

Control and Characterisation of Metal Oxide/Polymer Morphologies for Hybrid Photovoltaic Devices

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Abstract

The ready formation of nanostructures, combined with excellent optoelectronic properties has shown zinc oxide (ZnO) to be a promising material for use in photovoltaic devices. Hybrid photovoltaic (h-PV) devices composed of metal oxide-organic pairings are currently limited by ineffective charge transfer between the materials and by poor transport of free charge out of the active layer. Control of interfacial properties, and the structure and morphology of each component is key to device optimisation. In this thesis, ZnO nanorods are paired with the photoactive polymer, poly 3-hexylthiophene (P3HT) with two areas studied: i) nanorod alignment to aid polymer infiltration, and ii) elucidating optimum polymer processing conditions to prepare efficient devices.

Aligned nanorods are synthesised from ZnO coated substrates by a hydrothermal method. To understand the influence of ionic additives on morphological control, the addition of potassium chloride (KCl) to growth solutions is investigated. Films have been studied by SEM and XRD, with the correlation of these results (nanorod length, width, density vs (002) diffraction peak area) used to examine alignment, which increases at higher concentrations. This ordering is explained via a geometrical selection argument.

Effective polymer infiltration into nanorod arrays is found to be possible by spin coating and annealing above the polymer melting point. Extended annealing (> 60 seconds) is seen to reduce device performance. Small angle X-ray scattering and X-ray diffraction as a function of temperature was conducted to investigate polymer orientation and the kinetics of crystallisation within nanostructured films. These results are combined with device measurements to aid in understanding the relationship between morphological characteristics of the constituent materials and h-PV performance.

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Foreword

This thesis forms the written component of research undertaken in the period between October 2009 to December 2012 within the Department of Materials, Imperial College London. The work described is my own with the exception of the following; the transmission electron microscopy presented in figure 3.10 (section 3.5) was completed by Dr Mahmoud Ardakani and the gel permeation chromatography measurements (table 4.1, section 4.2) were recorded by Paul Westacott. In addition the experimental work presented in figure 4.1 (section 4.3) was completed by Thomas Schmaltz (Friedrich-Alexander-Universität Erlangen-Nürnberg, Supervisor: Prof. Dr. Christoph J. Brabec) as work towards his master's thesis under the supervision of myself and the Martyn McLachlan research group. Samples were made and characterised by Thomas Schmaltz, while analysis and formatting is my own.

The work presented in this thesis has been published in the following articles and form the basis of the results shown in chapters 3 and 4. Due to the slow nature of publication, work that has been submitted and is in review is included in this list.

1. Downing, J. M., Ryan, M. P., McLachlan, M. A. *Solution processed hybrid photovoltaics: Preparation of a standard ZnO template* Journal of Photonics for Energy 1(1), 011117 (2011)
2. Downing, J. M., Ryan, M. P., McLachlan, M. A. *Hydrothermal growth of ZnO nanorods: The role of KCl in controlling rod morphology* In review (Thin Solid Films) (2012)
3. Koch, F., Rivnay, J., Foster, S., Muller, C., Downing, J. M., Buchaca-Domingo, E., Westacott, P., Yu, L., Yuan, M., Baklar, M., Luscombe, C., McLachlan, M., Heeney, M., Rumbles, G., Silva, C., Salleo, A., Nelson, J., Smith, P., Stingelin, N. *Microstructure development with molecular weight in semicrystalline organic semiconductors and its influence on charge transport* In review (Progress in Polymer Science) (2013)

Work not presented in this thesis but completed in collaboration during this period of research has been published here –

- Franklin, J. B., Downing, J. M., Giuliani, F., Ryan, M. P., McLachlan, M. A. *Building on Soft Foundations – New Possibilities for Controlling Hybrid Photovoltaic Architectures* Advanced Energy Materials, 2, 5, 528-531 (2012)

Additionally experimental results shown in chapters 3 and 4 were the subject of oral presentations at the following conferences –

1. Downing, J. M., Ryan, M. P., McLachlan, M. A. *Hydrothermal growth of ZnO nanorods: The role of KCl for tailoring aligned morphologies* Symposium Z4: ZnO Functional Nanostructures I, Materials Research Society, Boston November 2011
2. Downing, J. M., Ryan, M. P., Payzant E. A., McLachlan, M. A. *Hybrid solar cells: Understanding the influence of conjugated polymer morphology on device performance* Symposium K: Hierarchically Structured Materials for Energy Conversion and Storage, Materials Research Society, Boston November 2012

