due to non-uniform build-up of charge densities in the device, corresponding to charge carrier concentration gradients, charge carriers will travel via a diffusion based charge transport process. Unless there are efficient layers to block collection of free charge carriers at the ‘wrong’ collecting electrodes, thereby providing electrode selectivity, diffusion (primarily) processes could result in charge carriers reaching their wrong collecting electrodes where they are extracted into the external circuit (‘leakage’ currents). This will lead to a photocurrent in the opposing direction, leading to a loss in the overall photocurrent output, thereby providing a possible loss mechanism in these BHJ solar cells.

Alternatively, if opposing charge carriers meet within the device, in the case where their coulombic binding energy exceeds that of their thermal energy, it is energetically favourable for them to recombine, and so, these charges are lost via a bimolecular recombination process. This will predominantly occur at the donor/acceptor interface. Bimolecular recombination, therefore, poses as a potentially major loss mechanism for such solar cells. To obtain efficient solar cells, it is essential that the transit time for electron and hole carriers to reach their collecting electrodes is faster than the corresponding lifetime of these charge carriers.

Charge collection at the wrong electrodes (leakage) and bimolecular recombination (see Fig. 1.8), combined with geminate recombination described in Section 1.2, represent three of the main possible loss mechanisms for charge carriers in organic BHJ solar cells.

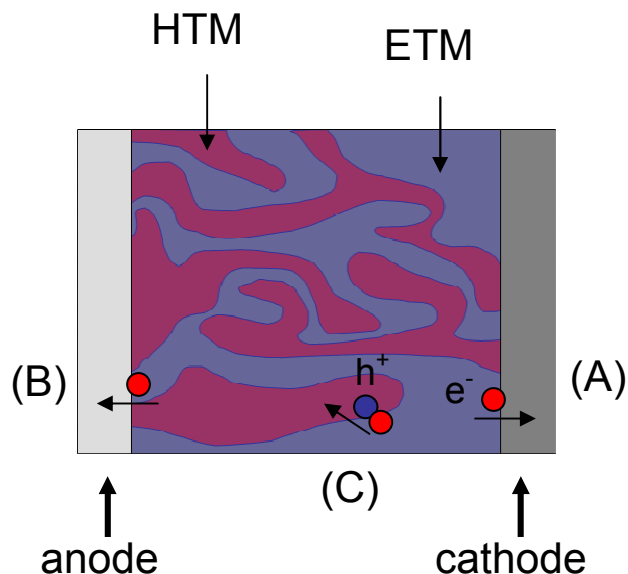


Fig. 1.8. Schematic of a BHJ solar cell, demonstrating the different possible current mechanisms. (A) In a solar cell electrons and hole charge carrier must travel to the cathode and anode respectively where they are extracted into the external circuit. However, if charge carriers reach the wrong collecting electrodes (B), i.e. electron charge carriers reach the anode and hole charge carrier reach the cathode, then they are also extracted resulting in a photocurrent which flows in the opposite direction to the net photocurrent, and hence, leads to a reduction in photocurrent output. An additional loss in current can result from the bimolecular recombination flux, which is generated when opposing charge carrier meet and recombine (C), which should predominantly occur at donor-acceptor interfaces.

1.6 Capacitance and charge storage

A solar cell can be considered as a capacitor as it consists of a dielectric sandwiched between two conductive plates. Its associated capacitance is given by $C = \epsilon A/d$, where ϵ is the effective dielectric constant of the active layer and A is the device area. When the device is subjected to an applied bias V , this leads to charge being present on the electrodes $Q = CV$.

When the device is illuminated, a steady state quasi-equilibrium will be reached in the device where generation, recombination and charge collection processes are all balanced. This results in a build-up of charge in the bulk of the device which leads to the ‘effective’ capacitance of the device under illumination to differ from its geometric capacitance in the dark.

1.7 Device operation

The objective of a solar cell is to convert the light energy of the sun into electrical power. To do this, the solar cell is connected in an electrical circuit in series with a load resistor, R_L , as shown in Fig. 1.9, which, when an incident light source is applied on the solar cell, results in producing electrical power per unit area P , given by the product of current density J with voltage V . The value of the load resistor used is chosen carefully to obtain the maximum power possible, known as peak power (PP).

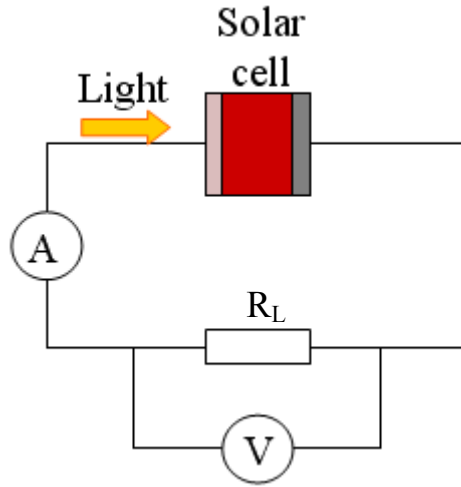


Fig. 1.9. Circuit diagram for the operation of a solar cell. A load resistance, R_L , is connected to the device which results in the production of power given by JV .

1.7.1 Device characterisation

To characterise device performance, the steady state electrical properties of the device are studied in the form of current voltage (J - V) curves. Figure 1.10 shows plots of the J - V curves, both in the dark and whilst under one sun simulated irradiation using an AM1.5 solar simulator. The fourth quadrant of the J - V curve measured whilst under light conditions serves as the operational region for the solar cell. The key parameters which influence device efficiency are given by the short-circuit current density J_{sc} , the open-circuit voltage V_{oc} , and the position of peak power PP which occurs at the maximum power point (V_{MPP} , J_{MPP}).

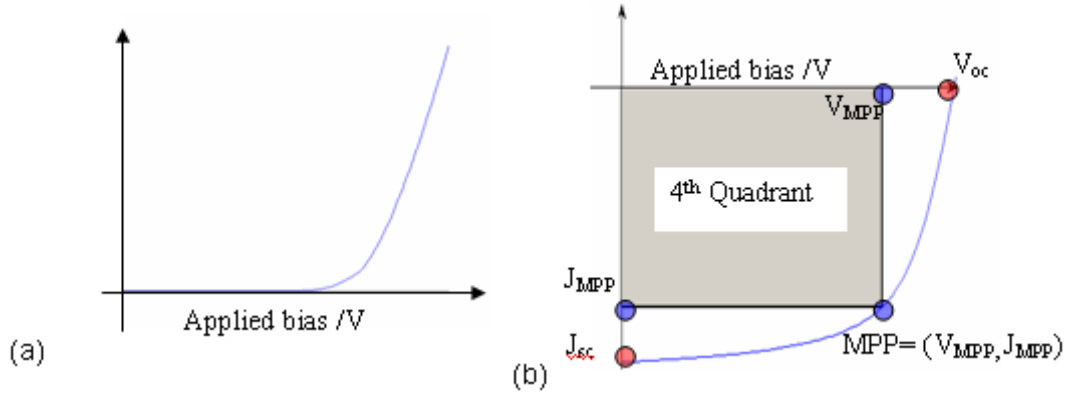


Fig. 1.10. J - V curves for a) a solar cell in the dark and b) under one sun illumination conditions.

1.7.1.1 Short-circuit

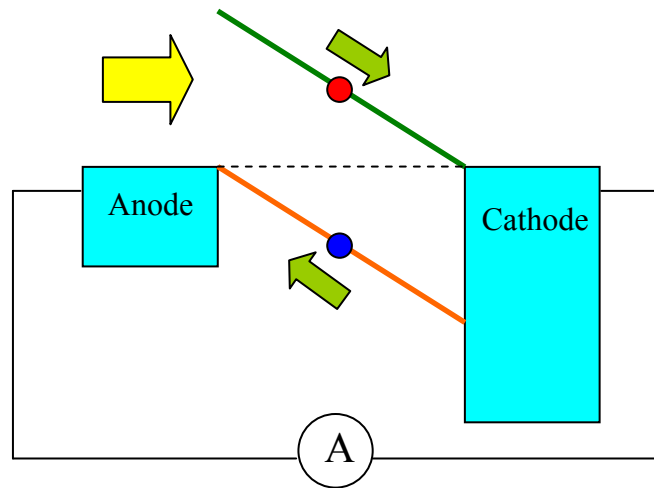


Fig. 1.11. Band diagram for a device under illumination under short-circuit conditions.

Short-circuit conditions serves as one limit for device operation. This corresponds to the case when the load resistance $R_L = 0$. At short-circuit, the electrodes are held at the same potential. The internal electric field is given by E_{BI} and provides a strong drift component of transport. Illumination causes the photogeneration of free charge carriers which will flow towards the electrodes through drift and diffusion processes. Charge carriers which reach the electrodes are collected, resulting in a short-circuit current, J_{sc} .

1.7.1.2 Open-circuit

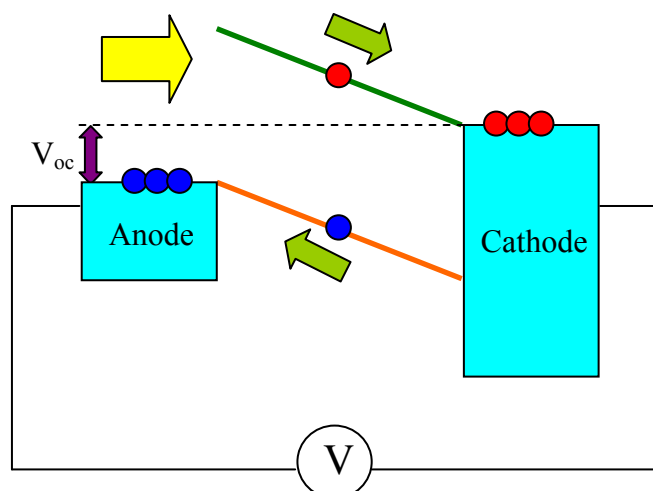


Fig. 1.12. Band diagram for a device under illumination under open-circuit conditions.

The second limit to solar cell operation is given by open-circuit conditions, corresponding to the case where $R_L = \infty$. At open-circuit, no current can flow through the external circuit. Due to the built-in electric field, photogenerated electrons will flow towards the anode, and holes to the cathode. However, as these charges cannot be collected at the electrodes a build-up of holes at the anode and electrons at the cathode results. This creates an electric field which acts in opposition to the built-in electric field. At steady state, the effective internal electric field in the device, E_{eff} , is now given by

$$E_{\text{eff}} = \frac{V_{\text{BI}} - V_{\text{oc}}}{d} \quad (1.2)$$

Therefore, illumination on a device at open-circuit results in a ‘light bias’. As the ‘light bias’ is increased, the internal electric field reduces. The maximum V_{oc} which is possible is given by the difference in energy levels between the HOMO of the donor and the LUMO of the acceptor, which provides the electronic bandgap of the blend.³² It has previously been demonstrated that there is a strong correlation between this electronic bandgap and the open-circuit voltage for 1 sun incident light conditions.^{32,33}

1.7.2 Efficiency

The product of J_{sc} with V_{oc} provides an upper limit to the maximum possible power a solar cell can provide. The peak power PP a solar cell can produce is given by

$$PP = -J_{MPP}V_{MPP} \quad (1.3)$$

The photovoltaic power conversion efficiency (PCE) of a solar cell is defined as the ratio of the maximum power a solar cell can produce to the incident optical power due to solar illumination, and is given by the following formula:

$$\eta_{AM1.5} = \frac{PP}{P_{in}} M = \frac{V_{oc} J_{sc} FF}{P_{in}} M \quad (1.4)$$

where $\eta_{AM1.5}$ is the PCE, P_{in} is the incident light power density due to the simulated solar illumination ($\sim 100 \text{ mWcm}^{-2}$), M is the spectral mismatch factor, which accounts for the deviations in the spectrum of the solar simulator from the solar spectrum and FF is the fill factor. The fill factor defines the ratio of peak power with the maximum power that a solar cell can produce by consideration of the maximum current and voltage of the fourth quadrant of the J - V curve, J_{sc} and V_{oc} respectively:

$$FF = \frac{PP}{J_{sc} V_{oc}} \quad (1.5)$$

It is not possible to obtain a fill factor of 100% due to the forward bias current in the dark, which is discussed in Section 1.9.1 below. To obtain an efficient solar cell, a high fill factor is a prerequisite, but does not guarantee it, as the J_{sc} and/or V_{oc} may be too small.

In analysing PV performance, it is also useful to consider the quantum efficiency (QE) of the device, of which there are two different forms: external quantum efficiency (EQE) and internal quantum efficiency (IQE). Traditionally, these quantum efficiencies are considered at short-circuit conditions, although we consider them herein as general QE 's. External quantum efficiency describes the density of photogenerated electrons with respect to the density of photons in the incident light

$$EQE = \frac{J}{J_{max}} \quad (1.6)$$

where $J_{\max}$ is the maximum possible current density if all the incident photons generated charge carriers in the external circuit. The internal quantum efficiency describes the efficiency of the current generation of only the absorbed photons, and is defined as

$$IQE = \frac{J}{J_{\max, \text{abs}}} \quad (1.7)$$

where $J_{\max, \text{abs}}$ is the maximum possible current density if all photons which are absorbed are converted into free charge carriers and are extracted by the electrodes into the external circuit. Both IQE and EQE are typically measured under monochromatic illumination. The quantum efficiency describes the quality of spectral matching between the solar spectrum and the absorption spectrum of the photo-absorbing material. In this thesis, when discussing quantum efficiency we consider IQE rather than EQE .

1.8 Design rules for efficient solar cells

From consideration of the energy levels of the semiconductors used for BHJ devices (see Fig. 1.13), it is apparent that to obtain an efficient solar cell, a compromise must be made between the maximum short-circuit current density the device can produce, which is dependent on the optical bandgap E_g of the donor (or acceptor) and the difference in electron affinities between the donor and acceptor which corresponds to the difference between their LUMO energy levels, and the maximum open-circuit voltage V_{oc} , which is given by the blends electronic bandgap describing the difference between the HOMO energy level of the donor and the LUMO energy level of the acceptor. For example, if the donor has a low E_g then this will increase the density of photons which can be absorbed from the solar spectrum, and so it may be possible to obtain a high photocurrent, as long as the driving force for exciton dissociation given by ΔE (difference between the electron affinities of the donor and acceptor) is sufficiently large. However, this limits the V_{oc} which is possible, and hence, may lead to a low efficiency despite the high photocurrent.

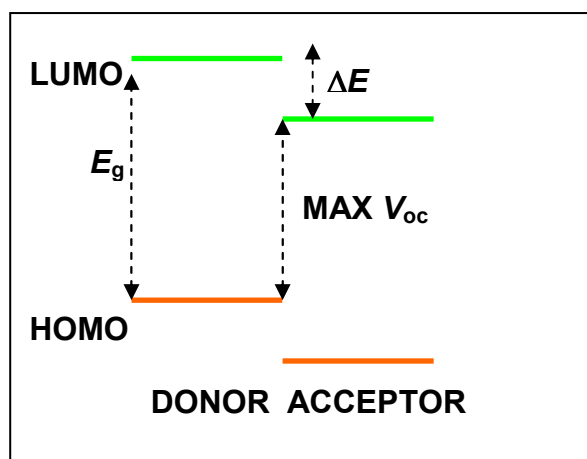


Fig. 1.13. Band diagram depicting the energy levels for a BHJ device.

Scharber³² presented a simple model based on this understanding, where he calculated the theoretically possible efficiency based on this simple energy diagram, assuming that the EQE at short-circuit is 65% and the $FF = 65\%$. We note that understood fundamental limit for the FF is $\sim 80\%$, depending on the V_{oc} of the device (see Section 1.9.1), and so it may be possible to obtain devices with a larger fill factor, resulting in higher obtainable efficiencies. Figure 1.14 shows the results of this model, which provide guidelines where it may be possible to increase device efficiency. For example, one of the best devices to date is based on a blend of P3HT:PCBM, which is studied in this thesis. However, a clear limitation of such a device is that the photoabsorbing material P3HT has an electronic bandgap $E_g \sim 1.9\text{eV}$, which only covers 30% of the solar spectrum,¹¹ thereby, limiting the photocurrent which is possible. If it was possible to obtain a device which absorbs at higher wavelengths, $>650\text{nm}$, it should be possible to obtain efficiencies which approach the desired 10% benchmark. Currently, this represents a strong direction for study in the organic solar cell community, with most recently device efficiencies reported in excess of 5%³⁴ based on a polymer: PCBM blend device, where the polymer absorption spectra is red-shifted compared to P3HT.

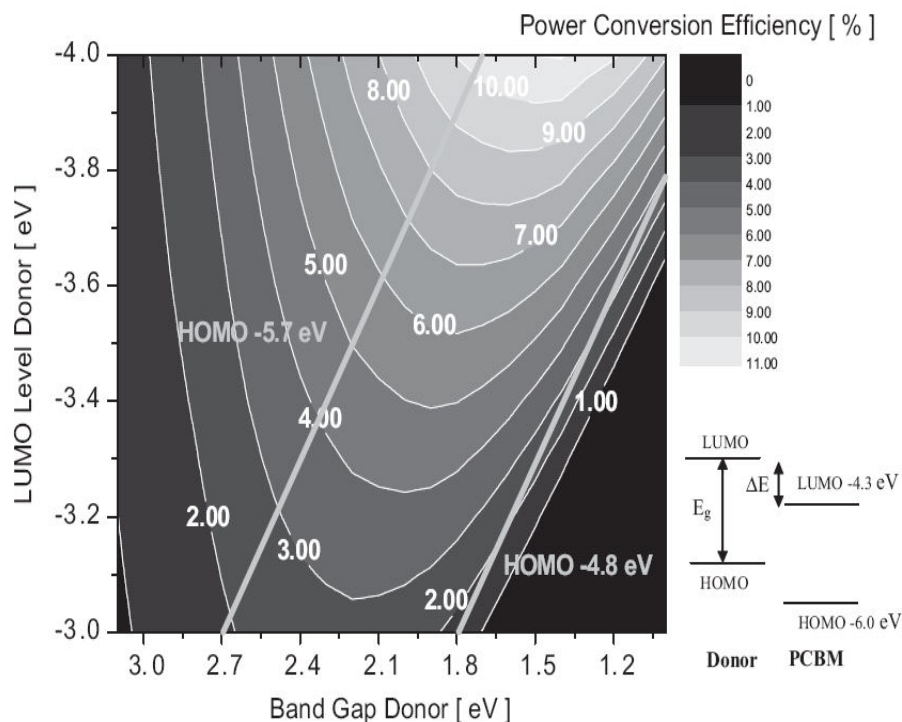


Fig. 1.14. Contour plot by Scharber *et al.*³² showing the calculated energy-conversion efficiency (contour lines) versus the bandgap and the LUMO level of the donor polymer. If it was possible to make a BHJ device with a donor with optical bandgap of 1.5eV, it may be possible to reach efficiencies as high as 10% based on this simple form of analysis.

1.9 The equivalent circuit of a solar cell

A common approach when considering real electrical devices is to consider an equivalent circuit to describe their electrical properties. Figure 1.15 shows the equivalent circuit used to describe a solar cell, where the solar cell is considered in terms of a diode in parallel with a constant photocurrent generator, with parasitic resistances given by a series and shunt resistance, R_s and R_{SH} respectively.³⁵

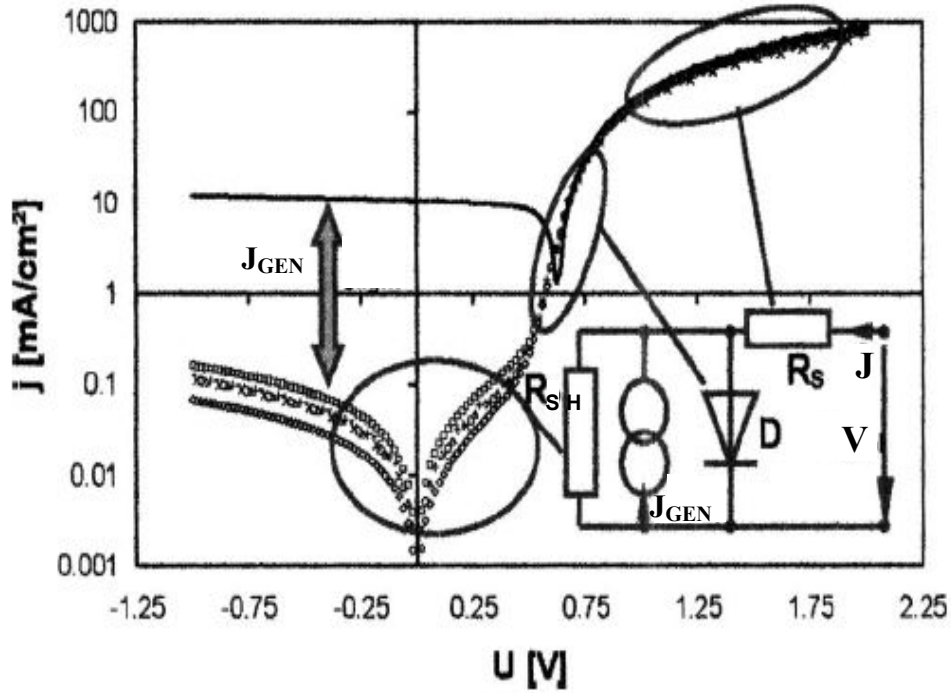


Fig. 1.15. Equivalent circuit for a solar cell.³⁵ This replacement circuit consists of a current generator, which provides J_{GEN} , a diode and both parasitic shunt and series resistances.

In this analysis, the corresponding J - V curve of a typical organic photovoltaic device in the dark is found to display three distinctive regimes, as shown in Fig. 1.15:^{35,36}

- 1) at negative voltages and low positive voltages the J - V curve follows ohmic behaviour where the current is limited by the shunt resistance R_{SH} , which describes electrical shorts in the device assigned to pure phase charge transport between the two electrodes.
- 2) at intermediate positive voltages, the current follows exponential behaviour, where the current is controlled by the diode behaviour of the solar cell.
- 3) at higher voltages the J - V curve is also found to follow ohmic behaviour, where the diode behaviour of the solar cell breaks down and the current becomes limited by the series resistance R_{S} . This serial resistance describes an ensemble of the contact resistivity, the bulk resistivity of the active layer and the circuit resistivity.

The series resistance results in a loss in voltage, whereas, the shunt resistance results in a loss in current, both of which lead to a reduction in FF and therefore, overall

device performance. In an ideal solar cell $R_s = 0$ and $R_{SH} = \infty$. However, for real device R_s is typically in the range $1 - 10 \Omega\text{cm}^2$, whereas R_{SH} take typical values in the range $1 \text{ M}\Omega - 1 \text{ G}\Omega$.

1.9.1 Shockley diode equation

It is common when considering the dark current to consider the formulation given by the Shockley diode equation,¹² which describes the behaviour of p-n junctions

$$J = J_0 \left(\exp \left(\frac{e(V - JAR_s)}{mk_B T} \right) - 1 \right) + \frac{(V - JAR_s)}{AR_{SH}} \quad (1.8)$$

where J_0 is the saturation current, e is the electronic charge, V is the applied voltage, A is the device area, m is the ideality factor, k_B is the Boltzmann constant and T is temperature. The first term refers to the diode properties of the device, whereas, the second term describes the current due to electrical shunts in the device. In this formulation, the ideality factor describes the originating process for the behaviour of the diode current. For an ideal diode $m = 1$ where the diode current results from a diffusion dominated process, where electron and hole free charge carriers are able to diffuse away from the p-n interface. Alternatively, the current can be dominated by an interfacial bimolecular recombination process, where the diode is described in terms of a Shockley Reed Hall recombination diode, $m = 2$. For solar cells the ideality factor m is typically found to be somewhere in between these two values, which indicates that the current consists of a combination of both of these effects.³⁵ Although the Shockley diode equation is derived based on the minority carriers in inorganic semiconductors rather than majority carriers which are important in organic semiconductors, and also, that it may be surprising for a BHJ device, unlike bi-layer devices, to have a well-defined separation due to the intimate blend, it has been suggested that an expanded p-n model may used to describe BHJ devices.³⁵

The Shockley diode equation has previously been extended to model the photocurrent for a solar cell, where an additional constant photo-generated current is introduced:³⁷

$$J = J_{\text{GEN}} + J_0 \left(\exp \left(\frac{e(V - JAR_s)}{mk_B T} \right) - 1 \right) + \frac{(V - JAR_s)}{R_{SH}} \quad (1.9)$$

This expression has been successfully used to recreate the J - V curves of inorganic devices. By considering the case for an ideal diode ($m=1$) where $R_s = 0$ and $R_{SH} = \infty$, this allows analytical expressions for J_{sc} , V_{oc} and FF to be obtained:

$$J_{sc} = J_{GEN} \quad (1.10)$$

$$V_{oc} = \frac{k_B T}{e} \ln \left(-\frac{J_{GEN}}{J_0} + 1 \right) \quad (1.11)$$

$$FF = \max \left(\frac{V}{V_{oc}} \left(\frac{\exp \left(\frac{eV_{oc}}{k_B T} \right) - \exp \left(\frac{eV}{k_B T} \right)}{\exp \left(\frac{eV_{oc}}{k_B T} \right) - 1} \right) \right) \quad (1.12)$$

Based on this formulation, the device current in the dark is indicative of a loss process limiting device performance, which limits the maximum possible fill factor. For instance, when $V_{oc} = 0.6V$ and $m = 1$ then the upper limit for the fill factor is given by $\sim 83\%$.¹²

Applying the same approach to model the J - V curves for organic solar cells has required a modification to Eqn. (1.9). Experimentally, it is found that the effective shunt resistance for a device under incident irradiation, i.e. the slope of the J - V curve under short-circuit conditions, is strongly dependent on the light intensity, significantly decreasing as the illumination intensity is increased.³⁶ To account for this effect, Eqn. (1.9) has been modified by introducing an additional light dependent parallel shunt resistance (R_p) which reflects both the change in conductivity of the device under illumination and selectivity for charge collection at the electrodes.^{31,38}

1.10 P3HT:PCBM BHJ devices

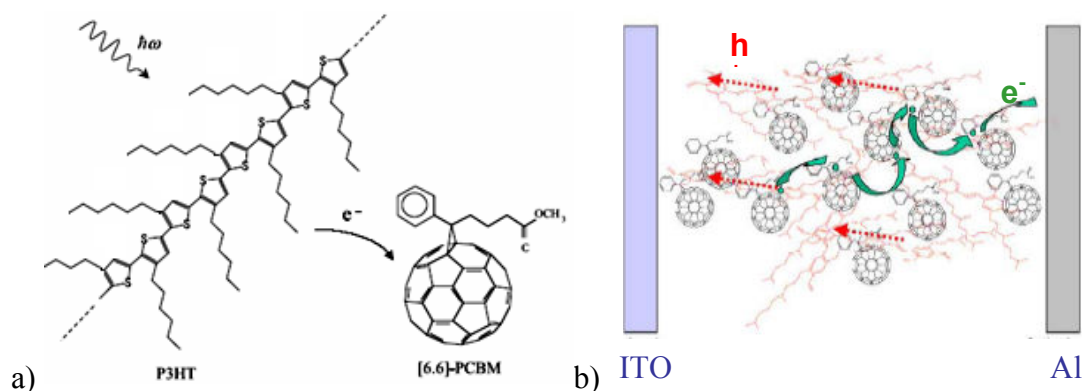


Fig. 1.16. a) Chemical structure of P3HT and PCBM and b) the basic design of a P3HT:PCBM device.² In a) light is absorbed by P3HT, which results in the formation of excitons. Due to the difference between the electron affinities between P3HT and PCBM, this results in the dissociation of excitons which diffuse to a P3HT:PCBM interface, where an electron transfers from the P3HT LUMO to the PCBM LUMO leaving a hole in the P3HT HOMO. When the P3HT:PCBM BHJ is sandwiched between two electrode, b) electron charge carriers travel to the cathode, whereas, hole charge carriers travel to the anode, through the interpenetrating networks of PCBM and P3HT respectively.

One of the most promising organic BHJ solar cells to date comprises devices based on blends of poly (3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methano fullerene (PCBM) with PCE's in excess of 4%.⁵⁻⁷ In this system the conjugated semiconducting polythiophene polymer P3HT, is used as the photo-absorbing HTM. and PCBM, a fullerene derivative, used as the ETM, as shown in Fig. 1.16, where electron charge carriers travel to the cathode, whereas, hole charge carriers travel to the cathode and anode, through the interpenetrating networks of PCBM and P3HT respectively. Figure 1.17 shows the absorption spectrum for pristine P3HT and for a typical annealed P3HT:PCBM blend. P3HT has an optical bandgap $E_g = 1.9$ eV with good absorption in the range 450nm – 650nm. P3HT also has a relatively high hole mobility (μ_p) with field effect transistor (FET) measured mobility as high as $\mu_p \sim 10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ³⁹ and time of flight (TOF) measured $\mu_p \sim 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.^{5,40} PCBM is used as the ETM as it has a lower LUMO level -4.3 eV than P3HT -3.3 eV,^{32,41} thus promoting exciton dissociation. It also has a relatively high electron mobility $\mu_n \sim 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ measured in FET's⁴² and $\mu_n \sim 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ from TOF measurements.⁵

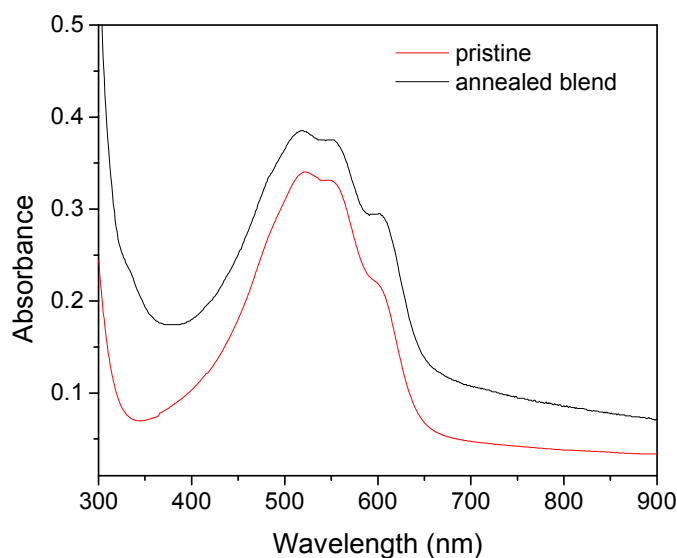


Fig. 1.17. Absorption spectrum for pristine P3HT, and for a 1:1 annealed (140°C, 20 min) P3HT:PCBM blend. P3HT has good absorption over the wavelength range 450 – 650 nm. However, its absorption is clearly limited into the red – infra-red range of the solar spectrum, which limits the current densities which are possible.

P3HT:PCBM photovoltaic device characteristics are highly dependent on the fabrication conditions used⁴³⁻⁴⁶ and the nature of the constituent materials, such as the polymer regioregularity⁵ and molecular weight.⁴⁷ A key feature involved in reaching high power conversion efficiencies for P3HT:PCBM devices is thermal or solvent annealing.^{6,7} Annealing significantly improves the efficiencies of P3HT:PCBM devices up to an order of magnitude (highly dependent on the efficiency of the initial un-annealed device),⁴⁸ with observed increases in both the short-circuit current density J_{sc} and the fill factor FF (see Fig. 1.18).⁴⁹ Morphology studies on films have revealed that the crystallinity of P3HT is increased upon thermal treatment^{46,50-52} due to the increased phase segregation of P3HT and PCBM, resulting in stronger interchain interactions⁵³ and enhanced hole mobility.⁵⁴

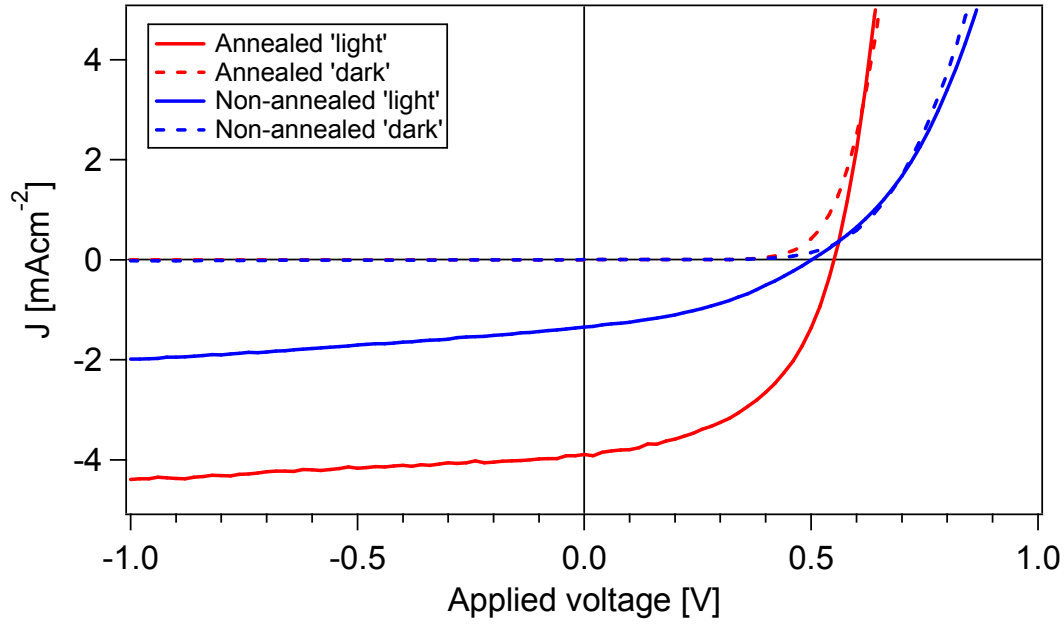


Fig. 1.18. J - V characteristics for an unannealed and an annealed (140°C for one hour) 1401:1 P3HT:PCBM BHJ device while under 50 mWcm⁻² AM1.5 simulated light (bold) and in the dark (dashed). For the un-annealed device, $V_{oc} = 0.54$ V, $J_{sc} = 3.9$ mAcm⁻², $FF = 51\%$ and $PCE = 0.53\%$, whereas, for the annealed device, $V_{oc} = 0.5$ V, $J_{sc} = 1.35$ mAcm⁻², $FF = 39\%$ and $PCE = 2.13\%$.

The improvement in the device efficiency upon annealing has most often been correlated with this increase in the charge carrier mobility,^{7,45,55,56} but also with the increase in crystallinity,⁶ vertical concentration gradients^{43,50} and the enhanced near-infrared optical absorption.⁵⁴ More recent optical transient absorption spectroscopy (TAS) studies have shown that the increase in the short-circuit current originates from a significant increase in the photogeneration yield upon annealing, which was correlated with an increase in the free energy of charge separation representing ΔE given in Section 1.8 (induced by a decrease in the ionisation energy of P3HT upon annealing, itself a result of the enhanced crystallinity).⁴⁹ Irrespective to the origin for the increased device performance for devices upon annealing, thermal treatment is an important procedure for the fabrication process, and thus for all the devices studied herein in this thesis a thermal annealing treatment was employed.

Figure 1.19 shows a schematic for the general device design for a P3HT:PCBM device consisting of a polystyrene sulphonate (PEDOT:PSS) coated indium tin oxide (ITO) glass substrate, a blend layer of P3HT:PCBM and an aluminium

electrode (Al), with a diagram showing its constituent energy levels (the values of which are found as varying in the literature).^{32,41}

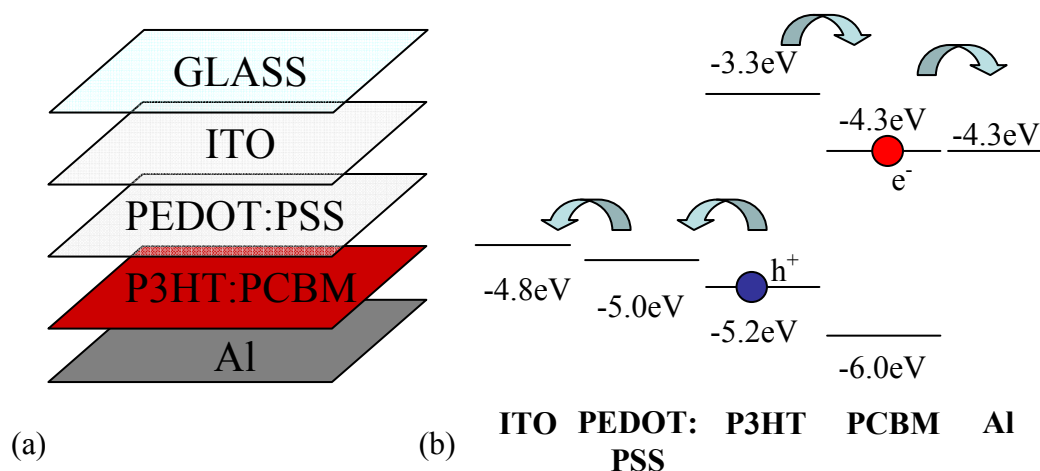


Fig. 1.19. (a) Schematic of the design of the P3HT:PCBM device studied herein and (b) an energy level diagram detailing the relevant energy levels.

1.11 Project objectives

The intention of this project is to investigate the physical processes which limit the performance of annealed P3HT:PCBM devices. To do this, a combination of numerical modelling and experimental studies are used. The overall objective will be to develop a simple model based on experimental measurements of physical quantities such as charge density in a standard device, able to recreate the $J-V$ curve, and so allowing an understanding of the origin of its behaviour. These studies are made on devices based on blends of P3HT:PCBM, but have been developed with the intention that they may be also applied to other organic based solar cells.

1.11.1 Numerical modelling

In this introduction it has been shown BHJ solar cells consist of a variety of different processes, with each of these processes resulting in different effects on device performance. To investigate the basic underlying processes involved in device function a simple drift-diffusion numerical model will be applied. The main focus of this work is to investigate the basic properties of the solar cell which are difficult to study experimentally, such as the spatial distributions of charge carrier densities,

electric field and current densities, and thus aid analyses of experimental J - V curves, and the effects of the possible loss mechanisms. We note it is not the intention to use this numerical model to provide a quantitative model of P3HT:PCBM J - V curves, but rather to explore the dependence of J - V curves upon specific processes and parameters.

1.11.2 Experimental studies

The remainder of this thesis, which represents the main part of this project, is based on developing a series of experimental procedures to determine values for physical quantities related to device function, such as charge densities and carrier lifetimes, for P3HT:PCBM solar cells while under operational conditions. By consideration of these determined values, we aim to investigate the charge carrier dynamics for these devices with the intention of trying to understand the mechanistic processes which limit device function in ‘standard’ P3HT:PCBM annealed devices such as bimolecular recombination and electric field dependent geminate recombination (see Section 3.1 for guidelines employed to determine ‘standard’ devices). By determining values for the physical properties of P3HT:PCBM devices, we intend on developing a relatively simple model able to recreate the J - V curves for P3HT based on the understanding of the loss processes in the device, in the absence of any fitting parameters.

Although these studies focus on investigating the specific properties of P3HT:PCBM devices, the techniques developed are designed with the intention to be applied for the study of organic photovoltaic devices in general.

An additional motivation for developing these direct measurements of the physical quantities which affect the behaviour of the J - V curve is to provide additional properties of solar cell operation other than J - V curves which should be reproducible by numerical models.



Chapter 2 Modelling bulk heterojunction solar cells using a drift-diffusion model

In this chapter, a simple drift-diffusion model is used to investigate bulk heterojunction (BHJ) solar cells. The BHJ device is treated as a single layer device, where microscopic properties of the blend, such as the electron and hole carrier mobilities, are included as device parameters. The aim of these studies, rather than attempt to model experimental data for a specific BHJ device, is to reach a basic understanding of the principles of solar cell operation. We assume non-selective electrodes, and so when charge carriers reach either electrode they are extracted immediately. Detailed studies are presented for a device under different incident light conditions. Initially, studies are made in the absence of bimolecular recombination, which allows us to investigate the role of alternative loss pathways. A bimolecular recombination process is then introduced, and its influence on the properties of the solar cell investigated.

When analysing the simulated current voltage (J - V) data, it is useful to consider a ‘corrected photocurrent’, obtained by subtracting the dark current from the photocurrent in order to remove the effects of carrier injection from the electrodes. These corrected photocurrent J - V curves are found to display symmetric behaviour over a wide range of incident light intensities, with a point of symmetry at an applied bias equal to the built-in potential. Despite the simplicity of the model, the general shape of the ‘corrected photocurrent’ is found to be in excellent agreement with recent experimental data collected by Ooi *et.al*⁵⁷ on devices based on blends of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO:PPV) and PCBM.

2.1 Background

A variety of techniques have been previously employed to model the behaviour of BHJ solar cells. These include parametric models based on an ‘equivalent circuit’ approach,^{38,58} microscopic numerical models based on Monte Carlo simulations,^{59,60} and drift-diffusion models.^{38,60-62} Studies of BHJ devices using the ‘equivalent circuit’ approach (see Section 1.9) have shown that it is possible to generate good fits for the current-voltage curves for organic BHJ devices, although these require modifications to be made to account for the light dependent shunt resistances in these devices.^{36,58} Numerical models based on Monte Carlo simulations provide a powerful numerical tool to describe the microscopic properties of solar cells and are particularly useful when including the effects of disorder or nano-morphology.^{59,60}

In this chapter we use a simple drift-diffusion model to investigate the basic properties of organic BHJ photovoltaic devices. In essence the behaviour of the solar cell is modelled using a system of coupled differential equations, which are solved to provide details concerning the device properties. This type of model allows one to study the spatial carrier and electric field distributions, potential loss mechanisms, and factors affecting the shape of the steady state J - V curve.

Organic solar cells can be modelled in a similar way to organic light emitting diodes (OLEDs), although an additional term must be included for photogeneration. Previous drift-diffusion modelling studies of organic LEDs differ in the boundary conditions which are employed, which are determined by the carrier injection and extraction processes at the electrodes.⁶³⁻⁶⁷ When modelling the behaviour of solar cells, it is common to initially model the diode properties of the solar cell in the dark, and then apply the same model to study solar cell behaviour while under incident illumination. For organic solar cells based on single layer⁶⁸ or bilayer devices,^{69,70} due to the relatively small exciton diffusion lengths of the photo-absorbing materials, when the device is illuminated, charge carrier generation has been considered to occur only near the electrode/semiconductor or the semiconductor/semiconductor interfaces.

When attempting to model BHJ devices, a common approach is to consider the blend in BHJ devices in terms of a single ‘virtual semiconductor’ (see Section 1.2), which has the LUMO energy level from the acceptor material and the HOMO energy level from the donor material.³¹ When the device is illuminated, generally either uniform or simple Beer Lambert absorption profiles are considered. However, this does not account for optical interference effects or the absorption profile properties of the blend structure. Optical models have been reported elsewhere where these effects are included.^{71,72} In BHJ devices, the blend morphology is controlled to achieve near-unity exciton dissociation, with reports of internal quantum efficiencies in P3HT:PCBM devices approaching unity,³⁰ and therefore many models, rather than include excitons explicitly, assign a simple probability for free carrier generation at the point of light absorption.^{62,73-75}

In this chapter, we describe a simple drift-diffusion model, which has been used to investigate the dynamics of BHJ solar cells. Similarly to previous modelling studies, the active layer of the BHJ devices is considered as a single layer ‘virtual semiconductor’ with a simple Beer Lambert absorption profile adopted. However, unlike previous models,^{61,62} we consider the ideal case where a fixed (electric field and spatially invariant) fraction of absorbed photons result in free carrier generation. We choose simple boundary conditions (injection by thermionic emission and perfect extraction at the counter electrodes) to ensure easy interpretation of the resultant simulations. We note that the focus of these studies is to reach a basic understanding of device function and not, like many of the previous models described, to reproduce experimental J - V data, which is dependent on already having an in-depth understanding of the physical processes which contribute to this J - V curve.

2.2 Model

A solar cell can be described using a one dimensional model in which the drift-diffusion equations are coupled to Gauss’s law. The time dependent continuity equations which describe the hole (p) and electron (n) distributions are given by

$$\partial_t p + \frac{1}{e} \partial_x J_p = G - R \quad (2.1)$$

$$\partial_t n - \frac{1}{e} \partial_x J_n = G - R \quad (2.2)$$

where t is time, x is position, ∂_t denotes $\partial/\partial t$, e is the electronic charge, G is the generation rate, R is the recombination rate, and J_p and J_n are the respective hole and electron current densities given by

$$J_p = e\mu_p \left(pE - \frac{k_B T}{e} \partial_x p \right) \quad (2.3)$$

$$J_n = e\mu_n \left(nE + \frac{k_B T}{e} \partial_x n \right) \quad (2.4)$$

where μ_p and μ_n are the respective hole and electron mobilities, E is the electric field, T is the temperature, k_B is Boltzmann's constant and Einstein's relationship⁷⁶ has been implicitly assumed, allowing us to rewrite the diffusivity D in terms of the mobility

$$D = \frac{k_B T}{e} \mu \quad (2.5)$$

In expressions (2.3) and (2.4), the first terms refer to the drift component of current density (which corresponds to the drift of charge carriers due to the local electric field) and the second terms refer to the diffusion component of current density (which corresponds to the diffusion of charge carriers due to charge carrier density gradients). The total current density J is equal to the sum of the hole and electron current densities

$$J = J_p + J_n \quad (2.6)$$

Gauss's law is then used to relate the electric field to the charge carrier densities

$$\frac{dE}{dx} = \frac{e}{\varepsilon} (p - n) \quad (2.7)$$

where $\varepsilon = \varepsilon_0 \varepsilon_r$ is the static dielectric constant, ε_0 is the permittivity of free space and ε_r is the relative permittivity.

2.2.1 Generation

We have previously introduced the photogeneration process for organic semiconductors in Section 1.2. Although, in organic semiconductors the absorption of light results in the formation of bound excitonic pairs rather than free carriers, BHJ are designed to ensure efficient conversion of the photogenerated excitons into free charge carriers. Hence in this study, rather than include the presence of excitons explicitly, we consider the simple case, in which a (electric field and spatially invariant) fixed fraction of absorbed photons result in free carrier generation. For simplicity, this fraction here is taken to be unity.

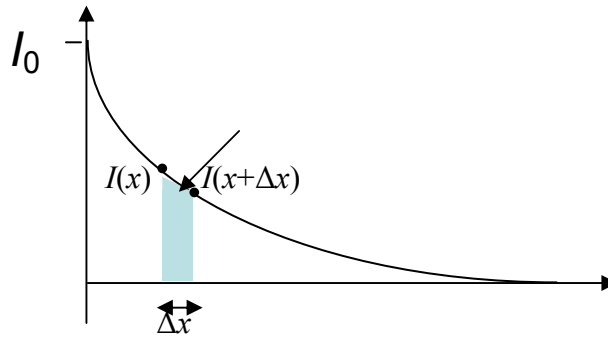


Fig. 2.1. The absorption profile of an incident light on a semiconductor.

In the following studies, a monochromatic light source is used to illuminate the device through a transparent anode. We consider the absorption profile to follow a simple Beer Lambert form

$$I(x) = I_0 \exp(-\alpha x) \quad (2.8)$$

where I is the light intensity at the position x , I_0 is the incident light intensity and α is the absorption coefficient. It is noted that the blend architecture can affect the absorption profile in BHJ devices⁷¹ but, such effects are neglected here as our intention is to obtain a generic understanding of device operation.