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Acronyms

Å	Angstrom
AAO	anodic aluminium oxide
BHJ	bulk heterojunction
CCD	charge coupled device
DSC	differential scanning calorimetry
EL	electroluminescence
FEG	field emission gun
FET	field effect transistors
FTO	fluorine doped tin oxide
FWHM	full width half maximum
GI-XRD	grazing incidence X-ray diffraction
GPC	gel permeation chromatography
h-PV	hybrid photovoltaic
HL	hole blocking layers
HH	head-to-head coupling
HMDS	hexamethyldisiloxane
HMT	hexamethylene tetramine
HOMO	highest occupied molecular orbits
HT	head-tail coupling
HyLEDs	hybrid light emitting diodes
ICBA	indene-C ₆₀ bis-adduct
ICDD	international centre for diffraction data
ITO	indium tin oxide
iPP	isotactic polypropylene
LEDs	light emitting diodes
LUMO	lowest unoccupied molecular orbital
MEH-PPV	poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene)
NBE	near band edge
NRA	nanorod arrays
ODT	1,8-octanedithiol
OTS	octadecyltrichlorosilane
OPV	organic photovoltaic

P3DDT	poly(3-dodecylthiophene-2,5-diyl)
P3HT	poly(3-hexylthiophene
PBTTT	poly[2,5-bis(3-alkylthiophen-2-yl)thieno(3,2-b)thiophene]
PCBM	phenyl-C ₆₁ -butyric acid methyl ester
PD	polydispersity
PDF	powder diffraction file
PEDOT/PSS	poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
PEI	polyethylenimine
PET	polyethylene terephthalate
PFO	polyfluorene
PL	photoluminescence
R2R	roll-to-roll processing
RR	regioregular
SAED	selected area electron diffraction
SAXS	small angle X-ray scattering
SE	secondary electrons
SEM	scanning electron microscopy
TAS	transient absorption spectroscopy
TEM	transmission electron microscopy
TFT	thin film transistor
TT	tail-to-tail
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1

Introduction

The development of renewable energy sources is driven not only by an increasing global population, but also by diminishing fossil fuel resources and attempts to mitigate the effect of anthropogenic climate change. Renewable technologies operate to generate usable energy and in operation require no additional expendable fuel and emit no carbon dioxide. Many technologies are available to harness energy from sunlight, wind, wave or biological sources. The topic of this thesis concerns devices that absorb light to create electricity; photovoltaics.

In the following pages the topic of photovoltaics is introduced in terms of historical development and scientific progress. These ideas are used to outline the aims and objectives of work presented in this thesis. In latter sections a literature review of the subject area concerning materials properties and deposition methods is completed as a preface to work which builds upon those that others have completed. Finally, this chapter concludes with an outline of the remaining chapters in the thesis.

1.1 Photovoltaics

1.1.1 Development of photovoltaic devices

Understanding processes that allow for the conversion of energy in the form of light to electrical energy has been the source of scientific curiosity and commercial interest for more than 150 years. Since the first observation of the photoelectric effect by Becquerel in 1839 [1] and later a fuller description of the phenomenon by Einstein in 1905 [2] there has been continued research to understand the materials that are able to absorb light and generate free charge. There is now a wealth of knowledge concerning the the physics of device operation and construction, much of which is the

subject of textbooks; two noteworthy publications are ‘The Physics of Solar Cells’ by Nelson [3] and ‘Organic Photovoltaics’ by Brabec et al. [4]. This section presents a brief introduction into the well-studied photovoltaic materials, with the aim to provide a suitable preface to a review of literature concerning bulk heterojunction (BHJ) organic photovoltaic (OPV) materials and devices. The topic of this thesis; hybrid photovoltaics (h-PV), a subset of OPVs, is then discussed.

It is easy to divide the main photovoltaic research themes chronologically and by active materials; these are outlined below with reference to the 1st generation, silicon solar cells, the 2nd generation, cells made from thin film technologies and 3rd generation, dye sensitised solar cells (DSSC). The development of each type of photovoltaic device can be described in three areas; the properties of the absorber material, device architecture and device operation (which varies for each materials combination), these are discussed below.