The number of photons per unit volume absorbed by the ‘virtual semiconductor’ can be determined from the decrease in light intensity with distance (see Fig. 2.1). Mathematically, this is described by

$$G = -\lim_{\Delta x \rightarrow 0} \left(\frac{I(x + \Delta x) - I(x)}{(x + \Delta x) - x} \right) = -\frac{dI}{dx} \quad (2.9)$$

Therefore, for the situation considered, the generation term is given by the (negative) spatial derivative of the Beer Lambert absorption profile given in Eqn. (2.8)

$$G = \alpha I_0 \exp(-\alpha x) \quad (2.10)$$

As organic solar cells are generally quite thin, typically 100-200nm, an additional generational component is required, to account for diffuse reflection of non-absorbed light at the opaque back cathode at $x = d$ (see Fig. 2.2), so we end up with:

$$G = \frac{dI}{dx} = \alpha I_0 [\exp(-\alpha x) + \exp(-2\alpha d) \exp(\alpha x)] \quad (2.11)$$

For simplicity we consider the ideal case where the anode is 100% transmissive and the cathode is 100% (diffusely) reflective.

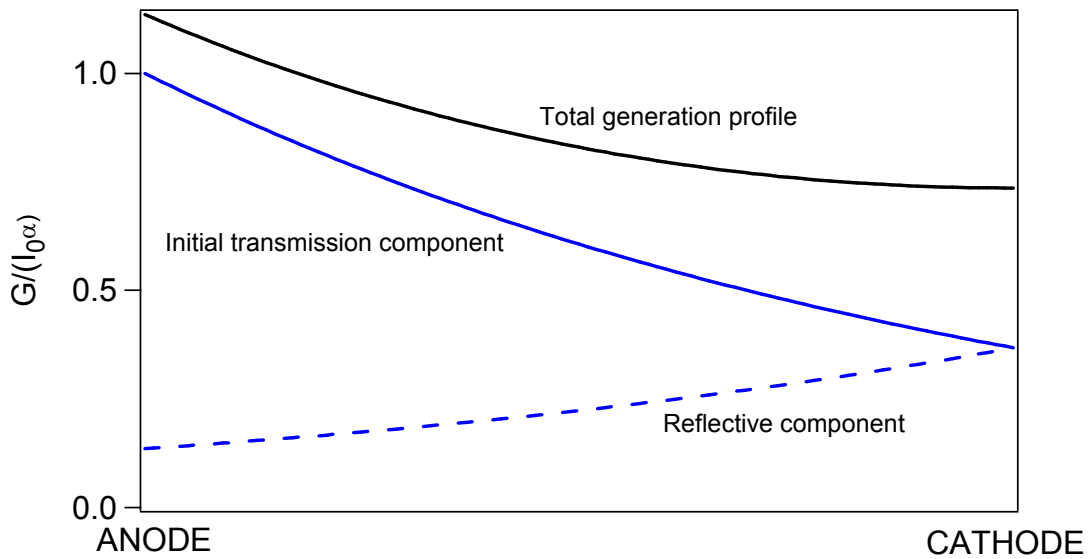


Fig. 2.2. A plot showing the contributions to charge generation from both the transmitted light and the diffuse reflection at the opaque cathode.

2.2.2 Recombination

An important loss process in organic semiconductors is bimolecular recombination R of free charge carriers which is proportional to the product of the hole and electron carrier densities with a corresponding bimolecular recombination coefficient k_{pn} :

$$R = k_{pn} pn \quad (2.12)$$

For pristine low mobility solids this bimolecular recombination process is frequently modelled by a Langevin description,⁷⁷ in which, free electrons and holes that come sufficiently close to each other will recombine if their Coulombic binding energy exceeds their thermal energy. In the Langevin model:

$$k_L = \frac{e(\mu_p + \mu_n)}{\varepsilon} \quad (2.13)$$

Recent experimental studies of bimolecular recombination in P3HT:PCBM blend devices have reported measurements of bimolecular recombination coefficients several orders of magnitude smaller than is predicted by using a Langevin bimolecular recombination coefficient.^{78,79}

In the case of blends, electrons and holes are confined to different phases, which means recombination of free electrons and holes occurs mainly across the donor/acceptor interface. Therefore, this process is likely to depend on the time it takes for charge carriers to reach these interfaces. This will be limited by the lowest mobility resulting in a modified expression for the Langevin recombination coefficient (k_L^{MOD}) in blends of the form:⁸⁰

$$k_L^{\text{MOD}} = \frac{e}{\langle \varepsilon \rangle} \min(\mu_p, \mu_n) \quad (2.14)$$

where $\langle \rangle$ denotes the spatial average. The studies presented here (where we consider equal electron and hole carrier mobilities) were based on the assumption of Langevin recombination process $k_{pn} = k_L$, but we also consider the recombination free case $k_{pn} = 0$. If $k_{pn} \ll k_L$, as reported for some blend devices,⁸¹ then device behaviour will be intermediate between these two cases.

2.2.3 Solving the equations

To investigate the steady state properties of the solar cell, the coupled differential equations (2.1), (2.2) and (2.7) are allowed to evolve in time from an arbitrary starting point until they reach steady state conditions, providing solutions for p , n and E . To

simplify the numeric procedure, we first rewrite Eqn. (2.7) as a first order time dependent equation in the following way

$$\frac{dE}{dt} = \frac{e}{\epsilon} \int_0^d \left(\frac{dp}{dt} - \frac{dn}{dt} \right) dx \quad (2.15)$$

to allow it to be easily integrated forward in time.

2.2.4 Boundary conditions

The boundary conditions have a critical influence on device behaviour. In the case of solar cells, the boundary conditions depend on the injection and extraction processes at the electrodes. Boundary conditions must be specified for the electric field and the electron and hole charge densities.

The injection processes from metals into disordered organic semiconductors are poorly understood. The density of charge carriers at the injecting electrodes are determined by the nature of the carrier injection processes which occur. Carrier injection is usually modelled using one of two processes, thermal activation over an energy barrier (which is known as thermionic emission) or tunnelling through.^{63-65,68,82}

Here we consider the simple case that the HOMO and energy level orbitals are matched to the work-functions of the electrodes enabling ohmic injection. The boundary conditions for the electric field are given by

$$E(0) = -\frac{\partial \phi(0)}{\partial x} \quad (2.16)$$

$$E(d) = -\frac{\partial \phi(d)}{\partial x} \quad (2.17)$$

where $E(0)$ and $\phi(0)$ describe the value of the electric field and electric potential in the semiconductor at the anode/semiconductor interface, and $E(d)$ and $\phi(d)$ describe the value of the electric field and electric potential in the semiconductor at the semiconductor/cathode interface respectively. At short-circuit, $\phi(0)$ and $\phi(d)$ are equal to the work-functions of the anode (ϕ_a) and cathode (ϕ_c) respectively.

As we assume the simple case where the work functions of the anode and cathode match the respective HOMO and LUMO energy levels of the single layer semiconductor, the effects of energy barriers on charge injection are not required, although we note the broader conclusions we draw are independent of the specific injection model employed.

We define the values of the hole and electron density on the semiconductor side of the semiconductor/anode and semiconductor/cathode interfaces as

$$p(0) = p_0 \quad (2.18)$$

$$n(d) = n_d \quad (2.19)$$

where p_0 denotes the hole density in the semiconductor at the anode and n_d denotes the electron density in the semiconductor at the cathode. In this model p_0 and n_d are user-defined electric field independent constants. The boundary conditions at the counter electrodes are given by:

$$p(d) = p(0) \exp\left(-\frac{eV_{\text{BI}}}{k_{\text{B}}T}\right) \quad (2.20)$$

$$n(0) = n(d) \exp\left(-\frac{eV_{\text{BI}}}{k_{\text{B}}T}\right) \quad (2.21)$$

where $eV_{\text{BI}} = \phi_{\text{a}} - \phi_{\text{c}}$ is the built-in potential determined by the difference between the work functions of the two electrodes. This formulation ensures the potential difference between the electrodes is V_{BI} under short-circuit conditions.

2.2.5 Simulation details

The algorithm to solve equations (2.1), (2.2) and (2.13) with corresponding boundary conditions (2.16-21) was written in Matlab code, using a robust Matlab built-in differential solver ODE15s. This code has been developed by members of the John de Mello research group at Imperial College. The algorithm is initialised using ‘dummy solutions’ for p , n and E at short-circuit, given by Boltzmann distributions and V_{BI}/d respectively. The time integrator is then allowed to evolve in time until the steady state solutions for p , n and E are found. A small electrical bias is then applied to the system, and the algorithm is re-initiated using the previous solutions as the new

‘dummy solutions’. By repeating this process over a range of applied biases we obtain solutions for p , n and E , which are then used to evaluate current densities using Eqn.s (2.3), (2.4) and (2.6), which allow the steady state J - V curves to be obtained.

2.2.6 Description of parameters used

In the studies presented here our intention is simply to obtain a basic understanding of the factors affecting device performance, and thus, we use matched device parameters for electrons and holes and the only asymmetry present is from the one-sided illumination. The carrier mobilities are considered to be equal and electric field independent.

The following values have been assumed:

Thickness	$d = 100 \text{ nm}$
Temperature	$T = 300 \text{ K}$
Dielectric constant	$\epsilon_r = 3.4$
Hole mobility	$\mu_p = 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$
Electron mobility	$\mu_n = 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$
Built in potential	$V_{BI} = 0.8 \text{ V}$
Hole density at the anode	$p_0 = 10^{15} \text{ cm}^{-3}$
Electron density at the cathode	$n_d = 10^{15} \text{ cm}^{-3}$
Illumination wavelength	$\lambda = 525 \text{ nm}$
Absorption coefficient	$\alpha = 10^5 \text{ cm}^{-1}$

2.3 Results

To verify the correctness of the numerical procedure we began by examining a situation for which exact analytical solutions are available. This was done by considering a device in the dark, under conditions of low carrier injection in the absence of recombination ($k_{\text{np}} = 0$).

We then investigated the effects of illuminating the device with a range of monochromatic light intensities in the range corresponding to $0 < I_0 < 1000$ Suns, again in the absence of bimolecular recombination. This provides useful information about non-recombination based losses in the device. The study is then extended to include the effect of bimolecular recombination. Lastly we consider the effects of charge carrier mobility on device function for a device operating under one sun conditions.

2.3.1 Solar cell properties in the dark with no recombination

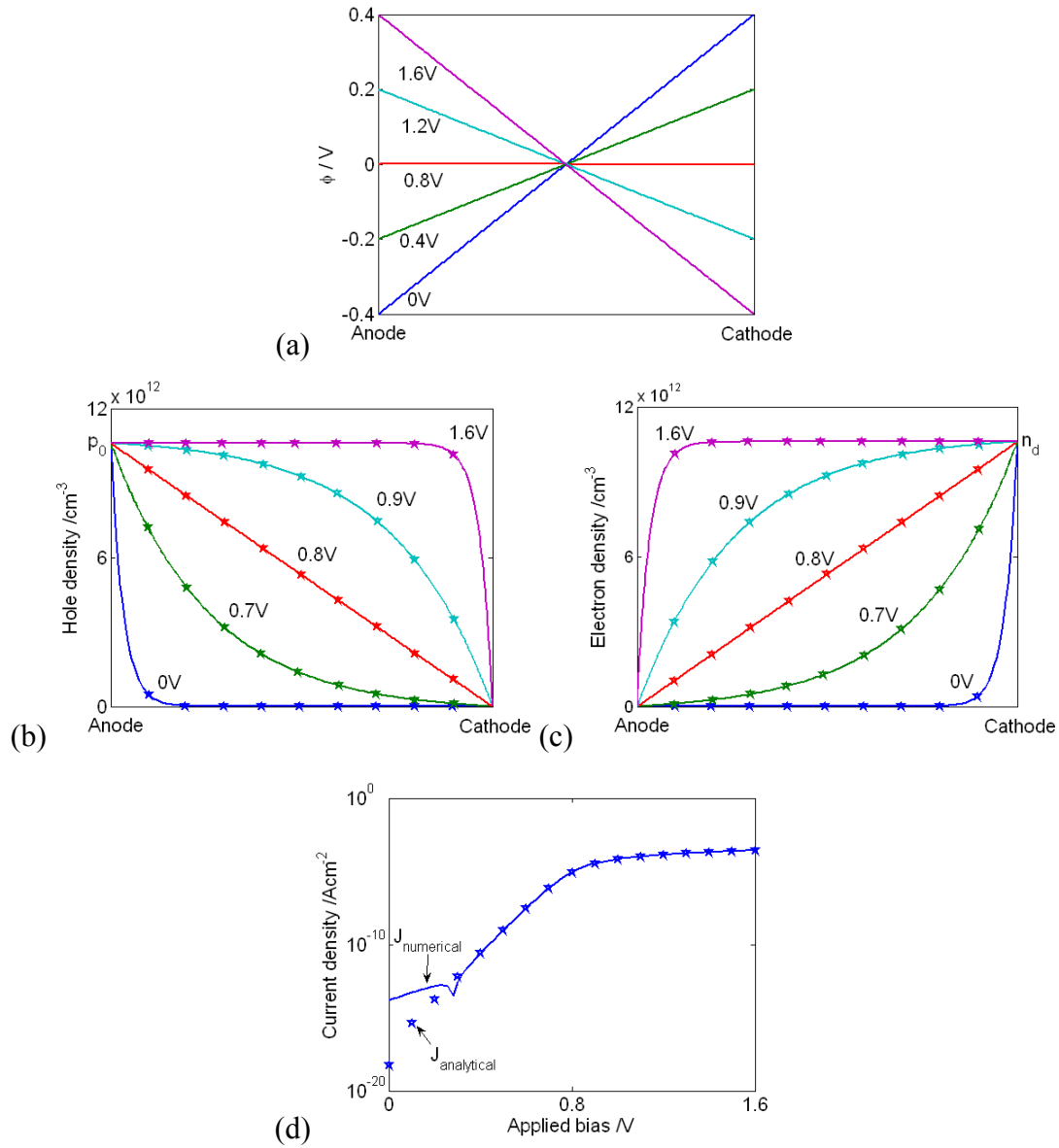


Fig. 2.3. Comparison of the analytical (markers) and numerical (solid lines) solutions for the steady state carrier distributions and current densities for a device in the dark, for low injection and no recombination. a) The electric potential profiles, b) hole and c) electron distributions, and d) current densities are all shown for different applied biases.

2.3.1.1 Testing the model

Previously, Malliaras has provided analytical solutions for the electron and hole carrier densities and the J - V curve for a single layer device in the dark assuming a constant electric field and no recombination:⁶⁸

$$n(x) = \frac{n_c - n_a}{e^{q_d} - 1} e^{qx} + \frac{n_a e^{q_d} - n_c}{e^{q_d} - 1} \quad (2.22)$$

$$p(x) = \frac{p_c - p_a}{e^{-q_d} - 1} e^{-qx} + \frac{p_a e^{-q_d} - p_c}{e^{-q_d} - 1} \quad (2.23)$$

$$J_{\text{dark}} = J_n + J_p = e \left(\frac{V_{\text{BI}} - V}{d} \right) \frac{(\mu_n n_c + \mu_p p_a) - (\mu_n n_a + \mu_p p_c) e^{q_d}}{e^{q_d} - 1} \quad (2.24)$$

where p_a and p_c are the respective hole densities at the anode and cathode, n_a and n_c are the respective electron densities at the anode and cathode, V is the applied bias, [$q = e(V_{\text{BI}} - V)/dk_B T$], d is the device thickness, e is the electronic charge, k_B is Boltzmann's constant, T is temperature and J_{dark} is the dark current. Figure 2.3 shows a comparison between the numerical and analytical solutions for a situation where the carrier densities at the electrodes ($p_0 = n_d = 10^{13} \text{ cm}^{-3}$) are sufficiently low to ensure that the electric field is constant throughout the device and that there is negligible recombination. The solutions for the hole and electron carrier densities are found to be in excellent agreement. The current densities also agree well for applied biases above 0.4V, but at lower biases the two sets of solutions diverge. This is due to the low current densities in this regime ($< \text{nAcm}^{-2}$), which means numerical errors dominate. We note that for ordinary solar illumination conditions currents of $\sim \text{mA/cm}^{-2}$ are obtained.

2.3.1.2 Discussion of distributions

The electric potential varies linearly with position indicating the electric field is constant due to the low charge density inside the device (see Fig. 2.3(a)). In the dark, the system modelled is completely symmetric, and hence, the hole and electron carrier densities are mirror images of each other, as shown in Fig. 2.3(b) and (c) at all applied biases. When the applied bias is equal to zero, the device is at equilibrium, thus the current density (in the dark) is equal to zero, where a balance exists between the drift and diffusion currents. The corresponding carrier distributions in the device take the form of approximately Boltzmann distributions. As the applied bias is increased the rates of charge injection at the two electrodes increases, and so, the charge density inside the device increases (see Fig. 2.3(b) and (c)). For applied biases smaller than the built-in potential, the current density is fairly small, but at higher biases it increases rapidly. This is because for applied biases below V_{BI} drift and diffusion

oppose each other, whereas, at applied biases above V_{BI} drift and diffusion are in the same direction.

In this section we have used relatively low charge injection values for $p_0 = n_d = 10^{13} \text{ cm}^{-3}$, allowing us to compare our numerical solutions with existing analytical solutions. This however leads to dark current densities (in the dark) far smaller than typically found in organic solar cells $\sim 0.01 \text{ mAcm}^{-2}$ compared to $\sim 1 \text{ mAcm}^{-2}$ (at $V=V_{BI}$). Thus, for the following studies we use larger values for $p_0 = n_d = 10^{15} \text{ cm}^{-3}$ (as shown in Section 2.2.6) to provide more reasonable values for $J_{\text{dark}} \sim 1 \text{ mAcm}^{-2}$ when $V=V_{BI}$, (the mobility values assumed in the simulations have previously been used when studying P3HT:PCBM devices).³¹

2.3.2 Study into the effects of incident light on the solar cell while recombination is absent

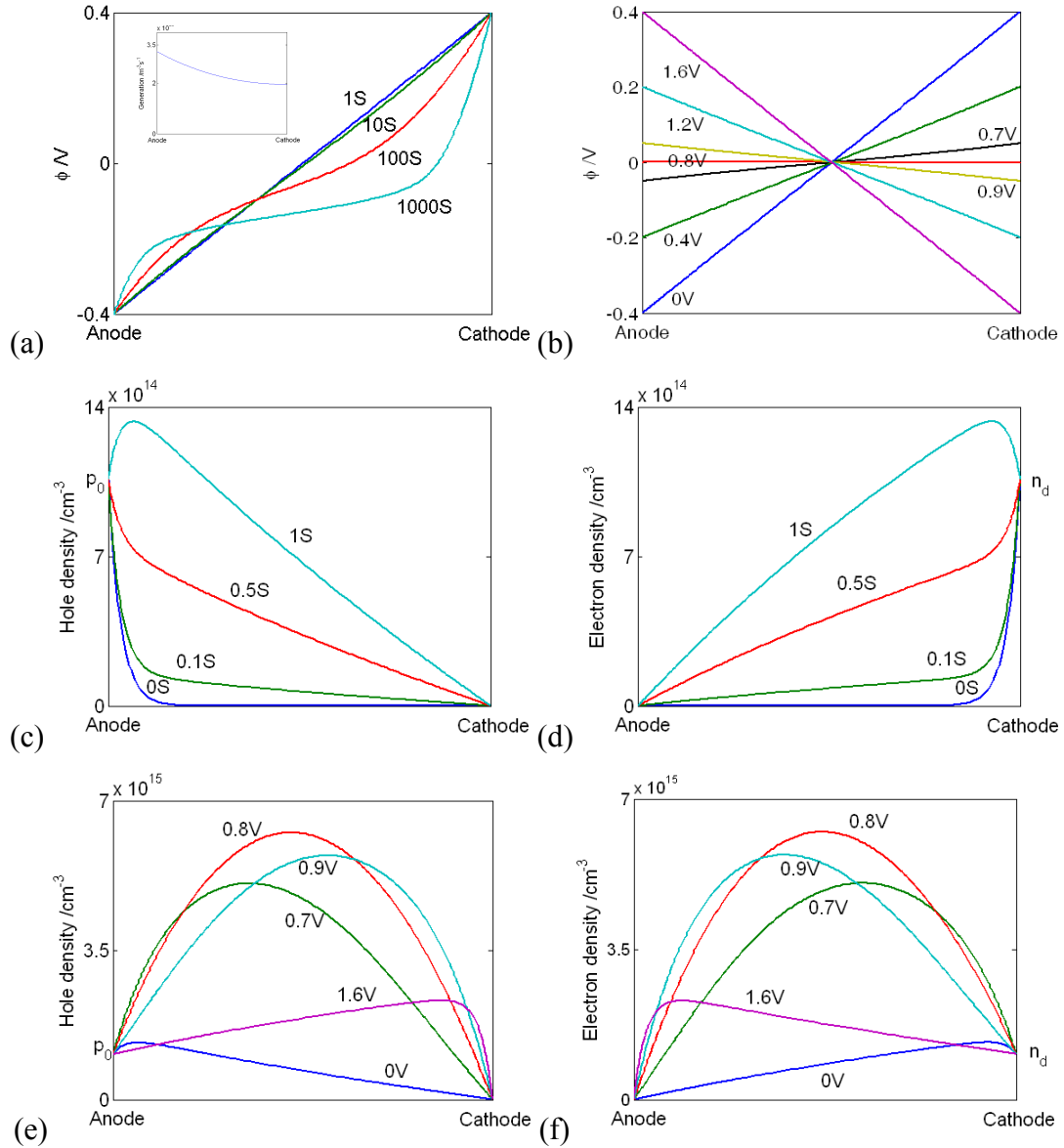


Fig. 2.4. Steady state solutions for the carrier distributions and electric profiles in a device while under light with no recombination. The electric potential profiles are shown a) at a variety of (high) illumination levels (with an inset displaying the generation profile employed) and b) for a 1 sun light at different applied biases. c) Short-circuit hole and d) electron distributions evolving from dark to 1 sun incident light conditions, and e) hole and f) electron distributions for applied biases in the range 0 - 1.6V under 1 sun light level are also shown.

In this section, we investigate the effects of illumination on the electric potential and carrier densities inside the device, again in the absence of bimolecular recombination. The generation profile employed in these studies is provided as an inset in Fig. 2.4(a).

We first consider the profiles of the electric potential for a device under illumination conditions. Similar to the case in the dark, under a 1 sun illumination level, the spatial profiles of the electric potential are largely linear, indicating that the electric field again is constant (see also Fig. 2.4(b)). However, as the light intensity is increased further, due to the low dielectric constant of the virtual semiconductor used, the profile of the electric potential changes as shown in Fig. 2.4(a), giving rise to a non-uniform electric field. We will see later that this effect is exacerbated for smaller carrier mobilities, which results in an increase in space charge build-up (see Section 2.3.5).

When the device is illuminated, photogenerated charge carriers are formed, which causes the total carrier concentrations in the device to increase. This is demonstrated in Fig. 2.4(c) and (d), where the evolution in $p(x)$ and $n(x)$ respectively is shown for a device under short-circuit conditions from dark to one sun incident light conditions. A small asymmetry is observed between the hole and electron distributions due to the asymmetric generation profile.

In Fig. 2.4(e) and (f), the effects of applied bias on the hole and electron distributions are shown for a device under a one sun light level. Increasing the applied bias up to V_{BI} causes the internal electric field in the device to reduce leading to a reduction in the drift driving force for charge collection, and hence, results in an increase in space charge within in the bulk of the device. When the applied bias equals the built-in potential of 0.8V, the hole and electron distributions become parabolic in shape. This behaviour can be explained analytically, assuming that the total carrier densities are dominated by photogenerated charge carriers, as opposed to injected charge carriers, and the generation profile is approximately flat across the device. We consider the case for p . When $V = V_{BI}$, the internal electric field $E = (V - V_{BI})/d$ is zero, and hence, the corresponding drift current density equals zero. Therefore, at steady state conditions $\partial p = 0$, and the hole continuity equation given in Eqn (2.1) reduces to:

$$\partial_x J_p = G = \mu_p \left(\frac{k_B T}{e} \partial_x^2 p \right) \quad (2.25)$$

Rearranging,

$$\partial_x^2 p = -G \frac{e}{k_B T \mu_p} = c_1 \quad (2.26)$$

where c_1 is a constant. By integrating Eqn. (2.26) w.r.t x twice, we obtain an expression for the hole distribution $p(x)$ when $V = V_{BI}$

$$p(x) = c_1 x^2 + c_2 x + c_3 \quad (2.27)$$

where c_2 and c_3 are constants of integration. By now applying the boundary conditions that all photogenerated carrier densities that reach the electrodes are immediately extracted into the external circuit ($p(0) = p(d) = n(0) = n(d) = 0$), then $c_3 = 0$ and $c_2 = -c_1 d$, and so, Eqn. (2.27) becomes

$$p = -G \frac{e}{k_B T \mu_p} x(x - d) \quad (2.28)$$

This is a parabola peaked at $x = d/2$ and broadly matches in shape the numerical solution. A similar analysis applies to the electron distribution also.

As the applied bias is increased above the built-in potential, the charge density inside the device reduces, due to the increasing field strength. This is true, as long as the injected carriers are outnumbered by photogenerated carriers.

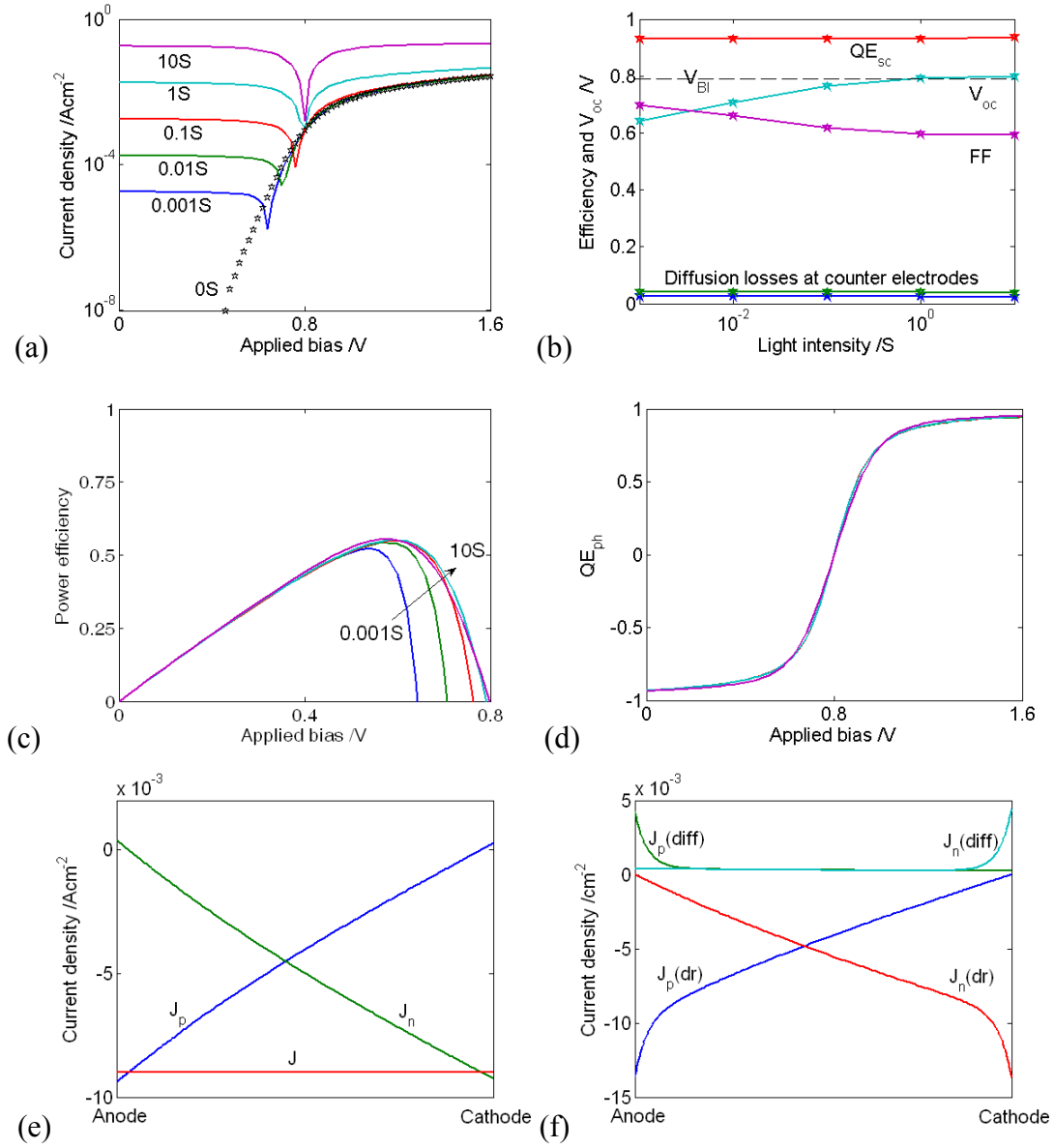


Fig. 2.5. J - V characteristics for a solar cell under illumination with no recombination for light intensities in the range 0.001 – 10 Suns. a) J - V curves b) FF , QE_{sc} , V_{oc} and leakage losses as a function of light intensity, plots of c) power (JV) d) QE_{ph} as a function of applied bias, e) hole and electron current densities and f) their corresponding drift and diffusion components are all shown.

Using the steady state solutions for p , n and E , J - V curves under illumination can be determined (see Fig. 2.5(a)). The dark current density is also shown, denoted by markers. As previously described in Section 1.7, the key figures of merit for J - V curves are the open-circuit voltage V_{oc} , the quantum efficiency at short-circuit $QE_{sc} = (J_{sc}/J_{max})$ (where J_{max} corresponds to the maximum photogenerated current density that is possible if all incident photons absorbed are converted into electrical current,

and J_{sc} is the short-circuit current density), and fill factor FF . These are shown in Fig. 2.5(b) as a function of incident light intensity. As the light intensity is increased, V_{oc} increases until it reaches a maximum value equal to V_{BI} ($= 0.8V$) which is its theoretical upper limit. The fill factor initially reduces but then also saturates. QE_{sc} is independent of light intensity but is determined to be smaller than 100%. The reasons for this behaviour are discussed below.

2.3.2.1 ‘Corrected Photocurrent’

A useful method to analyse J - V characteristics is to examine the ‘corrected photocurrent’.⁵⁷ The current J_{light} generated by a solar cell under illumination can be treated as the sum of a photogenerated current J_{ph} due to the flux of incident photons and a bias-induced current J_{Vphoto} due to the photovoltage V_{photo} across the electrodes:

$$J_{light} = J_{ph} + J_{Vphoto} \quad (2.29)$$

Assuming the rate of carrier injection is unaffected by the presence of photogenerated carriers, J_{Vphoto} will equal the current measured when the same device in the dark is subjected to an applied bias $V = V_{photo}$. J_{Vphoto} therefore equals the dark current J_{dark} and we can write:

$$J_{light} = J_{ph} + J_{dark} \quad (2.30)$$

Hence, J_{ph} can be determined by subtracting the dark current from the measured photocurrent.

$$J_{ph} = J_{light} - J_{dark} \quad (2.31)$$

The corrected photocurrent J_{ph} can be decomposed into drift and diffusion components for the respective photogenerated hole and electron current densities, $J_{ph,p}$ and $J_{ph,n}$

$$J_{ph} = J_{ph,p} + J_{ph,n} = e \left((\mu_p p_{ph} + \mu_n n_{ph}) E + \frac{k_B T}{e} (-\mu_p \partial_x p_{ph} + \mu_n \partial_x n_{ph}) \right) \quad (2.32)$$

where p_{ph} and n_{ph} represent the photogenerated hole and electron carrier concentrations respectively under steady state conditions. At steady state J_{ph} is spatially independent and so is constant throughout the device. Therefore, by considering the spatial average of J_{ph} , we can write

$$\langle J_{\text{ph}} \rangle = J_{\text{ph}} = e \left((\mu_p \langle p_{\text{ph}} \rangle + \mu_n \langle n_{\text{ph}} \rangle) E + \frac{k_B T}{e} \left(-\mu_p \langle \partial_x p_{\text{ph}} \rangle + \mu_n \langle \partial_x n_{\text{ph}} \rangle \right) \right) \quad (2.33)$$

where $\langle \rangle$ signifies the spatial average and we have assumed we are operating in the constant field regime. Over the range $a < x < b$ the spatial average for a spatial derivative is given by

$$\langle \partial_x f \rangle = \frac{f(b) - f(a)}{b - a} \quad (2.34)$$

Hence, we obtain

$$J_{\text{ph}} = e \left((\mu_p \langle p_{\text{ph}} \rangle + \mu_n \langle n_{\text{ph}} \rangle) E + \frac{k_B T}{e} \left(-\mu_p \left(\frac{p_{\text{ph}}(d) - p_{\text{ph}}(0)}{d} \right) + \mu_n \left(\frac{n_{\text{ph}}(d) - n_{\text{ph}}(0)}{d} \right) \right) \right) \quad (2.35)$$

In the model we assume non-selective charge collection at the electrodes, and so, when photogenerated holes or electrons carriers reach either electrode they are immediately extracted into the external circuit. Therefore, at the electrodes the photogenerated carrier concentrations fall to zero: $p_{\text{ph}}(0) = p_{\text{ph}}(d) = n_{\text{ph}}(0) = n_{\text{ph}}(d) = 0$. Substituting these values into Eqn. (2.35), the first term drops out and we obtain

$$J_{\text{ph}} = e (\mu_p \langle p_{\text{ph}} \rangle + \mu_n \langle n_{\text{ph}} \rangle) E \quad (2.36)$$

In the voltage range $0 \leq V \leq V_{\text{BI}}$, the electric field $E = (V - V_{\text{BI}})/d$ is negative, whereas μ , p and n by definition take positive values, and so J_{ph} is negative and is largest at short-circuit where $E = V_{\text{BI}}/d$. When the applied bias equals the built-in potential, the electric field equals zero, hence J_{ph} equals 0. Due to the non-selective electrodes, the charge densities $\langle p_{\text{ph}} \rangle$ and $\langle n_{\text{ph}} \rangle$ should be approximately even functions of the electric field since they are determined by the averaged dwell times of the electron and holes in the device, which vary inversely with the drift speed and therefore electric field. The bracketed term in Eqn. (2.36) is also an even function. Therefore, as the electric field $E = (V - V_{\text{BI}})/d$ is an odd function, this results in J_{ph} must also be odd with respect to the electric field, J_{ph} must therefore be an anti-symmetric function of the applied bias with a symmetry point at $(V_{\text{BI}}, 0)$.⁵⁷

In Fig. 2.5(d), plots of the internal quantum efficiency corrected photocurrent J - V curves ($J_{\text{ph}}-V$) are shown (corresponding to $QE_{\text{ph}}(V) = (J_{\text{ph}}(V)/J_{\text{max}})$). It is apparent that

at all light intensities studied, the numerically simulated $J_{\text{ph}} - V$ curves have a symmetric profile with a symmetry point $(V_{\text{BI}}, 0)$ as predicted above. By removing the effects of J_{dark} , an alternative form of the fill factor can be defined on the shape of the $J_{\text{ph}} - V$ curve. For light intensities ≤ 10 suns, these $J_{\text{ph}} - V$ curves overlay each other indicating that the ‘corrected’ fill factor is independent of incident light intensity. The change in the ordinary fill factor with increasing light intensity (in this range) is attributable to changes in the relative importance of the dark current.

2.3.2.2 Light intensity dependence of V_{oc}

For each of the $J_{\text{ph}} - V$ curves, J_{ph} equals zero when the applied bias equals V_{BI} . This indicates the open-circuit voltage would reach a limiting value of V_{BI} in the absence of the dark current density. The effect of J_{dark} is to reduce the open-circuit voltage V_{oc} (which occurs when $J_{\text{ph}} = -J_{\text{dark}}$) to a value less than V_{BI} . As the light intensity is reduced, J_{ph} decreases, and so requires a smaller compensatory dark current density to null the corrected photocurrent causing the V_{oc} to shift to lower voltages as seen in Fig. 2.5(b). This leads to the conclusion that J_{dark} should be considered as a loss mechanism, which will limit the device efficiency.

2.3.2.3 Origin for $QE_{\text{sc}} < 100\%$

Under short-circuit conditions the quantum efficiency is less than 100%, i.e. $J_{\text{sc}} < J_{\text{max}}$, indicating a loss in current. However, as these studies are performed in the absence of bimolecular recombination, and J_{dark} equals zero under short-circuit conditions, this indicates that an additional loss pathway must exist. To understand where this loss in current originates from we consider the individual components of J_{sc} , given by the hole and electron current densities J_{p} and J_{n} respectively (see Fig. 2.5(e)). At both electrodes we observe a positive current component, indicating there is a loss in current density at the electrodes. The two currents can be further decomposed into individual drift and diffusion components, as shown in Fig. 2.5(f). It is evident that diffusion drives electrons and holes out of both electrodes causing some charge carriers to be extracted by the wrong electrodes. As shown in Fig. 2.5(b), these diffusion losses (referred hereafter as ‘leakage’ losses) are proportional to the light intensity, which explains why QE_{sc} does not vary with light intensity.

These leakage losses explain the shape of the $J_{\text{ph}}-V$ curves and why their fill factor is less than 100%. The internal electric field in the devices gets weaker as the applied bias is increased towards the built-in potential and so is less effective at driving charges to the correct electrodes. This leads to increased leakage currents resulting in the decrease in the quantum efficiency with increasing applied bias ($\leq V_{\text{BI}}$).

2.3.2.4 Light intensity dependence of fill factor

The fill factor of the (non-corrected) $J-V$ curve compares the ratio of the peak power PP with the maximum power the device could produce on the base of its values for J_{sc} and V_{oc} . To obtain an efficient solar cell, a high fill factor is required, but this is not in itself a sufficient condition as large losses in efficiency can arise due to low short-circuit currents or open-circuit voltages. The fill factor depends on a range of parameters, peak power, J_{dark} , J_{sc} and V_{oc} . Thus, to understand its behaviour as a function of light intensity, it is useful to consider each of these components individually. We have already considered the light intensity dependence of both J_{sc} (in terms of QE_{sc}) and V_{oc} . Figure 2.5(c) shows a further plot of the electrical power (JV) as a function of applied bias. As the light intensity is increased, the peak power initially increases, but then saturates at higher light intensities. As indicated above, this can be explained due to the behaviour of the $J_{\text{ph}}-V$ curve, and how it compares in magnitude to the dark current. At higher light intensities, the shape of the $J-V$ curve is predominantly determined by the shape of the $J_{\text{ph}}-V$ curve and is only weakly influenced by the comparatively small dark current. Even at high light intensities the fill factor is smaller than 100% due to the diminishing value of J_{ph} with applied voltage resulting from increased leakage losses.

In the above discussion the properties of a solar cell have been studied in the absence of bimolecular recombination, highlighting that there are two additional loss mechanisms that must be taken into account when considering device operation, the dark current J_{dark} and carrier leakage at the ‘wrong’ electrodes. The effects of bimolecular recombination will now be considered, based on similar studies of solar cell behaviour in the dark and under illumination.

2.3.3 Solar cell studies under dark conditions with recombination

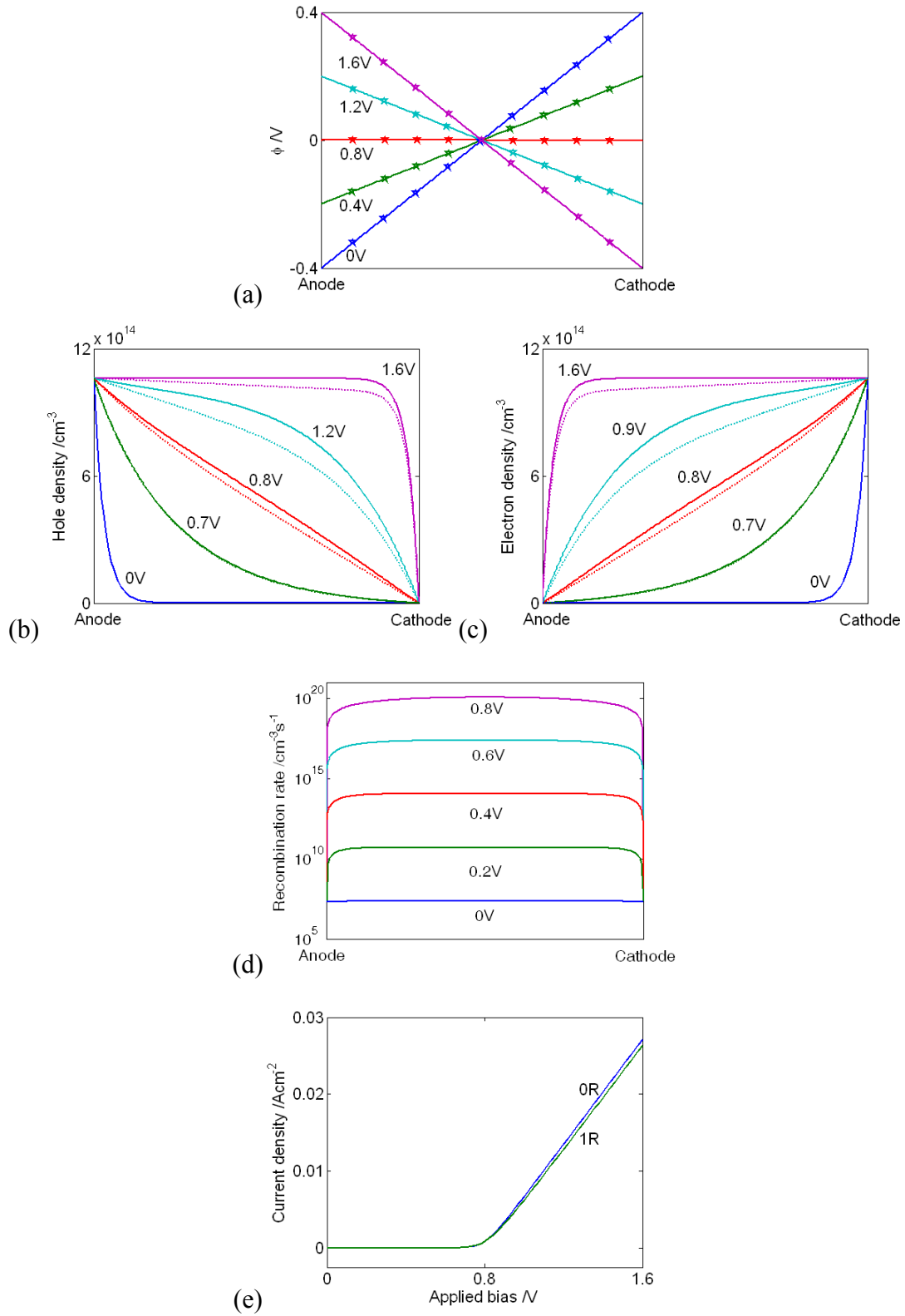


Fig. 2.6. Device properties in the dark showing the a) electric potential profiles, b) hole and c) electron distributions, d) recombination densities with (lines) and without (dashed or markers) recombination for various applied biases, and e) a comparison between J - V curves with and without recombination.

As described in Section 2.2.2, we consider the bimolecular recombination process to follow a Langevin description with a corresponding bimolecular recombination coefficient $k_L = e (\mu_p + \mu_n) / \varepsilon \sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ using $\mu_p = \mu_n = 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Figure 2.6(a) shows a comparison of the electric potential profiles for a device in the dark with (solid lines) and without (markers) recombination and it is apparent that there is no significant change in the electric potential due to recombination. Under short-conditions the inclusion of bimolecular recombination has a negligible influence on the carrier distributions, shown in Fig. 2.6(b) and (c). However, at higher applied biases, recombination leads to a discernible reduction in the carrier densities compared to the recombination free case. Figure 2.6(d) further highlights the behaviour of recombination with increasing applied bias, which increases due to the increasing charge densities present in the bulk. This results in a reduction in the steady state current density, as shown in Fig. 2.6(e).

2.3.4 Effects of recombination on the solar cells in the light

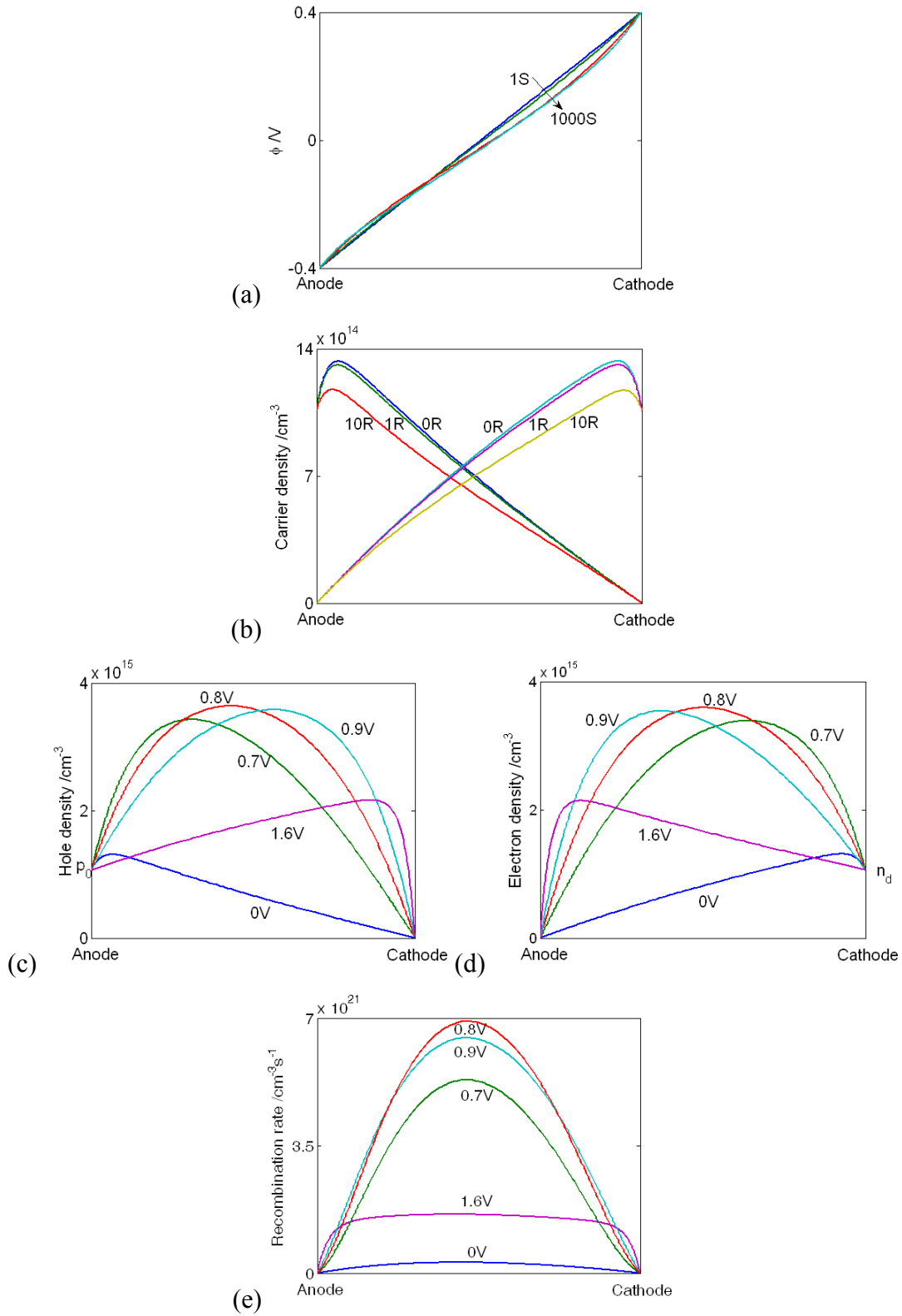


Fig. 2.7. Steady state distributions for a device in the light with recombination, showing a) the electric potential profile under high light intensities, b) short-circuit hole and electron distributions when $k_{\text{pn}}=0$, k_{L} and $10k_{\text{L}}$, and c) hole, d) electron and e) recombination distributions under various applied biases.

Similar to the recombination-free case, the density of photogenerated charge densities is insufficient to affect the internal electric field and so the potential profiles until the incident light intensity becomes excessively high (see Fig. 2.7(a)). Figure 2.7(b) shows a comparison of the hole and electron distributions for a device under short-circuit conditions while under one sun illumination for 3 different situations: 1) $k_{\text{pn}} = 0$, 2) $k_{\text{pn}} = k_{\text{L}}$ and 3) $k_{\text{pn}} = 10 k_{\text{L}}$ (i.e. a process in which the recombination rate is ten times larger). For ‘normal’ Langevin recombination the additional recombination-induced losses under one sun illumination at short-circuit are relatively small. If the light intensity is increased further, then the effects of bimolecular recombination become more evident. It is apparent that bimolecular recombination causes a reduction in the amount of charge carriers present in the device, and hence, leads to much weaker changes in the internal electric potential compared to the recombination free situation.

As with the recombination free case, the carrier densities within the bulk of device increase as the applied bias is increased up to the built-in potential (see Fig. 2.7(c) and (d)). This results in increased bimolecular recombination losses as the V_{BI} is approached (see Fig. 2.7(e)). For applied biases larger than the built-in potential, the rate of charge collection increases due to an increase in the electric field which drives the charge to the electrodes, leading to recombination losses to reduce.

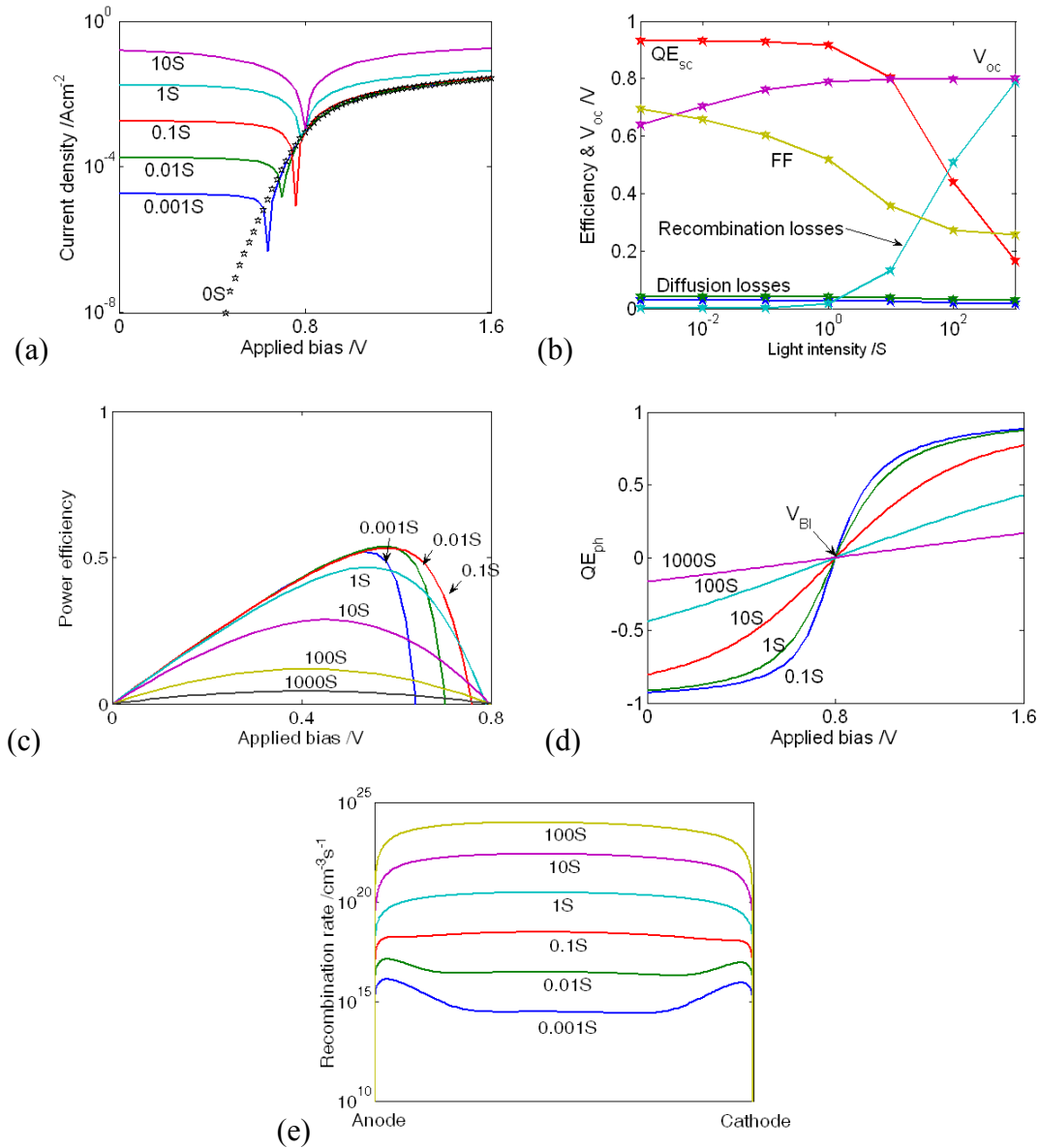


Fig. 2.8. $J-V$ characteristics for a solar cell under illumination in the presence of recombination ranging from dark to 1000 suns. a) $J-V$ curves b) FF , QE_{sc} , V_{oc} , diffusion losses and recombination losses for as a function of light intensity, c) a plot of $PP/V_{BI}J_{max}$ against applied bias, d) QE_{ph} against applied bias and e) recombination rates at short-circuit conditions.

Figure 2.8(b) shows how the fill factor, the quantum efficiency at short-circuit, open-circuit voltage and short-circuit leakage losses vary with light intensity under the assumption of Langevin recombination. Recombination leads to reductions in both the fill factor and QE_{sc} as the light intensity is increased, but has only a marginal effect on the open-circuit voltage and the leakage losses under short-circuit conditions. The reduction in the fill factor as the light intensity is increased originates primarily from

the dependence of the corrected photocurrent on bimolecular recombination shown in Fig. 2.8(e) (except at low light intensities where the fill factor is strongly influenced by J_{dark}). As the light intensity increases, bimolecular recombination losses increase, which leads to a large reduction in overall quantum efficiency. We note however that, irrespective of these bimolecular recombination losses, the symmetric form of these $J^{\text{ph}}-V$ curves is conserved with a symmetry point at $(V_{\text{BI}}, 0)$.

2.3.5 Studying the effects of carrier mobility on the properties of a solar cell

In this section we investigate the effect of carrier mobility on device performance, assuming Langevin recombination in which the bimolecular recombination coefficient is proportional to carrier mobility and still assuming matched mobilities.

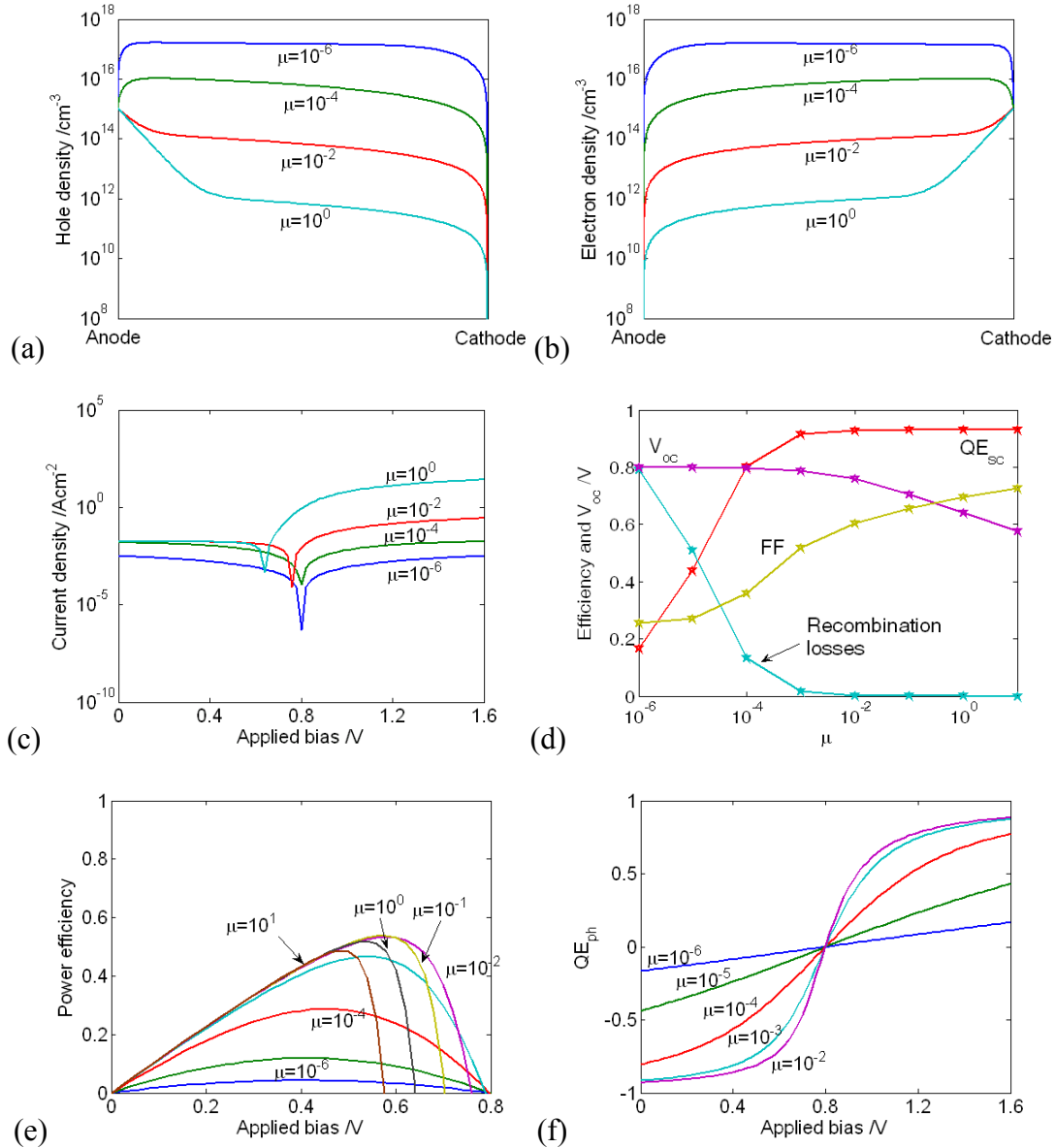


Fig. 2.9. Studying device behaviour for different matched charge carrier mobilities ranging from 10^{-6} - 10 cm²V⁻¹s⁻¹, when bimolecular recombination effects are included. In a) and b) the hole and electron carrier distributions are shown for different carrier mobilities (matched) respectively. c) and d) show the J - V curves and the key features thereof respectively. In e) and f) plots of the power against applied bias and the J_{ph} - V curves are shown for different carrier mobilities.

As the carrier mobilities are increased, the charge carrier densities inside the device reduce, as shown in Fig. 2.9(a) and (b), due to charges being swept more quickly from the device. Figures 2.9(c) and (d) show the J - V characteristics as a function of carrier mobility while under a 1 sun illumination level. As the carrier mobility is increased the fill factor increases, whereas the V_{oc} decreases. The reduction in V_{oc} is due to the increased dark current (which is proportional to the carrier mobility). The optimal mobility is one that it is just high enough to ensure that the charge carriers are swept rapidly to their parent electrode (without having the opportunity to recombine) without causing the dark current to become unnecessarily high. Since the fill factor increases with increasing carrier mobility, device performance will initially improve, until the carrier mobility is so large that the reduction in V_{oc} outweighs any further improvements in J_{ph} . In the system modelled we find the optimum carrier mobility to be $\sim 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (see Fig. 2.9(e)).

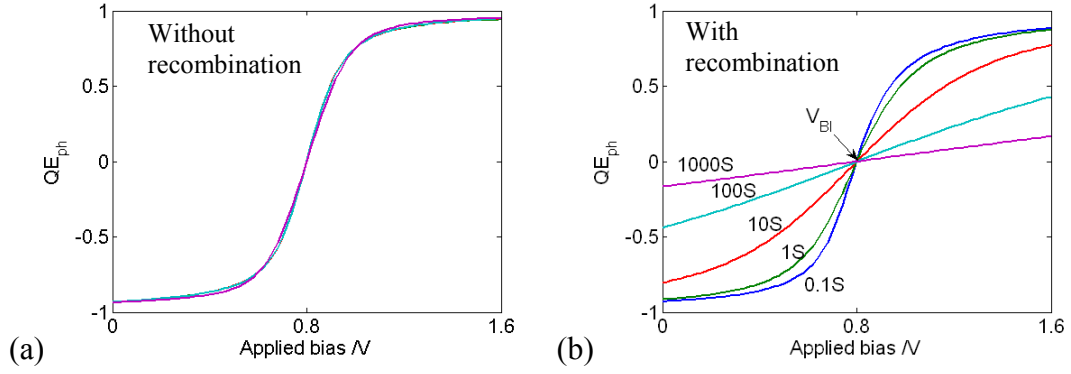
2.3.6 Comparison of numerical and with experimental studies of the ‘Corrected Photocurrent’

The above modelling studies were undertaken to provide a conceptual understanding of device operation in an idealised single layer solar cell. As mentioned previously, the focus of these studies was to arrive at a basic understanding of the main physical processes involved in device function, and not to model the behaviour of a specific BHJ device. As these studies were made in the absence of experimental data, without experimental verification, it is difficult to carry forward these findings to real BHJ devices. In this section, we compare the behaviour of our modelled J_{ph} - V curves with recently performed experimental studies of the ‘corrected photocurrent’ in two common donor/ acceptor systems: MDMO:PPV/PCBM and P3HT:PCBM solar cells.

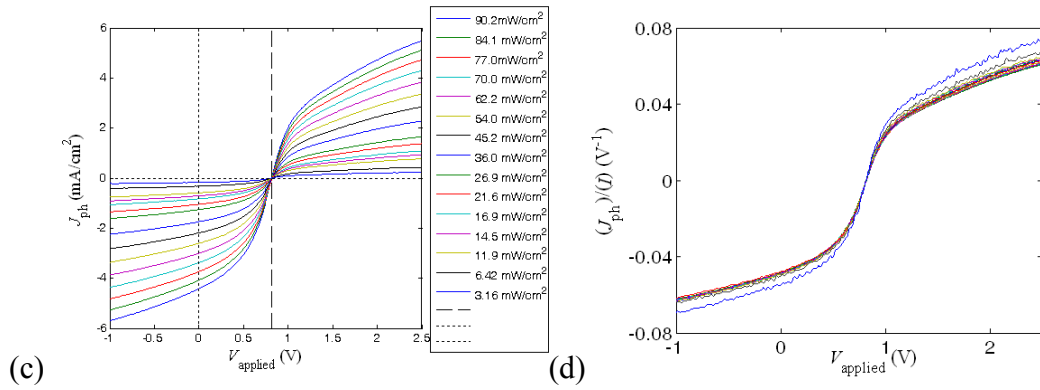
In Section 2.3.2.1, the ‘corrected photocurrent’ concept was introduced and was shown to be a particularly useful tool for understanding device behaviour. For the single layer device the corrected photocurrent takes a symmetric form with a symmetry point at the built-in potential where $J_{ph} = 0$ (see Fig. 2.10(b)). The normalised (i.e. internal quantum efficiency) J_{ph} - V curves overlap each other over a large range of light intensities (≤ 10 suns) when bimolecular recombination is

negligible. When bimolecular recombination is important however, this is no longer true, and the normalised $J_{\text{ph}}-V$ curve changes shape. Hence, studying experimental $J_{\text{ph}}-V$ curves as a function of light intensity offers a way to study bimolecular recombination effects, assessing the extent to which bimolecular recombination influences device function. This notion has prompted the experimental study of BHJ devices by using this corrected photocurrent procedure. This work has been performed by Ooi,⁵⁷ who has developed an AC temperature controlled setup to measure the corrected photocurrent experimentally and we gratefully acknowledge his contribution of the experimental data presented in this section. Although this was not the first time $J_{\text{ph}}-V$ curves had been studied experimentally,^{75,83} Ooi took care in his studies to eliminate a number of experimental artefacts that had rendered many previous studies invalid. In particular he was careful to measure the dark and light currents at the same temperature eliminating an important cause of systematic error.

MODEL



MDMO:PPV/PCBM



P3HT:PCBM

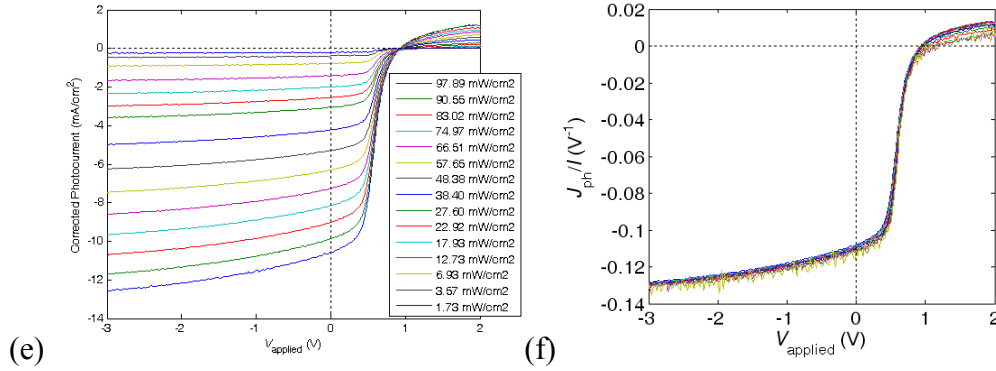


Fig. 2.10. Comparison of our numerical simulated J_{ph} - V curves with experimental studies performed by Ooi on MDMO:PPV/PCBM and P3HT:PCBM blend devices. In a) and b) the numerically modelled corrected photocurrent are given for the single layer system modelled without and with the presence of bimolecular recombination effects respectively. c) and d) show the unnormalised and normalised (with light intensity) J_{ph} - V curves as a function of light intensity for MDMO:PPV/PCBM devices. And e) and f) show the unnormalised and normalised J_{ph} - V curves as a function of light intensity for P3HT:PCBM devices.

Figure 2.10 shows experimental J_{ph} - V curves for a BHJ device based on a blend of MDMO:PPV and PCBM, together with the numerically generated J_{ph} - V curves presented earlier. There is excellent qualitative agreement between the analytical and experimental data with both exhibiting a symmetric profile centred about $J_{ph}=0$. This suggests that this symmetry point in the experimental data occurs when the applied bias is equal to the built-in potential. It also suggests that the MDMO:PPV/PCBM blend behaves like the single layer ‘virtual semiconductor’ of our numerical analysis, in which there is no selectivity for charge collection at either electrode. Figures 2.10(a) and (b) show the respective unnormalised and normalised J_{ph} - V curves obtained from the numerical treatment. There is a small reduction in quantum efficiency as the light intensity is increased towards the 1 sun level which indicates that there are some small losses due to bimolecular recombination.

In the case of P3HT:PCBM devices (and for some other BHJ devices), the profile of the corrected photocurrent differs materially from the MDMO:PPV :PCBM devices. Typical corrected photocurrent data for P3HT:PCBM devices is given in Fig. 2.10(e-f). Although the J_{ph} - V curves follow a symmetric form their point of symmetry occurs for a negative current and not when $J_{ph} = 0$, as predicted by our numerical treatment and seen for MDMO-PPV:PCBM. To rationalise this different behaviour, we consider again the expression for the corrected photocurrent in terms of the spatially averaged drift and diffusion current components is considered (see Section 2.3.2.1).

$$J_{ph} = e \left((\mu_p \langle p_{ph} \rangle + \mu_n \langle n_{ph} \rangle) E + \frac{k_B T}{e} \left(-\mu_p \left(\frac{p_{ph}(d) - p_{ph}(0)}{d} \right) + \mu_n \left(\frac{n_{ph}(d) - n_{ph}(0)}{d} \right) \right) \right) \quad (2.37)$$

We previously assumed there is no selectivity for electron and hole extraction at either electrode, and thus, all photogenerated charges are immediately extracted on reaching an electrode. In this situation the spatially averaged diffusion current terms equal zero, and so, the expression of the corrected photocurrent is dependent only on the spatially averaged contributions of the drift current. This is a reasonable model for a single layer device. For device systems with selective electrodes the diffusion terms in Eqn. (2.37) take non-zero values. However, Eqn.(2.37) still predicts J_{ph} - V curve to be approximately symmetric but, due to the non-zero diffusion term, the point of symmetry would be translated to negative currents, in good agreement with

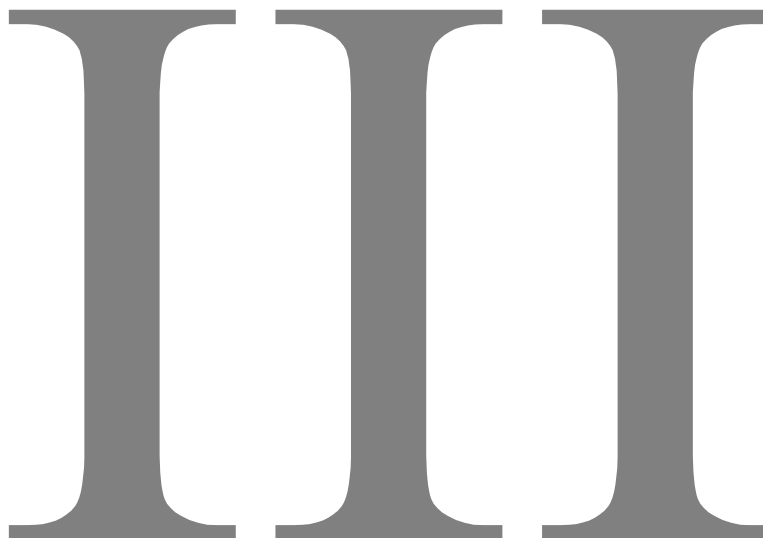
experimental $J_{\text{ph}}-V$ data for P3HT:PCBM devices. Therefore, this suggests that for P3HT:PCBM devices, the blend morphology promotes charge selectivity at the electrodes. One possible explanation for selective electrodes for these devices is that at the ITO anode and/or the Al cathode, there is a pure phase layer of pristine P3HT or PCBM respectively. This would result in charge carriers being prevented from reaching their wrong collecting electrodes, thus reducing the leakage losses. This is consistent with previous reports of vertical separation in these devices which leads to thin layers of P3HT and PCBM forming close to the anode and cathode respectively.^{43,50}

If we now consider the intensity dependence of the corrected photocurrent, the normalised (by light intensity) $J_{\text{ph}}-V$ curves overlay each other for P3HT:PCBM devices, but vary slightly with increasing light intensity for MDMO:PPV/PCBM devices. This suggests for P3HT:PCBM devices there is no bimolecular recombination, whereas, for MDMO:PPV/PCBM devices, there is a small influence due to bimolecular recombination. This is in good agreement with previous experimental studies of bimolecular recombination by Pivrikas⁷⁹ and Jūska⁷⁸ who determined the bimolecular recombination coefficient for P3HT:PCBM devices to be a factor of 1000 times smaller than the predicted Langevin bimolecular recombination coefficient based on TOF measurements of charge carrier mobility, where it was suggested that this reduction in bimolecular recombination may arise due to the morphology of the blend promoting separated bi-continuous pathways for charge transport, but found for MDMO:PPV/PCBM devices the bimolecular recombination coefficient to display Langevin behaviour.⁸¹

2.3.7 Future work

For the numerical studies presented in this chapter, we have treated a BHJ blend device as a single layer ‘virtual semiconductor’ sandwiched between two non-selective electrodes. We found good qualitative agreement between the simulated $J_{\text{ph}}-V$ curves with those of real MDMO:PPV/PCBM devices. Clear differences were observed with P3HT:PCBM devices. Although these too exhibited symmetric behaviour $J_{\text{ph}}-V$ curves, the point of symmetry occurred at a negative current rather than the expected $J_{\text{ph}} = 0$ is translated. As described above, one possible explanation

for this behaviour is that a non-uniform blend induces selectivity at one or both electrode with electrons being blocked at the anode and/or holes at the cathode. This yields a beneficial increase in the size of the (negative) photocurrent. In future numerical studies, non-selective electrodes should be considered, to investigate whether the behaviour of this experimental data can be explained in this manner.



Chapter 3 Experimental Methods

In this section we provide details concerning the P3HT:PCBM devices which were studied in this PhD thesis, and describe the main four experimental techniques which were used to study them; transient photovoltage (TPV), transient photocurrent (TPC), transient absorption spectroscopy (TAS) and charge extraction (CE).

3.1 Device details

The main focus of this thesis was to study the behaviour of ‘standard’ annealed P3HT:PCBM devices. Due to the extensive range of factors that influence the performance of such devices, including the fabrication conditions used,⁴³⁻⁴⁶ and the constituent materials used (P3HT regio-regularity RR^5 and molecular weight M_w ⁴⁷) (see Section 1.10), to define what constitutes a ‘standard’ device is difficult. In this section we begin by describing details for the devices which were studied, and

provide the guidelines which we used to determine when a device could be considered as a ‘standard’ device based on their photovoltaic characteristics.

For this thesis, devices were supplied primarily from other members of Imperial College, with several additional devices also supplied from external sources, such as Konarka Technology Ltd. Devices produced internally (Imperial College) were fabricated by Dr. Amy M. Ballantyne, Dr. Youngkoo Kim, Dr. Lichun Chen, Dr. Yeni Astuti, Dr. Richard Hamilton and Mikeal Portman, all gratefully acknowledged here. All of these devices employed similar fabrication processes and material sources. In principle these devices should be similar, and thus results obtained on them are comparable. Thus, for this thesis we primarily discuss results obtained on these ‘Imperial College’ fabricated devices. For devices supplied externally, the fabrication procedures and the material sources used are different (unknown, except that the devices were much thicker $\sim 500\text{nm}$), which results in it being difficult to relate data obtained on these devices, with those on Imperial College devices.

Devices fabricated at Imperial College⁵ consisted of 1:1 blend films of regioregular P3HT and PCBM and had typical thicknesses ranging from 70 – 200 nm. Regioregular P3HT was synthesized by Merck Chemicals Ltd ($M_w = 26.2$ kDa and $RR = 94.4\%$). Blend solutions (P3HT:PCBM=1:1 by weight) were prepared in chlorobenzene at a concentration of 30-50 mg/ml. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron P standard grade, HC Stark) was spin-coated at 1500 rpm on top of indium-tin oxide (ITO) coated glass ($25 \Omega\text{cm}^{-2}$) that had been cleaned by sonicating with acetone and isopropyl alcohol, and subsequently “annealed” at 230°C in air for 15 min. P3HT:PCBM blend films were then spin-coated on the annealed PEDOT:PSS layer (75nm thick). A $\sim 1500 \text{ \AA}$ thick aluminium (Al) electrode was deposited on the blend film by thermal evaporation at $\sim 3 \times 10^{-6}$ Torr, defining an active area of 0.045 cm^2 , followed by thermal annealing at $140\text{--}150^\circ\text{C}$ for 1 hour using a hotplate. Devices were made in batches of six for each substrate area 1cm^2 . Devices were left un-encapsulated. Devices were studied under nitrogen conditions using a nitrogen filled sample holder. Experimental measurements were performed at room temperature, illuminating through the ITO.

Devices supplied externally were already encapsulated. These devices were used primarily for the development of the experimental transient analysis techniques employed in this thesis, as their encapsulation provided greater flexibility for study.

The photovoltaic characteristics were measured in the following way. A silicon diode calibrated to the solar spectrum using band pass filtering (previously calibrated at the Fraunhofer ISE), was positioned in front of a Model SS150W solar simulator (Sciencetech) with 150 W xenon lamp equipped with an IR filter (water filter) and an AM1.5 filter. The power of the lamp was varied until the light incident on the photodiode corresponded to 100mWcm^{-2} AM1.5 simulated irradiation. The silicon diode was replaced with the device electrically contacted in a suitable sample holder in the same position. J - V curves were measured using a Keithley 2400 Sourcemeter while under both (100mWcm^{-2}) AM1.5 conditions and in the dark (blocking the light source).

In Section 1.7 the important parameters used to characterise device function were described. These included the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), the power conversion efficiency (PCE). Based on these device parameters, devices were considered as ‘standard’ if $J_{sc} \geq 3\text{ mAcm}^{-2}$, $V_{oc} \geq 0.55\text{V}$, $FF \geq 40\%$, and the corresponding PCE was $\geq 1.5\%$, with typical devices having a $J_{sc} \sim 6\text{ mAcm}^{-2}$, $V_{oc} \sim 0.6\text{V}$, $FF \sim 50\%$ and $PCE \sim 2\%$. Figure 1.1 shows several J - V curves for typical annealed P3HT:PCBM devices considered suitable for study in this thesis.

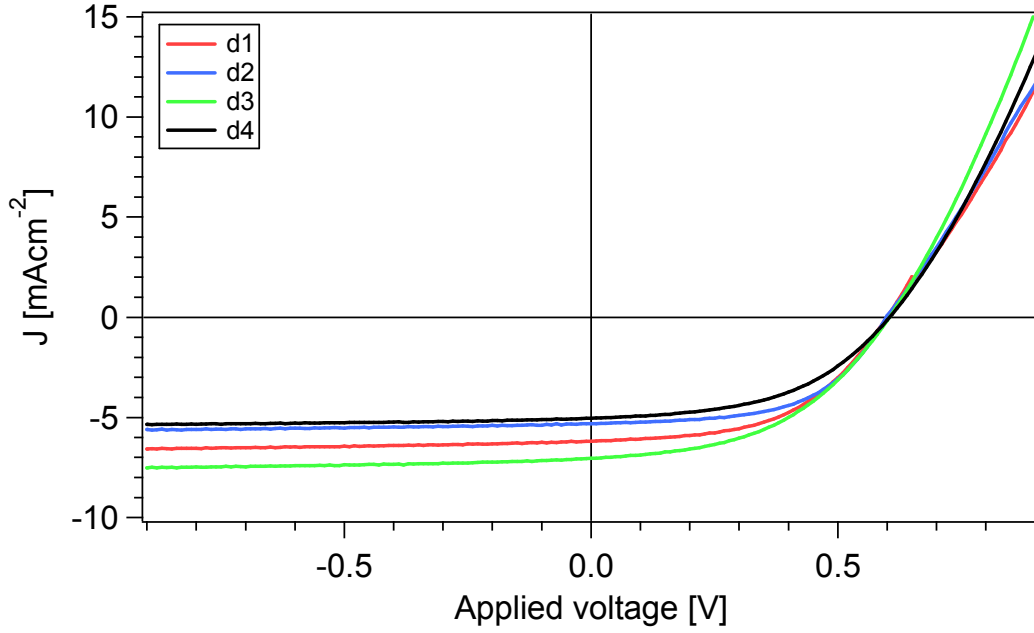


Fig. 3.1. J - V characteristics for ‘standard’ annealed devices while under 100mWcm^{-2} AM1.5 simulated irradiation. For the J - V curves shown, the values of importance were: d1: $J_{\text{sc}} = 6.2 \text{ mAcm}^{-2}$, $V_{\text{oc}} = 0.60\text{V}$, $FF = 51\%$ and $PCE = 1.9\%$. d2: $J_{\text{sc}} = 5.3 \text{ mAcm}^{-2}$, $V_{\text{oc}} = 0.60\text{V}$, $FF = 56\%$ and $PCE = 1.8\%$. d3: $J_{\text{sc}} = 7.0 \text{ mAcm}^{-2}$, $V_{\text{oc}} = 0.61\text{V}$, $FF = 47\%$ and $PCE = 2.0\%$. d4: $J_{\text{sc}} = 5.0 \text{ mAcm}^{-2}$, $V_{\text{oc}} = 0.61\text{V}$, $FF = 49\%$ and $PCE = 1.5\%$.

Additional device properties, such as the series and shunt resistances were also found to vary between devices. As we describe later in Section 3.2.1, the value of the shunt resistance effects how we determine what light intensities we can use to study transient photovoltage measurements. In the case of some of the device studied the shunt resistance was relatively small $\sim 0.1 \text{ M}\Omega$. However, based on the guidelines presented above, all of these devices were still considered suitable for study. Experimental data obtained on devices with low ($0.1 \text{ M}\Omega$) and high ($1 \text{ G}\Omega$) shunt resistances was similar. We thus do not believe that for the broader conclusions obtained in this work should in anyway be influenced by the shunt resistances of the devices studied.

3.2 Transient photovoltage (TPV)

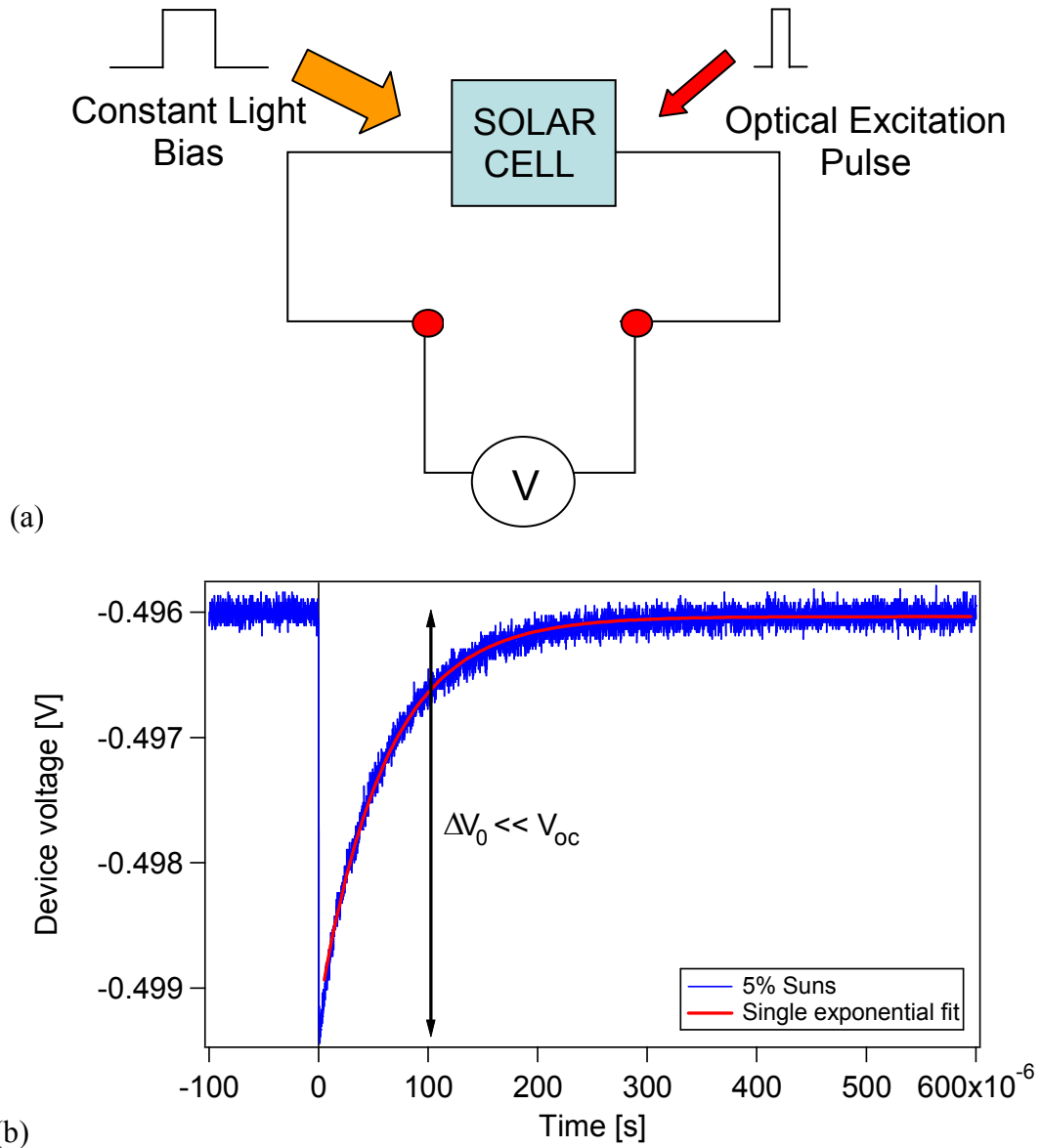


Fig. 3.2. (a) A basic schematic of the experimental setup used to measure transient photovoltage with (b) a typical TPV transient with a voltage amplitude ΔV and a baseline V_{oc} . The red line represents a single exponential fit of the TPV decay showing that in this small perturbation approach, the form of the TPV transient is well-describe by a single exponential, greatly simplifying data analysis.

TPV is a relatively simple small perturbation opto-electronic transient photovoltage measurement of carrier lifetime in a device held at open-circuit conditions. It has been previously been employed primarily to study dye sensitized solar cells.^{84,85} For the TPV measurements reported herein, the devices were connected to the 1 M Ω input terminal of a TDS 3032B Tektronix digital storage oscilloscope, and illuminated with

continuous white light using a 10W ‘Solarc’ metal halogen bulb, the intensity of which was used to control the open-circuit voltage V_{oc} (attenuated with neutral density filters). The photovoltage generated by the white light source is referred to here as a ‘light-bias’. A small optical perturbation was applied using a GL-330 PTI nitrogen laser pumped – GL-301 PTI dye laser as an excitation source with wavelength 620 nm (frequency 4 Hz, pulse duration < 1 ns), which resulted in a voltage transient with an amplitude $\Delta V_0 \ll V_{oc}$. The intensity of the laser pulse was attenuated as necessary to keep ΔV_0 smaller than typically ≤ 10 mV. At V_{oc} , no external current can flow through the external circuit so charge carriers generated are forced to remain in bulk of the device and/or the electrodes. The TPV decay can therefore be used to monitor the loss kinetics. Importantly, by restricting measurements to the small perturbation regime employed, the profile of the measured decay is forced to take the form of a single exponential (i.e.: pseudo-first order behaviour), simplifying quantitative analysis (see Section 4.3). A schematic describing the basic experimental setup and a typical photovoltage transient are provided in Fig. 3.2.

3.2.1 Experimental requirements: Ensuring open-circuit conditions

In this simple TPV measurement, the internal resistance of the oscilloscope, $R_{osc} = 1$ M Ω , was used to provide open-circuit conditions in the device ($J \sim 0$). To determine under which conditions open-circuit conditions are met, we employed two different guidelines which were dependent on whether the devices shunts resistance R_{SH} was a) $R_{SH} > 1$ M Ω and b) $R_{SH} < 1$ M Ω .

a) $R_{SH} > 1$ M Ω

For a device with a shunt resistance larger than the internal resistance of the oscilloscope, at relatively low light intensities it was found that R_{osc} was not large enough to enforce open-circuit conditions in the device. This behaviour was verified by comparing the voltage measured using an oscilloscope ($R_{osc} = 1$ M Ω) and an AVO Megger MS091 digital voltmeter (DVM) which has a larger resistance equal to 10 M Ω . At relatively low light intensities, the voltage measured using these two instruments deviated, as shown in Fig. 3.3. For light intensities where these two curves deviate the internal resistance of the oscilloscope is insufficient to provide

open-circuit conditions in the device, as it will allow current to flow through it. Therefore, at these light intensities TPV is unable to study the open-circuit properties of the device.

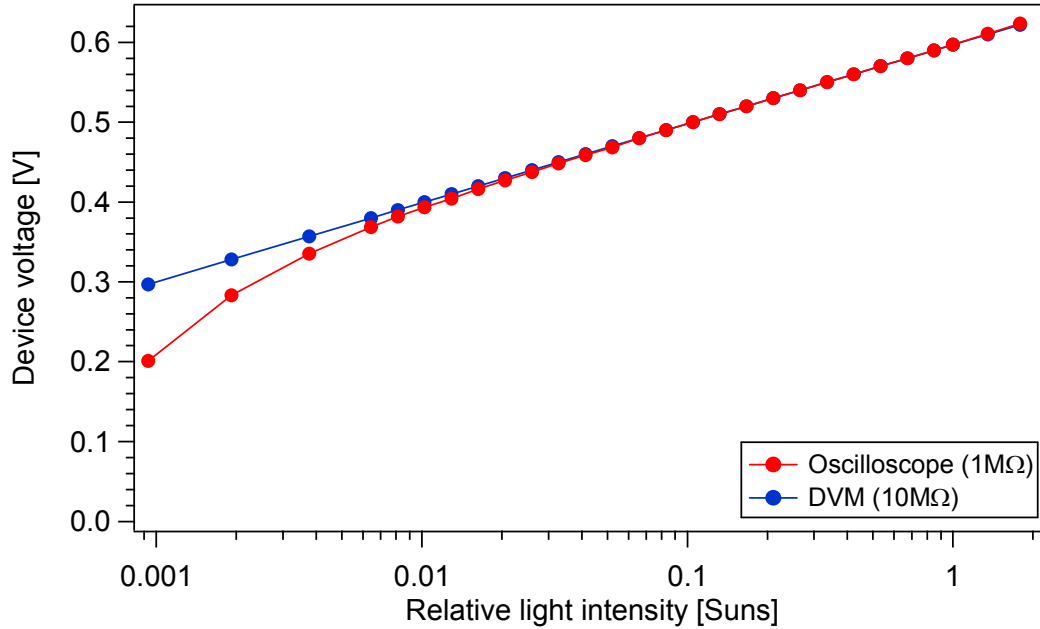


Fig. 3.3. Comparison of the light intensity dependence of V_{oc} measured using an oscilloscope ($R_{OSC} = 1 \text{ M}\Omega$) and a digital voltmeter ($R_{DVM} = 10 \text{ M}\Omega$). At relatively low light intensities, as the light intensity is reduced further, the voltage measured by the oscilloscope and the DVM deviates. This indicates in this regime, that the resistance of the oscilloscope is insufficient to provide open-circuit conditions in the device.

At these relatively low light intensities, larger resistances may be used to enforce open-circuit conditions. However, we found that when we increased the circuit resistance, the TPV transients reduced in size. As we already confine these transients to be small ($\leq 10 \text{ mV}$), then further reduction in size leads to the signal to noise of such transients to be a compromised. One solution to this problem could be using an amplification system. However, as this effect is only observed at relatively low light intensities and the basis of this TPV measurement is to provide simple measurements of charge carrier lifetime, we deemed this additional complication to the experimental setup to not be necessary. Instead, we imposed a lower limit for the light bias we used for our TPV study, which was determined using the plot given in Fig. 3.3, typically for an incident light intensity $\sim 0.01 \text{ suns}$.

b) $R_{SH} < 1 \text{ M}\Omega$

For devices with a shunt resistance $R_{SH} < 1 \text{ M}\Omega$, a similar comparison was made between the V_{oc} determined using an oscilloscope and a DVM as was done in Fig. 3.3. In both cases, the V_{oc} was determined to be the same for all light intensities. This implies that the internal resistance of the oscilloscope will always determine the device to be held at open-circuit conditions for all light bias conditions. Figure 3.4 shows a typical plot of V_{oc} versus light intensity for such devices. We observed that a biphasic relationship is observed, which is different to that found for devices with larger shunt resistances where a single exponential relationship was observed (see Fig. 3.3, DVM data). By considering the corresponding J - V curves for relatively low light intensities (< 0.025 suns) where the V_{oc} is found to reduce rapidly with decreasing light intensity, it is evident that these curves are linear. At these low light intensities the photocurrent is small, and thus these light J - V curves resemble that of the dark current, which due to the low shunt resistance is linear over a relatively large range of voltages $< 0.4\text{V}$ (see Section 1.9). We therefore assert that for these low light intensities in these devices the V_{oc} is shunt resistance limited, and thus any open-circuit measurements performed for these low light biases will reflect properties of the electrical shunts present rather than probe photovoltaic behaviour. Thus, for devices with $R_{SH} < 1 \text{ M}\Omega$, we restrict our measurements to light biases where the light intensity is exponentially related to the incident light intensity.

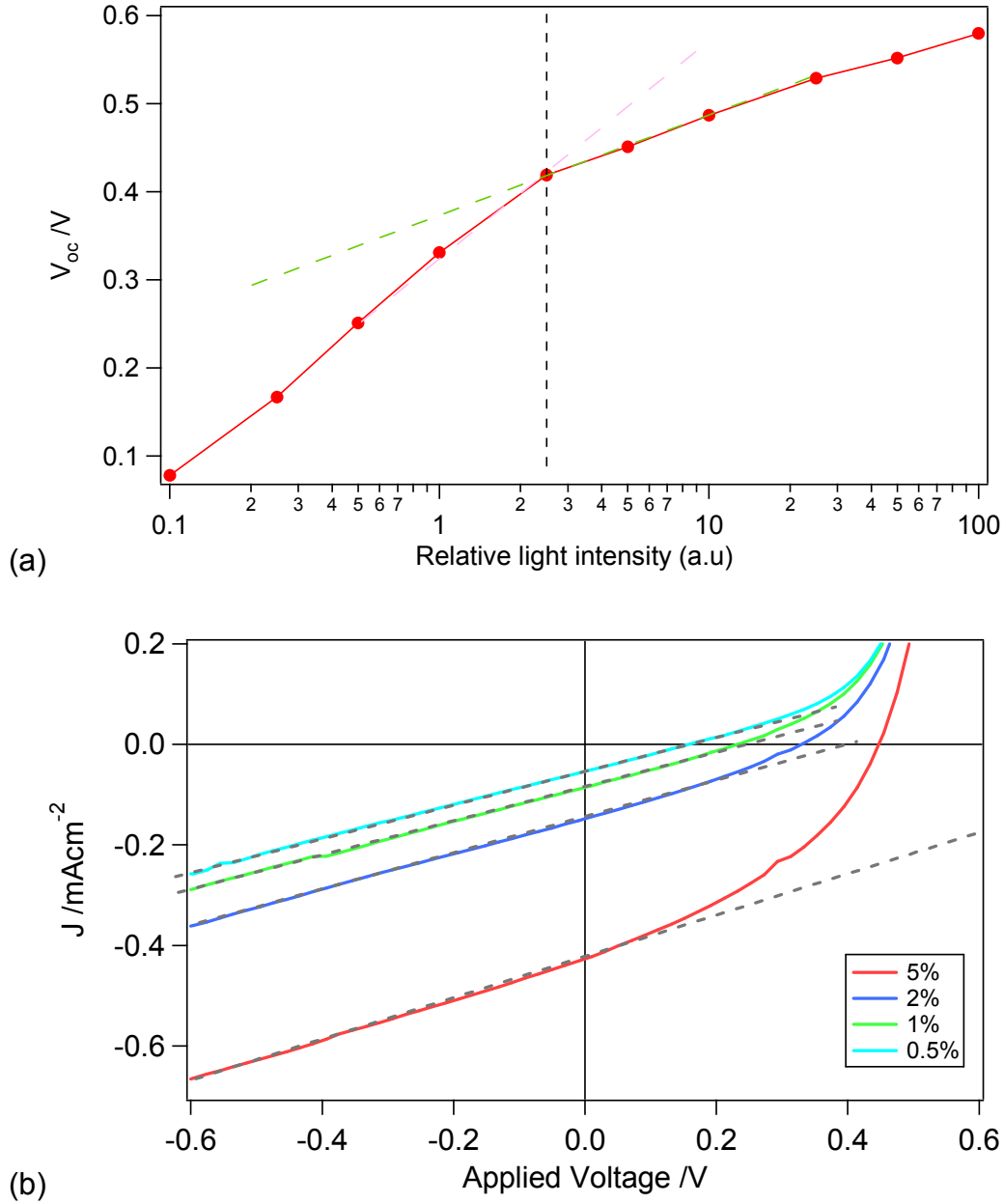


Fig. 3.4. (a) Light intensity dependence of the open-circuit voltage for a device with a relatively low shunt resistance $R_{SH} \sim 0.1 \text{ M}\Omega$. It is found to take the form of a biphasic curve is found with an observed transition occurring for a light intensity $\sim 2.5\%$ suns. (b) The corresponding J - V curves are displayed for relatively low light intensities $\leq 5\%$ suns. It is apparent that for light intensities $< 2\%$ suns the J - V curves are linear, which would be consistent with the effects of an electrical shunt limited dark current over the voltage range these low light intensity J - V curves cover.