Silicon solar cells

The majority of research has been completed in devices made from silicon, such devices perform with high efficiencies and are commercially competitive ($\sim 1 \text{ } \$ \text{ W}^{-1}$). The best laboratory cell (test areas = 4 cm^2) to date operate with 25.0 % efficiency [5]. In addition commercial modules are widely available, the best in production being those from SunPower which operate with efficiencies (η) $> 20 \text{ } \%$ over areas $> 1 \text{ m}^2$ [6]. In operation, crystalline silicon is an excellent choice for absorber material as it has a low band gap of 1.12 eV, which is well matched to the solar spectrum allowing for high absorption. The band gap however, is indirect resulting in a low optical density and thick layers are required ($> 200 \text{ } \mu\text{m}$ [7]). Apart from materials cost, film thickness is not a problem as charge mobilities within crystalline Si are high ($\mu_{electrons} = 1200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\mu_{holes} = 400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K [8]) and the material can be doped to further tailor these properties.

Under illumination, photons are absorbed by Si to generate hole-electron pairs. Due to the low coulombic attraction in high dielectric materials these charges are freely mobile within the crystal. The separation of free charges occurs at a junction between negatively doped (n-type) and positively doped (p-type) materials (Fig. 1.1). At this interface an electric field is generated, driving electrons into the conduction band of the n-type layer and holes into the valence band of the p-type material. The loss mechanisms in these devices; surface reflection, low absorption co-efficient and charge loss through exciton recombination, are well understood and have been systematically addressed by research employing innovative solutions such

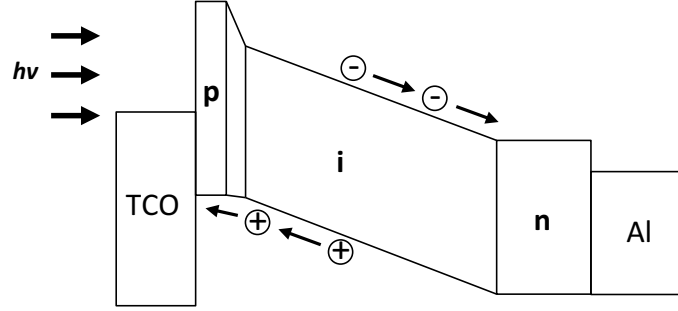


Figure 1.1: Band diagram showing silicon p-i-n junction architecture and operation. Under illumination light passes through the transparent conductive oxide layer (TCO) before being absorbed by the silicon which is either p-type (p), undoped/intrinsic (i) or n-type (n). Charge separation occurs as shown. Adapted from ref. [9].

as anti-reflection coating, novel device architectures and extended p-n junctions [10], to achieve efficiencies close to the thermodynamic maximum for PV devices (30 %, for single junction cells [11]).

Thin film solar cells

Second generation photovoltaic devices concern the use of chalcogenide based absorbing materials, of interest are cadmium telluride (CdTe) [12] and copper indium gallium diselenide (CIGS) [13] compounds. These materials have high absorption co-efficients (CdTe, 10^3 cm^{-1} [14]) and so thin films (as low as $0.7 \mu\text{m}$, $\eta = 11.2 \%$ CdTe [15]) can be applied to devices. These devices are seen to perform well; at 19.9 % when prepared under laboratory conditions [16] and 15.7 % for large area modules [6]. Such devices are commercially competitive because of the low use of active material that accounts for a large proportion of the construction cost.

Dye sensitised solar cells (DSSCs)

Work by Gratzel and O'Regan introduced the first dye sensitised solar cell (DSSC) [17]. DSSCs use an absorbing dye coated to a semiconducting nanostructured template (typically metal oxides, TiO_2 , ZnO). On absorption, dye molecules photoexcite and transfer photoelectrons rapidly to the oxide scaffold. The dye is regenerated by a liquid electrolyte (typically I^-/I_3^- [18]), and is a slow process resulting in a cell where electron transfer is favoured over regenerative loss from electrolyte to dye. Photochemical cells are of interest for their light weight and potential use with flexible substrates.

Understanding the roles of electrolytes, dyes and scaffold materials has been the concern of two decades of DSSC research. This has resulted in production of devices

with efficiencies $\approx 11\%$ [19]. Commercialisation of DSSCs has been difficult owing to the liquid electrolytes employed in these cells. DyeSol have made progress in the manufacturing of these cells and see a market for devices [20] that are semitransparent and work well in low light conditions [21].