We thus conclude that in either case, when performing TPV studies, there is a lower limit to the light bias that should be used, which is typically around 1 -5 % suns

depending on the device tested, and whether the devices shunt resistance is smaller or larger than the oscilloscopes $1\text{ M}\Omega$ resistance.

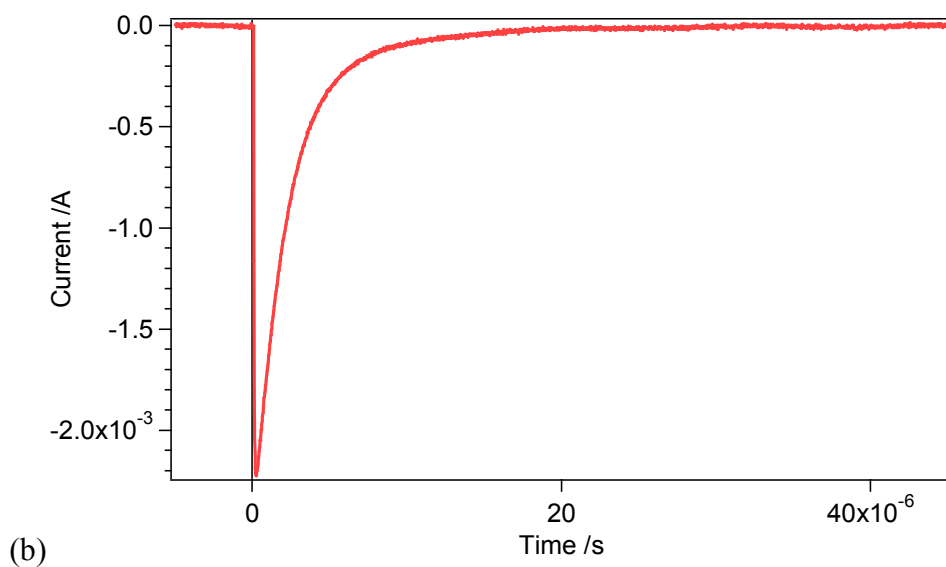
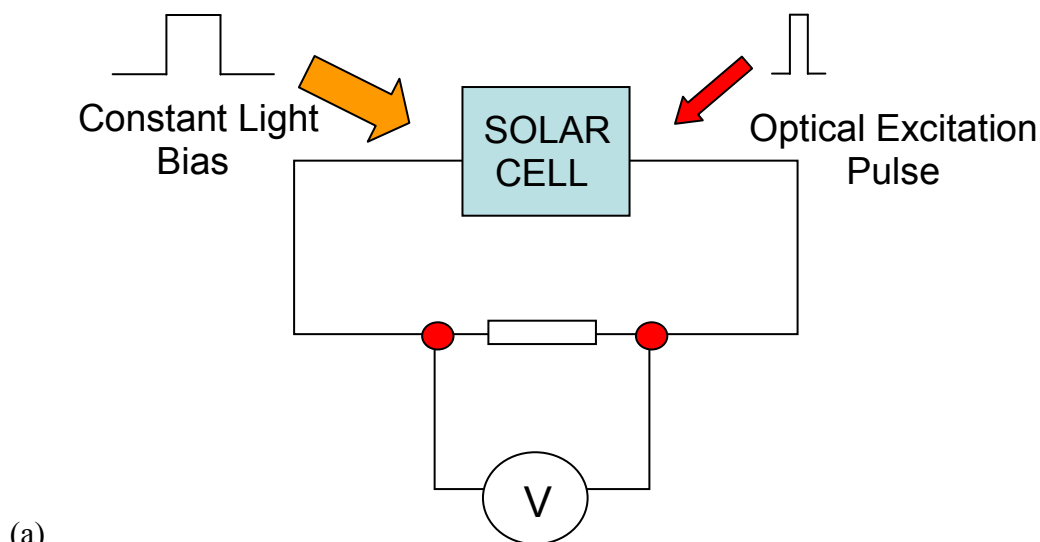
3.2.2 Temperature effects on measurements

In TPV studies the device is subjected to continuous illumination. This can lead to the device temperature increasing by heating effects. As the light bias is increased, this effect becomes more evident. To attempt to reduce this effect, various approaches have been employed, including placing the solar cell on to a metal plate which has cold water continually flowing through it during measurements and using a cryostat. These approaches have proved relatively effective when working with encapsulated devices. However, most of the performed studies were performed on un-encapsulated devices, and therefore required that they be tested in nitrogen filled sample holders, limiting the extent of temperature control which could be implemented. Instead, in the earlier studies presented in this thesis, prior to Chapter 6, special attention was paid to measurements of TPV transients at higher light intensities ≥ 0.5 suns, where the behaviour of the data was compared to the TPV data at lower light biases, where the effects of heating will be significantly reduced. In TPV studies obtained in Chapter 6 and for future studies, the constant light source used was replaced with pulsed light emitting diodes, which greatly reduces the heat flux on the sample, and hence, allows TPV to be measured more reliably at higher light biases, ≥ 1 sun.

3.3 Transient photocurrent (TPC)

Transient photocurrent (TPC) is used to obtain an estimate of the amount of the additionally photogenerated charge carriers ΔQ which are created due to the laser intensity employed in the TPV studies. TPC employs the same experimental setup as used to measure TPV transients, except an additional small load resistor, typically 50Ω , is inserted in series with the device, and the voltage across the load resistor is monitored using an oscilloscope (see Fig. 3.5). When the device is excited by the laser pulse, the additionally photogenerated charge carriers created are able to flow out of the device, and the oscilloscope measures a current transient which corresponds to the current flow $I = V/R_L$ through the load resistor. Integrating this current transient with

respect to time provides a measure of the amount of charge which was collected as a direct result of the incident excitation pulse. Unlike TPV measurements which are made for varying light biases, these TPC measurements were made either in the dark or under low incident light intensity (typically 0.01 suns) so that the incurred recombination losses are small in these measurements. Fig. 3.5 (b-c) shows a typical photocurrent transient and the corresponding time integrated form.



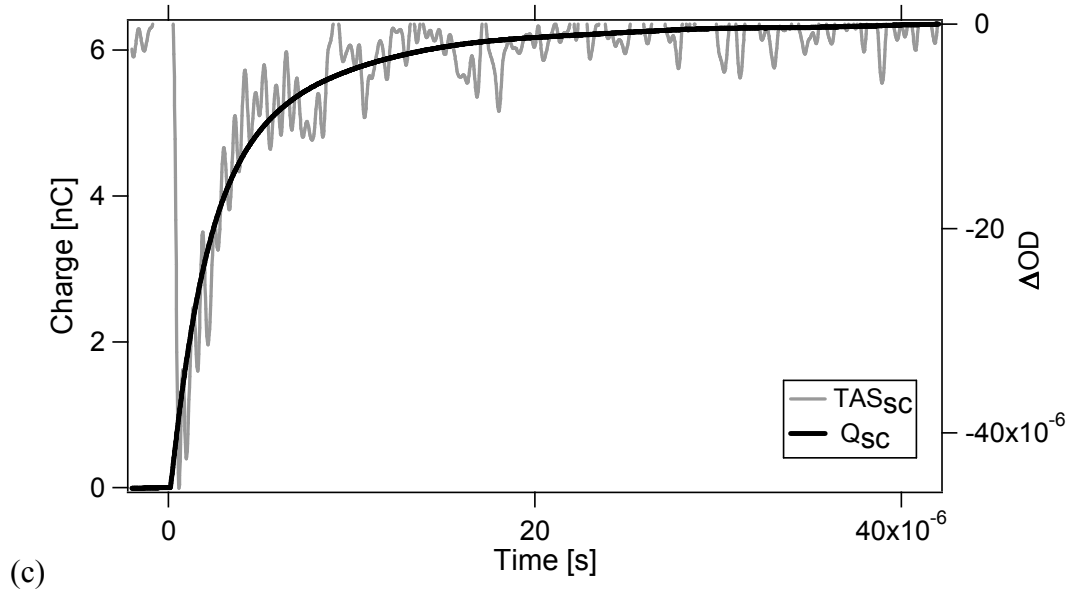


Fig. 3.5. a) Basic schematic of the transient photocurrent experimental setup. b) Transient photocurrent measured under at low light intensity (~ 0.01 suns) at approximately short-circuit conditions (50Ω) using the same intensity laser pulse as Fig. 3.2. (a). c) Time-integrated data ($Q_{sc}(t)$) derived from Fig. 3.5 (b) confirmed as a measure of charge through comparison with TAS performed under identical conditions.

This estimate of ΔQ is required, to allow a calculation of the effective capacitance ($C = \Delta Q / \Delta V_0$) of the device to be made for the different light biases studied, which then can be used to determine the charge density present in the active layer of the device (see details on this differential charging procedure in Section 4.5). To limit the experimental errors in the calculation of C , the excitation intensity is purposely chosen to allow a complete TPV study (typically over a light intensity range $0.01 - 1$ suns) where the TPV peak voltage amplitude is still confined to be small, $\Delta V_0 \leq 10 - 20$ mV, without requiring this excitation intensity to be varied. As a result, only a single TPC measurement is required per TPV study. Therefore, even if there are errors in the measurement of ΔQ , this error will be present for all light biases, allowing at least a comparison of qualitative trends.

3.4 Transient absorption spectroscopy (TAS)

Transient absorption spectroscopy (TAS) is an optical measurement in which changes in optical density upon photoexcitation are used to monitor the population of transient

species. TAS has previously been used to monitor polaron decay dynamics in a range of polymer: PCBM thin films.^{60,86,87} When performed on devices, TAS must be performed in reflection mode due to the opacity of the cathode. For the measurements reported in this thesis, a 100 mW 980 nm laser diode (#LD 0975-0100-1 Toptica) probe operated using a LDC 500 Thorlabs laser diode controller and a TEC 2000 Thorlabs temperature controller and a TCLDM9 TEC LD Thorlabs mount was used to monitor absorption of the P3HT⁺ polarons⁸⁸ generated by either the same 620 nm laser pulses used for the TPV experiments for the small perturbation TAS measurements described in Chapter 4, or, when performing large perturbation measurements (no background light, relatively higher laser intensities 4-60 μJcm^{-2}) in Chapter 5, using the same GL-3000 PTI nitrogen laser pumped – GL-301 PTI dye laser as an excitation source, but with 520nm laser pulses (peak absorption of P3HT) using a TDS 3032B Tektronix digital storage oscilloscope. A basic schematic for the experimental TAS setup is given in Fig. 3.6. A graded neutral density wheel was used in between the laser diode and the sample to reduce the amount of probe light incident on the sample. To reduce the amount of scatter/emission reaching the photodetector, the photodetector was placed in a separate black metal box, with several 830nm high pass filters placed in between the sample and the photodetector along the optical path of the probe beam. A high gain photodiode equipped with appropriate low and high pass filtering was employed as the detection unit (Costronics Electronics optical transient amplifier (2004) and per-amplifier Mk2 (2002)). The instrument response was of the order of 300 ns. Data were collected on time scales from 1 μs - 1 ms, averaging typically 500-1000 laser shots on each time scale, yielding a sensitivity of 10^{-6} to 10^{-4} depending upon the time scale under study. Experiments as a function of the excitation intensity described in Chapter 5 employed neutral density filters to vary the laser intensity from 4 - 60 μJcm^{-2} per pulse. Data are plotted as the change in sample optical density ΔOD , which is related to the change in sample transmission ΔT by $\Delta OD \times \ln 10 = -\Delta T/T$. This ΔOD is related to the voltage monitored by the oscilloscope ΔV_{osc} by

$$\Delta OD = -\frac{1}{\ln(10)} \frac{\Delta V_{\text{osc}}}{V_{\text{DC}}} \quad (3.1)$$

where V_{DC} is the voltage measured in the absence of the excitation pulse. Reflection mode TAS data were collected either by using the Al electrode to reflect the probe

beam when studying devices, or by directing the probe beam between the Al electrodes, and using a mirror placed directly behind the sample to reflect the beam back when studying the thin film component of the device (see Section 5.2, Chapter 5).

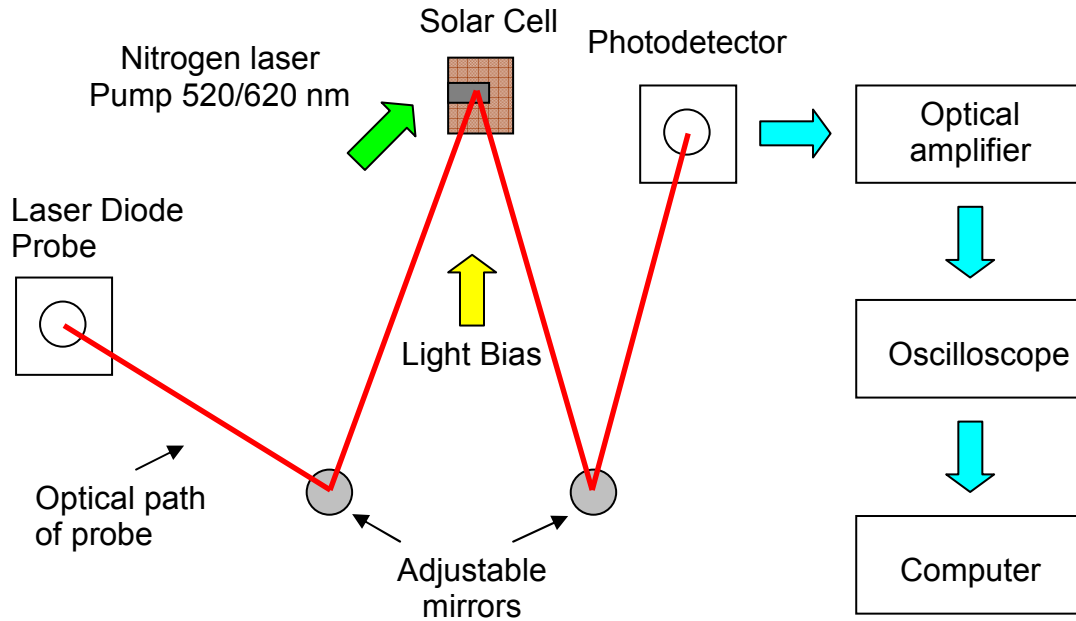


Fig. 3.6. Schematic of the experimental TAS setup in reflective mode.

3.5 Charge extraction (CE)

The charge extraction technique^{89,90} is a simple measurement in which a solar cell is initially at a fixed point on the J - V curve, either in the dark or under illumination, and then is switched to short-circuit (zero bias) while at the same time the light (if any) is switched off.

The switch to short circuit creates a current transient as the cell discharges. The integral of this current transient provides an estimate of the excess charge in the cell under the J - V condition specified before the switching, minus any charge losses incurred during the measurement. Fig. 3.7 shows typical charge extraction transients for a device held at approximately 1 sun V_{oc} and short-circuit conditions. We note that this experiment also collects the capacitive charge resident on the electrodes and thus

requires to be accounted for when considering charge extraction data, which was done using a simple estimate of the geometric capacitance as described in Section 6.3.2.

It may be argued that the incurred charge losses in these CE measurements are likely to be relatively large. Thus, by using the CE data combined with TPV lifetime measurements, we have determined the incurred charge losses using an iterative procedure as outlined in Section 6.3.1, and have made a correction for these charge losses. These losses were found to be relatively small, $\sim 10\%$ for 1 sun V_{oc} conditions.

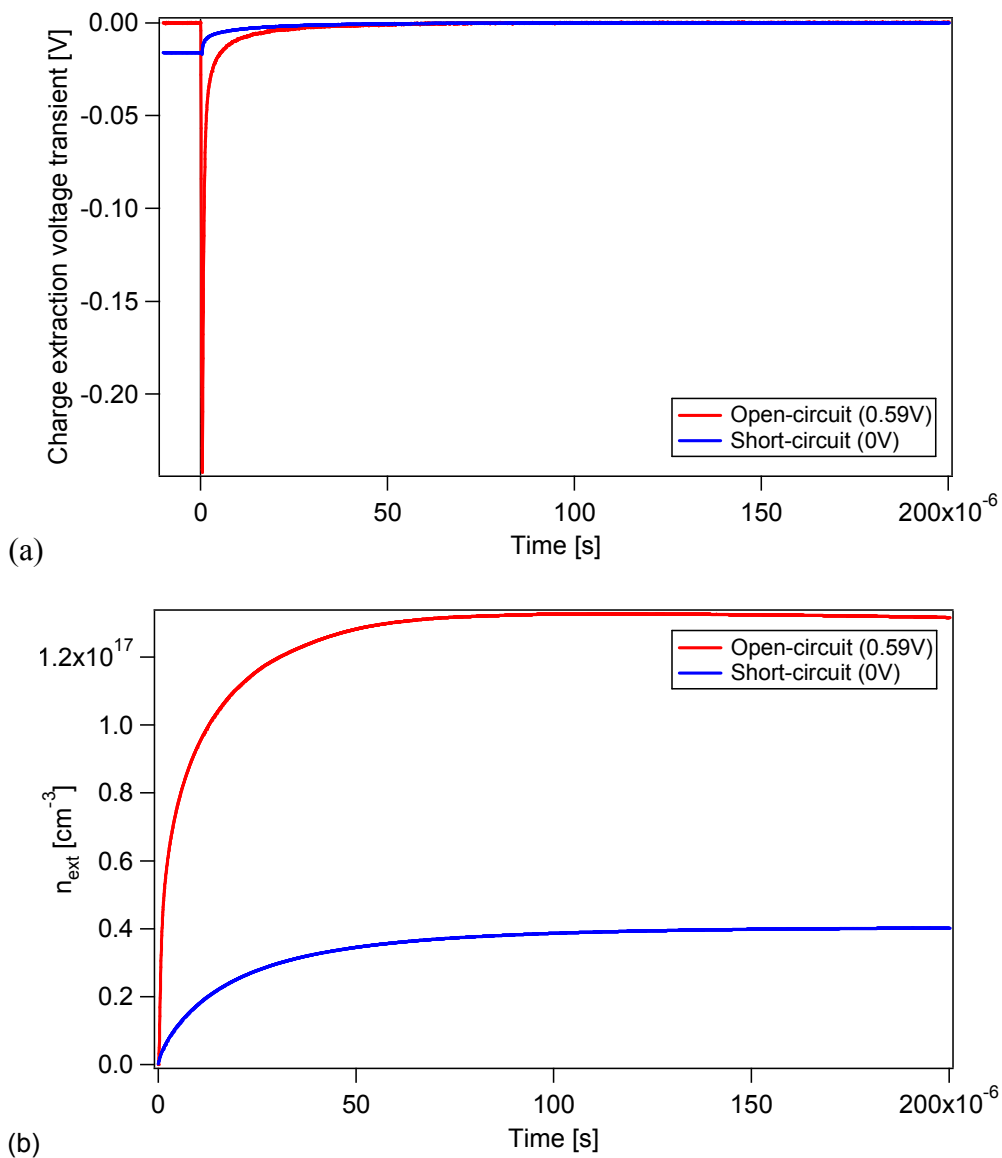
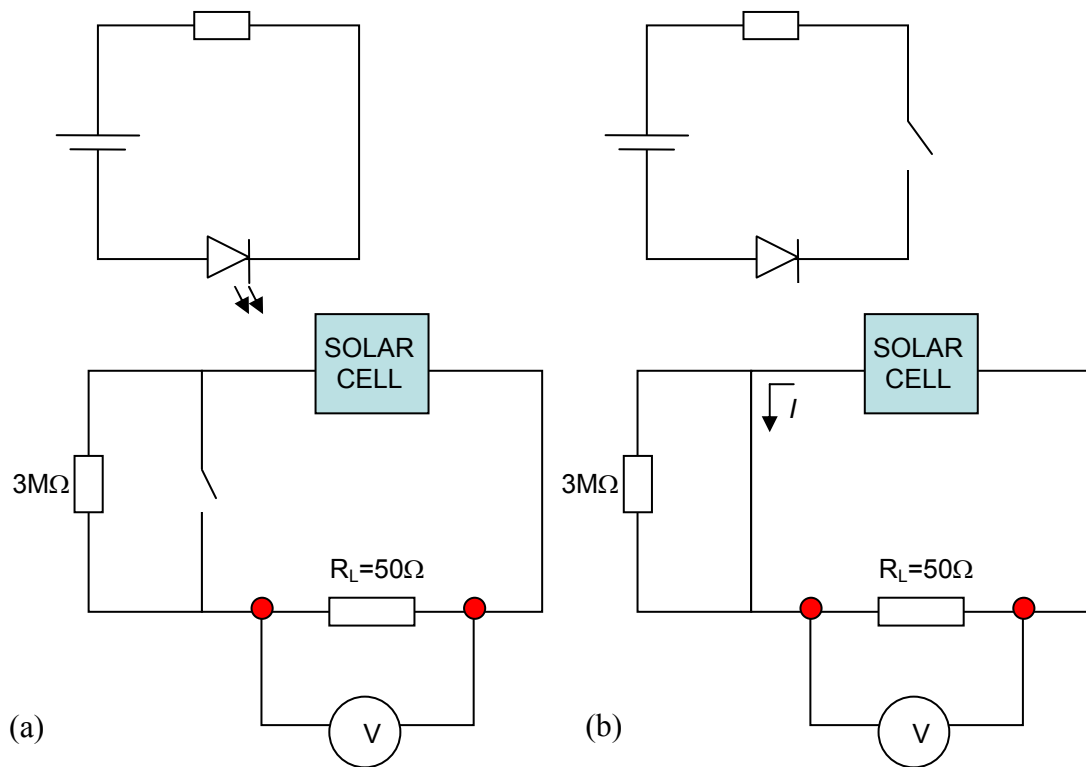


Fig. 3.7 Typical charge extraction transients displaying the measured current transient for a device under approximately 1 sun (a) open-circuit and short-circuit conditions, and the time integrated form, which depicts plots of the corresponding (b) charge extraction 'charge' transients.

For the charge extraction studies reported herein, the devices were short-circuited using a typical MOSFET (on time ≤ 100 ns, $R_{\text{open}} \sim 3 \text{ M}\Omega$ $R_{\text{closed}} \sim 0.5 \Omega$) in series with a 50Ω measuring resistor R_L . Illumination was provided by four 1 watt white LEDs (Lumileds) with focusing optics. These LEDs have intrinsic turn off times ≤ 200 ns. The lights were switched off with an identical MOSFET. The output of the LEDs can be varied over 3 orders of magnitude. Illumination time before switching was typically 100 ms, which was enough to achieve steady state conditions while minimizing heating. When measuring charge at V_{oc} the transistor open resistance of the transistor provided open-circuit conditions, where the V_{oc} was determined by the light intensity employed. When measuring charge at points on the J - V curves (dark/light), the initial device voltage was controlled using a Keithley 2400 sourcemeter (dark/light) or a variable resistor (light), connected in parallel with the transistor switch. Simplified schematics of the basic experimental circuits for charge extraction studies at open-circuit, mapping of the J - V curve for a device under illumination (shown using a variable resistor) and dark conditions are shown in Fig. 3.8 (a-b), (c-d) and (e-f) respectively.



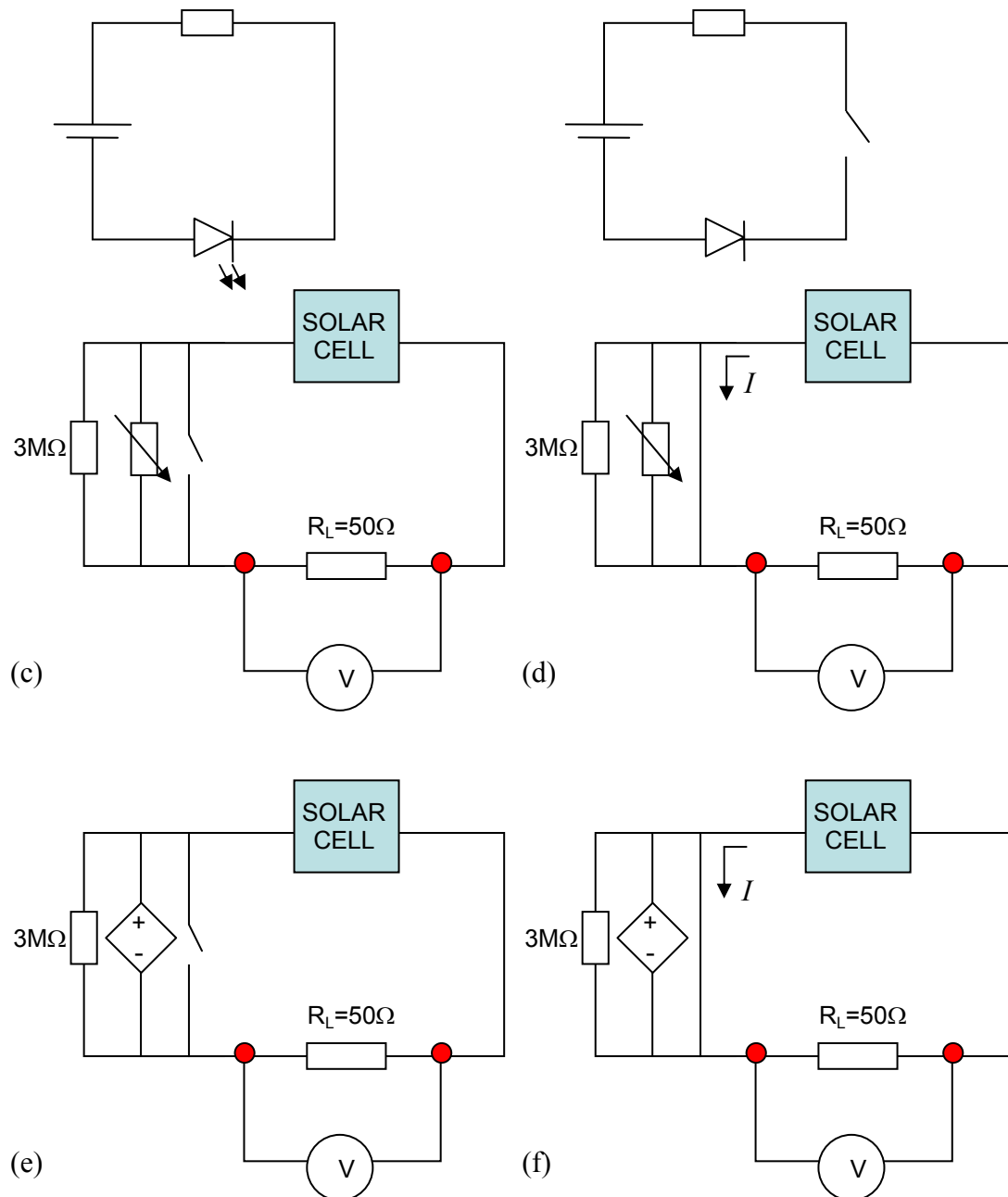


Fig. 3.8 Basic experimental schematics are given for charge extraction studies at V_{oc} (a-b), and mapping of the J - V curves for a device whilst under illumination (c-d) and for dark conditions (e-f). (a) Initially the device is held at open-circuit conditions through the transistors internal resistance, under constant light bias conditions in the form of white LED's. (b) Simultaneously these LED's are switched off, whilst the device is shorted, which allows the charge density in the device to be collected by the device electrodes, and a voltage transient is measured by an oscilloscope. This voltage transient represents a current transient $I = V/R_L$. In the case of mapping the J - V curves in terms of charge density, (c) a variable resistor or (d) a voltage source is used to control the initial device voltage conditions.

IV

Chapter 4 Experimental determination of the rate law for charge carrier decay in a polythiophene : Fullerene solar cell

We use transient photovoltage and differential charging experiments, complemented by transient absorption data, to determine charge carrier lifetimes and densities in a poly(3-hexylthiophene): methanofullerene solar cell at V_{oc} as a function of white light bias intensity. Using these measurements, the rate law for charge carrier decay dynamics are determined, which, for a typical device, are observed to exhibit an approximately third order dependence on charge density ($dn/dt \propto n^3$).

4.1 Introduction

Improvements in performance on organic solar cell are dependent on developing a better understanding of the pertinent loss processes such as bimolecular recombination, geminate recombination, shunts, and leakage.⁶² This in turn requires the ability to reliably determine charge densities (n) and carrier lifetimes (τ_n) in real devices under standard operating conditions.

Many techniques have been employed to obtain values for n and τ_n , including Photo-CELIV,⁹¹ double injection currents (DOI)⁷⁸ and integral mode time of flight (Q -TOF),⁷⁹ although it has proved difficult to relate such measurements directly to device photovoltaic operation under continuous irradiation. A recent review provides a good summary of this work.⁸¹ In this Chapter we present a method for studying the steady-state carrier lifetimes and charge densities in optimised polymer solar cells under continuously illuminated open-circuit conditions using transient photovoltage (TPV) measurements,^{84,85,92} complemented with the use of transient absorption spectroscopy (TAS).^{5,60,86,87} We report measurements on poly (3-hexylthiophene) (P3HT): 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methano fullerene (PCBM) bulk heterojunction devices and find that the loss processes at open-circuit in a typical P3HT:PCBM device follows an approximately third order dependence on charge density.

This chapter investigates the charge carrier dynamics in ‘standard’ P3HT:PCBM devices (see Section 3.1) with the main aim of determining the rate law describing the charge carrier decay dynamics for the device at V_{oc} conditions. We begin by showing that small perturbation opto-electronic transient photovoltage measurements provide a direct measure of the carrier lifetime for these devices by making a direct comparison with TAS data obtained under identical light bias conditions. We show that due to the small perturbation regime employed the decay of these TPV transients should take the form of a single exponential, as is found experimentally. The behaviour of these TPV data under varying light bias conditions is determined, from which a plot of the small perturbation carrier lifetime as a function of light bias is obtained. To determine the corresponding steady state charge densities present in the device for the same light

bias conditions we employed a differential charging procedure, which is based on TPV data combined with a single short-circuit transient photocurrent measurement. By combining the measured small perturbation carrier lifetimes and the determined corresponding steady state charge densities, we derive an empirical expression for the carrier decay dynamics for the device at V_{oc} in terms of charge density.

For experimental details concerning the transient photovoltage, transient absorption spectroscopy, transient photocurrent and the devices studied, please refer to the experimental methods chapter 3, where these are given in the respective Section's 3.2, 3.3, 3.4 and 3.1.

In this and all consequential chapters, we employ experimental study to determine the 'total' charge density in P3HT:PCBM devices, which we refer to herein as n . This is not to be confused with the previous computing studies (Chapter 2), where we considered the respective electron and hole spatial charge distributions $n(x)$ and $p(x)$ separately.

4.2 Determining whether transient photovoltage can be used as a direct measure of carrier lifetime

To determine whether transient photovoltage decay transients is indeed a measure of polaron density, rather than alternative processes such as dielectric relaxation,⁹³ a direct comparison was made between the TPV and TAS signals obtained under identical light-bias and probe beam conditions. Typical data are shown in Fig. 4.5. Excellent agreement is found between the shape of the transients recorded by the two techniques, consistent with the small perturbation regime employed and confirming that TPV does indeed provide us with a measure of the polaron populations and, therefore, can be used as a direct measure of carrier lifetimes. As expected in the small perturbation regime, both transients exhibited single exponential decays (see below), consistent with a pseudo-first order rate equation of the form

$$\frac{d\Delta V}{dt} \propto \frac{d\Delta n}{dt} = -k_{\text{eff}}\Delta n = -\frac{\Delta n}{\tau_{\Delta n}} \quad (4.1)$$

where ΔV is the photovoltage, t is the time, k_{eff} is the pseudo first-order rate constant, Δn is change in the density of photogenerated carriers due to the laser pulse and $\tau_{\Delta n}$ is the corresponding carrier lifetime. TPV measurements provide a superior signal-to-noise resolution, as is clear from Fig. 4.1, whilst also having the merit of being considerably simpler to carry out practically.

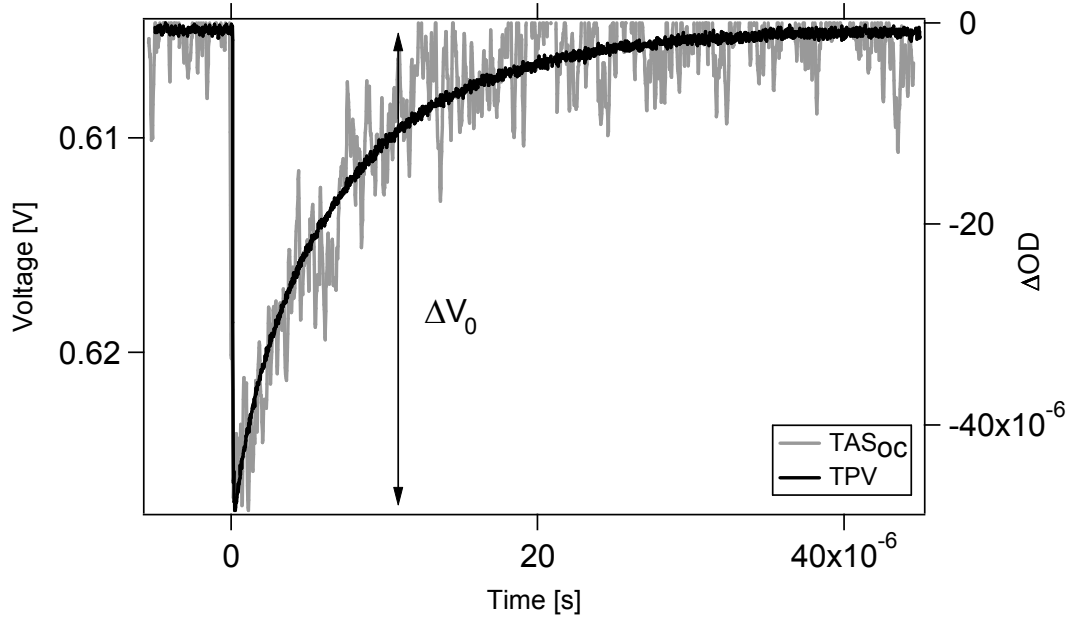


Fig. 4.1. The transient photovoltage (left, black) and transient absorption signals (right, grey) obtained in the small perturbation regime. Measurements were made under 1 sun illumination, $V_{\text{oc}} = 0.59\text{V}$, using a pump of wavelength 620 nm and a probe of 980 nm.

4.3 Verifying that by employing a small perturbation regime the transient photovoltage decays should take the form of single exponentials

In TPV, as a result of the small perturbation regime employed, we find that the measured transients are well-described by single exponentials. To verify the origin of this behaviour, we consider a generalised form for the origin of losses at V_{oc} , in terms of the total (spatially averaged) electron and hole carrier concentrations

$$\frac{dn}{dt} = -\sum_{ij} k_{ij} n^{\phi_i} p^{\phi_j} = -(k_{00} + k_{10} n^{\phi_1} + k_{01} p^{\phi_1} + k_{11} n^{\phi_1} p^{\phi_1} + \dots) \quad (4.2)$$

where n is the electron carrier concentration, p is the hole carrier concentration, t is time, and i, j, k_{ij}, ϕ_i and ϕ_j are all constants. In the transient photovoltage measurements described in this chapter, a small perturbation regime is employed in which the steady state charge concentrations are perturbed by a small additional amount of photogenerated electron and hole charge carriers, Δn and Δp respectively, where $\Delta n = \Delta p \ll n, p$. By applying this to Eqn. (4.2), we obtain,

$$\begin{aligned} \frac{d(n + \Delta n)}{dt} &= - \sum_{ij} k_{ij} (n + \Delta n)^{\phi_i} (p + \Delta p)^{\phi_j} \\ &= - \left(k_{00} + k_{10} (n + \Delta n)^{\phi_1} + k_{01} (p + \Delta p)^{\phi_1} + k_{11} (n + \Delta n)^{\phi_1} (p + \Delta p)^{\phi_1} + \dots \right) \end{aligned} \quad (4.3)$$

which can be rewritten

$$\begin{aligned} \frac{d(n + \Delta n)}{dt} &= - \sum_{ij} k_{ij} (n + \Delta n)^{\phi_i} (p + \Delta p)^{\phi_j} \\ &= - \left(k_{00} + k_{10} n^{\phi_1} \left(1 + \frac{\Delta n}{n} \right)^{\phi_1} + k_{01} p^{\phi_1} \left(1 + \frac{\Delta p}{p} \right)^{\phi_1} + k_{11} n^{\phi_1} p^{\phi_1} \left(1 + \frac{\Delta n}{n} \right)^{\phi_1} \left(1 + \frac{\Delta p}{p} \right)^{\phi_1} + \dots \right) \end{aligned} \quad (4.4)$$

As $\Delta n/n \ll 1$, we can apply the binomial expansion, where non-linear terms of $\Delta n/n$ are small, and so neglected.

$$\begin{aligned} \frac{d(n + \Delta n)}{dt} &= \\ &= - \left(\left(k_{00} + k_{10} n^{\phi_1} \left(1 + \frac{\phi_1 \Delta n}{n} \right) + k_{01} p^{\phi_1} \left(1 + \frac{\phi_1 \Delta p}{p} \right) + k_{11} n^{\phi_1} p^{\phi_1} \left(1 + \frac{\phi_1 \Delta n}{n} \right) \left(1 + \frac{\phi_1 \Delta p}{p} \right) \right) + \dots \right) \end{aligned} \quad (4.5)$$

When the system is excited, this results in a small additional amount of equal photogenerated electron and hole free charge carriers $\Delta n = \Delta p$. Thus:

$$\begin{aligned} \frac{d(n + \Delta n)}{dt} &= \\ &= - \left(\left(k_{00} + k_{10} n^{\phi_1} + k_{01} p^{\phi_1} + k_{11} n^{\phi_1} p^{\phi_1} \right) + \Delta n \left(k_{10} n^{\phi_1-1} + k_{01} p^{\phi_1-1} + k_{11} n^{\phi_1} p^{\phi_1} \left(\frac{\phi_1}{n} + \frac{\phi_1}{p} \right) + \dots \right) \right) \end{aligned} \quad (4.6)$$

The first term on the RHS is equal to dn/dt (see Eqn (4.2)), and so by subtracting dn/dt from both sides we obtain

$$\frac{d\Delta n}{dt} = -\Delta n \left(k_{10} n^{\phi-1} + k_{01} p^{\phi-1} + k_{11} n^{\phi} p^{\phi} \left(\frac{\phi_1}{n} + \frac{\phi_1}{p} \right) + \dots \right) \quad (4.7)$$

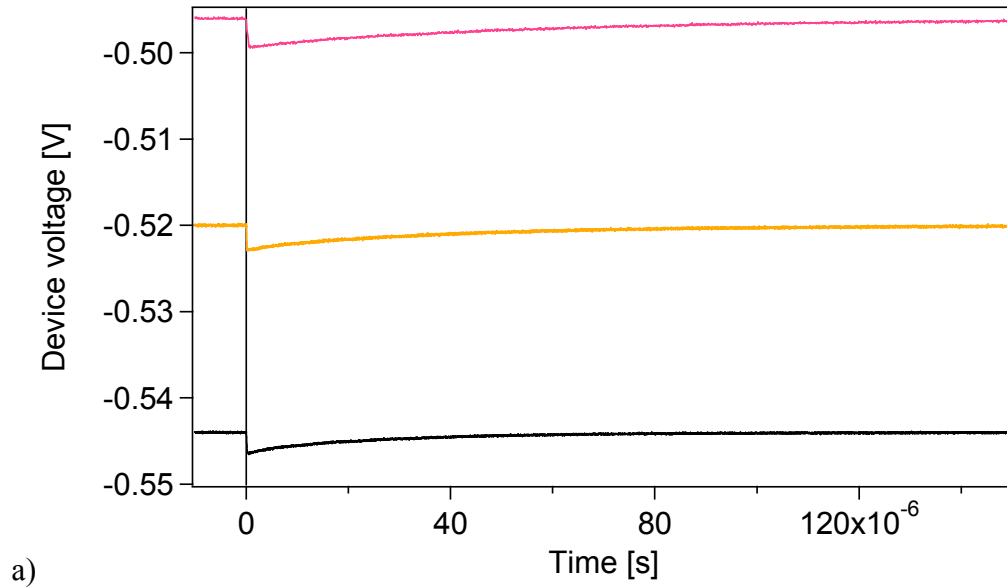
All the terms present in the bracket on the RHS of the equation represent constants, and thus this equation can be rewritten in terms of a single exponential, with a corresponding pseudo-first order rate constant given by

$$\frac{d\Delta n}{dt} \approx -k_{\text{eff}} \Delta n \quad (4.8)$$

$$k_{\text{eff}} = \left(k_{10} n^{\phi-1} + k_{01} p^{\phi-1} + k_{11} n^{\phi} p^{\phi} \left(\frac{\phi_1}{n} + \frac{\phi_1}{p} \right) + \dots \right) \quad (4.9)$$

Thereby demonstrating that by employing a small perturbation regime, the TPV transient should take the form of a single exponential.

4.4 TPV studies as a function of light bias



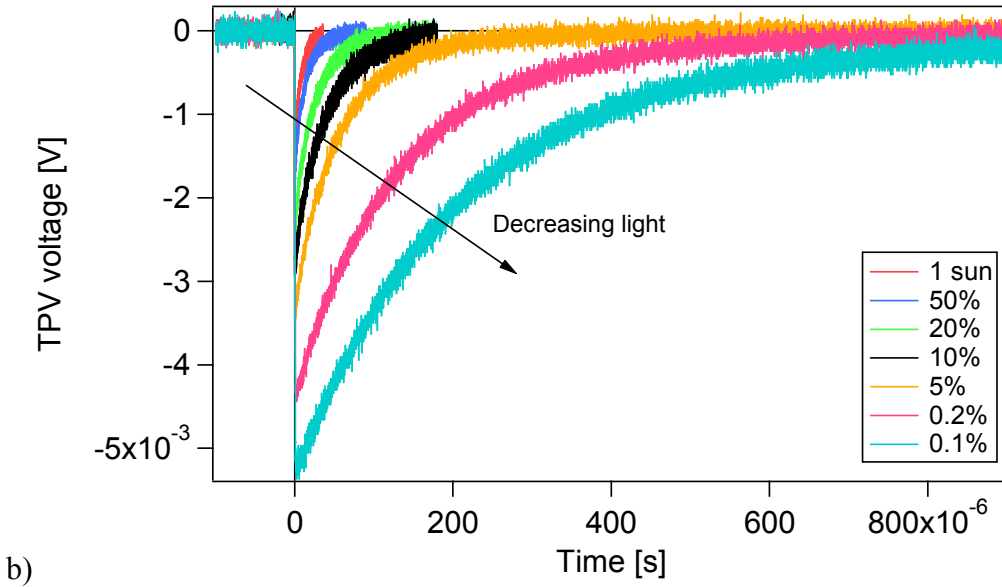


Fig. 4.2. a) A plot demonstrating the typical TPV transients measured over a range of light biases. b) Comparison of TPV transients measured over a range of light intensities 0.1 – 1 suns, by plotting them using the same baseline for each. It is found that as the light bias is increased, both the TPV lifetime and the initial signal amplitude decrease.

Photovoltage transients were measured over a range of light intensities, ranging from approximately 0.01 - 1 sun, corresponding to a V_{oc} range of 0.4 - 0.59V. As the light bias was increased, the TPV decays become faster, whereas the initial signal size ΔV_0 is found to become smaller, as shown in Fig. 4.2. In general, the excitation intensity is chosen appropriately, to allow a complete TPV study over a wide range of light biases, without needing to change this intensity. In Fig. 4.3 a plot of $\tau_{\Delta n}$ is given as a function of V_{oc} . $\tau_{\Delta n}$ was found to vary exponentially with V_{oc}

$$\tau_{\Delta n} = \tau_{\Delta n0} \exp(-\beta V_{oc}) \quad (4.10)$$

where $\tau_{\Delta n0}$ is $\sim 1.7 \times 10^5 \mu s$ and β is ~ 16 . As the light intensity is increased, $\tau_{\Delta n}$ decreases, reaching $\sim 10 \mu s$ at an approximate intensity of one sun.

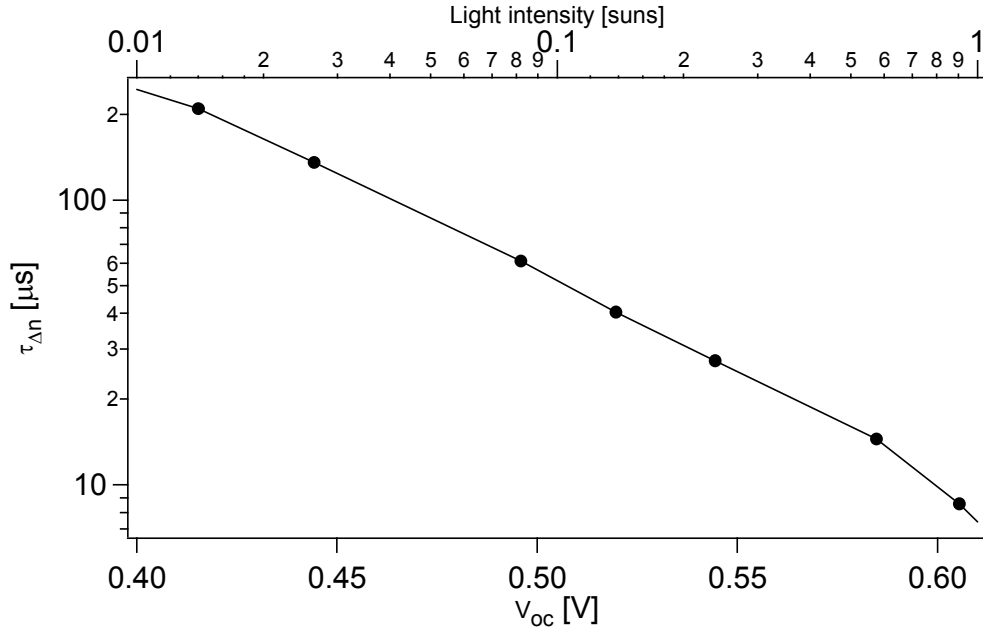


Fig. 4.3. The variation of the carrier lifetime $\tau_{\Delta n}$ with light intensity (bold, left) in the range 0.01 - 1 sun, which corresponds to an open-circuit voltage range 0.4 – 0.59 V (secondary axis).

To verify that this represents a typical result, TPV studies were made on a wide range of different ‘standard’ P3HT:PCBM devices (see Fig. 4.4). In all cases, similar behaviour was observed, with $\tau_{\Delta n}$ following an exponential dependence on V_{oc} .

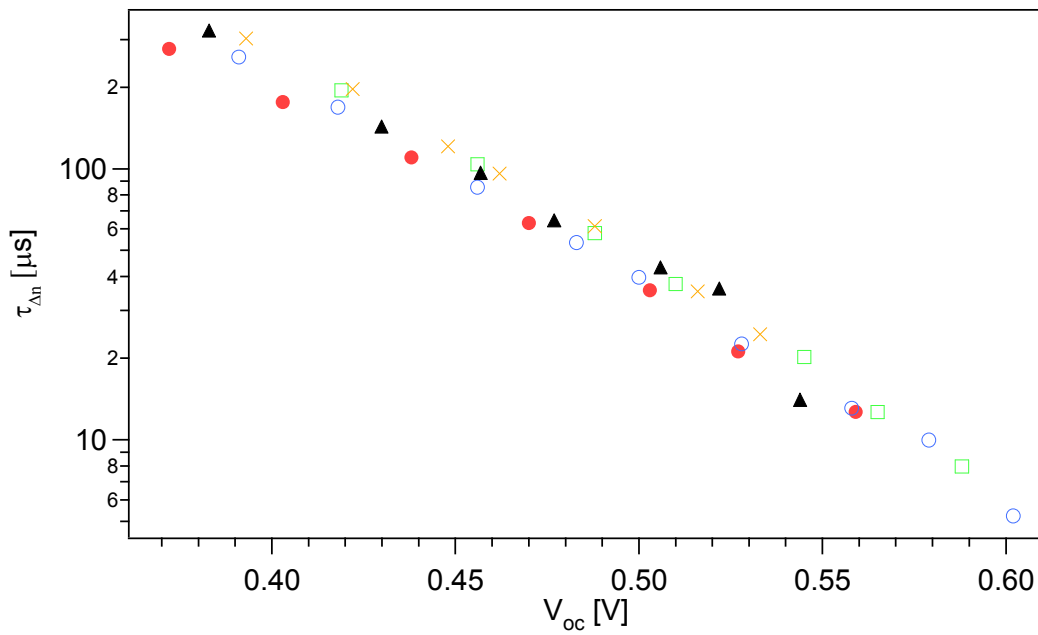


Fig. 4.4. Plots of carrier lifetime versus open-circuit voltage for several different devices. It is apparent that the results from the TPV studies are similar.

4.5 Differential Charging

Photovoltage transients can also be used to determine the steady-state carrier concentration (n) at open-circuit using a procedure known as ‘differential charging’. The differential capacitance C is defined as the voltage change ΔV_0 when a small amount of charge ΔQ is added to the device.

$$C = \Delta Q / \Delta V_0 \quad (4.11)$$

The determination of charge density using this differential charging procedure is based on several key elements:

4.5.1 Obtaining an estimate for ΔQ

To calculate the ‘differential charging’ requires an estimate of the amount of additionally photogenerated charge carriers ΔQ due to the excitation pulse. ΔQ was obtained by integrating with respect to time the short-circuit photocurrent transient (TPC) for the same laser pulse as used in TPV studies, but importantly is measured either at low incident light intensity or in the dark (see Section 3.3 in Chapter 3 for experimental details). This requires the assumption that charge pair generation in P3HT:PCBM devices is independent of electric field and that the recombination losses at short-circuit under the low incident light intensity conditions employed are small. We purposely measured TPC for the device while under low incident intensity or dark conditions to ensure the incurred recombination losses are low.

In the next chapter we experimentally investigate whether that in the case of the standard P3HT:PCBM devices studied there are effects of electric field on the charge pair generation using applied bias TAS studies, and conclude that there are no significant effects observed (see Section 5.3). Thus, this allows us to obtain an estimate of ΔQ by employing photocurrent measurements at short-circuit rather than at open-circuit (where the electric field is smaller) where the TPV transients are measured.

To confirm that the time integral form of the TPC data monitors charge collection, a comparison was made between the charge transient $Q_{sc}(t)$ obtained from the time

integral of the TPC data and the corresponding short-circuit TAS data measured under the same excitation conditions (see Fig. 4.5). It is apparent that $Q_{sc}(t)$ and TAS data are in excellent agreement. The short-circuit TAS data reflects the loss in charge density in the device either due to charge collection or recombination effects. Therefore, this indicates that TPC data can indeed be used to estimate ΔQ .

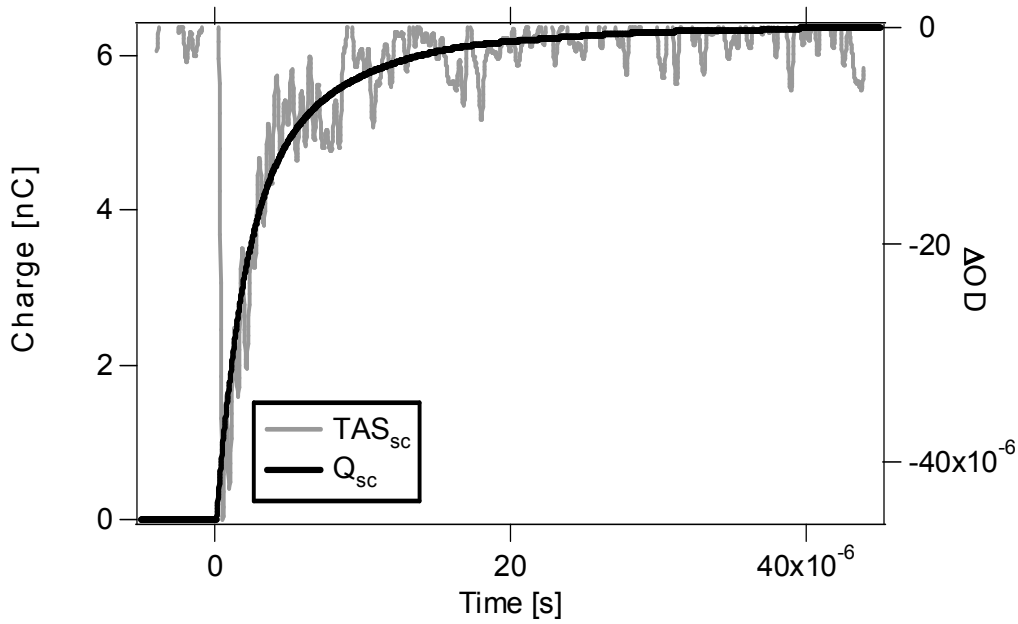


Fig. 4.5. Comparison of time-integrated TPC data (Q_{sc}) with TAS performed under identical conditions. It indicates that Q_{sc} provides a direct measure of the loss in charge in the device.

In an attempt to reduce the errors involved in the determination of the differential charging C , when performing TPV studies the same excitation pulse intensity was used for all light bias conditions studied while still ensuring that all the TPV data abide to the small perturbation regime. This means by assuming that the quantum yield for charge pair generation is light intensity independent, then we can use the same value of ΔQ to determine C for all light biases, and thus, only a single measurement of ΔQ is required.

4.5.2 Determining the appropriate value for ΔV_0 to use

We now turn our attention to address the resultant small change in photovoltage ΔV_0 , due to the small additional amount of charge photo-generated ΔQ . An initial estimate

of the resultant change in voltage due to the excitation pulse is given by the peak photovoltage of the TPV data. However, as charge separation can be considered ‘instantaneous’ relative to the timescales for the voltage transients studied, then recombination will commence at time zero. This means that the peak voltage of the TPV transient represents an under-estimate for ΔV_0 , due to incurred charge losses in the time it takes for the peak voltage to have developed. Rather than use the peak voltage, the change in voltage ΔV_0 which resulted due to the excitation pulse was determined by extrapolating the exponential TPV decay back to $t = 0$:

$$\Delta V(t) = \Delta V_0 \exp\left(-\frac{t}{\tau_{\Delta V}}\right) \quad (4.12)$$

where $\tau_{\Delta V}$ is the lifetime of the TPV decay.

4.5.3 Determining the charge density present in the photoactive layer of the device

Over the range of background intensities employed, C was found to be orders of magnitude larger, $\sim \mu\text{Fcm}^{-2}$, than would be predicted from the electrode capacitance, $\sim 16 \text{ nFcm}^{-2}$ (using a dielectric constant $\varepsilon = 3$, and device thickness $d = 170\text{nm}$). It is therefore assigned to a measure of charge carriers present within the photoactive layer of the device. This is confirmed by comparing the differential charging C data before and after making a correction for the geometric capacitance to account for the charge which should be present on the electrodes, where, as expected, only a minor effect is observed (see Fig. 4.6). We note that for devices where the charge densities present in the active layer of the device are smaller, due to low photogeneration yields and/or faster recombination rates, then this correction will be more significant, and thus must be considered for each device studied.

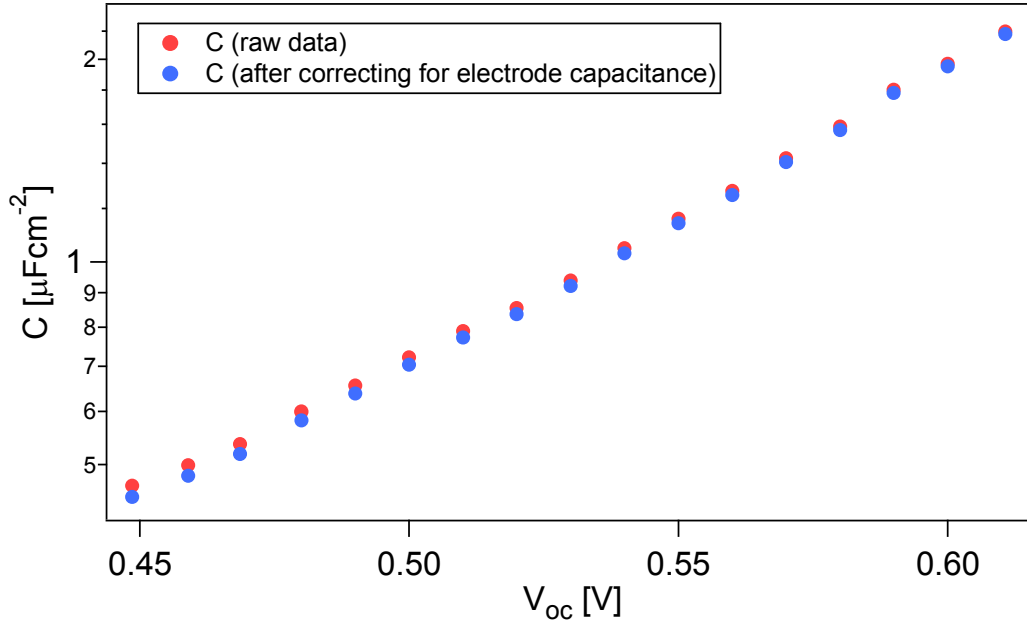


Fig. 4.6. Comparison of differential charging data, before and after making a correction for the electrode capacitance to take account of the charge which should be present on the device electrodes.

C is found to increase exponentially with increasing V_{oc} which we extrapolate back to $V = 0$. Integrating C with respect to voltage provides us with a measure of n (V_{oc})

$$n = \frac{1}{Aed} \int_0^{V_{oc}} C(V) dV = n_0 \exp(\gamma V_{oc}) \quad (4.13)$$

where A is the device area, e is electronic charge, d is the device thickness, n_0 is the carrier concentration prefactor and γ is a constant. In Fig. 4.7, both plots of C and n as a function of V_{oc} are shown for the same device as studied by TPV in Fig. 4.3. This figure shows a three fold increase in charge density between 0.4 and 0.6 V with a value of 7.9 found for γ . Similar values for charge density were obtained using the complementary method of charge extraction,⁹⁴ which will be discussed in detail in Chapter 6.

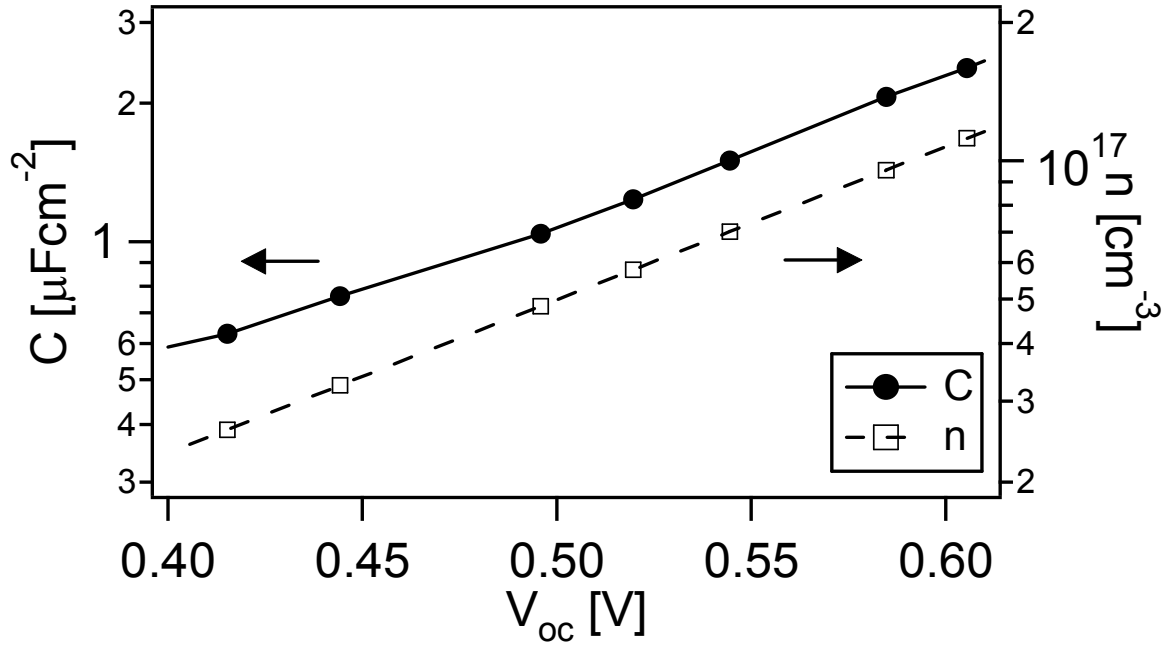


Fig. 4.7. Plots of differential charging (bold, left) and carrier concentration (dashed, right) as a function of V_{oc} for light intensities ranging from 0.01 - 1 sun. Both follow the same exponential dependence with V_{oc} .

In Fig. 4.8, several examples of the differential charging C are given for different devices. Unlike for the TPV measurements of carrier lifetime, in which, for different devices we did not observe significant variations, it is apparent that there is a larger variation in C between different devices.

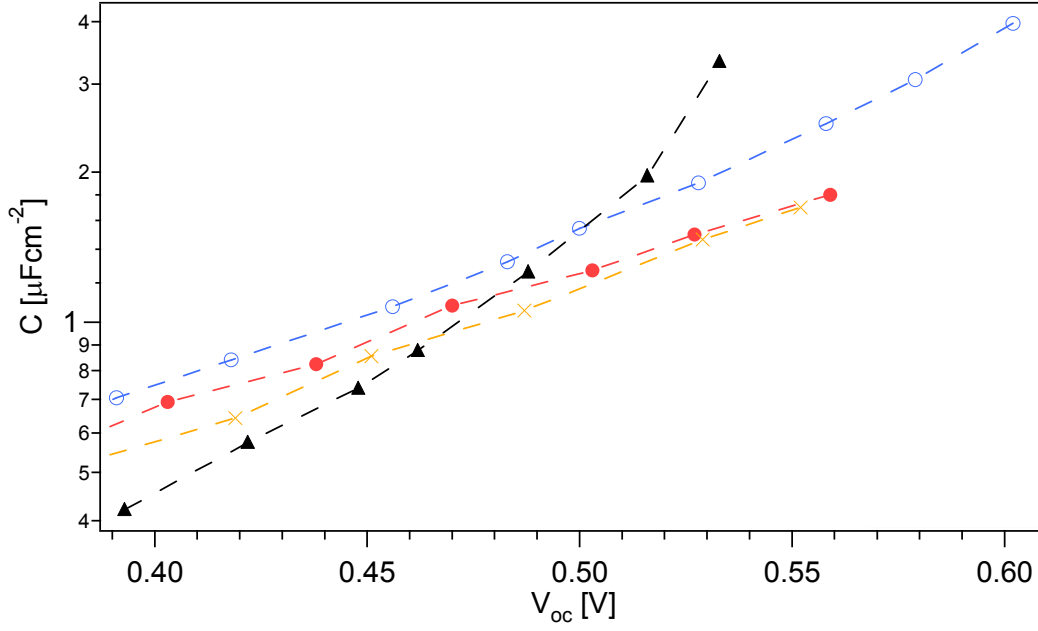


Fig. 4.8. Several examples of differential charging data as a function of light bias, V_{oc} , for a range of different P3HT:PCBM devices.

4.6 Derivation of the rate law for carrier decay dynamics at the open-circuit voltage

If the small perturbation carrier lifetime $\tau_{\Delta n}$ is now plotted against n , Fig. 4.9 (a), we find that $\tau_{\Delta n}$ is strongly related to the charge density, following an inverse square relationship with increasing charge density $\tau_{\Delta n} = \tau_{\Delta n0} (n_0/n)^\lambda$ with $\lambda = 2$. Rearrangement of Eqn.'s (4.10) and (4.13) shows $\lambda = \beta/\gamma$. Studies of a range of devices gave values for λ in the range 1.15 – 2.9 (see Fig. 4.9 (b)), dependent upon the details of device fabrication. We note here that there was not a clear correlation between the value for λ and the corresponding device efficiencies for the devices studied.

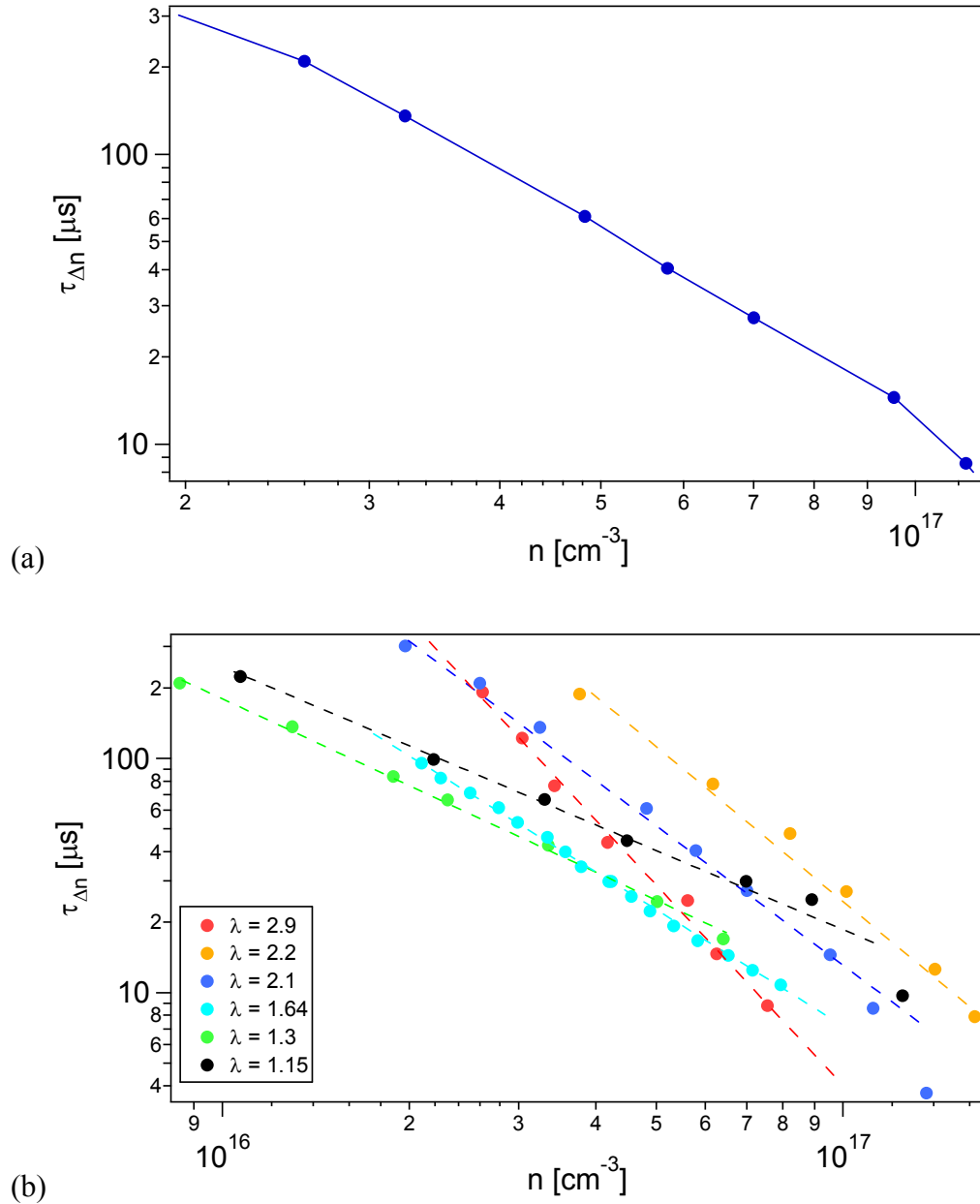


Fig. 4.9. Small perturbation carrier lifetime as a function of charge density for light intensities from 0.01 - 1 sun. (a) The carrier lifetime is found to follow an inverse square relationship with increasing charge density n . (b) Values for λ are found to typically be in the range 1.15 – 2.9.

Equation (4.1) expresses the transient photovoltage in terms of the decay dynamics of the excess charge density $d\Delta n/dt$. As was shown previously in a TPV study of dye sensitised solar cells,⁹⁵ these decay dynamics can be directly related to the total population dynamics, such that:⁹⁶

$$\frac{dn}{dt} \approx \frac{d\Delta n}{dt} \times \frac{n}{(1+\lambda)\Delta n} \quad (4.14)$$

Substitution of Eqn.'s (4.10), (4.13) and (4.14) into Equation (4.1), we obtain:

$$\frac{dn}{dt} \approx -\frac{n^{1+\lambda}}{(1+\lambda)\tau_{\Delta n 0}n_0^\lambda} \quad (4.15)$$

Our empirical observation, for a typical device, of $\lambda = 2$ leads us to the conclusion that the charge carrier decay dynamics exhibit a third order dependence on charge density ($dn/dt \propto n^3$). This strong carrier dependency is striking, and has not been reported previously for P3HT:PCBM devices. One possible interpretation for this strong carrier density dependence is that it corresponds to a bimolecular recombination process in which the corresponding bimolecular recombination coefficient is carrier dependent $k(n)$. Such an interpretation would be consistent with previous reports of TAS studies on polymer:fullerene blend thin films, where dispersive bimolecular decay dynamics were observed, attributed to an exponential tail of sub-bandgap localised ('trap') states.⁶⁰ This trap distribution was shown to be sensitive to film preparation conditions, consistent with our observation of range of values for λ .

Due to the range of processes which can contribute to this empirically derived rate law for the charge carrier decay dynamics at V_{oc} , such as the effects of electric field dependent geminate recombination⁵⁹ and leakage current (see Chapter 2), etc., due to the presence of the electrodes, we are unable to conclude from the data shown in this chapter alone whether this possible interpretation is appropriate. In the next chapter we employ an all optical technique (TAS) to study both thin films and devices, which allows us to investigate the effects due to the presence of the electrodes while under similar open-circuit conditions. By relating these measurements with the TPV data presented here, we will investigate how to interpret the origin of the rate law determined here.

At the beginning of this chapter, a comparative study between TAS and TPV data obtained using the same small perturbation conditions was used to assign the decay of the photovoltage transient as a direct measure of carrier lifetime. TAS measurements

using a large perturbation regime have previously been used to study the carrier decay dynamics in polymer: fullerene blend thin films.^{5,60,86} In these measurements relatively high excitations are employed, where the transient decay is used to monitor the large photogenerated polaron populations falling back to zero. As such it is difficult to relate the carrier lifetimes obtained from these measurements directly with device function, as unlike TPV measurements described here which probe the steady state conditions for specific V_{oc} light bias conditions, this measurement scans a wide range of continually changing charge densities present in the film, making it difficult to know which device conditions the decay lifetime corresponds to. Furthermore, these studies were made on thin films rather than devices, thus, it is also not clear whether the dynamics in the devices we study will be the same as for thin films due to the presence of the electrodes. In the next chapter where we relate large perturbation TAS data on thin films and devices with TPV data, we investigate how to relate large perturbation TAS data with device function.

In the case of other experimental techniques which have been used to study the carrier decay dynamics in similar P3HT:PCBM devices such as Integral mode Q-TOF, photo-CELIV and DOI currents,⁸¹ these techniques have been employed to determine the bimolecular recombination coefficient in these devices. Such measurements have been designed so that the dominant charge decay mechanism is given by bimolecular recombination by employing suitable conditions, such as high excitation intensities in the case of Q-TOF measurements. It is difficult to directly compare these data to the TPV studies presented here, as we must first assert whether we are able to assign the carrier decay dynamics we have described in this chapter at V_{oc} to follow a bimolecular recombination process. Secondly, we know by probing device function at the steady state V_{oc} conditions that our results provide direct measurements of the J - V curve properties under these conditions, whereas it is not clear what device conditions these alternative measurements correspond to.

4.7 Conclusion

In conclusion, a method for probing the steady state charge densities and carrier lifetimes under illumination at open-circuit has been demonstrated on a standard P3HT:PCBM device. Strikingly, it is found that the carrier lifetime follows a strong, non-linear dependence on charge density. This results in the rate law, which describes the charge carrier decay dynamics at V_{oc} , to follow an approximately third order dependence on charge density. In the next Chapter, the origin of this relationship is investigated.



Chapter 5 Bimolecular recombination losses in polythiophene: fullerene solar cells

Transient absorption spectroscopy is employed to monitor charge carrier decay dynamics in a poly(3-hexylthiophene): methanofullerene solar cell. Comparisons of device and film data and data under applied bias demonstrate that these dynamics are dominated by bimolecular recombination. These data are employed to determine the rate constant for bimolecular recombination, found to be strongly carrier density dependent, allowing calculation of the recombination flux. By comparison with the device short-circuit photocurrent we conclude that the open-circuit voltage is primarily limited by bimolecular recombination.

5.1 Introduction

A key advance in the development of organic solar cells was the introduction of donor:acceptor blend films, or ‘bulk heterojunctions’, which enable efficient exciton diffusion to the charge separation interface. However, a drawback of such intimate mixing of donor and acceptor material is that photogenerated charge carriers may be lost via interfacial bimolecular recombination:

$$\frac{dn}{dt} = -knp \quad (5.1)$$

where n, p are the electron and hole carrier concentrations, respectively, t is time and k is the bimolecular recombination coefficient (or ‘rate constant’).

There have been extensive studies of the importance of bimolecular recombination in limiting the performance of organic bulk heterojunction solar cells, focusing in particular on devices based on poly (3-hexylthiophene) (P3HT): 1-(3-methoxycarbonyl) propyl-1-phenyl-[6,6]-methanofullerene (PCBM) blend films. However, quantification of magnitude of bimolecular recombination losses in such devices remains controversial. It has, for example, been reported that the bimolecular recombination coefficient for P3HT:PCBM devices is several orders of magnitude smaller than that predicted using a Langevin description (see Section 2.2.2), and thus it was concluded that bimolecular recombination may be unimportant in such devices.^{78,79,91} This contrasts with analyses of device current voltage data which have typically been indicative of significant bimolecular recombination losses.^{80,97} One complication with experimental studies to date is that they have all been based on optoelectronic studies of complete devices, where interpretation of the data is complicated by the range of other processes which may contribute to charge carrier losses in addition to bimolecular recombination (e.g.: short circuits and device shunts (leakage), recombination at device electrodes, electric field dependent geminate recombination, etc.) or under conditions which are difficult to relate directly to device photovoltaic performance under solar irradiation.^{32,59,62} This explains why in the previous chapter, although we obtained an empirical form for the charge carrier decay dynamics at V_{oc} , we were unable to make any conclusions concerning the originating process(es) for these dynamics.

The main focus of this chapter is to try and understand the origin of the rate law for the total population carrier decay dynamics determined in Chapter 4. Herein we employ an all optical technique, transient absorption spectroscopy (TAS), to monitor charge carrier decay dynamics both in thin P3HT:PCBM blend films and complete P3HT:PCBM devices in order to attempt to investigate the origin of these dynamics. TAS has previously been used to monitor polaron decay dynamics in a range of polymer: PCBM thin films.^{5,60,86} By studying both thin films and devices, we are able to determine whether the presence of the device electrodes has an impact upon the observed carrier decay dynamics, as compared to the thin film component of the same device. Furthermore, by using this optical TAS approach, we are also able to investigate whether, in the standard P3HT:PCBM devices studied herein, there are effects of electric field dependent geminate recombination, achieved by performing TAS studies of ‘charge generation’ under different applied electrical bias.

By comparison of this film and device data, and by consideration of data collected under applied bias, we conclude that the charge carrier decay dynamics at open circuit in the P3HT:PCBM devices studied herein are indeed dominated by bimolecular recombination. These decay dynamics are shown to exhibit an approximately third order dependence upon charge density ($dn/dt \propto n^3$), which is in agreement with our previous transient photovoltage studies given in the previous chapter. Analysis of these dynamics in terms of bimolecular recombination allows us to quantify a carrier dependent bimolecular rate coefficient $k(n)$ which, based on a microscopic model previously developed to explain the origin of the carrier decay dynamics observed in ‘similar’ TAS data for MDMO:PPV/PCBM thin films,⁶⁰ is interpreted in terms of a thermally activated de-trapping bimolecular recombination process. By using the values for this determined $k(n)$, combined with the charge densities determined to be present in the device at V_{oc} , we thus obtain an estimate for the overall bimolecular recombination flux under device operation, and by comparison with the device photocurrent, conclude that the device open circuit voltage (V_{oc}) is primarily limited by this bimolecular recombination process.

Transient absorption spectroscopy is an all optical technique which monitors the change in optical density (ΔOD) of a sample upon pulsed photoexcitation due to the generation of transient species. As such it is a ‘contactless’ technique and can therefore be employed both on complete devices and on the photoactive layer in the absence of electrodes. For experimental details concerning transient absorption spectroscopy and the devices studied, please refer to Section 3.4 in Chapter 3.

5.2 Comparison of thin film and device TAS data

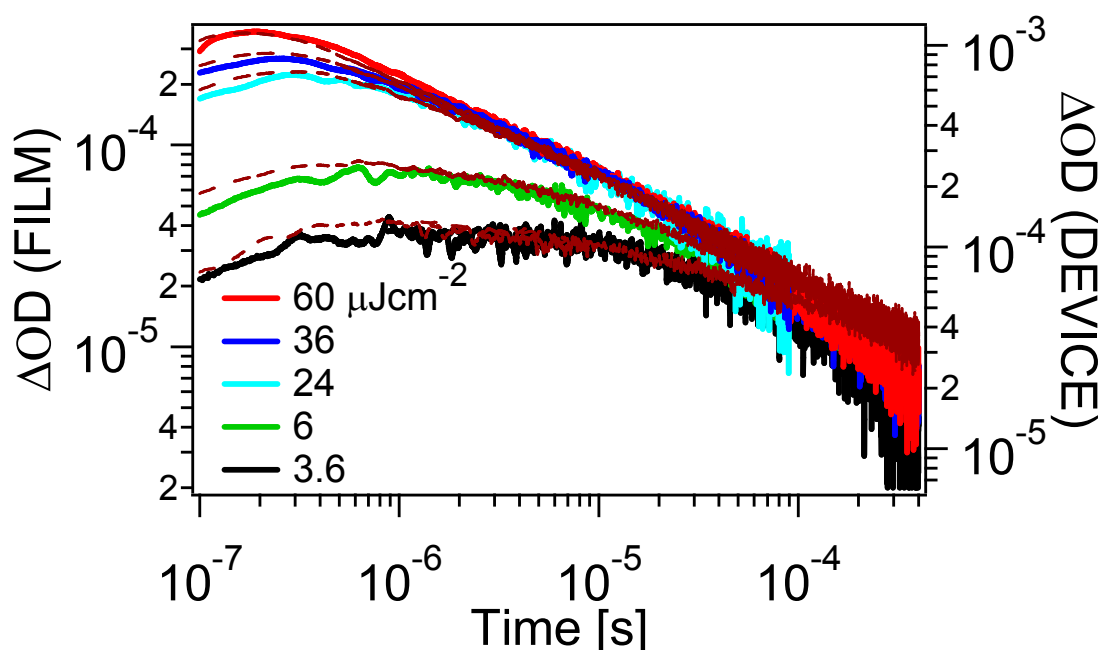


Fig. 5.1. Comparison of reflection-mode TAS film (left) and device data (right - brown dashes) using a 520nm pump and 980nm probe. In both cases, a power law decay $\Delta OD \propto t^{-\alpha}$ with $\alpha \sim 0.47$ is found at relatively high pump intensities/long timescales.

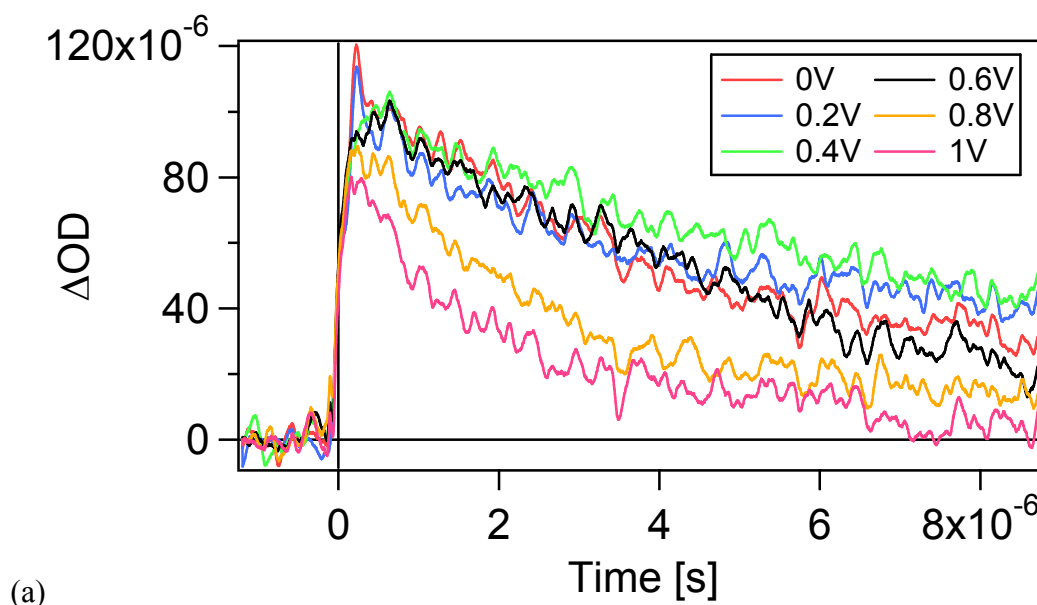
Figure 5.1 shows a comparison of film and device TAS data collected as a function of excitation density under open circuit conditions. These data monitor the decay dynamics of P3HT⁺ polaron photo-induced absorption at 980nm,⁸⁸ observed following excitation at 520nm. The film data, and its dependence upon excitation density, are qualitatively similar to those that were reported previously for PPV/PCBM blend films,^{60,86,87} exhibiting a power law decay $\Delta OD \propto t^{-\alpha}$ with $\alpha \sim 0.47$. In this previous work, a comprehensive study was made into the effects of excitation intensity,

background light and temperature dependence on this power law TAS decay and it was shown that this power law behaviour for each of these conditions can be successfully simulated by a bimolecular recombination model incorporating an exponential tail of polaron trap states providing compelling evidence that the TAS data on these thin films originate due to a bimolecular recombination process.^{60,86} The exponent in such power law decays for P3HT:PCBM films has also been shown to be dependent upon the P3HT regio-regularity and film processing conditions, ranging between 0.3 - 0.7, attributed to variations in trap density.^{5,98} From Fig. 5.1, it is apparent that the thin film and device data show almost identical TAS decay dynamics (note there is a difference in signal amplitude attributed to optical interference effects influencing the device data). It can be concluded that the presence of the device Al electrode has no influence upon the polaron decay dynamics, and therefore that the device data are also consistent with this bimolecular recombination model. In general, the presence of the device electrodes is expected to generate electric fields between the device electrodes which might be expected to result in n and p both being position (x) dependent as found for our computing studies in Chapter 2, thereby directly influencing the bimolecular recombination process given in Eqn. (5.1). However, as the observed recombination dynamics appear to be independent of the presence of device electrodes, we conclude that any such spatial dependencies can be neglected for the decay dynamics addressed herein.

5.3 Applied electrical bias TAS studies of electric field assisted charge generation

In addition to bimolecular recombination losses, geminate (or monomolecular) recombination has also been reported to be an important loss mechanism in OPV in particular. Device electric fields have been suggested to have a strong influence on such geminate recombination losses.^{59,61,75,99,100} For electric field dependent geminate recombination, the resultant reduction in internal electric field with increasing applied bias towards open-circuit this leads to a reduction in the quantum yield of free charge carriers, thus this type of process can alternatively be considered in reverse as an electric field assisted charge generation process. Such geminate recombination processes occur primarily on sub-microsecond timescales,⁹⁸ and would therefore, in

the experiments reported herein, result in a loss of initial signal amplitude. In order to investigate this possibility further, the initial ($\sim 0.5 \mu\text{s}$) TAS amplitude was monitored in devices as a function of applied electrical bias. Low density excitation conditions were employed to ensure to avoid any possible effects of saturation or space charge screening. Typical data are shown in Fig. 5.2. It is apparent that in the range 0 - 0.6 V ($\sim 1 \text{ sun } V_{\text{oc}}$) there is no notable change in the initial signal amplitude. It can be concluded that over this voltage range geminate losses do not significantly change, and so the loss in photocurrent at open-circuit cannot be explained by this process. It should be noted that this observation does not imply that geminate recombination dynamics are in themselves negligible, but only that, for the P3HT:PCBM devices studied herein, any such losses are independent of device macroscopic electric field.⁹⁸ At higher applied biases (above flat-band), we do observe a loss of initial signal amplitude; however this is coupled with accelerated (μs) decay dynamics, and can most probably be attributed not to enhanced geminate recombination but rather either to rapid charge extraction by the device electrodes or accelerated bimolecular recombination.



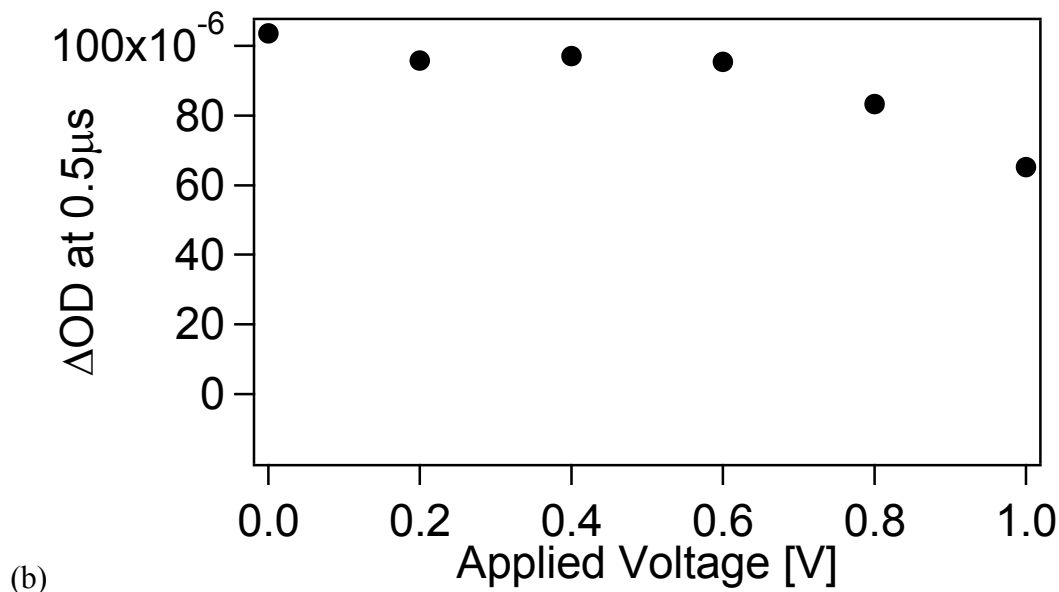


Fig. 5.2. (a) Reflection-mode TAS data for a P3HT:PCBM device under different applied electrical bias. (b) Over the voltage range 0 – 0.6V (~ 1 sun V_{oc}), there is no significant variation in initial (~ 0.5 μ s) signal amplitude, indicating that geminate recombination losses do not strongly increase.

5.4 Converting the TAS $\Delta OD(t)$ data into charge carrier density

The $\Delta OD(t)$ data shown herein can be converted directly into charge carrier dynamics $n(t)$ by using the Beer-Lambert law and employing a suitable value for the molar extinction coefficient (ϵ_M) for photogenerated polarons. For this purpose, the effective ϵ_M under the measurement conditions employed was determined (see below) to be $4 \pm 1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ by comparison of the initial ΔOD amplitude with an integrated short-circuit photocurrent transient for a device under the same low excitation density conditions.

5.4.1 Determination of the effective P3HT⁺ polaron molar extinction coefficient

The Beer-Lambert law is the linear relationship between absorbance (ΔOD) and concentration (c) of an absorbing species

$$\Delta OD = \epsilon_M c l \quad (5.2)$$

where ε_M is the extinction coefficient of the absorbing species and l is the optical path length. An estimate of the effective P3HT⁺ polaron extinction coefficient can be found by correlating the amplitude of the transient absorption spectroscopy (TAS) signal (ΔOD_{PEAK}) using a pump intensity in which the initial signal amplitude is not saturated with the corresponding integrated short-circuit photocurrent (Q) for the same pump intensity. In Eqn. (5.2) the concentration of the absorbing species c can be rewritten in terms of charge Q

$$c = \frac{1000}{N_A} n = \frac{1000}{N_A} \frac{Q}{Aed} \quad (5.3)$$

where n is the carrier concentration, N_A is Avogadro's constant, A is the device area, e is the electronic charge and d is the device thickness. By combining Eqn.'s (5.2) and (5.3), we arrive at an expression for ε_M in terms of ΔOD_{PEAK} and Q

$$\varepsilon_M = \frac{\Delta OD_{\text{PEAK}}}{2d} \frac{Aed}{Q} \frac{N_A}{1000} \quad (5.4)$$

where the optical path length l in the reflective TAS measurements is given by $2d$. Substituting values for $\Delta OD_{\text{PEAK}} = 2 \times 10^{-4}$ and $Q = 9.3 \times 10^{-9}$ nC (Fig. 5.3) with $A = 0.045 \text{ cm}^2$ and $d = 170 \text{ nm}$, we determine an upper estimate for the effective P3HT⁺ polaron extinction coefficient in the device tested, $\varepsilon_M \sim 4.66 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. As the Q found calculated by integrating the photocurrent transient at short-circuit provides us with an under estimate of the total charge corresponding to ΔOD_{PEAK} , due to recombination losses at short-circuit, this provides an upper limit for ε_M . By consideration of experimental errors in the measurements (particularly in the resolution of the TAS signal, measured under these relatively low excitation conditions) we arrive at an estimate for ε_M given by $\varepsilon_M \sim 4 \times 10^4 \pm 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

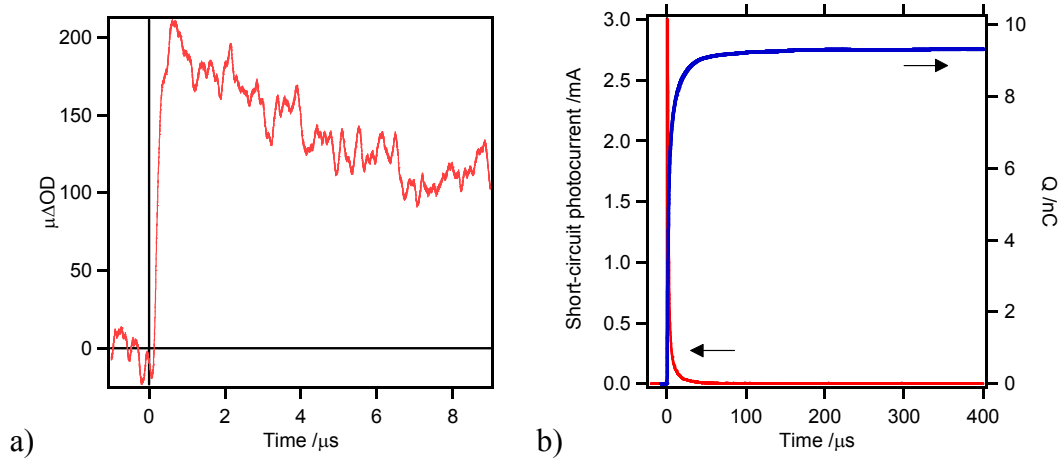


Fig. 5.3. a) Plot of μs -TAS device data at a relatively low pump intensity ($6 \mu J cm^{-2}$) in which the initial signal amplitude is not saturated, and b) the corresponding short-circuit photocurrent (red, left) and total charge Q (blue, right) transients measured under the same excitation conditions.

We note that optical interference effects are well known to influence light absorption within complete photovoltaic devices. The value of ϵ_M for $P3HT^+$ polarons is determined here within the device and is therefore only used in calculations of device data (and not the thin film data). It is likely that these optical interference effects increase the effective strength of polaron absorption, and therefore this value for ϵ_M is specific to the devices studied herein.

5.5 Relating large perturbation TAS data with small perturbation TPV data

The resultant polaron density transients are plotted in Fig. 5.4. It is apparent that the densities monitored are in the range $10^{16} - 10^{18} cm^{-3}$, spanning the steady state charge density observed for $P3HT:PCBM$ devices in the previous chapter at one sun V_{oc} ($10^{17} cm^{-3}$).

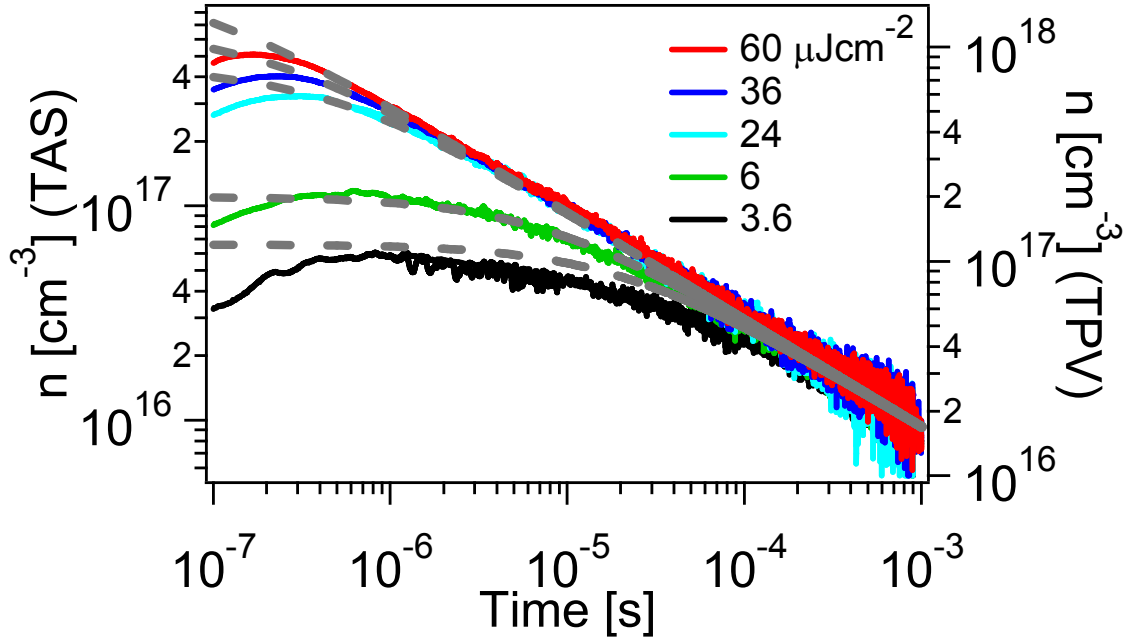


Fig. 5.4. Reflection-mode TAS device $n(t)$ data (left) compared to the simulated TAS data derived from TPV data (right - grey dashes).