Research on DSSC-absorbing dyes, as well as early work by Tang et al. on functional PV bilayer devices of copper phthalocyanine (CuPc) and a perylene tetracarboxylic derivative [22], showed the feasibility of using organic materials as absorber and inorganic acceptor materials in photovoltaic devices. In the former case, research has gone further to employ polymeric absorber materials for use in photovoltaic devices, these are termed organic photovoltaics and are discussed in the next section.

1.1.2 Organic photovoltaics

The solubility of organic materials and the ease with which thin films can be processed over large areas and at low cost is one reason for their current popularity in the scientific community. If devices can be created with modest efficiencies and shown to operate with reasonable lifetimes then organic photovoltaic (OPV) devices can become commercially viable. Organic photovoltaics are lightweight and can be processed on flexible substrates, allowing devices made from these materials to be integrated into products where application of traditional photovoltaics would be infeasible.

Photoexcitation in organic materials is different from the aforementioned inorganic and photochemical devices. Organic materials, which have low dielectric constants, absorb photons to create tightly bound Frenkel excitons. A high attraction between the opposite charges binds excitons around similar lattice positions and confines the diffusion of excitons to small distances within the material ($\approx 10\text{ nm}$ [23]). The creation of free charges in these materials is possible through the dissociation of the exciton at an interface between acceptor and donor materials which occur due to the energy difference in the band structure of the two materials. Excitons that do not diffuse to these interfaces recombine (geminate recombination) and the potential energy is lost as phonon or photon emission. If an exciton does reach an interface, electrons will move to the lower energy of the conduction band in the acceptor material and holes continue within the donor conduction band. These charges can diffuse under

the inbuilt field of the cell which is provided by the difference in the work function of the electrodes to the corresponding electrodes.

Efficient OPV devices require fine mixing of acceptor and donor materials. Such films are termed bulk heterojunctions and provide a high interfacial area between the acceptor-donor materials while allowing for charge collection through so-called ‘bi-continuous pathways’ for electron and hole conduction to the device electrodes. Numerous material combinations have been investigated, including small molecule-small molecule [24], polymer-polymer [25], polymer-nanoparticles [26] and polymer-small molecule blends [27]. The best studied of these combinations are polymer-small molecule blends using poly(3-hexithiophene) (P3HT) and the fullerene derivative, phenyl-C₆₁-butyric acid methyl ester (PCBM). A typical device architecture is shown in figure 1.2. The highest reported devices are seen to operate with 6.5 % efficiency [27], however, these devices have very small active areas (1.5 mm x 1.5 mm) and feature advanced processing conditions and interlayers, more often efficiencies of $\sim 4 - 5$ % are reported [28].

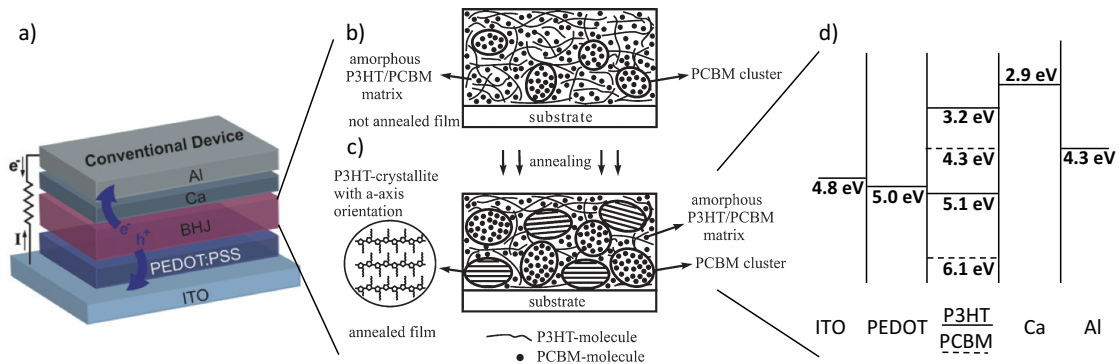


Figure 1.2: a) BHJ device in conventional architecture, ITO / PEDOT:PSS / BHJ / Ca / Al, reproduced from ref. [29] b,c) schematic diagram showing film morphology before and after annealing step, reproduced from ref. [30] d) band diagram showing for BHJ cell, active layer P3HT shown in bold and PCBM in dashed lines. Adapted from ref. [31].