In the previous chapter we presented an alternative small perturbation optoelectronic measurement of charge carrier dynamics in P3HT:PCBM solar cells, based upon transient photovoltage (TPV) data obtained from devices held at open circuit under continuous white light bias. Employing this methodology, we determined an empirical rate law for charge carrier decay dynamics in a P3HT:PCBM device at V_{oc} given by

$$\frac{dn}{dt} \approx -\frac{n^{1+\lambda}}{(1+\lambda)\tau_{\Delta n0}n_0^\lambda} \quad (5.5)$$

where λ , n_0 and $\tau_{\Delta n0}$ are experimentally determined constants and $(1+\lambda)$ corresponds to the empirical reaction order with respect to n . By integrating this rate law, we obtain an expression for the total carrier decay dynamics $n(t)$, which can be used to simulate the $n(t)$ transients determined from the large perturbation ΔOD transients.

$$n(t) \approx n_{t=0} \left(1 + \frac{\lambda n_{t=0}^\lambda t}{(1+\lambda)\tau_{\Delta n0}n_0^\lambda} \right)^{-1/\lambda} \quad (5.6)$$

where $n_{t=0}$ corresponds to the initial charge density. This comparison is shown in Fig. 5.4, employing TPV data collected for the same device employed in the TAS studies ($\lambda \sim 2$, $n_0 = 1.1 \times 10^{15} \text{ cm}^{-3}$, $\tau_{\Delta n0} = 0.17 \text{ s}$ and using $n_{t=0}(60 \mu\text{Jcm}^{-2}) = 2 \times 10^{18} \text{ cm}^{-3}$,

which is scaled with excitation energy). It is striking that the charge carrier decay dynamics obtained from the large perturbation all optical TAS studies are in excellent agreement with the small perturbation optoelectronic TPV data. Given this agreement and the agreement between our film TAS decays, which we have previously assigned to bimolecular recombination, we conclude that the charge carrier dynamics observed by the TPV technique in devices under continuous bias irradiation at V_{oc} are also dominated by bimolecular recombination.

5.6 Bimolecular recombination coefficient k

5.6.1 Calculating k using TAS and TPV data

We now turn to calculation of the bimolecular rate constant for the decay dynamics shown in Fig. 5.4. Rearrangement of Eqn. (5.1), employing the Beer-Lambert law to relate the observed optical density change ΔOD to charge density n and assuming charge neutrality ($n = p$), allows this coefficient to be determined directly from the TAS data, Fig. 5.5:

$$k = -\frac{d\Delta OD}{dt} \frac{2d\varepsilon_M}{\Delta OD^2} \frac{1000}{N_A} \quad (5.7)$$

where d is the device thickness and N_A is Avogadro's constant. Alternatively this rate constant can be calculated from consideration of the empirical rate law obtained from TPV transients given in Eqn. (5.5):

$$k = \frac{n^{\lambda-1}}{(1 + \lambda)\tau_{\Delta n0} n_0^\lambda} \quad (5.8)$$

Figure 5.5 shows the results of the calculations of the bimolecular rate constant k both from the large perturbation TAS data and from the small perturbation TPV data presented in the previous chapter, plotted as a function of film charge density n . It is apparent that the two methodologies are in excellent agreement, both indicating that k is strongly carrier dependent, increasing almost linearly with increasing n ($k \propto n$), thereby resulting, for the typical device studied herein, in an overall third order reaction rate law.

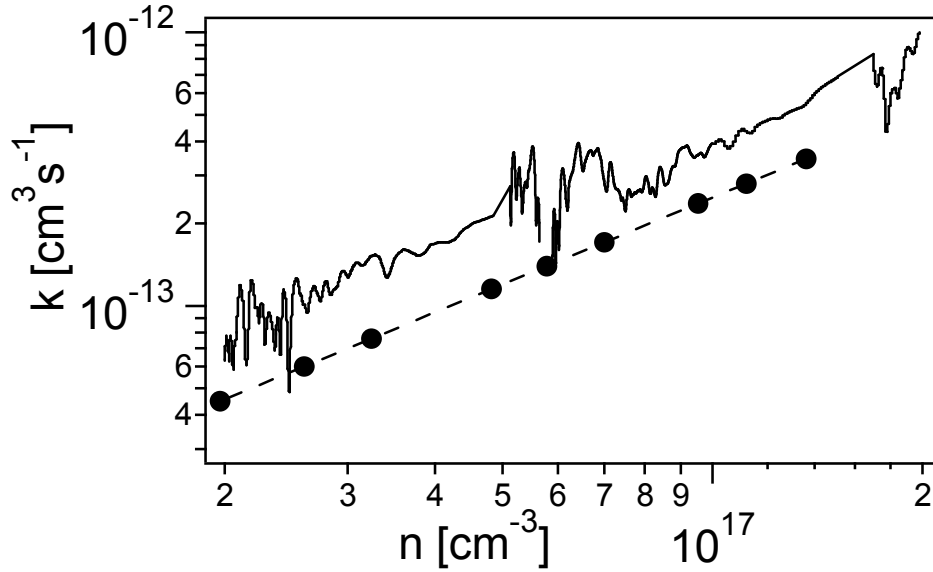


Fig. 5.5. Plots of bimolecular recombination coefficient, k , as a function of carrier concentration, n , calculated from measurements of TAS (bold) and TPV (dashed).

As we described previously in the last chapter, the charge density dependence of the rate law for the carrier decay dynamics at V_{oc} derived from TPV data allows the bimolecular recombination coefficient k (see Eqn. (5.8)) to be determined. The charge density dependence of the bimolecular rate constant $k \propto n^{\lambda-1}$, determined from this equation, was found vary for different devices, where as previously (see Section 4.6) λ was in the range 1.15 – 2.9 resulting in the carrier dependence of k to be in the range 0.15 - 1.9. Figure 5.6 shows some typical examples for k determined for a range of different devices. However, most devices exhibited λ 's in the middle of this range (approximately $\lambda = 2$), corresponding to the 'typical' cells focused upon in this thesis. We note, as we discuss below, that this variation of λ between devices most probably results from variations in the crystallinity of the photoactive layer of the device, although it has not yet been possible to undertake a systematic study of this effect.

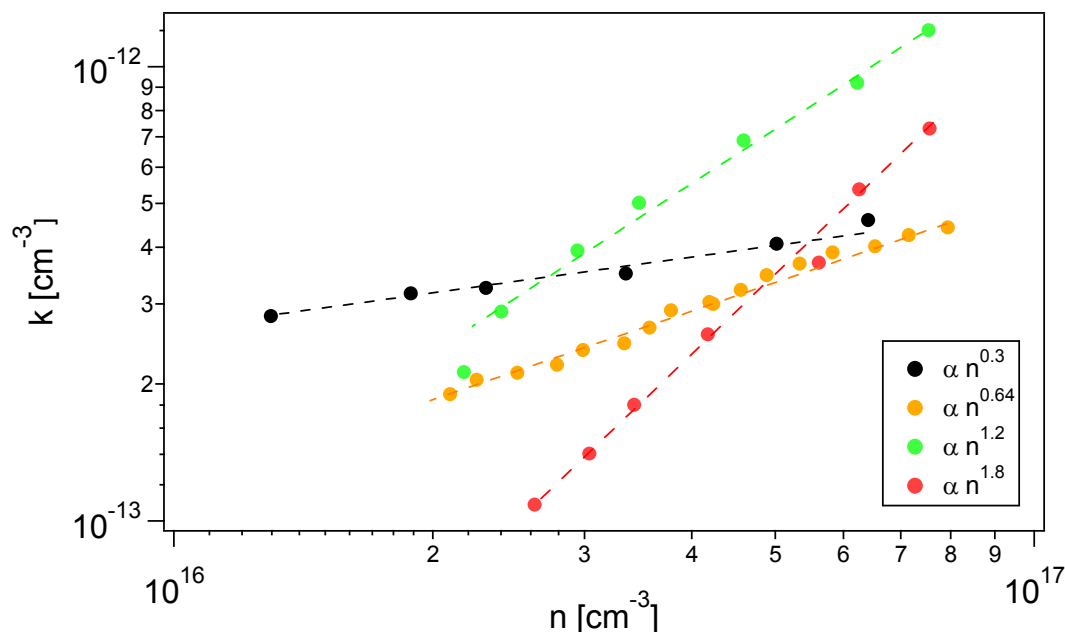


Fig. 5.6. Several examples of plots of the charge density dependence of the bimolecular recombination coefficient in standard annealed P3HT:PCBM devices.

We are also now able to rationalise the behaviour of the power law decay exponent α obtained from TAS data already reported on thin films of P3HT:PCBM in terms of the charge density dependence of the bimolecular recombination coefficient. It was shown that the power law exponent was dependent on crystallinity.^{5,98} More specifically, as the crystallinity of these films increased α also increased. Therefore, using Eqn. (5.8) this leads to k to become less charge density dependent with an increase in crystallinity, where for non-annealed low crystalline films $\alpha \sim 0.3$, corresponding to $k \propto n^{2.3,5}$, whereas, for annealed films which have higher crystallinity α has been reported as high as 0.7 resulting in a corresponding charge density dependence for k of $k \propto n^{0.4,98}$.

5.6.2 Discussion concerning this carrier dependent bimolecular rate constant

Our observation that the bimolecular rate constant is charge density dependent is in agreement with the previously reported microscopic model for this process incorporating an exponential tail of trapped hole states in the conjugated polymer, with thermally activated de-trapping resulting in carrier concentration dependent recombination kinetics.⁶⁰ In Fig. 5.7 a diagram describing this model is given. This model corresponds to a diffusional description of bimolecular recombination, where

the rate constant is proportional to the effective polaron diffusion constant (or, by Einstein's relationship, the mobility), and this effective diffusion constant is charge density dependent. Carrier concentration dependent mobilities have also been reported from FET mobility data for P3HT thin films.¹⁰¹ Our observation that k increases with n is important for device function, as it results in a strongly non-linear increase in bimolecular recombination losses with increasing charge density. It is important to note that $k(n)$ does not continue to increase indefinitely, but instead, for sufficiently large n , where all the trapped states in P3HT will become filled, a regime will be reached where the bimolecular rate constant k is no longer charge carrier density dependent. This is consistent with the fast phase 'trap-free' bimolecular recombination component of TAS decay reported previously for large charge densities.⁸⁶ This value of k serves as the maximum value this recombination coefficient can take.

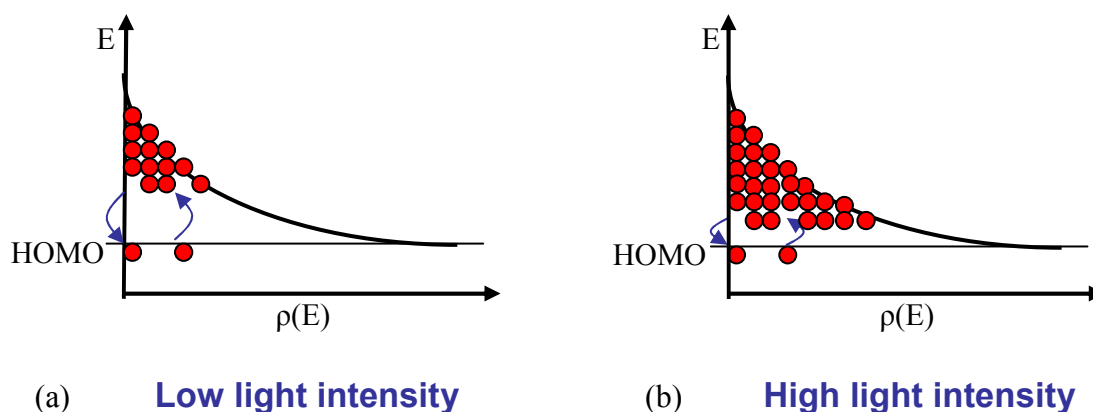


Fig. 5.7. Microscopic model of a bimolecular recombination process incorporating an intra-band exponential density of trapped states ρ in P3HT. (a) At low light/excitation intensity, a low number of these trapped states are filled, and thus, this leads to slow de-trapping times, and therefore, the holes spend less time at the mobility edge. As a result, this will lead to slower recombination dynamics and lower charge carrier mobility. (b) At high light/excitation intensity, much more of these trapped states are filled. Therefore, the de-trapping times become much faster, which leads to faster bimolecular recombination dynamics, and a higher charge carrier mobility.

At the end of this chapter, we offer an alternative explanation for the origin of this 'third order' behaviour of the charge carrier dynamics, where we consider that rather than explain this behaviour in terms of a bimolecular recombination process with a corresponding coefficient which is carrier dependent, it may instead be due to a

traditional second order bimolecular recombination process, in which this additional empirically observed third charge contribution originates from variations in the spatial overlap between the electron and hole charge distributions. This represents future work as, at present, it is unverified, and so requires further study.

The bimolecular rate constant k determined herein is significantly smaller (even for the highest charge densities studied) than that calculated for the Langevin recombination coefficient ($k_L = e(\mu_n + \mu_p)/\epsilon\epsilon_0$) where e is the electronic charge, $\epsilon(\epsilon_0)$ is the relative (absolute) dielectric permittivity and $\mu_n(\mu_p)$ is the electron (hole) mobility.⁷⁹ Time of flight (TOF) studies of similar blend films indicate polaron mobilities on the order of $\sim 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ ⁵ which predict $k_L = 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, 2 - 3 orders of magnitude higher than the values of k determined herein (see Fig. 5.4). This conclusion is consistent with previous double injection and integral mode TOF studies.^{78,79} The relatively low value for the observed bimolecular rate constant has been suggested to result from phase separation of the polymer and PCBM components of the film. Whatever its origin, the observation that $k \ll k_L$ is critical to reducing bimolecular losses and enabling efficient device performance.

5.7 Calculating the loss in photocurrent at open-circuit due to bimolecular recombination

We have shown above that the charge carrier decay dynamics in the P3HT:PCBM studied herein under open circuit conditions are dominated by bimolecular recombination. We note that the observed strong carrier dependence of these bimolecular losses is consistent with such bimolecular recombination losses being relatively unimportant at short circuit, where charge extraction by the electrodes results in significantly lower charge carrier densities. We turn now to quantification of J_{BI} , the bimolecular recombination flux at V_{oc} :

$$J_{BI} = -knpde \quad (5.9)$$

J_{BI} acts in the opposite sense to the photocurrent, hence reducing the net current density extracted under operating conditions. For determination of J_{BI} , we use values for n , p determined from differential charging (previous chapter) and charge

extraction (see next Chapter) techniques, TPV data for k , assuming $n = p$ and neglecting (see above) any spatial dependence of n or p . This recombination flux is compared in Fig. 5.8 against the short circuit photocurrent J_{sc} measured under the same light conditions. We find that over the whole range of light intensities studied, J_{BI} at V_{oc} is approximately equal to J_{sc} , further supporting our conclusion that the primary factor resulting in loss of photocurrent output at open-circuit is bimolecular recombination.

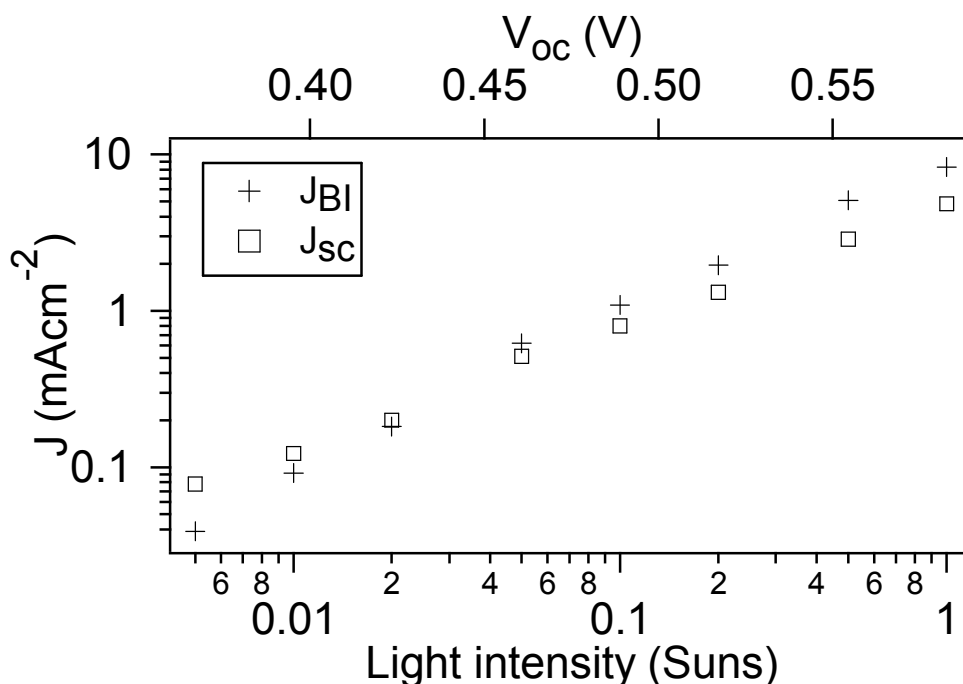


Fig. 5.8. Comparison of the calculated bimolecular recombination flux at open-circuit J_{BI} (crosses) with the corresponding short-circuit photocurrent, J_{sc} (open squares).

Previous studies of the factors limiting the open-circuit voltage of bulk heterojunction solar cells have shown a correlation between V_{oc} and the separation of the donor HOMO and acceptor LUMO levels.³² The results we report herein suggest this dependence originates from bimolecular recombination losses, with shifts in HOMO/LUMO levels modulating charge carrier densities and thereby the bimolecular recombination flux J_{BI} . We note this correlation has previously been related to dark current diode losses limiting V_{oc} , suggesting that the dark current may (over the conditions studied herein) originate from a bimolecular recombination process as we describe in more detail in the next chapter. In any case, given the relatively modest voltage output of P3HT:PCBM solar cells (0.6 V compared to the blend electronic

bandgap of 1.1 eV), we conclude that minimisation of such bimolecular losses is likely to be essential to improve the voltage output, and therefore power conversion efficiency, of P3HT:PCBM solar cells. For example, the data we present herein (see Fig. 5.8) indicates that a reduction of the bimolecular rate constant by 10 in Eqn. (5.9) should result in a 0.1V increase in device open circuit voltage as long as all other features in the device remain unchanged. However a reduction in the bimolecular recombination coefficient will likely to lead to an increase in the charge densities in the device, and so resulting in less of a significant increase in V_{oc} . We believe this factor may have been neglected in the work by Pivrikas *et.al.*⁷⁹ where they have claimed that bimolecular recombination was unimportant in P3HT:PCBM devices due to the ‘non-Langevin’ behaviour of the bimolecular recombination coefficients, as they assumed relatively low device charge densities.

5.8 Future Work: Alternative explanation for the origin for the third order charge carrier decay dynamics

In this Chapter, we have concluded that the origin of the rate law describing the charge carrier decay dynamics at V_{oc} described previously in the last Chapter corresponds to a bimolecular recombination process with a strongly carrier dependent bimolecular recombination coefficient. Our experimental data to date indicates that consideration of the spatial dependence of $n(x)$ and $p(x)$ is not required for this interpretation of the data reported herein. Nevertheless, for completeness we now also consider the potential impact of such spatial dependencies on our analysis.

The resultant macroscopic electric fields introduced by the device electrodes would have been expected to change the spatial overlap between the electron and hole distributions as previously observed in our numerical studies presented in Chapter 2, where we modelled a BHJ solar cell using a simple single layer drift diffusion model. Figure 5.9 shows a comparison of the numerically simulated electron and hole carrier distributions for a device both under 1 sun and 0.01 sun V_{oc} conditions which shows that as the light bias is increased the spatial overlap between the electron and hole carrier distributions also increases, leading to faster recombination dynamics. Consequently, this suggests that in general considering bimolecular recombination in

terms of total charge densities rather than their constituent spatial distributions may lead to determining an inappropriate value for the recombination coefficient.

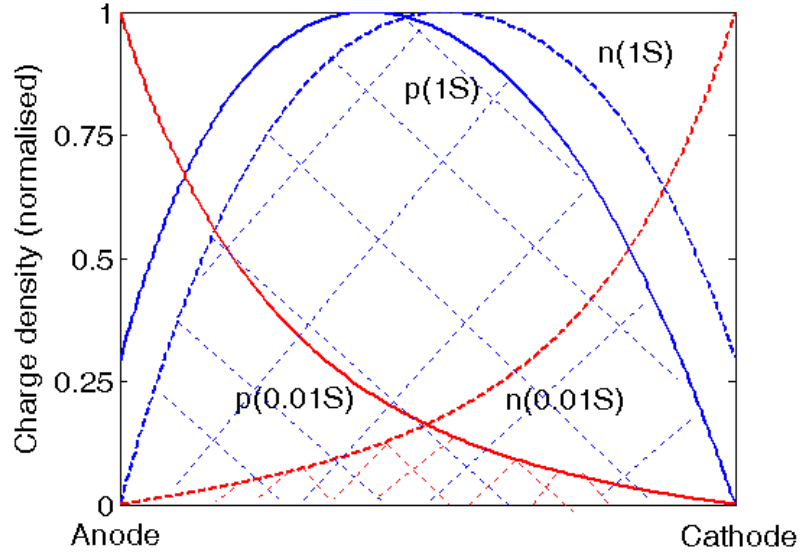


Fig. 5.9. Plot of the electron (solid) and hole (dashed) distributions (normalised) under 1 sun (blue) and 0.01 sun (red) V_{oc} conditions, obtained from the numerical studies presented in Chapter 2. It is found that the area of spatial overlap for 1 sun conditions (given by the blue dashed area) is much larger than under 0.01 sun conditions (given by the red dashed area).

We consider this behaviour algebraically by considering the case of a ‘pure’ bimolecular recombination process in terms of the spatial charge distributions and a constant bimolecular recombination coefficient k_0 ,

$$\frac{dn(x)}{dt} = -k_0 n(x)p(x) \quad (5.10)$$

As we are unable to investigate these spatial distributions experimentally, we instead must consider the total recombination across the thickness of the active layer, which is given by

$$\frac{d\bar{n}}{dt} = \frac{1}{d} \int_0^d \frac{dn(x)}{dt} dx = -\frac{k}{d} \int_0^d n(x)p(x) dx \quad (5.11)$$

where $\bar{n}$ is the spatially averaged electron hole charge densities, and d is the device thickness. This can be rewritten in terms of the spatially averaged electron and hole charge densities, $\bar{n}$ and $\bar{p}$ respectively, and a function $f(V, I)$ describing the spatial

overlap between $n(x)$ and $p(x)$ dependent both on the applied voltage and the illumination level

$$\frac{d\bar{n}}{dt} = -\frac{k_0}{d} \int_0^d n(x)p(x)dx = -k_0 \bar{n} \bar{p} f(x) = -k_0 \bar{n}^2 f(V, I) \quad (5.12)$$

where we have assumed charge neutrality $\bar{n} = \bar{p}$. At high light intensities and applied biases (approaching the built-in potential) the spatial overlap f will approach 1, which corresponds to the case where the spatial overlap between both carrier distributions is total.

We can now compare this analytical expression with the rate law determined for the carrier decay dynamics at V_{oc} from both large perturbation TAS data and small perturbation TPV data, which is now rewritten using similar notation:

$$\frac{d\bar{n}}{dt} \sim -c_1 \bar{n}^3 = -k_0 \bar{n}^2 f(V, I) \quad (5.13)$$

where c_1 is a constant. Therefore, an alternative interpretation for the origin for $k(n)$ could be that $f(V, I) \propto \bar{n}$, i.e. the area of the spatial overlap scales with the charge density present in the device. Whether this is the case for an intimate blend such as P3HT:PCBM is debateable.

In this alternative description, as we have already pointed out, as the light bias is increased, the spatial overlap between the charge distributions will approach completeness. Therefore, for high light bias conditions we would expect the carrier decay dynamics to display behaviour of a pure second order recombination process. By consideration of large perturbation TAS data under similar conditions which occur for high excitation intensities ($60 \mu\text{Jcm}^{-2}$) on early time scales ($\sim \text{ns}$), it has indeed been reported previously that the TAS decay has a fast phase characteristic of a pure bimolecular recombination process in thin films.⁸⁶

This interpretation also seems to be consistent with the results for the bimolecular recombination coefficient obtained from other experimental techniques, such as integral mode TOF⁷⁹ and photo-CELIV,⁹¹ which employ high excitation intensities or are studied at approximately flat-band conditions. In these studies they have reported

‘carrier independent’ bimolecular recombination coefficient for P3HT:PCBM devices contrary to our findings presented herein. If the spatial distributions are indeed important for the determination of k , then this would suggest that we are unable to correctly determine the ‘real’ bimolecular recombination coefficient using our TPV and TAS data, but instead we actually determine an effective one encompassing both the bimolecular rate constant as well as the effects of spatial overlap between $n(x)$ and $p(x)$. To determine the ‘real’ bimolecular recombination coefficient, we would instead need to either consider the fast phase of the large perturbation TAS data under high excitation intensity or perform measurements such as integral mode TOF⁷⁹ or DOI⁷⁸. However, to relate the ‘real’ rate constant to experimental J - V curves would require an additional measurement of this spatial overlap, which is not the case for our TPV data. Therefore, the effect of spatial overlap does not in anyway reduce the importance of these measurements we have presented herein. This will become further clear in the final two chapters, where we relate the empirically determined carrier decay dynamics to recreate ‘light’ J - V curves. This provides a possible direction for future study.

We emphasize our assumption that the spatial dependence of n and p can be neglected appears to provide sufficient explanation for the data presented herein and is moreover consistent with the previously reported model of polaron dynamics in such films.

VI

Chapter 6 Charge extraction studies of charge density

In the last chapter we considered analyses of P3HT:PCBM J - V curves at V_{oc} from which a charge density dependent bimolecular recombination coefficient was determined. This chapter provides analysis of a new method to measure charge density, ‘charge extraction’, which can be applied to the device across the J - V curve for both incident light/dark conditions. First of all we employ this technique at open-circuit and demonstrate good agreement with differential charging data, which was previously described in Chapter 4. Then by applying charge extraction to the device under forward bias in the dark an expression relating the dark current with charge density is obtained. By measuring the charge as a function of V_{oc} (under varying light intensities), we determine a similar expression relating the loss in photocurrent at V_{oc} with charge density for different light intensities. Strikingly, these two currents are found to follow the same relationship with charge density, $J \propto n^\alpha$, where $\alpha \sim 2.6$. This suggests that the two processes, the forward bias current in the dark and photocurrent losses, represent identical physical processes and can be treated

uniformly when expressed as a function of charge. This indicates that the J - V curves for a device under incident light can be modeled using the forward bias current in the dark, but which is scaled directly with the charge densities present in the device under illumination conditions.

6.1 Introduction

A key physical parameter determining OPV (organic photovoltaic) device performance is the charge density (n) present in the device under operation. The ability to measure charge densities across the J - V curve will greatly facilitate the interpretation of J - V data, and also provide an additional parameter which should be reproducible by numerical device models, such as the one presented in Chapter 2, thereby significantly enhancing the validity of such models. Previously we have described studies of the carrier decay dynamics at V_{oc} in the last two chapters, where we obtained an expression for these dynamics in terms of charge density. By studying the charge densities across the J - V curve, it may be possible to determine the charge density losses in general, rather than specifically be confined to open-circuit conditions.

A variety of techniques have previously been employed to obtain values for n in organic electronic devices, including charge extraction with a linear increasing voltage for a device under illumination Photo-CELIV,⁹¹ double injection currents (DOI)⁷⁸ and integral mode time of flight (Q -TOF).⁷⁹ In general the focus of these studies have been to interrogate charge carrier decay dynamics and charge carrier mobilities simultaneously, rather than specifically focus on providing a direct description of the J - V curve in terms of charge density at standard operation voltages and currents. In this Chapter we apply a ‘charge extraction’ (CE) technique^{90,94,102} to determine charge densities in a solar cell while under steady state operating conditions. This measurement is frequently used in the dye sensitized research community,^{89,102} but has not, to our knowledge, been previously applied to polymer/fullerene cells. CE represents an analogous measurement to CELIV, but employs a significantly simpler experimental setup. In CELIV, a linearly increasing voltage is applied to the device when extracting the charge from the device.^{91,103-105}

This is done to limit the extent of the charge losses incurred during the measurements, and also allows the introduction of time delays, thereby allowing the investigation of recombination. As we show in this chapter, we believe the charge extraction technique reported herein determines charge densities for these P3HT:PCBM efficiently allowing charge densities to be determined across the J - V curve, thus not requiring the additional complications involved in the CELIV setup.

Charge extraction is a simple measurement in which a solar cell is initially at a fixed point on the J - V curve, either in the dark or under illumination, and then is switched to short-circuit (zero bias) while at the same time the light (if any) is switched off. Schematically, this is shown in Fig. 6.1.

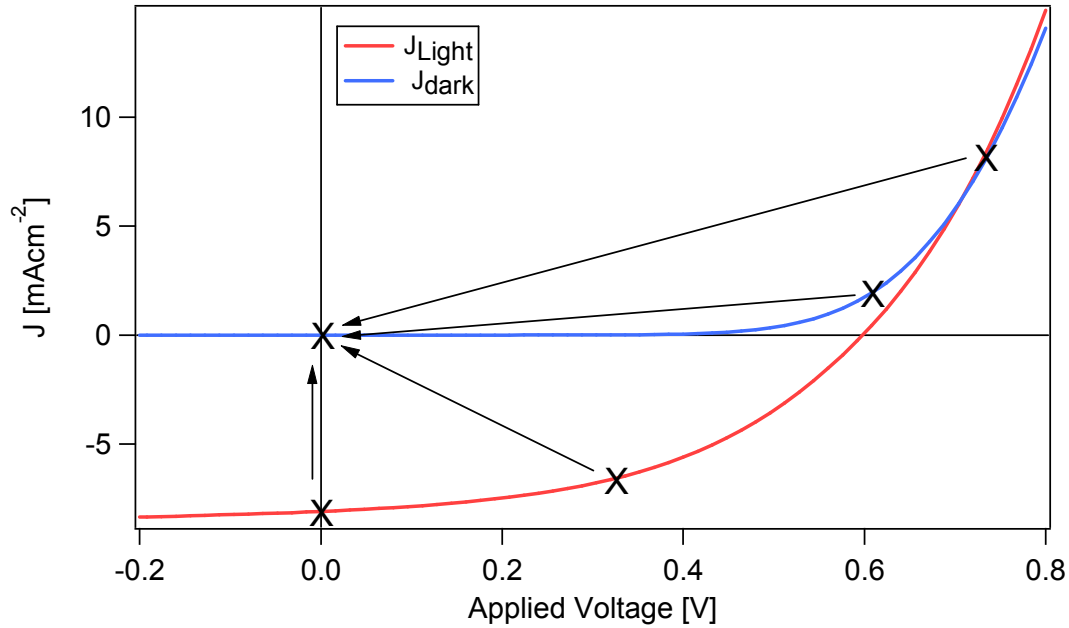


Fig. 6.1. Schematic of the charge extraction measurement. Initially the device is positioned at a fixed point on either the ‘light’ J - V curve J_{light} , or the dark J - V curve J_{dark} . The device is then shorted whilst being placed under dark conditions, which allows the charge density in the device to be extracted in the form of a current transient.

The switch to short circuit creates a current transient as the cell discharges. The integral of this current transient provides an estimate of the excess charge in the cell under the J - V condition specified before the switching, minus any charge losses incurred during the measurement. We note that this experiment also collects the capacitive charge resident on the electrodes.

Charge extraction was initially employed to study the charge densities in the device/on the electrodes under light bias V_{oc} conditions. The carrier losses incurred during these CE measurements were quantified using an iterative procedure based on the expression for the charge carrier decay dynamics derived from the small perturbation TPV studies previously described in Chapter 4, and are found to be relatively small. By correcting for these incurred losses and the charge which would be present on the device electrodes based on the capacitive structure of the device using an estimate of the geometric capacitance, we obtain an estimate of the charge density present in the active layer of the device. By comparison with the charge densities determined using the complementary differential charging procedure, as described in Chapter 4, we find that the charge densities determined by both techniques are in excellent agreement, which suggests that the CE technique is able to determine the charge densities present in the active layer correctly.

We then apply the CE technique to the device under forward bias in the dark. By relating the current density with the charge density present in the active layer of the device, and by comparing this relationship, with that found between the loss in current at V_{oc} and charge density, we show that these relationships follow the same rate law with charge density. This strongly suggests that the forward bias current in the dark is governed by the same physical process which determines the loss in current at V_{oc} , which in the previous chapter we concluded was controlled by a bimolecular recombination process. Finally, we relate our findings concerning this forward bias current in the dark with the widely used formulation of the Shockley diode equation.^{12,38}

For experimental details concerning the CE technique and for fabrication details on the devices studied, please refer to Section's 3.5 and 3.1 respectively, given in the experimental methods chapter, Chapter 3. As previously, all data were collected on annealed P3HT:PCBM solar cells.

6.1.1 Diagnostic test for the charge extraction technique

To determine whether the experimental setup used for charge extraction was working appropriately we performed a simple test measurement on a test circuit. CE measurements were made on a capacitor C where the charge $Q = CV$ residing on the electrodes is known, where V is the applied voltage. It was found that the CE current transient obtained was able to account entirely for the capacitive charge that would be resident on the electrodes, thus verifying the CE setup was working appropriately and could be applied to study standard P3HT:PCBM devices.

6.2 Charge extraction measure of the charge density stored in the device at V_{oc}

Figure 6.2 shows typical charge extraction data for a device held at approximately 1 sun V_{oc} conditions. The inset displays the time integrated form of the CE current data, where it has been converted into the extracted carrier concentration $n_{ext} = Q_{ext}/Aed$, where Q_{ext} is the charge extracted A is the device area, d is the device thickness and e is the electronic charge.

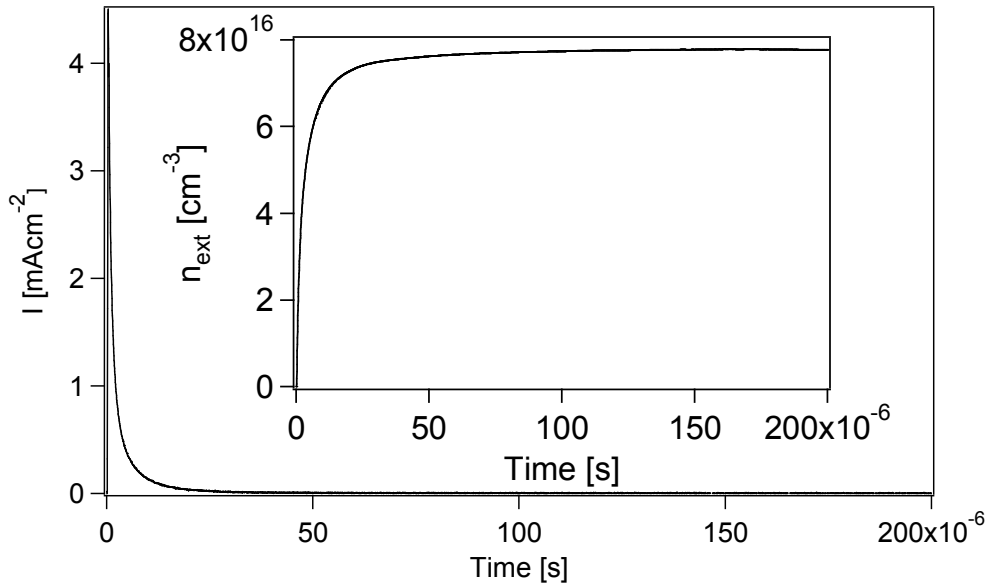


Fig. 6.2. A typical charge extraction current transient for a device under approximately 1 sun open-circuit conditions, with inset displaying the corresponding time integrated form.

A typical CE result as a function of V_{oc} is shown in Fig. 6.3. It is apparent that it follows an approximately exponential relationship with V_{oc} , as previously described in the complementary measurement of differential charging described in Chapter 4.

$$n_{ext} = n_0 \exp(\gamma V_{oc}) \quad (6.1)$$

where $n_0 = 7.3 \times 10^{14} \text{ cm}^{-3}$ and $\gamma = 7.8$. We have previously presented charge measurements based on another method ‘differential charging’ in Chapter 4, where $n(V_{oc})$ was found to follow a similar exponential expression. Before we make a direct comparison between these two complementary measurements, the CE data must be corrected for the charge losses incurred during the transient, either due to recombination or charge collection at the ‘wrong’ electrodes, and for the charge resident on the device electrodes. We first evaluate the charge losses before considering the charge present on the electrodes, as this charge will also be able to recombine as the total excess charge is extracted from the device.

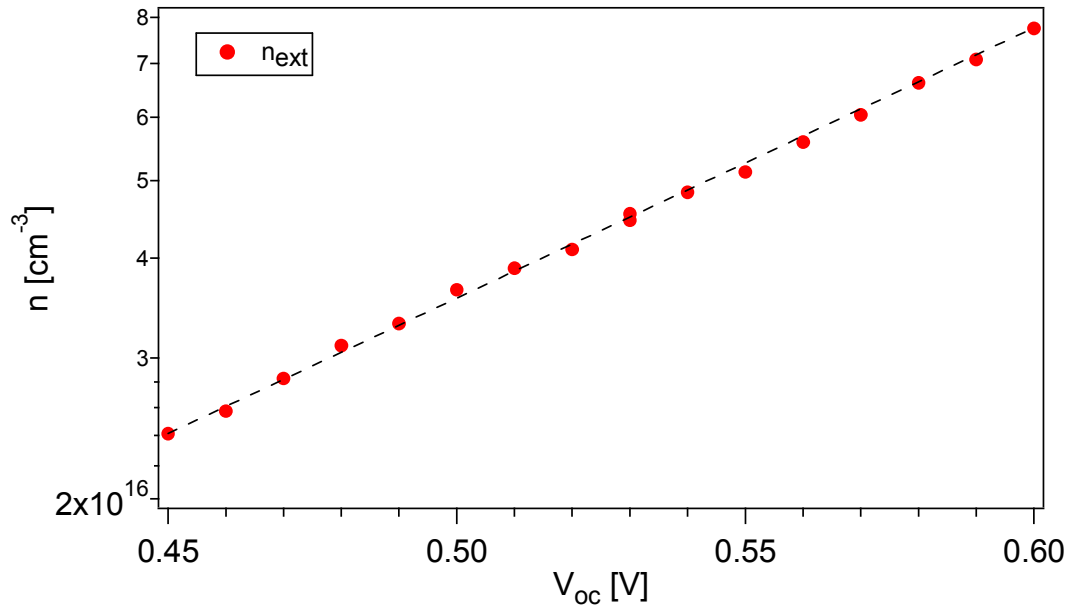


Fig. 6.3. Initial charge extraction data on a typical P3HT:PCBM solar cell, before making corrections for the incurred carrier losses and for the charge which would be present on the device electrodes.

6.2.1 Evaluation of the incurred charge losses

It might be argued that the CE measurement will underestimate the total charge due to recombination occurring during the complex evolution from light V_{oc} to dark short

circuit conditions. Qualitatively one can see that this error will be small for the cells studied herein. The time to extract 50% of the charge in these cells is ($\sim 2 \mu\text{s}$) for the device at 1 sun V_{oc} (see Fig. 6.2), compared to a corresponding carrier lifetime at V_{oc} equal to the product of the small perturbation carrier lifetime $\tau_{\Delta n}$ ($\sim 8 \mu\text{s}$), determined from TPV data (see Chapter 4) and the small perturbation factor $\delta = (1+\lambda)$ ($\lambda = 1.86$, see below), as described previously in Chapter 4, which for this cell gives ($\sim 23 \mu\text{s}$).

We can furthermore quantify the incurred charge losses using the following scheme. The extracted charge as a function of time gives a first estimate of the initial charge $n_{\text{ext}}(\infty)$ and the remaining charge density $n_{\text{device}}(t)$ at each time (see Fig. 6.4(a))

$$n_{\text{device}}(t) = n_{\text{ext}}(t = \infty) - n_{\text{ext}}(t) \quad (6.2)$$

where $n_{\text{ext}}(t = \infty)$ represents the total charge density extracted. By performing TPV studies on the same device (see Fig. 6.4(b)), combined with this initial estimate of the charge densities present in the device at V_{oc} , we obtain an expression for the carrier decay dynamics in the device at V_{oc} in terms of charge density, as outlined in Chapter 4:

$$\frac{dn}{dt} = -\frac{n}{(1+\lambda)\tau} = -\frac{n^{1+\lambda}}{(1+\lambda)\tau_{\Delta n_0} n_0^\lambda} \quad (6.3)$$

where t is time, $\lambda = \beta/\gamma \sim 1.86$, where $\beta = 14.53$ and $\gamma = 7.8$, $\tau_{\Delta n_0} = 0.066 \text{ s}$ and $n_0 = 7.3 \times 10^{14} \text{ cm}^{-3}$. As TPV is performed as a function of ‘light bias’, which represents a simultaneous study of the effects of light intensity and applied bias, then dn/dt , in principle, should describe the carrier decay dynamics across the whole J - V , and thus, may be used to determine the incurred losses during these CE transient measurements.

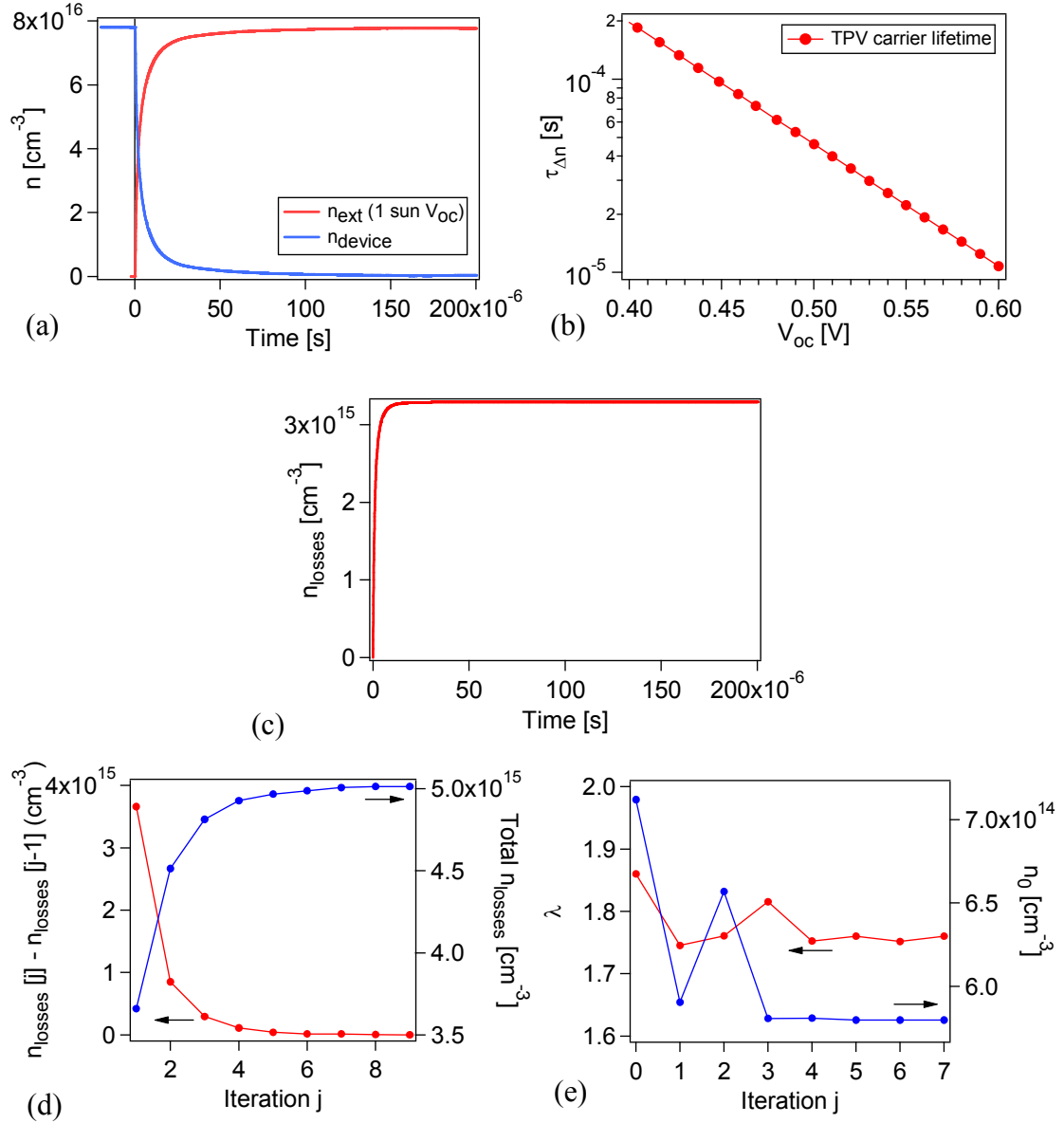


Fig. 6.4. The main plots involved in the iterative procedure used to evaluate the incurred carrier losses during the charge extraction transients. (a) A typical initial CE plot is shown for a device under initial 1 sun V_{oc} conditions. Based on the initially measured charge extraction transient, we obtain an initial estimate of the amount of charge present in the device n_{device} as a function of time. (b) TPV determined carrier lifetimes as a function of V_{oc} , $\tau_{\Delta n} = \tau_{\Delta n0} \exp(-\beta V_{\text{oc}})$ with $\beta = 14.53$. (c) By using the derived expression for the carrier decay dynamics dn/dt , an initial mapping of the incurred carrier losses n_{losses} was made. The charge extraction transient is then corrected for these losses and the same procedure repeated. In (d), a plot is given which shows that the additional incurred losses $n_{\text{losses}} [j] - n_{\text{losses}} [j-1]$ between iteration $j-1$ and j converges to zero after several iterations (left axis), and therefore, by summing these losses, the total losses incurred during the charge transient based on the expression of dn/dt converges to a fixed value (right axis). This procedure was repeated for each of the light biases studied, with each of the initial CE determined charge densities then corrected for these incurred carrier losses. The expression dn/dt was then modified to take into account for this correction for the charge

density and the same method was then repeated for several iterations. In (e) plots of the determined values for λ and n_0 are shown as function of iteration, showing that after several iterations, these values converge to a fixed value, resulting in a fixed expression for dn/dt .

At each time interval of the CE transients, the incurred charge carrier losses n_{losses} are evaluated based on the derived expression for the carrier decay dynamics dn/dt at each of the light biases for which TPV is studied, as shown in Fig 6.4(c).

$$n_{\text{losses}} = \sum_{t=0}^{\infty} \frac{dn_{\text{device}}(t)}{dt} \Delta t = \sum_{t=0}^{\infty} \frac{n_{\text{device}}^{1+\lambda}}{(1+\lambda)\tau_{\Delta n_0} n_0^{\lambda}} \Delta t \quad (6.4)$$

where $\Delta t = 4 \times 10^{-8}$ s is the time interval between each point for the charge extraction transient. The expression for $n_{\text{device}}(t)$ was then corrected for these losses, and the same process repeated for several iterations j until the evaluated carrier losses are convergent, $n_{\text{losses}}[j] - n_{\text{losses}}[j-1] \rightarrow 0$, which was found to typically require 4 - 6 iterations, although, to ensure convergence, the procedure was repeated for 9 iterations, as shown in Fig. 6.4(c). This same method was repeated for each of the light biases studied using CE.

The values obtained for n_{losses} were then added to the initial charge densities n_{ext} , from which a new expression for dn/dt was then re-evaluated to account for this modification. The procedure was then repeated iteratively until self consistency is achieved, which provides the finalised values for n_{losses} to use and a finalised expression for dn/dt which could now be employed to determine n_{losses} for the other conditions studied using charge extraction. By correcting for the determined n_{losses} , we obtain an estimate of the total excess charge density present in the device/on the electrodes given by

$$n_{\text{device}}(V, I) = n_{\text{ext}}(V, I) + n_{\text{losses}} \quad (6.5)$$

The main graphs, which form the basis of this iterative process, are supplied in Fig. 6.4.

Figure 6.5 shows a comparison between $n_{\text{ext}}(V_{\text{oc}})$ before and after correcting for the total determined charge losses n_{losses} . It is apparent that this correction of n_{losses} is relatively small. At 1 sun V_{oc} conditions, representing the condition for which the

charge densities present in the device under operating conditions will be maximum, and so, we would expect to find the incurred carrier losses to be largest, we find that $n_{\text{losses}} \sim 10\%$ of n_{device} . Therefore, even without correcting for these carrier losses for the devices studied herein, the charge extraction measurements provide a good estimate for the charge density stored in the device/on the electrodes.

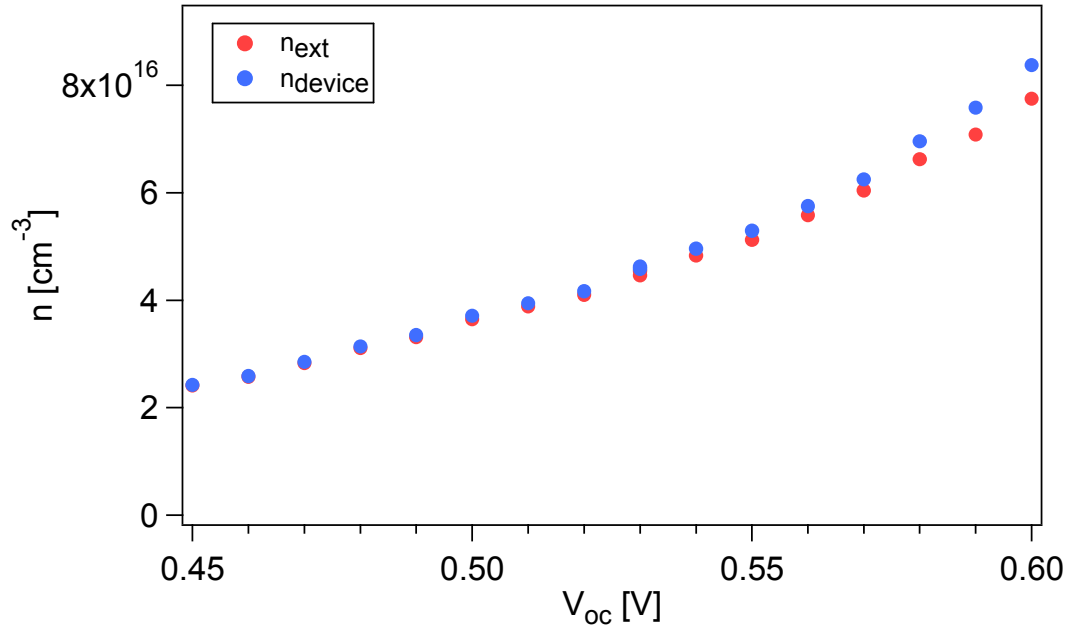


Fig. 6.5. Comparison of the charge densities determined in the device by charge extraction before and after correcting for the evaluated carrier losses, n_{ext} and n_{total} respectively.

6.2.2 Correction of electrodes

By using the initial CE data, and correcting for the incurred charge losses as just described, we obtain an estimate of the total excess charge density present in the device/on the electrodes. However, this includes the charge which will also be present on the electrodes as a result of the device's capacitive structure, which requires to be corrected for. By using the device thickness $d = 150$ nm, the device area $A = 0.045$ cm^2 , combined with an estimate of the dielectric constant as 3, we estimate the geometric capacitance as $C = 0.8$ nF. The charge density which would be present in the photo-active layer n_{active} of the device is given by

$$n_{\text{active}} = n_{\text{device}} - \frac{CV}{eAd} \quad (6.6)$$

Figure 6.6 shows a comparison of the charge densities before and after correcting for the charge resident on the electrodes. It is apparent that this correction is most important at low device voltages (corresponding to low active layer charge densities. For instance, for a light bias $V_{oc} = 0.45V$ n_{active} is $\sim 15\%$ smaller than n_{device} . We find that the charge density present in the active layer is exponentially related to open-circuit voltage.

$$n_{active}(V_{oc}) = n_0 \exp(\gamma V_{oc}) \quad (6.7)$$

where $n_0 = 3.85 \times 10^{14} \text{ cm}^{-3}$ and $\gamma = 8.88$.

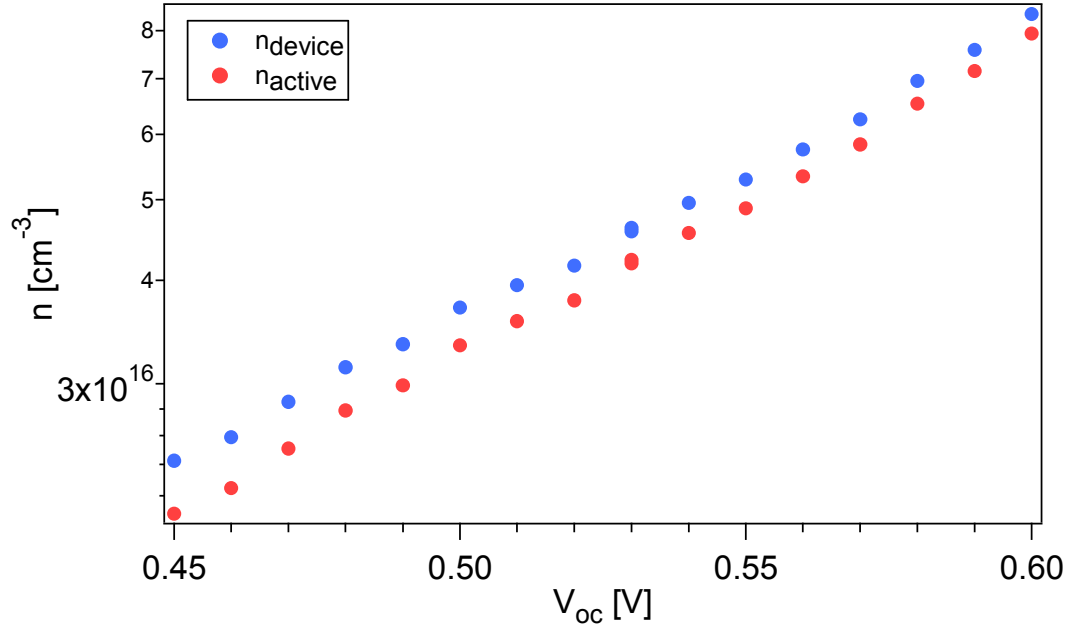


Fig. 6.6. Comparison of the charge densities n determined by the charge extraction technique in the device as a function of light bias V_{oc} before and after correcting for the charge which will be present on the device electrodes given by n_{device} and n_{active} respectively.

Hereafter, in referring to charge densities n_{active} , we employ n , dropping the ‘active’ subscript.

6.2.3 Comparison of differential charging and charge extraction to measure the charge densities in the device at V_{oc}

In Chapter 4, a ‘differential charging’ method was used to determine the charge density stored in the device/on the electrodes at V_{oc} conditions. In this procedure, an

evaluation of the differential charging $C = \Delta Q / \Delta V_0$ is determined by measuring the amount of additional charge density ΔQ that results in a small change in the device voltage ΔV_0 , where ΔQ and ΔV_0 are found by measuring short-circuit photocurrent transients (under dark conditions) and small perturbation TPV transients. By integrating C with respect to V_{oc} , an estimate for the charge carrier densities stored in the device at V_{oc} ($n(V_{oc})$) was found. Charge extraction provides an alternative method to determine the same charge densities. A comparative study was made between the charge densities determined via both techniques, using the same ‘light bias’ experimental conditions on the same device. Figure 6.7 shows a comparison between $n(V_{oc})$ obtained by using these two different techniques. We find that the determined charge densities from both techniques are in excellent agreement. This suggests that both measurements correctly determine the charge densities present in the photoactive layer of the device, as both methods represent independent methods and require different assumptions. For instance, the differential charging procedure is based on the assumption that the charge generation process is electric field independent and that recombination losses at short-circuit are low for low light conditions. In contrast the charge extraction method assumes that we are able to evaluate the incurred charge losses during the measured transients using the derived expression for the carrier decay dynamics at V_{oc} based on combined TPV and CE data. We note that for both methods we have accounted for the charge resident on the electrodes. The fact that we find good agreement between both data is supportive that the assumption that the charge generation process is electric field dependent in the case of differential charging, as previously concluded in the last chapter.

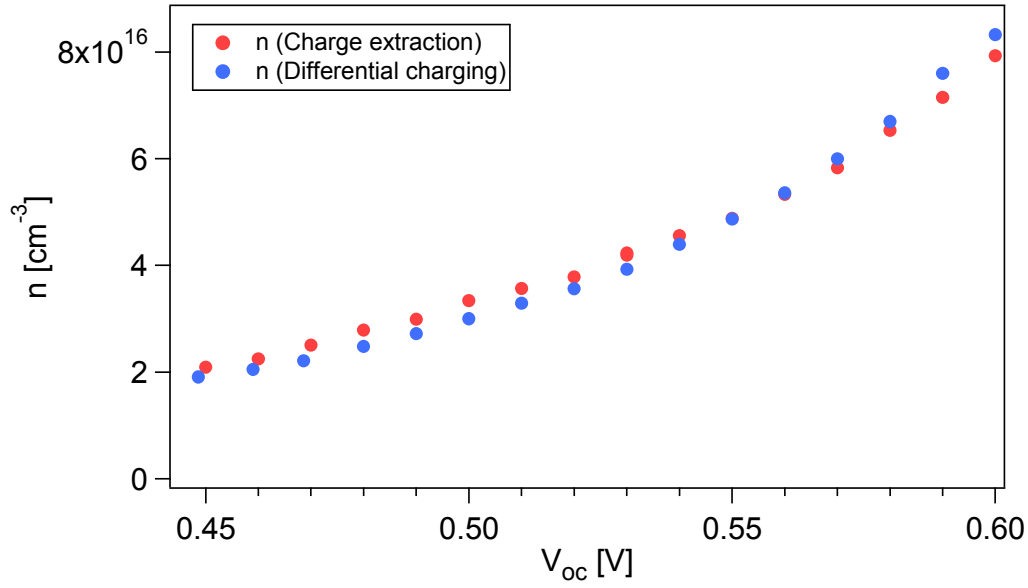


Fig. 6.7. Comparison of the charge densities determined in the active layer of the device using charge extraction (red) and differential charging measurements (blue). All data have been corrected for the charge resident on the electrodes.

6.3 Self-consistency test to check the validity of the analysis

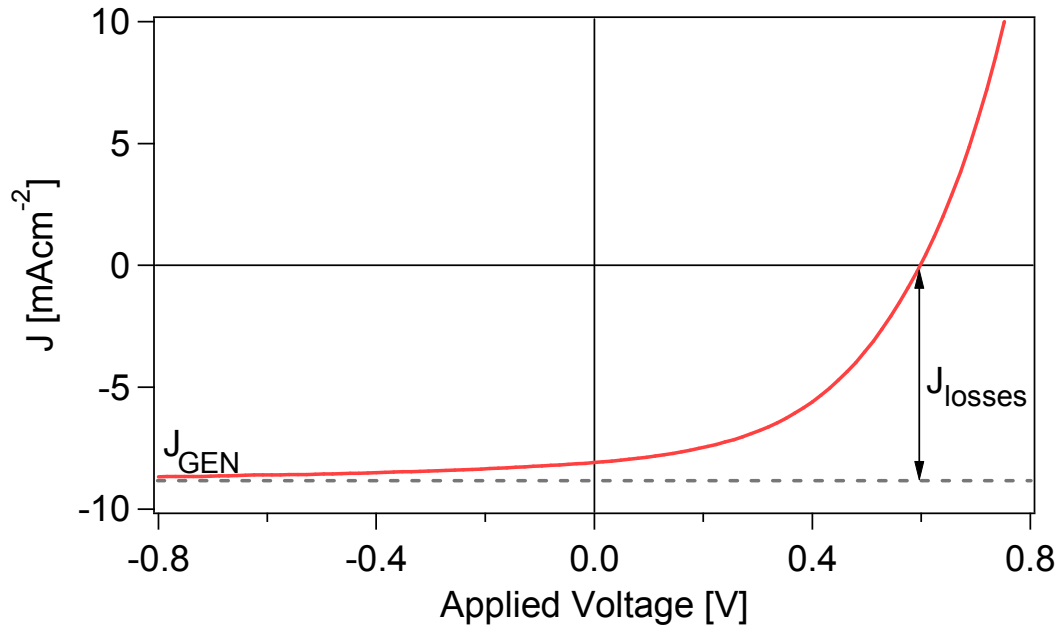


Fig. 6.8. A J - V curve depicting the loss in photocurrent at V_{oc} . In the absence of an electric field assisted charge generation then this loss in photocurrent will equal the photocurrent.

A general test to check the validity of the analysis for charge density n and carrier lifetime τ is to calculate the loss in photocurrent at V_{oc} (J_{losses}) and compare it to the device's corresponding photocurrent. In the absence of an electric field assisted charge generation process, the loss in current at V_{oc} (J_{losses}) must equal the corresponding photogenerated current for the device under the same light conditions (see Fig. 6.8). In the previous chapter we attributed the loss in photocurrent at V_{oc} to a bimolecular recombination dominated current based on combined TAS and TPV study. Thus when considering the loss in photocurrent at V_{oc} , we evaluated the bimolecular recombination flux (J_{BI}). However, we note here that for other device systems that charge collection at the wrong electrodes could provide a significant loss pathway, and so, herein, we consider a more general case for determining the loss in photocurrent at V_{oc} based entirely on empirical data, not requiring any assertions concerning the determining loss mechanism(s). The loss in current at V_{oc} is defined as

$$J_{losses}(V_{oc}) = ed \frac{n(V_{oc})}{\tau(V_{oc})} \quad (6.8)$$

In our measurements we do not measure the carrier lifetime, but instead determine the small perturbation carrier lifetime using TPV data. In Chapter 3, we showed that we can rewrite the carrier lifetime as the product of the small perturbation carrier lifetime with a 'small perturbation' factor δ representing the order of the process (i.e. if $J_{GEN} \propto n^\delta$, then $\tau = \tau_{\Delta n} \delta$). Thus, Eqn. (6.8) becomes

$$J_{losses}(V_{oc}) = ed \frac{n(V_{oc})}{\tau_{\Delta n}(V_{oc}) \delta} \quad (6.9)$$

Based on our applied electrical bias studies of electric field assisted charge generation presented in the previous chapter, now combined with the good agreement between CE and differential charging, where, unlike CE, differential charging requires the assumption that charge generation is electric field independent, this indicates that in the case of the 'standard' P3HT:PCBM devices studied, that $J_{losses}(V_{oc})$ must equal the photocurrent $J_{GEN}(V_{oc})$ (referring to the photocurrent at V_{oc}), so we obtain

$$J_{GEN}(V_{oc}) = ed \frac{n(V_{oc})}{\tau_{\Delta n}(V_{oc}) \delta} \quad (6.10)$$

Importantly, this expression only requires experimentally determined quantities with no additional assumptions required.

6.3.1 Determination of the small perturbation factor δ

In Chapter 4, an expression for the small perturbation factor δ was determined based on the exponential gradients for n and $\tau_{\Delta n}$, given by γ and β respectively,

$$\begin{aligned} n &= n_0 \exp(\gamma V_{oc}) \\ \tau_{\Delta n} &= \tau_{\Delta n 0} \exp(-\beta V_{oc}) \\ \delta &= 1 + \frac{\beta}{\gamma} \end{aligned} \quad (6.11 - 6.13)$$

where n_0 , $\tau_{\Delta n 0}$, γ and β are all constants. Based on the expression given in Eqn. (6.10), the small perturbation factor can be determined in two additional ways, where now only one of these values for β and γ are now required. This requires the use of the relationship of open-circuit voltage with light intensity, which represents a simple directly measurable relationship, and is likely to be more reliable than the measurements of n and $\tau_{\Delta n}$. Figure 6.9 shows a plot of open-circuit voltage versus light intensity. Over a relatively large voltage range, corresponding to the light conditions where a solar cell would be operated under, the light intensity is found to follow an exponential dependence on V_{oc}

$$I = I_0 \exp(SV_{oc}) \quad (6.14)$$

where I_0 and S are constants.

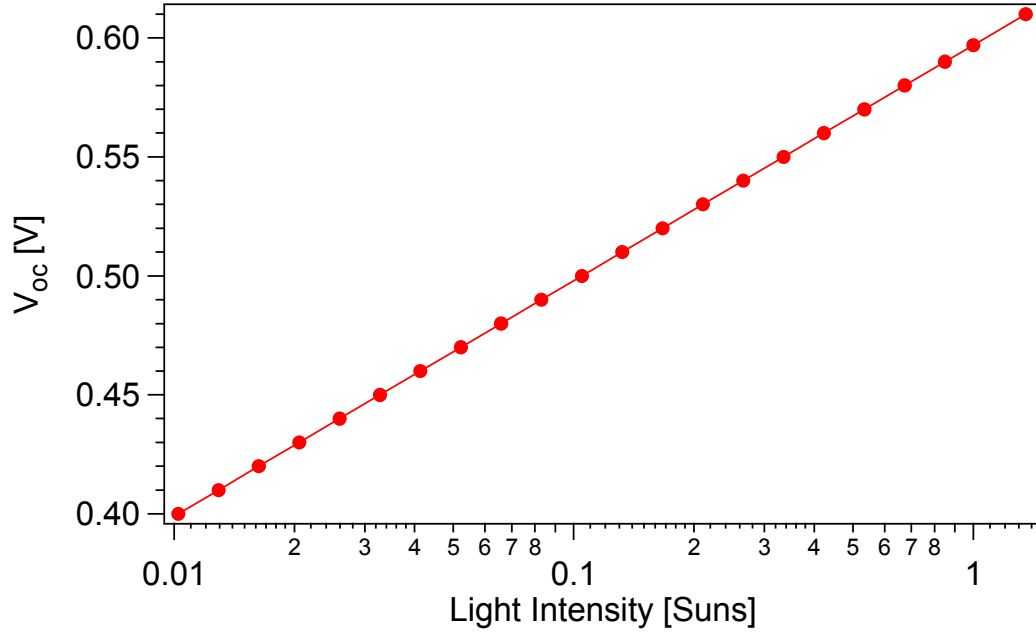


Fig. 6.9. A plot of light intensity versus open-circuit voltage. The open-circuit voltage is found to follow an inverse exponential voltage with incident light intensity.

Assuming the quantum yield of photogenerated free charge carriers is light intensity independent, then the photogenerated current J_{GEN} will be proportional to the incident light intensity, and thus, Eqn (6.12) can be rewritten as

$$J_{\text{GEN}}(V_{\text{oc}}) = J_{\text{GEN0}} \exp(SV_{\text{oc}}) \quad (6.15)$$

where J_{GEN0} is a constant. By substituting this expression for J_{GEN} into Eqn. (6.10) we obtain,

$$J_{\text{GEN}}(V_{\text{oc}}) = J_{\text{GEN0}} \exp(SV_{\text{oc}}) = ed \frac{n(V_{\text{oc}})}{\tau_{\Delta n}(V_{\text{oc}}) \delta} \quad (6.16)$$

As J_{GEN} is described by an exponential relationship with V_{oc} , this indicates the functional forms of charge density and small perturbation carrier lifetime, when combined, must also be given by the same exponential relationship. This is most readily understood if both n and $\tau_{\Delta n}$ are also described in terms of an exponential relationship with V_{oc} , as suggested by our experimental studies. Thus, we substitute the expressions for $n(V_{\text{oc}})$ and $\tau_{\Delta n}(V_{\text{oc}})$, given in Eqn. (6.11) and (6.12) respectively, into Eqn. (6.16).

$$J_{\text{GEN}} = J_{\text{GEN0}} \exp(SV_{\text{oc}}) = ed \frac{n_0 \exp(\gamma V_{\text{oc}})}{\tau_{\Delta n0} \exp(-\beta V_{\text{oc}}) \delta} = ed \frac{n_0 \exp((\gamma + \beta)V_{\text{oc}})}{\tau_{\Delta n0} \delta} \quad (6.17)$$

This provides us with an expression relating S with the values γ and β

$$S = \gamma + \beta \quad (6.18)$$

Using the expression for the correction factor given in Eqn. (6.13), as previously derived in Chapter 4, then we obtain three different formulations for this correction factor, by rearranging the expression for S and substituting in values for γ and β

$$\delta = 1 + \frac{\beta}{\gamma}, \quad \delta = \frac{S}{S - \beta} \text{ and } \delta = \frac{S}{\gamma}. \quad (6.19-21)$$

Importantly, each of these values are dependent on two experimentally determined values, and so, in the case, where one of these measurements yields incorrect values for S , β or γ , then this would become evident when comparing these values these values. Using the experimentally determined values $S = 23.26$, $\beta = 14.53$ and $\gamma = 8.88$, we are able to determine three different values for δ given by 2.64, 2.66 and 2.62 corresponding to Eqn.'s (6.19 – 6.21) respectively. This strong agreement between each of these three values, suggests that the values for S , β and γ are determined accurately, and the value for δ is also determined accurately.

6.3.2 Comparison of $J_{\text{losses}}(V_{\text{oc}})$ with $J_{\text{GEN}}(V_{\text{oc}})$

We are now able to calculate $J_{\text{losses}}(V_{\text{oc}})$ using $\tau_{\Delta n}$ obtained from TPV data, n determined from charge extraction, and the determined value for δ (using the averaged value of 2.64), and compare it with $J_{\text{GEN}}(V_{\text{oc}})$ for the corresponding light intensities (see Fig. 6.10). We estimate $J_{\text{GEN}}(V_{\text{oc}})$ here by considering the ‘saturation’ photocurrent (approximately) of the device ‘light’ J - V curves in reverse bias ($\sim -2V$).

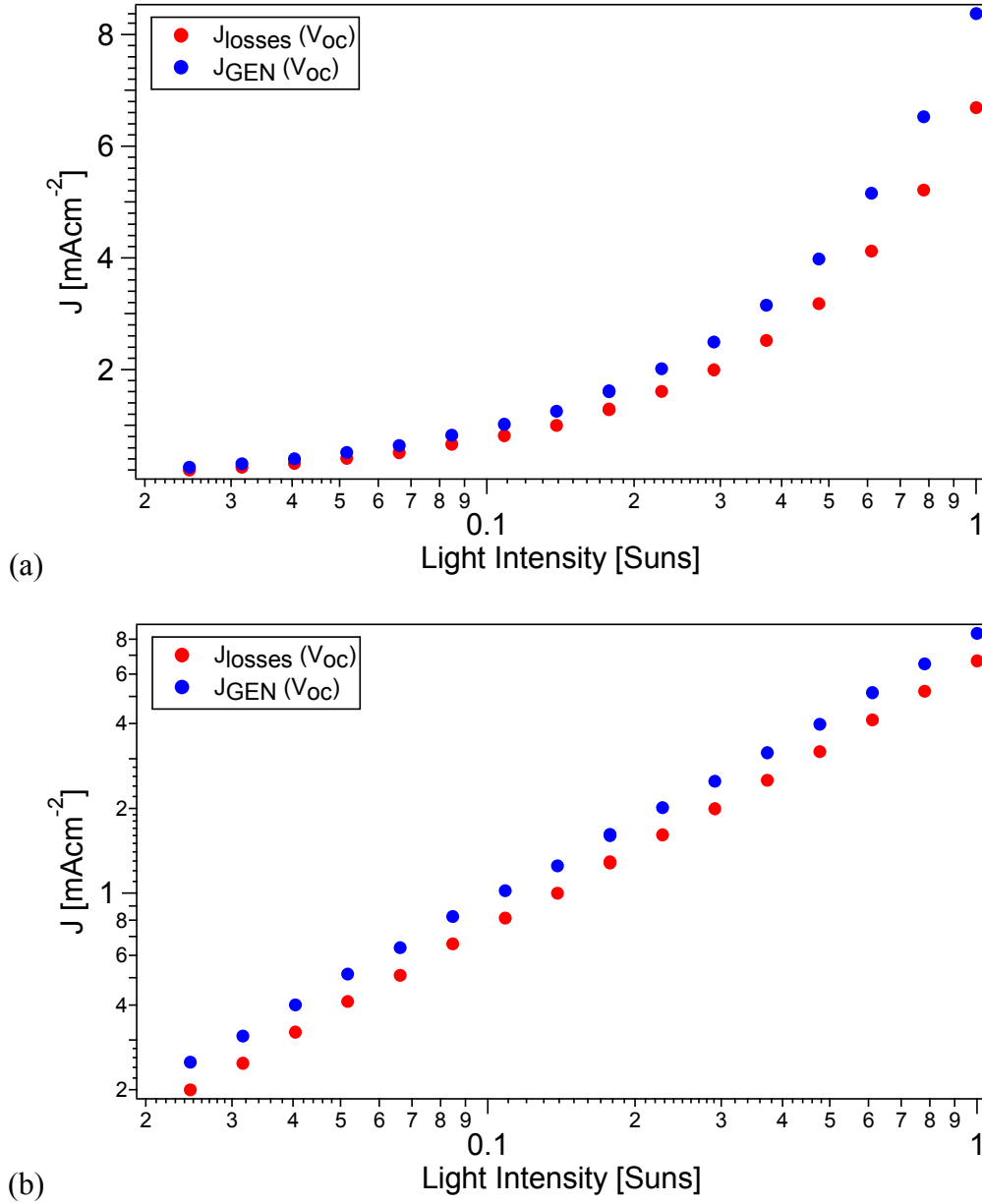


Fig. 6.10. Comparison of the photo-generated current (estimated by using the current density in reverse bias at -2V) with the calculated loss in current at open-circuit, over a range of light intensities 0.02 – 2 suns. This comparison is made on both (a) a linear – linear scale and (b) a log – log scale.

We find that there is a relatively good qualitative agreement between both curves, similarly as found for the previous chapter where we considered J_{BI} . We find that the error in J_{losses} is approximately 25% for all light biases, which based on the values for n , $\tau_{\Delta n}$ and δ which are all experimentally determined values, is relatively small. For all devices studied, similar findings were found. However, these errors were highly sensitive to the quality of the transient data measured. In the next section we consider

the possible limitations of the precisions in our calculation of $J_{\text{losses}}(V_{\text{oc}})$ to see whether in the future it may be possible to obtain even greater precision.

6.3.3 Potential limitations to our empirical results

In the determination $J_{\text{losses}}(V_{\text{oc}})$ we require values for charge density, the small perturbation carrier lifetime and the small perturbation factor. By employing two different methodologies, charge extraction and differential charging, we have found good agreement between the determined charge densities, thus suggesting that these values for the charge densities should be relatively accurate. Furthermore, if these charge densities are accurate, then this implies that the small perturbation factor should also be accurate as it can be determined using this charge density data combined with V_{oc} versus light intensity data (which is also expected to be relatively accurate). Therefore, this leaves only the small perturbation carrier lifetime, which we now consider in more detail (below).

In Section 4.2 of Chapter 4, we performed a comparative study between TPV and TAS data obtained using the same small perturbation conditions. This comparison is re-plotted here in Fig. 6.11. Based on the excellent qualitative agreement between these two data, we concluded that the lifetime of the voltage decay can be used to estimate the corresponding carrier lifetime. We now inspect whether this TPV and TAS data is identical, as opposed to agree qualitatively, as this would provide an obvious limitation in our calculation of $J_{\text{losses}}(V_{\text{oc}})$. Directly fitting both TPV and TAS data with single exponentials, as shown in Fig. 6.11, it is apparent that the TAS decay lifetime $6.5 \mu\text{s}$ is faster than of the TPV decay, $7.4 \mu\text{s}$ by $\sim 15\%$. Such an observation would result in an increase of $J_{\text{losses}}(V_{\text{oc}})$ thereby reducing the error when compared with $J_{\text{GEN}}(V_{\text{oc}})$. It is clear however, that the signal to noise resolution of the TAS data measured under these small perturbation conditions is particularly bad, and as such, it is difficult to make any significant conclusions based on this comparison. This is a possible direction for future study to attempt to improve the precision of our calculations of $J_{\text{losses}}(V_{\text{oc}})$.

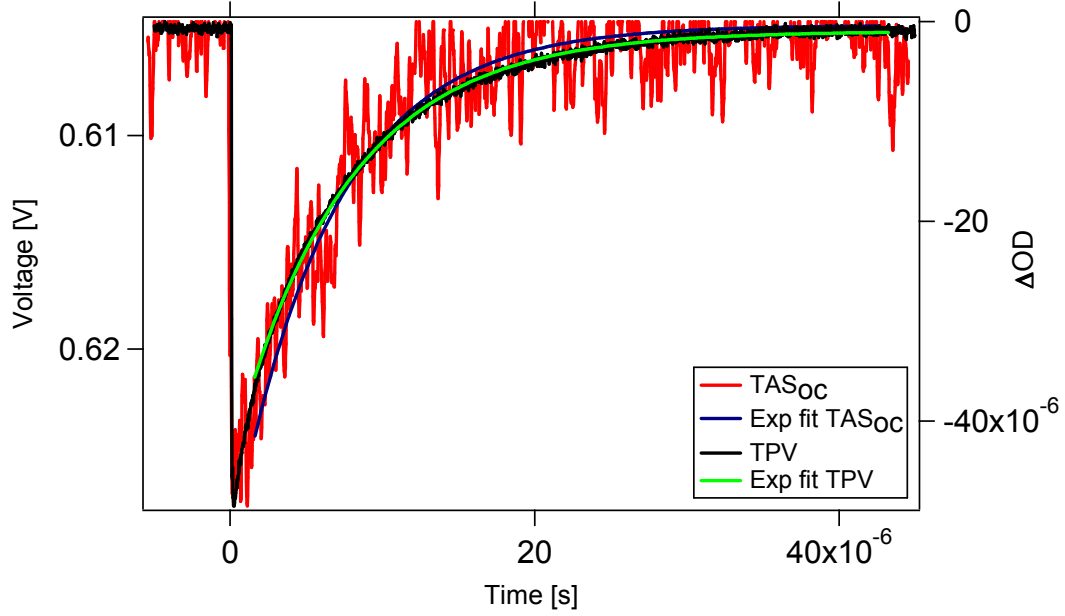


Fig. 6.11. Comparison of transient photovoltage (left, black) and transient absorption signals (right, red) obtained in the small perturbation regime. Measurements were made for an open-circuit voltage 0.6V (~ 1 sun), using a pump of wavelength 620 nm and a probe of 980 nm.

6.3.4 General conclusions for $J_{\text{losses}}(V_{\text{oc}})$

We conclude that the internal consistency is good between the calculated $J_{\text{losses}}(V_{\text{oc}})$ and $J_{\text{GEN}}(V_{\text{oc}})$, with reasonable error, typically 30%, dependent on the quality of the data obtained. Although in the previous chapter, we determined the loss in photocurrent at V_{oc} to be bimolecular recombination dominated and so considered it in this manner, we have shown here that mathematically it is not necessary to assign this loss in current to an originating loss mechanism(s). For the standard P3HT:PCBM devices we have studied for this thesis, we have concluded that V_{oc} is primarily determined by bimolecular recombination, however we are able to perform similar analysis for other device systems, where alternative current loss mechanisms such as charge collection at the wrong collecting electrode may be more prominent.

In the next section where we relate the loss in photocurrent at V_{oc} with the forward bias current in the dark, we consider this in terms of $J_{\text{GEN}}(V_{\text{oc}})$ and not $J_{\text{losses}}(V_{\text{oc}})$.

6.4 Mapping the J - V curve for a device in the dark in terms of charge density, measured using charge extraction

As we have been able to demonstrate that this relatively simple charge extraction technique can be used to measure the charge densities present in a device, we have applied charge extraction to determine the charge density n_{dark} in the same device in the dark.

6.4.1 Introduction

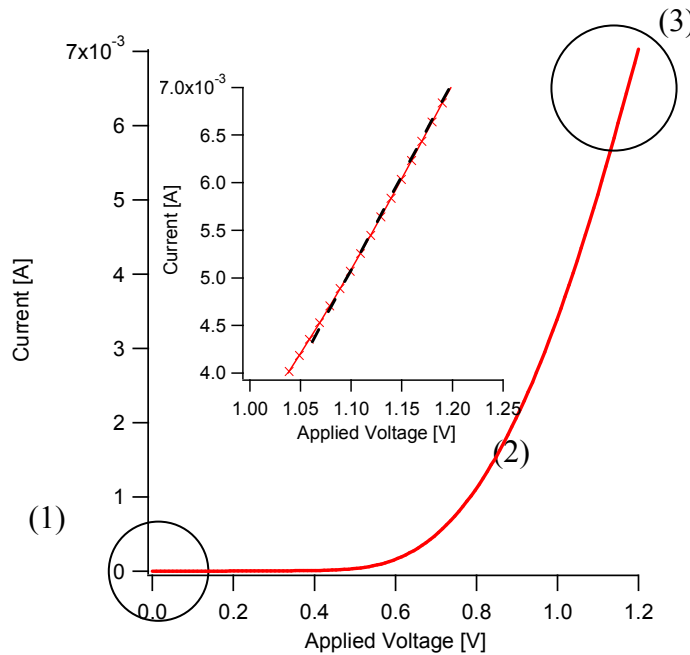


Fig. 6.12. Typical J - V curve for a device in the dark. It consists of a (1) ohmic shunt limited current at low applied voltages, an (2) exponential regime and a ohmic at high applied voltages where the current is limited by the internal serial resistance R_s (this behaviour is amplified in the inset displaying its linear behaviour from which we determine a value for R_s which is required for our studies (below)).

The electrical response for solar cells in the absence of light is given by the ‘dark current’. Whenever studying the photovoltaic characteristics of solar cells, it is commonplace to also measure current-voltage characteristics of a solar cell in the dark. Figure 6.12 shows a typical J - V curve in the dark for one of the standard P3HT:PCBM devices studied herein, identifying three distinct regimes:^{35,36} (1) For low applied voltages close to $V = 0$ the current displays ohmic (linear) behaviour as a

result of electrical shunts, (2) at intermittent applied voltages the device current displays ‘diode’ exponential behaviour, and (3) at high applied voltages the dark current also displays ohmic (linear) behaviour, where the current is limited due to the serial resistance of the solar cell. For solar cell operation, it is the ‘diode’ exponential current which is likely to be most important for device function.³⁵

The dark current reflects the current resulting from charge carriers injected at the device electrodes. The ‘diode’ current generated in the dark can be determined primarily by two possible processes. Either electrons are injected into PCBM and holes into P3HT and these charge carrier subsequently undergo bimolecular recombination at the polymer/PCBM interface,^{35,106} or the injected charge carriers are able to flow through a single organic phase from the injecting electrode the opposite electrode and are collected (‘leakage’ currents) (e.g. holes injected at the ITO/PEDOT:PSS electrode flow through the polymer HOMO orbitals to the Al electrode). As the dark current flows in the opposite direction (positive) to the photocurrent (negative) it represents a ‘loss’ process, which as we see later is dependent on the incident light conditions.

6.4.2 Charge extraction study of the forward bias current in the dark

In Fig. 6.13, plots of n_{dark} are shown over the voltage range 0.3 – 0.9V, after correcting for both the charge losses using the procedure outlined in Section 6.3.1 using the finalised expression for the open-circuit charge carrier dynamics and for the charge which would be present on the electrodes (using the ‘effective’ cell voltage – see next paragraph). As expected, as the applied voltage (V) is increased, n_{dark} increases, as a result of increased carrier injection. Figure 6.13 shows the raw data, and also the charge when the applied voltage has been corrected for the voltage loss in the series resistance R_s using $V_{\text{int}} = V - IR_s$, where I is the current. The series resistance $R_s = 9 \Omega\text{cm}^2$ was determined from the by consideration of the devices forward bias current in the dark, where the current displays linear (‘ohmic’) behaviour (see Fig. 6.12). We note that for the previous studies discussed in this thesis, this correction was not required as these measurements were made under open-circuit ($I = 0$) conditions. We find that the charge densities present in the device under dark forward bias are not much different of those present when the same voltage is created as V_{oc} by

illumination. For instance, at an approximately 1 sun ‘light bias’ $V_{oc} = 0.6V$ $n \sim 8 \times 10^{16} \text{ cm}^{-3}$, whereas, for the corresponding applied electrical bias $V_{int} = 0.6V$ in the dark, $n_{dark} \sim 4 \times 10^{16} \text{ cm}^{-3}$, which is only a factor of 2 smaller (see Fig. 6.14).

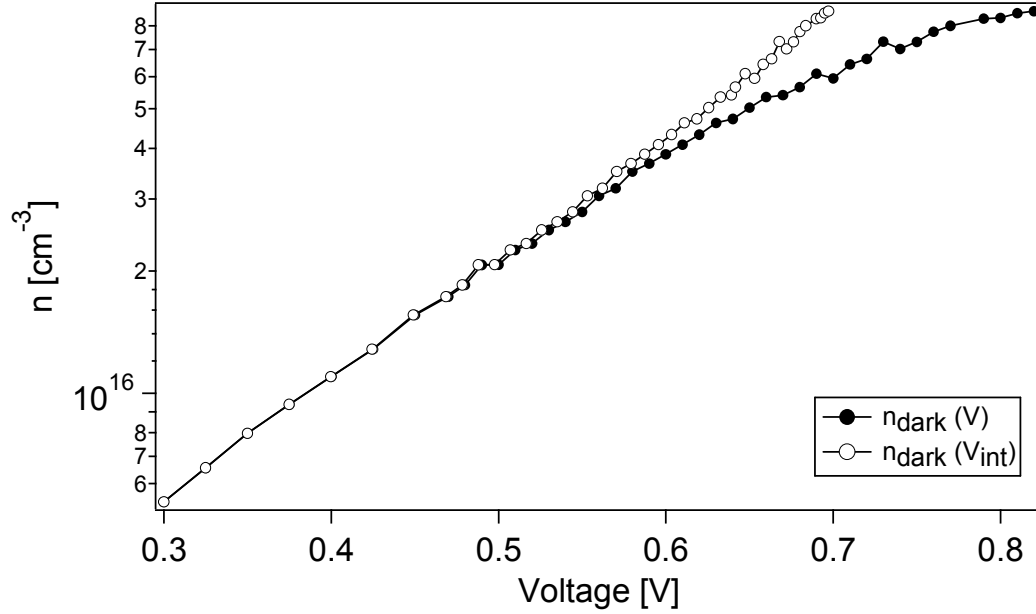


Fig. 6.13. Charge extraction determined values for the charge densities in the active layer of the device as a function of the applied voltage and the cell voltage while under dark conditions.

From Fig. 6.13 we can see that the charge densities in the device in the dark follow an exponential relationship with cell the voltage V_{int} which can be expressed as:

$$n_{dark} = n_{dark0} \exp(\gamma_{dark} V_{int}) \quad (6.22)$$

where $n_{dark0} = 6.7 \times 10^{14} \text{ cm}^{-3}$ and $\gamma_{dark} = 7.0$. This expression is analogous to the expression for the charge concentrations present in the device at open-circuit $n(V_{oc})$ as a function of ‘light bias’, where $n(V_{oc})$ was found to also follow an exponential form with V_{oc} (see Eqn.(6.7)). To determine whether the CE data in the dark appears reasonable a direct comparison was made with $n(V_{oc})$ (see Fig. 6.14). For the light bias (V_{oc}) studies, as the light intensity is reduced, the device approaches dark conditions, therefore, we should expect that $n_{dark}(V_{int})$ and $n(V_{oc})$ will converge as the device voltage is reduced, as found. This provides additional support that these charge extraction measurements appear to be working appropriately.

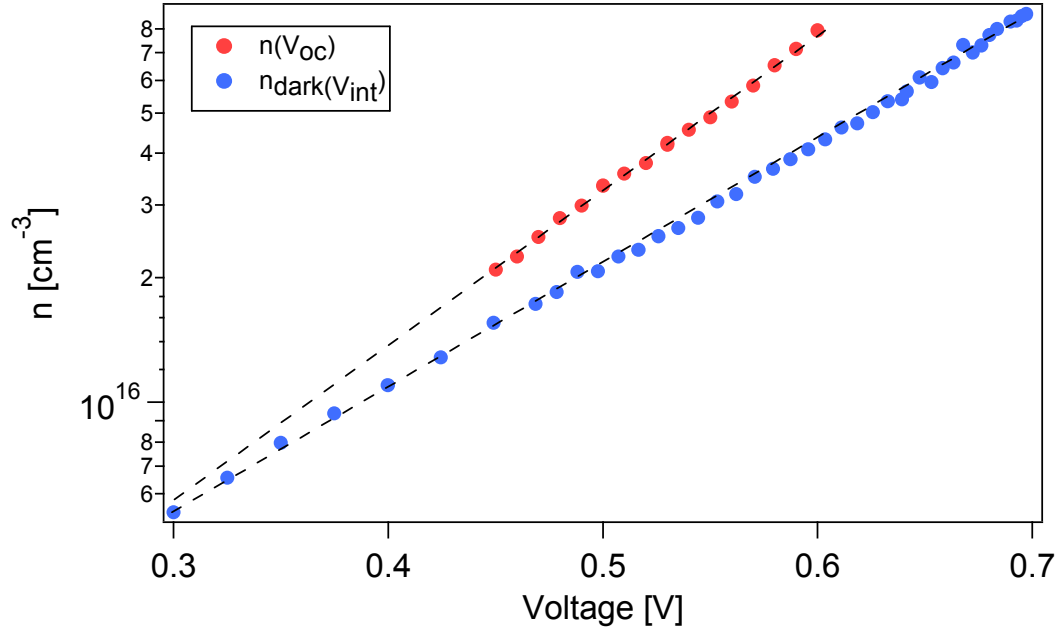


Fig. 6.14. Comparison of the charge density present in the device as function of applied electrical and applied light biases. As the applied voltage is reduced, these two curves converge as expected, due to the reduction in light bias indicating that the device is approaching dark conditions.

We now turn our attention to examine the relationship between charge density and current density. Figure 6.15 shows a plot of the devices current density measured under forward bias in the dark $J_{FW, \text{dark}}$ versus n_{dark} (here we purposely use the notation $J_{FW, \text{dark}}$ rather than the familiarly used J_{dark} to highlight that the ‘dark’ current represents the forward bias current in the dark, but does not necessary represent the same current while under light conditions). We find that $J_{FW, \text{dark}}$ follows a power law relationship with n_{dark} , which is given by

$$J_{FW, \text{dark}} = dek_{\text{dark}0} n_{\text{dark}}^{\phi_d} \quad (6.23)$$

where $k_{\text{dark}0} = 1.2 \times 10^{-23}$ and $\phi_d = 2.64$. We note this comparison does not require any corrections to be made for R_s as $J_{FW, \text{dark}}$ and n_{dark} are measured under the same applied voltage conditions.

A similar equation can be written for the ‘loss in photocurrent’ that occurs at forward bias under light, $J_{FW, \text{losses}}(V)$. Specifically, at V_{oc} , all the photogenerated charge is recombining via one or more ‘loss’ pathways, therefore $J_{FW, \text{losses}}(V_{oc}) = J_{\text{GEN}}(V_{oc})$ (see Section 6.4). As we have found the charge generation is not potential dependent in these cells, we can estimate $J_{\text{GEN}}(V_{oc})$ for a given light level from the saturation

photocurrent at -2V. In Fig. 6.15 we plot $J_{\text{GEN}}(V_{\text{oc}})$ vs. the measured charge density, $n(V_{\text{oc}})$. The resulting power law (Eqn. 6.24) is almost identical to that found for $J_{\text{FW,dark}}$

$$J_{\text{GEN}}(V_{\text{oc}}) = dek_{\text{Voc0}} n(V_{\text{oc}})^{\phi_{\text{L}}} \quad (6.24)$$

where $k_{\text{Voc0}} = 1 \times 10^{-23}$ and $\phi_{\text{L}} = 2.64$.

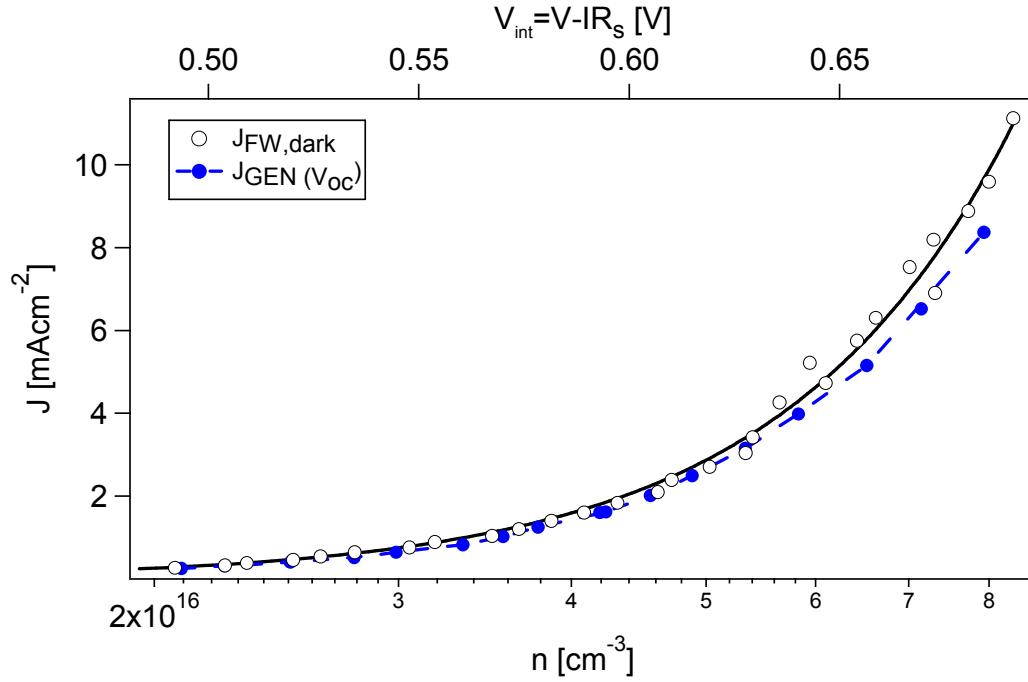


Fig. 6.15. Comparison of the current density as a function of charge density for the forward bias current density in the dark and the loss in current at V_{oc} , given by $J_{\text{GEN}}(-2\text{V})$. The vertical axis corresponds to the effective cell voltage for $J_{\text{FW,dark}}$.

The nearly identical relationship of $J_{\text{FW,dark}}$ and $J_{\text{GEN}}(V_{\text{oc}})$ to charge density gives fundamental insight into processes occurring inside the cell. It indicates strongly that the physical process by which charge crosses a P3HT:PCBM device under dark bias is identical to that by which photogenerated charges are lost at V_{oc} . Thus, $J_{\text{FW,dark}}$ describes the loss mechanism which results in the loss in photocurrent for the device. Second, it strengthens the case for any dark current and loss mechanisms that lead directly to power law behaviour with respect to charge. It also suggests that by applying charge extraction to determine the charge densities in the device while under incident light conditions, we may be able to simulate the ‘light’ J - V curve based on this expression for the loss in current when considered specifically in terms of charge

density as given in Eqn.'s (6.23) and (6.24), which will be studied in the following chapter.

In the previous chapter, we have used transient absorption and transient photovoltage data to argue that the loss mechanism at V_{oc} in these standard P3HT:PCBM annealed cells is bimolecular recombination, where the bimolecular recombination coefficient is charge density dependent $k(n)$.⁶⁰ From Fig. 6.15, we reason that $J_{FW, dark}$ is also determined by this same bimolecular recombination process, at least for voltages between 0.45 and 0.8V. In support of this assertion the ideality factor of the dark current in this voltage range is $m = 2.1$ (see next section). In p-n junction theory, a ideality factor of 2 indicates that the current is dominated by bimolecular recombination, equivalent to a Shockley Reed Hall diode.^{107,108}

As Fig. 6.15 suggests that the forward bias current in the dark is dominated by a bimolecular recombination process, this suggests that alternate loss mechanisms such as charge collection by the 'wrong' electrodes and electrical shunts are unimportant in these devices over the voltage range studied. We reason that this behaviour could be due to at least partially selective contacts (electrodes). This is consistent with recently reported 'corrected photocurrent' studies of P3HT:PCBM devices where it was concluded that P3HT:PCBM devices displayed characteristics of selective electrodes, limiting the extent charge carriers can be collected at the 'wrong' collecting electrodes (leakage).⁵⁷ A possible explanation for the device to have selective contacts, even though there are no specific blocking layers used in the device design, is the effects of vertical segregation in these devices, which could result in relatively pure phases of P3HT at the anode and/or PCBM at the cathode.^{43,50} In the case where there is complete charge selectivity at both electrodes, then the loss in current density for a device under illumination and the forward bias current in the dark must be described entirely by bimolecular recombination. Although it is unlikely that this is completely the case in P3HT:PCBM devices based on the limited morphology control of the P3HT:PCBM blend, our results that $J_{FW, dark}$ is dominated by a bimolecular recombination process is consistent with at least partial selectivity for charge collection at the electrodes. In Chapter 2 we performed modelling studies of the 'corrected photocurrent' for devices with non-selective contacts. Based on the comparison with experimental data collected on MDMO:PPV/PCBM and

P3HT:PCBM blend devices we concluded that these device systems materially behaved differently. MDMO:PPV/PCBM devices displayed behaviour consistent with non-selective contacts, whereas, P3HT:PCBM devices displayed behaviour consistent with selective contacts. The CE studies in P3HT:PCBM blend devices presented here further emphasize the importance of extending these modelling studies to include selective contacts.

It is possible that at lower applied voltages, where the charge density present in the device is smaller, the relationship between $J_{FW, \text{dark}}$ and n_{dark} shown in Eqn. (6.23) may change as a result of a reduced bimolecular recombination contribution to the current. By extending our study to lower applied voltages/charge densities (0.3 - 0.5 V, $n \leq 2 \times 10^{16} \text{ cm}^{-3}$) for this device studied, we find that the relationship between current density and charge density does indeed change. Figure 6.16 shows a plot of $J_{FW, \text{dark}}$ versus n_{dark} over an extended voltage range to include the lower charge density measurements. We observe a change in the exponent ϕ_d given in Eqn. (6.23) from 2.64 to 3.47, which when considered in terms of a ideality factor then for these lower charge densities corresponding to $m \sim 1.6$ (see next section).

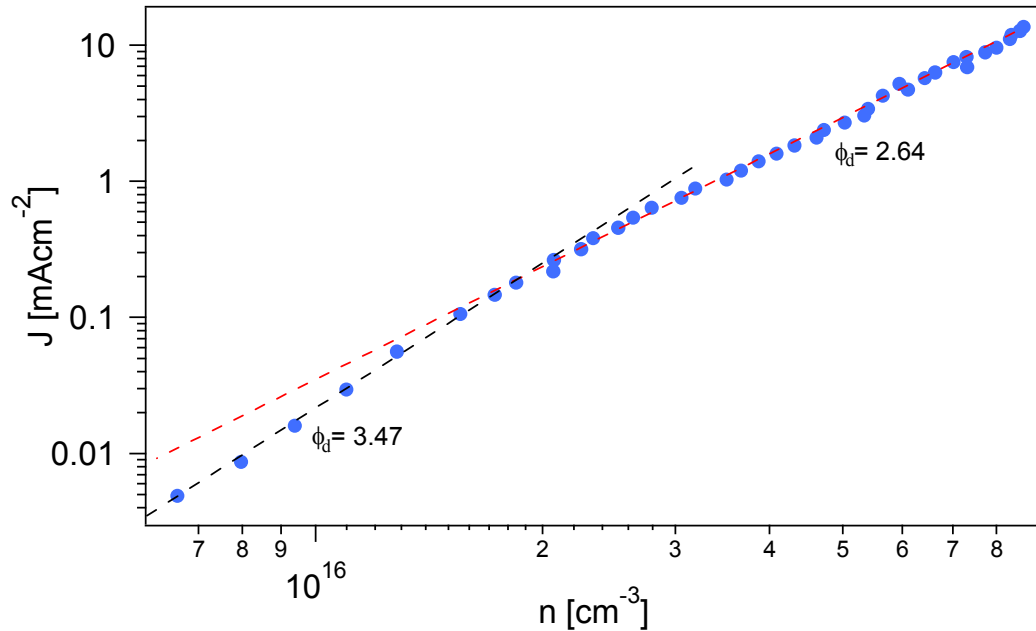


Fig. 6.16. Plot of the forward bias current density in the dark against n_{dark} for an extended range of charge densities. It is found that at lower charge densities, the exponent for the observed power law relationship relating $J_{FW, \text{dark}}$ with n_{dark} increases from 2.64 to 3.47.

6.4.3 Further Analysis:

Correlating CE results with the Shockley diode equation

A common approach when analysing dark J - V curves is the use of the Shockley diode equation.^{37,108} The Shockley ideal diode equation (named after William Bradford Shockley) is used to describe the J - V characteristic of an ideal diode:

$$J_{\text{dark}} = J_0 \left[\exp\left(\frac{V}{mV_T}\right) - 1 \right] \quad (6.25)$$

where J_0 is the saturation current, m is the ideality factor ($=1$ for an ideal diode), $V_T = k_B T/e$ is the thermal voltage, where k_B is Boltzmann's constant, T is temperature, e is the electronic charge. It is derived with the assumption that the only processes giving rise to current in the diode are drift, diffusion, and thermal recombination-generation. It also assumes that the recombination-generation (R - G) current in the depletion region is insignificant. It is based on the injection and diffusion of injected minority carriers by the application of a forward bias. This means that the Shockley equation doesn't account for the processes involved in reverse breakdown and also does not include the effects of the internal resistances which limit the current at high forward bias as well as the influence of electrical shunts. Thus, for a real device, these effects must also be included:

$$J_{\text{dark}} = J_0 \left[\exp\left(\frac{(V - IR_s)}{mV_T}\right) - 1 \right] + \frac{(V - IR_s)}{R_{\text{SH}}} \quad (6.26)$$

where I is the current, R_s is the series resistance and R_{SH} is the shunt resistance. When the recombination effects in the depletion width are also included, then the ideality factor $m = 2$. The recombination current flows under forward bias to replenish recombining in the depletion layer. In general photovoltaic devices display non-ideal behaviour with an ideality factor is between 1 and 2, resulting from both types of behaviour to be present, with the specific values determining which behaviour is more prominent. Alternate studies have included two diode descriptions in which the second diode is implemented as a Shockley Reed Hall recombination diode^{107,108} where the ideality factor m is pre-defined as 2.

$$J_{\text{dark}} = J_{01} \left[\exp\left(\frac{(V - IR_s)}{V_T}\right) - 1 \right] + J_{02} \left[\exp\left(\frac{(V - IR_s)}{V_T 2}\right) - 1 \right] + \frac{(V - IR_s)}{R_{\text{SH}}} \quad (6.27)$$

where the first diode describes the behaviour of a diffusion dominated diode, whereas, the second diode is used to include the additional effects of the recombination.

Previously the Shockley diode equation has been employed to study organic photovoltaic devices,^{36,38} with the overall intention to model J - V curves for devices under illumination (discussed in more detail in the next chapter). In the case of P3HT:PCBM both single diode and two diode models have been used to study the dark J - V curve. It has been shown that such BHJ devices can be described reasonably as an internal p-n junction with a clearly defined interface for charge separation, followed by single phase transport along pure phases of the constituent semi-conducting layers.³⁵ However, as organic devices are based on majority charge carriers, rather than the minority charge carriers from which the Shockley diode equation is derived, then in some ways, the Shockley diode equation represents more a ‘fitting’ routine, where the respective saturation current and ideality factor m act more as fitting parameters without a clear physical meaning. It is argued that for these BHJ devices, the exponentially based dark current results from the parallel annihilation of an electron and hole of an electron and hole at a donor/acceptor interface, with the ideality factor m describing the shape of the interface between the constituent donor and acceptor layers.³⁵

In this thesis we have not focussed on applying Shockley diode analysis to J - V curves, thus our data is limited on this subject. However, by combining our experimental studies that provide physical insight in the mechanisms contributing to the current for these P3HT:PCBM devices with the Shockley diode equation analyses, we should be able to give more physical meaning to the Shockley diode equation when applied to BHJ devices. In this chapter we have applied CE to study the forward bias current in the dark, which has allowed us to make physical interpretation of this dark current. In this section we relate our results with the commonly employed Shockley diode equation, thus allowing us to provide a physical interpretation of the relevance of this equation to organic solar cells.

The studies presented herein suggest that rather than consider the current density in terms of applied voltage, it may be better considered in terms of charge density instead. This will become of great importance when attempting to model J - V curves

for a device under illumination, which is discussed in the next chapter. By combining the expression for the dark current in terms of charge density given in Eqn. (6.23) with the expression for charge density in terms of the applied voltage V given in Eqn. (6.22) and including additional terms for the leakage current $(V - IR_s)/R_{SH}$ and a '-1' correction factor required to take account of the leakage current due to electrical shunts and the fact that the current in the dark equals zero when $V = 0$, we obtain a modified version of the Shockley diode equation in terms of charge density,

$$J_{\text{dark}} = dek_{\text{dark}0} n_{\text{dark}0}^{\phi_d} [\exp(\gamma_{\text{dark}} (V - IR_s) \phi_d) - 1] + \frac{(V - IR_s)}{R_{SH}} \quad (6.28)$$

$$J_{\text{dark}} = J_0 \left[\exp\left(\frac{(V - IR_s)}{V_T m}\right) - 1 \right] + \frac{(V - IR_s)}{R_{SH}} \quad (6.29)$$

By comparison of these two equations, we obtain expressions for the ideality factor m and the saturation current J_0 in terms of experimentally determined constants γ_{dark} and ϕ_d :

$$J_0 = dek_{\text{dark}0} n_{\text{dark}0}^{\phi_d} \quad (6.30)$$

$$m = \frac{1}{V_T \gamma_{\text{dark}} \phi_d} \quad (6.31)$$

When we fit the J - V data with the Shockley diode equation we find that when using a single diode representation ($m = 1.6$) we are able to reproduce the behaviour of the J - V data for low applied biases, but not at higher applied biases. At higher applied biases it is apparent that the gradient of the J - V curve decreases which suggests that over this region the ideality factor increases. Therefore, even by considering a two diode representation of the Shockley diode equation, we would still be unable to reproduce the J - V data, as in this representation the diode with the lower rather than higher ideality factor is more dominant at higher applied voltages contrary to that observed.

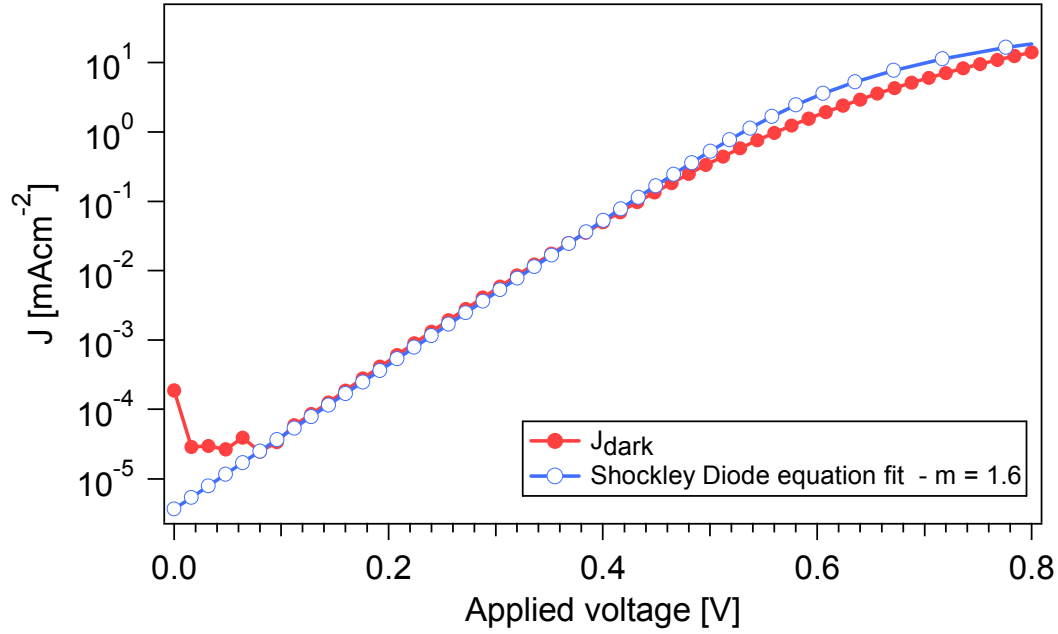


Fig. 6.17. Modelling the dark current using a Shockley diode equation with $m = 1.6$.

In the previous section, we observed that the relationship between $J_{FW, \text{dark}}$ and charge density displayed two distinct phases, where for cell voltage $< 0.5\text{V}$ (corresponding to charge densities $\leq 2 \times 10^{16} \text{ cm}^{-3}$) $\phi_d = 2.64$, whereas, for higher charge densities $\phi_d = 3.47$ (see Fig. 6.16). This indicates, that we must consider two sets of values for J_0 and m to describe these distinct phases and not the single set as used in the Shockley diode fitting routine:

$$J_{01} = dek_{\text{dark}01} n_{\text{dark}0}^{\phi_{d1}}, m_1 = \frac{1}{V_T \gamma_{\text{dark}} \phi_{d1}} \quad (6.32)$$

$$J_{02} = dek_{\text{dark}02} n_{\text{dark}0}^{\phi_{d2}}, m_2 = \frac{1}{V_T \gamma_{\text{dark}} \phi_{d2}} \quad (6.33)$$

By substituting our values for $\gamma_{\text{dark}} = 7.0$ and $\phi_{d1} = 3.47$ and $\phi_{d2} = 2.64$, we find that for $V < 0.45\text{V}$ the ideality factor $m_1 = 1.6$, whereas, for $V > 0.45\text{V}$ $m_2 = 2.1$. If we were to employ a simple p-n junction description,³⁷ although debatable, this suggests that for higher applied voltages the dark current represents a bimolecular recombination current ($m = 2$), whereas, at lower voltages, the current could possibly interpreted as a diffusion dominated current ($m = 1$). We have previously concluded that the forward bias current in the dark for cell voltages above 0.5V is dominated by a bimolecular recombination process, thus, consistent with the p-n junction

interpretation of the $m = 2.1$. At lower applied voltages where $m_1 = 1.6$, it is possible that such behaviour may be explained in terms of an alternate loss mechanism such as leakage currents governed primarily by a diffusion based process, which also could be considered consistent with a p-n junction type interpretation. We note previously in the correlations made between BHJ device data and p-n junction theory, selective contacts are assumed, leading to the conclusion that the ideality factor in BHJ devices refers to the shape of the interface where interfacial bimolecular recombination occurs, rather than describing an alternate loss mechanism.^{31,35} We also note that ideality factors much larger than two have previously been observed in some device systems, which would be difficult to rationalise in terms of p-n junction theory.^{109,110}

6.5 General applicability of CE study to different organic solar cells systems

The charge extraction studies presented in this chapter were demonstrated on standard P3HT:PCBM annealed cells. In principle however, all the methods studied are directly applicable to be used to study other organic solar cell systems. It may be possible that relatively low reduced bimolecular recombination coefficient in these cells allows us to determine the charge densities efficiently using charge extraction because the evaluated charge losses are small. For other device systems where the bimolecular recombination coefficient k may be larger, the charge losses which will be significantly larger, which may make it more difficult to correct for these incurred losses. In addition, for devices with a larger k and/or lower internal quantum efficiencies, the charge densities in the device are likely in general to be smaller, resulting to lower signal to noise resolution for the CE current transients measured. An alternative issue may also occur if the carrier mobilities of the device are larger, as this will lead to an accelerated charge extraction and so may require more sophisticated experimental apparatus with faster response times. Nevertheless, studies of the same measurements presented herein on other device systems represents an obvious direction for future study.

In Chapter 2, we presented a drift-diffusion model to study organic BHJ solar cells using a single layer device with a ‘virtual semiconductor’ and non-selective

electrodes. On comparison of experimental with numerically simulated ‘corrected photocurrent’ data for MDMO:PPV/PCBM BHJ devices,⁵⁷ we concluded that unlike P3HT:PCBM device, it was apparent there are non-selective contacts for these devices, thus leakage currents represent a significant loss mechanism in these devices. Performing similar studies as those outlined in this thesis for this device system may therefore be of great interest. In addition, it may also be of interest to employ the same studies for bi-layer devices, where leakage currents are likely to be negligible, which may aid the interpretation of studies on BHJ devices.

6.6 Summary

In conclusion, we have demonstrated that a simple charge extraction technique can be used to determine the charge densities which are stored in a P3HT:PCBM device. By applying charge extraction to map the J - V curve for a device in the dark in terms of charge density, we find that $J_{FW, \text{dark}}$ follows the same relationship with charge density as the carrier decay dynamics at V_{oc} . As we have previously concluded in the last Chapter that the origin of the open-circuit voltage is dominated by a bimolecular recombination process, we must further conclude that $J_{FW, \text{dark}}$ follows the same bimolecular recombination process. We propose that rather than consider the devices current in terms of applied voltage as done traditionally, that it should instead be considered in terms of charge density. This will be studied in more detail in the next chapter where we will attempt to apply these findings to simulate a J - V curve under 1 sun incident light based on charge extraction data.

VII

Chapter 7 Future Studies: Recreating the J - V curve for a device under illumination using charge extraction studies

In the previous chapter we concluded that for the case of the standard annealed P3HT:PCBM BHJ devices studied, the forward bias current in the dark followed the same relationship with charge density as the loss in current at V_{oc} with charge density in the light. This indicates that not only do these currents represent the same physical process, but it also suggests that it may be possible to simulate the light J - V curve by applying our expression for these currents in terms of charge density over the whole J - V curve for devices under light conditions. This requires charge extraction to be applied to determine the charge densities across the ‘light’ J - V curve.

7.1 Introduction

One of the simplest descriptions of a current-voltage curve for a device under incident light conditions is found by considering the current as the sum of a constant photocurrent J_{GEN} , which is determined by the incident light intensity, and a loss in current J_{losses} resulting from the physical loss mechanisms present (see Fig. 7.1):

$$J_{\text{light}} = J_{\text{GEN}} - J_{\text{losses}} \quad (7.1)$$

where J_{light} is the current in the light. We note that in the case where there is an effect of electric field assisted charge generation present, J_{GEN} should no longer be considered as constant, but instead will contain a dependence on the applied voltage, where, as the applied voltage approaches the built-in potential V_{BI} , there is a reduction in the photogenerated current.^{59,99} As we have previously concluded this effect not to be significant in the standard annealed P3HT:PCBM device studied in this thesis, this is neglected in the analysis reported herein.

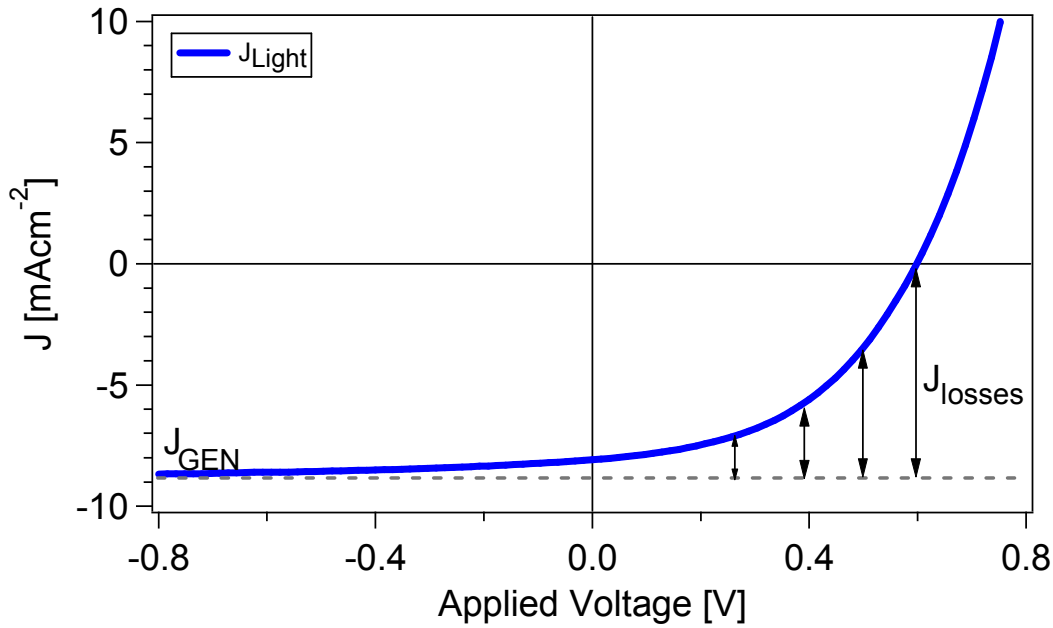


Fig. 7.1. Basic description of a ‘light’ J - V curve in terms of a constant photocurrent J_{GEN} and a loss in current J_{losses} .

In the previous Chapter we found an excellent agreement between the expressions relating the loss in photocurrent at V_{oc} and the forward bias current in the dark with

charge density n . It suggests that as both of these current expressions are determined for variations in both light intensity and applied bias conditions, that we may be able to consider the general loss in current across the whole J - V curve $J_{\text{losses}}(V)$ depicted in Fig. 7.1 using the same expression:

$$J_{\text{losses}}(V) = dek_0 n(V)^\phi \quad (7.2)$$

where d is the device thickness, e is electronic charge and k_0 and ϕ are experimentally determined constants from either our charge extraction studies of the forward bias current in the dark or the loss in photocurrent at V_{oc} (subscripts have been dropped). Therefore, by mapping the ‘light’ J - V curve in terms of charge density, then we may be able to simulate the J - V curve using

$$J_{\text{light}} = J_{\text{GEN}} - dek_0 n(V)^\phi \quad (7.3)$$

In this chapter, we perform preliminary charge extraction studies of the device J - V curve under 1 sun incident light conditions, and attempt to recreate the 1 sun J - V curve using the expression given in Eqn. (7.3). We then consider the implications of this approach by considering the commonly employed Shockley diode equation, and providing a modified version of this Shockley diode equation based on the CE studies presented herein. We note the studies presented herein are preliminary, and should be studied in greater detail in future studies, where thorough investigation of the light dependency of the charge densities present in the device should also be made. Finally, we make a brief discussion concerning other future studies which can be made using charge extraction and end with some closing remarks concluding this PhD project.

For experimental details of charge extraction and device details, please refer to Section’s 3.5 and 3.1 in the experimental method chapter, Chapter 3.

7.2 Mapping the J - V curve for a device under illumination in terms of charge density using charge extraction

We have applied the CE technique to determine the charge densities present in the active layer of the P3HT:PCBM device studied in the previous chapter, while under 1 sun incident light conditions. CE measurements were performed using a voltage source operated in constant current mode and a variable load resistor to control the initial device voltage conditions as described in Section 3.5. In principle, using a voltage source should be sufficient for all these CE measurements, and so not requiring the use of a variable resistor which restricts CE study to a limited voltage range $V = 0 - V_{oc}$. We observed however, that when employing the voltage source to make CE measurements in the light at applied voltages in the range $0 - 0.5V$, the applied voltage was found to fluctuate significantly. So instead, over this voltage range we employed a variable resistor, whereas, for higher voltages we used a voltage source. This observation is most likely to stem from the fact that the voltage source is used in constant current mode where, due to small fluctuations in the device current, this results in the initial voltage conditions of the device to vary. This effect becomes increasingly prominent when the gradient of the J - V curve becomes smaller and thus prevents us from determining the voltage at which the device held. In future studies to avoid this issue, when performing CE studies the voltage source could be switched off in parallel with the light source, allowing all measurements to be made using a voltage source.

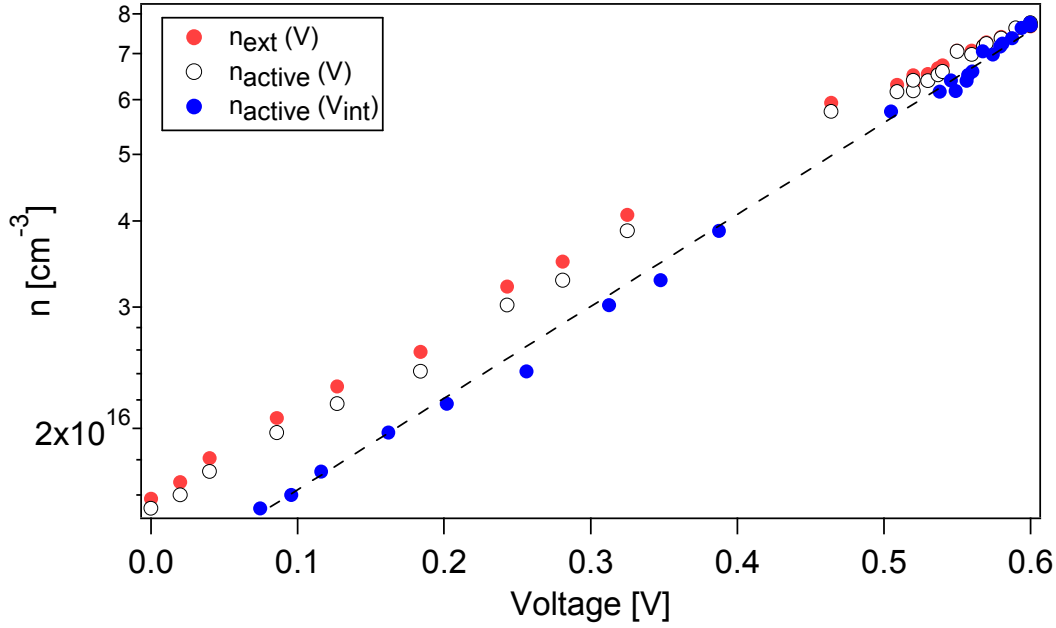


Fig. 7.2. Charge extraction measurements of the charge density present in an annealed P3HT:PCBM device under approximately 1 sun incident light intensity. It shows plots of the CE initial data (red), the charge densities after correcting for the incurred carrier losses and the electrode capacitance (black, open circles), and after correcting these charge densities for the influence of the series resistance on the applied voltage (blue), $V_{\text{int}} = V - IR_s$.

Figure 7.2 shows the CE data before and after making corrections for both charge losses incurred during measurement and the charge residing on the electrodes (see Section 6.3). As in the previous chapter, when referring to n_{active} we drop the subscript ‘active’. As the applied voltage is increased, the charge density in the device is found to increase, which is consistent with both reduced carrier collection and increased carrier injection at the electrodes. It is apparent that when the corrected CE data is plotted against the cell voltage $V_{\text{int}} = V - IR_s$ (see Section 6.5.2), $n(V_{\text{int}})$ appears to follow an exponential dependence on the cell voltage similarly to both $n(V_{\text{oc}})$ and $n_{\text{dark}}(V_{\text{int}})$ shown previously in the last chapter,

$$n(V_{\text{int}}, I = 1\text{sun}) = n_{1\text{sun}0} \exp(\gamma_{1\text{sun}} V_{\text{int}}) \quad (7.4)$$

where $n_{1\text{sun}0} = 1.2 \times 10^{16} \text{ cm}^{-3}$ is the charge density present in the device for a cell voltage $V_{\text{int}} = 0$ whilst under 1 sun constant irradiation, and $\gamma_{1\text{sun}} = 3.1$.

7.3 Simulating the device ‘light’ J - V curve under 1 sun incident light conditions

In Section 7.1 we described an expression Eqn. (7.3), derived from our studies of photocurrent losses and forward bias current in the dark when considered in terms of charge density. Using Eqn. (7.3) with values of k_0 and ϕ determined using the expression for the loss in photocurrent at V_{oc} $J_{GEN}(V_{oc})$ given in the previous Chapter (or equally the forward bias current in the dark), and the charge densities in the active layer of the device determined in Section 7.2, and using an estimate of the photogeneration, determined by consideration of the saturation current in reverse bias (i.e. the EQE reaches a maximum), then this allows us attempt to simulate the J - V curve. We note that in this approach, when attempting to simulate the J - V curve, the applied voltage does not need to be adjusted for to account for the voltage drop across the serial resistance as both the current and charge densities are measured under the same applied voltage conditions (see Section 7.2).

Figure 7.3 shows a comparison of the simulated J - V curve using $J_{GEN} = -8.68 \text{ mAcm}^{-2}$ $k_0 = 1 \times 10^{-23}$ and $\phi = 2.64$ in Eqn. (7.3) with the CE data obtained in Section 7.2, with experimental data for the J - V curve under 1 sun irradiation. We note that due to the incurred problems when collecting CE data using a voltage source, this has led to a limited number of data points. Nevertheless, it is apparent that we find quite a good agreement between the simulated J - V curve and experimental data, especially close to V_{oc} , which suggests that this approach may be valid. Based on our previous conclusions in the previous chapter that both the forward bias current in the dark and the loss in current at V_{oc} are determined by the same bimolecular recombination process, this work further suggests that the losses across the whole J - V curve for the 1 sun conditions considered here, are also of the same bimolecular recombination process origin. This requires further study in the future.

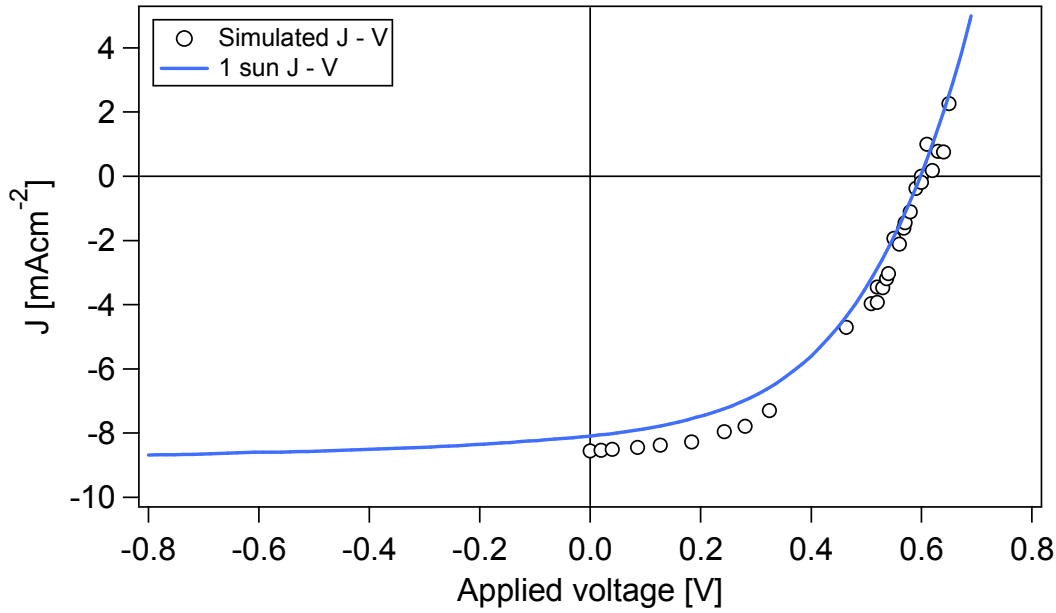


Fig. 7.3. Simulation of the J - V curve for a solar cell under approximately 1 sun conditions, based on the forward bias current in the dark as a function of charge density in the device for 1 sun conditions, found from charge extraction measurements.

7.4 Modifying the Shockley diode equation for the simulation of ‘light’ J - V curve data

Based on this preliminary data presented herein, it suggests that it may be possible to simulate ‘light’ J - V curves using either expressions for the loss in photocurrent at V_{oc} or the forward bias current in the dark when considered in terms of the charge density in the device. We now turn our attention to relate this representation of the ‘light’ J - V curve given in Eqn. (7.3) with the Shockley diode equation¹⁰⁸ when employed to simulate ‘light’ J - V curve for organic solar cells.^{37,38}

$$J_{\text{light}} = J_{\text{GEN}} + J_{\text{FW,dark}} = J_{\text{GEN}} + \left[J_0 \left(\exp \left(\frac{(V - IR_s)}{V_T m} \right) - 1 \right) \right] + \frac{V - IR_s}{R_{\text{SH}}} \quad (7.5)$$

where J_0 is the saturation current, I is the current, V_T is the thermal voltage, m is the ideality factor and R_{SH} is the shunt resistance. To account for the behaviour of the J - V curve under illumination, an additional light dependent parasitic resistance was placed in parallel with the shunt resistance and a light dependency is incorporated into the value for J_0 .³⁸ Here, the J - V curve has been considered in terms of applied voltage.

However, based on our studies presented herein, we conclude that it may be more insightful to consider the J - V curve in terms of the charge density presented within the device, as detailed in Eqn. (7.3).

In the previous chapter we discussed a modified expression for the forward bias current in the dark based on the Shockley diode equation, where, for the purposes of this chapter, this is now rewritten,

$$J_{FW, \text{dark}} = \left[J_0 \left(\exp \left(\frac{(V - IR_s)}{V_T m} \right) - 1 \right) \right] + \frac{V_{\text{int}}}{R_{SH}} = J_0 \exp \left(\frac{V_{\text{int}}}{V_T m} \right) - J_{00} + \frac{V_{\text{int}}}{R_{SH}} \quad (7.6)$$

where

$$m = \frac{1}{\gamma_{\text{dark}} V_T \phi} \quad (7.7)$$

$$J_0 = dek_{\text{dark}0} n_{\text{dark}0}^{\phi} \quad (7.8)$$

where J_{00} represents the $-J_0$ correction factor, which will be invariant under all incident conditions, and so it is rewritten as J_{00} to avoid any confusion. It is important to note, that this correction factor has negligible effect on the resulting current, except for very small applied voltages close to zero.

By substituting the expressions for $n_{\text{light}}(V_{\text{int}})$ (see Eqn. (7.4)) into Eqn (7.3) including the J_{00} correction and the current due to electrical shunts, we obtain

$$J_{\text{light}} = -J_{\text{GEN}} + dek_{\text{dark}0} \left[n_{\text{light}0}^{\phi} \left(\exp(\gamma_{\text{lsun}} V_{\text{int}} \phi) \right) \right] - J_{00} + \frac{V_{\text{int}}}{R_{SH}} \quad (7.9)$$

By rearranging Eqn. (7.7) to make ϕ as the subject, and substituting into Eqn. (7.9), we obtain

$$J_{\text{light}} = -J_{\text{GEN}} + dek_{\text{dark}0} \left[n_{\text{light}0}^{\phi} \left(\exp \left(\frac{\gamma_{\text{lsun}} V_{\text{int}}}{\gamma_{\text{dark}} V_T m} \right) \right) \right] - J_{00} + \frac{V_{\text{int}}}{R_{SH}} \quad (7.10)$$

which is rewritten in the form of a familiar representation of the Shockley diode equation as given in Eqn. (7.6)

$$J_{\text{light}} = -J_{\text{GEN}} + J_0' \left(\exp \left(\frac{V_{\text{int}}}{V_T m'} \right) \right) - J_{00} + \frac{V_{\text{int}}}{R_{SH}} \quad (7.11)$$

where

$$J_0' = J_0 f(I) = J_0 \left(\frac{n_{\text{light0}}}{n_{\text{dark0}}} \right)^\phi > J_0 \quad (7.12)$$

$$m' = mg(I) = m \left(\frac{\gamma_{\text{dark}}}{\gamma_{\text{light}}} \right) > m \quad (7.13)$$

where $f(I)$ and $g(I)$ are light dependent terms, which are determinable by comparison of the charge densities present in a device in the dark and whilst under illumination for various light intensities. In this representation, as the light intensity is increased, this results in an increase in both the effective saturation current J_0' and effective ideality factor m' , which will directly influence the behaviour of the resultant J - V curve. In this representation of the device current density, the parameters which are important (neglecting the leakage current term J_{SH}) are given by the familiar saturation current J_0 , the ideality factor m and J_{GEN} terms, and additional 'light dependent' terms $g(I)$ and $f(I)$. By investigating these functional forms, we hope that we may be able to gain further insight into the parameters controlling device performance. Most importantly though, this representation removes the unphysical parameter employed to describe J - V curves in terms of a light dependent shunt resistance. Based on this new formulism, it is straightforward to obtain expressions for J_{sc} , V_{oc} and FF (where for simplicity J_{SH} is neglected) which are given by

$$J_{\text{sc}} = -J_{\text{GEN}} + J_0' - J_0 = -J_{\text{GEN}} + dek_{\text{dark0}} (n_{\text{light0}}^\phi - n_{\text{dark0}}^\phi),$$

$$V_{\text{oc}} \approx \frac{k_B T m'}{e} \ln \frac{J_{\text{GEN}}}{J_0'} = \frac{k_B T m'}{e \alpha} \ln \frac{J_{\text{GEN}}}{dek_{\text{dark0}} n_{\text{light0}}^\phi},$$

$$FF = \max \left[\frac{V_{\text{app}}}{V_{\text{oc}}} \left(\frac{\left(\exp \left(\frac{e V_{\text{oc}}}{k_B T m'} \right) - \exp \left(\frac{e V_{\text{int}}}{k_B T m'} \right) \right)}{\left(\exp \left(\frac{e V_{\text{oc}}}{k_B T m'} \right) - 1 \right)} \right) \right] \quad (7.14-7.16)$$

An observed feature of P3HT:PCBM devices is that, although one of the best organic solar cells to date,^{6,7} fill factors remain smaller than the previously understood fundamental limit of 83%¹² (reported as high as 70%).⁶ This modified formulation for the fill factor may provide an explanation for the limited fill factors observed, because

the effective ideality factor increases with increasing incident light intensity, and therefore, unless all the photogenerated charge carriers are collected at the peak power point, i.e. n_{light} and n_{dark} are equal, this fundamental limit will never be reachable. Figure 7.4 shows plots of the optimum fill factor FF which is possible considering the ideal case that $R_s = 0$ and $R_{\text{SH}} = \infty$, based on the value for the modified ideality factor m' using the typical 1 sun $V_{\text{oc}} \sim 0.6\text{V}$ found for a P3HT:PCBM device. By consideration of the case where $m' = m = 2$, i.e. the case where all the photogenerated charge carriers are collected at the peak power point and the forward bias current is governed by a bimolecular recombination process ($m = 2$), then this would lead to $FF = 72\%$, which feasibly may provide the actual limit for the maximum FF which is possible. In the case of the device studied $m' = m(\gamma_{\text{dark}}/\gamma_{\text{light}}) = 4.74$ (where $m = 2.1$, $\gamma_{\text{dark}} = 7$ and $\gamma_{\text{light}} = 3.1$), thus, this predicts a $FF = 54\%$, which is in excellent agreement with the $FF = 53\%$ determined directly from the J - V curve (using the cell voltage $V_{\text{int}} = V - IR_s$). These studies therefore indicate that to maximise the fill factor, it is important to reduce the ratio of γ_{dark} with γ_{light} , which would occur by improving the collection efficiency of photogenerated free charge carriers at the correct collecting electrodes, thereby reducing the effective ideality factor for light conditions. Such a representation of the fill factor given in Eqn. (7.16) also explains why the fill factor is found to decrease with increasing light intensity,¹¹¹ as the ideality factor m' increases with light intensity. whereas, if $m' = m$ for all light intensities, then this would predict that the fill factor should increase with increasing light intensity due to the increase of V_{oc} with light intensity.

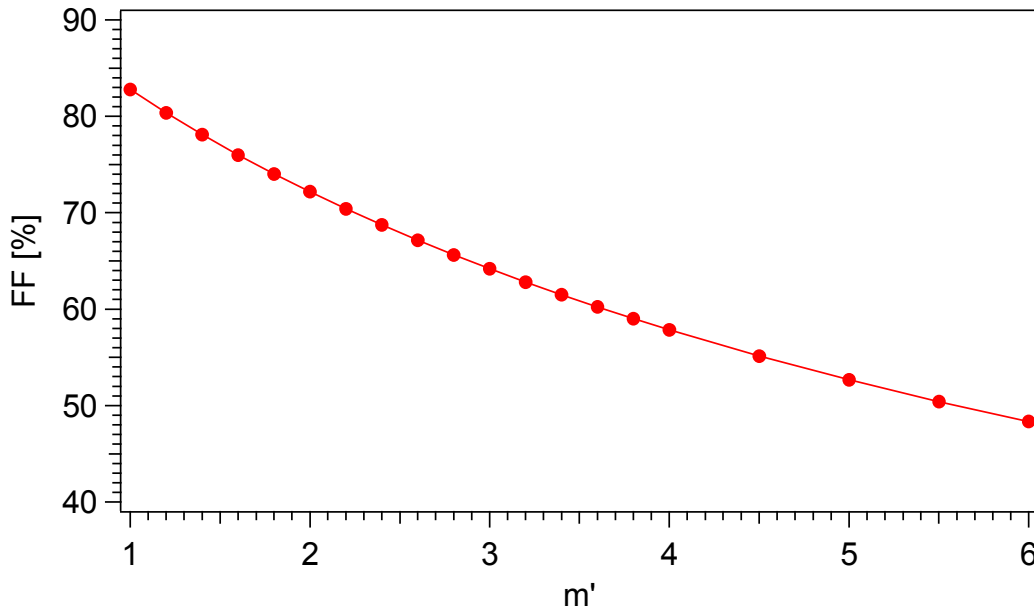


Fig. 7.4. The relationship of fill factor with the effective ideality factor m' found under light conditions for a $V_{oc} = 0.6V$.

7.5 Future charge extraction studies

In this and the last chapter we have employed charge extraction to determine charge densities in the device across their J - V curves. We have shown several applications of this CE data to understand the properties of both the ‘dark’ and ‘light’ J - V curves. In addition to the experimental and analysis approaches already described, there are several additional forms of investigation which charge extraction studies can be used for, with particular focus on understanding the light intensity dependence of the charge density in the device. Above, charge extraction has been used to investigate the charge density in a device in forward bias. Similarly, it should also be possible to investigate the device charge density in reverse biases, in which, charge extraction is performed in the reverse manner, where instead of extracting charge from the device, the measured current transients describe the charging of the device.

In the numerical studies presented in Chapter 2, the concept of the ‘corrected photocurrent’ procedure was outlined, and was shown to be particularly useful when attempting to analyse device dynamics. In this work, it was shown that the corrected

photocurrent can be considered in terms of the spatially averaged drift and diffusion based current densities.

$$J_{\text{ph}} = e \left((\mu_p \langle p_{\text{ph}} \rangle + \mu_n \langle n_{\text{ph}} \rangle) E + \frac{k_B T}{e} \left(-\mu_p \left(\frac{p_{\text{ph}}(d) - p_{\text{ph}}(0)}{d} \right) + \mu_n \left(\frac{n_{\text{ph}}(d) - n_{\text{ph}}(0)}{d} \right) \right) \right) \quad (7.17)$$

By comparison with experimental studies performed by Ooi,⁵⁷ it is apparent that this expression correctly describes the experimentally determined ‘corrected photocurrent’ data. As it is now possible to map the J - V curves for a device in the dark and under illumination in terms of charge density, we are now also able to consider the ‘corrected photocurrent’ and the expression depicted in Eqn. (7.17) in terms of photogenerated charge densities n_{ph}

$$n_{\text{ph}}(V_{\text{int}}) = n_{\text{light}}(V_{\text{int}}) - n_{\text{dark}}(V_{\text{int}}) \quad (7.18)$$

where n_{light} is the charge density in the device at a given voltage under light conditions and n_{dark} is the charge density in the device at the same voltage under dark conditions, both of which are measured using the charge extraction measurement. Such studies can be easily employed in parallel with ‘corrected photocurrent’ experimental studies.

VIII

Chapter 8 Final Conclusions

The primary focus of this PhD thesis was to study the charge carrier decay dynamics in standard annealed P3HT:PCBM devices and obtain a device model to describe their light J - V curves. This was done by initially using a simple drift-diffusion model to investigate the basic processes that may contribute to device function and then employing a wide range of experimental techniques to determine and study the physical parameters which are influential on device function, such as carrier lifetime and charge density.

In Chapter 2 a simple drift-diffusion model was employed to study the basic processes that may influence device function in organic bulk heterojunction (BHJ) solar cells. The BHJ blend device was treated as a single layer ‘virtual semiconductor’ sandwiched between two non-selective electrodes. In our studies of the corrected photocurrent (J_{ph}) where the effects of dark injection are removed we found that we were able to obtain good qualitative agreement between the simulated J_{ph} - V curves with those of real MDMO:PPV/PCBM devices. These J_{ph} - V curves follow symmetric behaviour with the point of symmetry when the applied voltage equals the built-in potential and $J_{ph} = 0$. Clear differences were observed with P3HT:PCBM devices

however. Although these too exhibited symmetric behaviour $J_{\text{ph}}-V$ curves, the point of symmetry occurred at a negative current rather than the expected $J_{\text{ph}} = 0$ is translated. One possible explanation for this behaviour is that a non-uniform blend induces selectivity at one or both electrode with electrons being blocked at the anode and/or holes at the cathode. This yields a beneficial increase in the size of the photocurrent and may partly explain the high efficiencies in P3HT:PCBM devices.

In Chapter 4 we determined the rate law describing the charge carrier decay dynamics at open-circuit on standard P3HT:PCBM solar cells by while under illumination by studying the steady state charge densities and carrier lifetimes. This rate law was found to follow strong non-linear behaviour, typically following an approximately third order dependence on charge density.

Chapter 5 investigated the origin of this rate law through combined studies of optical transient absorption spectroscopy (TAS) on devices and thin films with the opto-electronic studies described in Chapter 4. The rate law describing the charge carrier decay dynamics at V_{oc} were shown to be equivalent to those observed in TAS studies of thin films. Based on the microscopic model that has been previously used to describe TAS data for polymer: PCBM thin films these carrier decay dynamics in P3HT:PCBM devices are understood to be governed by a bimolecular recombination process in which the rate constant is charge density dependent due to thermally activated de-trapping from an intra-band exponential tail of trapped states in the conjugated polymer.⁶⁰ We have determined this bimolecular recombination coefficient and found it to be several orders of magnitude smaller than the Langevin recombination coefficient consistent with previously reported findings.⁸¹

By employing applied electrical bias studies of charge generation we demonstrated that in the voltage range 0 – 0.6V (~ 1 sun V_{oc}) there were no significant variations in charge generation, indicating that it is not possible to explain the loss in photocurrent that occurs at open-circuit in terms of an electric field dependent geminate recombination process. Therefore, this indicates that the primary loss in current at V_{oc} can be attributed to bimolecular recombination which we confirmed by comparing the evaluated loss in current due to bimolecular recombination to the short-circuit photocurrent.

In Chapter 6 we demonstrated the use of a relatively simple charge extraction technique to determine the charge densities in standard P3HT:PCBM devices. We showed the charge densities determined in devices under the same light bias V_{oc} conditions using charge extraction with those determined using differential charging were in good agreement, thus providing support that charge extraction may be employed to study charge density in these devices. This charge extraction technique was applied to study the charge densities present in the device while under fixed conditions on the dark J - V curve. Strikingly, we found that the dark current followed the same relationship with charge density as that found for the charge carrier decay dynamics at V_{oc} . We thereby conclude that the dark current and the loss in current at V_{oc} in fact represent the same trap limited ‘bimolecular’ process, which simply scales with the charge density present in the device. Furthermore, it suggests that if we were to map the light J - V curve in terms of charge density, that we may be able to simulate the J - V curve by employing the expression for bimolecular recombination determined either from the charge carrier decay dynamics at V_{oc} or from the dark current. This was studied in Chapter 7 where we found that we were able to find a good agreement between our simulated light J - V curve using this bimolecular recombination process alone with the real light J - V curve. Therefore, we conclude that the predominant loss mechanism in the standard annealed P3HT:PCBM studies is due to a bimolecular recombination process in which the rate constant is charge density dependent.

By performing studies of the open-circuit charge carrier decay dynamics at V_{oc} , combined with studies of the forward bias current in the dark and also the ‘light’ J - V curve has led to the conclusion the predominant loss mechanism observed in the J - V curve for annealed P3HT:PCBM devices is bimolecular recombination. Finally, as a result of this thesis, based on the understanding of these studies, we have obtained a simple expression based on a trap-limited bimolecular recombination that is able to recreate light J - V curves, thereby reaching the primary goals of this project.

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