The modest performance of these devices is reasonably well understood and can be explained due to the morphology formed by the intermixing and crystallisation of annealed bulk heterojunction blends (Fig. 1.2b,c). As-cast films are primarily a mixture of small molecules dispersed in an amorphous polymer matrix. On heating, the materials self segregate as crystallisation occurs to form semicrystalline polymer, small molecule crystals and intermixed amorphous regions [30]. The optimum internal structure is seen to be a meta-stable state where some crystallisation of the two

components has occurred but not so to allow for the growth of overly large grains [4]. Balancing the rate of crystallisation of polymer and small molecule is dependent on the molecular weight, poly dispersity (PD) and regioregularity of the polymer. For P3HT:PCBM annealing is completed in the temperature range 110 - 150 °C [28] and seen to yield approximate domain sizes of 6 nm and 23 nm for P3HT and PCBM respectively [32, 33].

Research towards increasing device efficiency further has seen the development of novel low bandgap polymers, which perform with efficiencies of 6.1 % [34]. For these systems it is now understood that the position of the donor HOMO-LUMO levels with respect to acceptor LUMO level is important in terms of the driving force for exciton dissociation and the open circuit voltage (V_{OC}) of the device [35]. Optimised acceptor molecules energy levels can dramatically enhance OPV performance, one such example is indene- C_{60} bisadduct (ICBA), which is seen to work exceptionally well with P3HT ($\eta = 6.5$ %) to increase the V_{OC} in these OPV devices [36]. Low work function electrodes are also employed to increase the built in voltage across the device (Fig 1.2d).

1.1.3 Towards hybrid photovoltaics

The development of photovoltaic technologies from cells made from silicon to those made from organic materials has been discussed. Through the early work on molecular thin films and dye sensitised solar cells, organic photovoltaic devices are becoming increasingly well understood and are seen to operate now with modest efficiencies. Novel photovoltaic devices made from inorganic and organic components borrow from both DSSCs and OPV to create functional composites with the advantageous properties of each component. The desirable properties for a hybrid photovoltaic (h-PV), in terms of inorganic materials are, a high n-type conductivity, transparency and structural stability; each of which are discussed in section 1.2.1. The polymer component acts as a strong optical absorber with the ability to transfer charge to the oxide, it has p-type conductivity and can be processed by a variety of low temperature methods. Polymer properties are discussed in section 1.2.5. The study of composite metal oxide-polymer films and h-PV devices are presented in section 1.2.6 and 1.3 respectively.

The development of organic (and hybrid) photovoltaics is part of a wider interest in organic materials for optoelectronic applications, these include thin film transistors (TFT) and organic light emitting diodes (OLED). Such a field is inter-disciplinary,

requiring knowledge of chemical synthesis, device physics and investigation of film morphology on nanometer to micron length scales.

1.2 Materials properties and processing methods

The physical properties of the materials zinc oxide (ZnO) and poly-3-hexylthiophene (P3HT), used in later experiments are presented in sections 1.2.1 and 1.2.5 respectively. The properties of interest are those that pertain to optoelectronic applications. For the inorganic the role of defects in conductivity is discussed (section 1.2.1.3) along with the processes by which nanostructured growth can occur (section 1.2.3). For the conjugated polymer, the process of photonic excitation and conduction mechanism within the polymer are discussed (section 1.2.5.1) and these properties are linked to processing methods and polymer molecular weight (section 1.2.5.4). In the final subsection (1.2.6.2) pairings of inorganic and organic materials are discussed, with the aim to review literature relating to the infiltration of polymeric materials within inorganic nanostructures with the properties of confined polymers within small pore sizes being of specific interest.

1.2.1 Zinc oxide (ZnO)

Zinc oxide has been chosen for this research because it is a wide band gap material with intrinsic n-type properties. The transparency and conductivity make ZnO suitable for hole blocking layers in photovoltaics [37, 38]. In addition to photovoltaic applications [37, 38, 39], ZnO has been applied to light emitting diodes [40, 41], thin film transistors [42, 43] and gas sensors [44, 45].

This section will focus on the applicable properties of ZnO for PV and in the initial paragraphs provide a comparison with titanium dioxide (TiO_2) to show the advantageous material properties of ZnO. In later sections the crystal structure of ZnO (section 1.2.1.2), nanostructure growth mechanisms (section 1.2.2.5) and optoelectronic properties (section 1.2.1.3) are discussed before presenting possible processing methods for ZnO thin films and nanostructures (section 1.2.2).

1.2.1.1 Motivation for ZnO in hybrid photovoltaics

To achieve a well functioning h-PV device, the inorganic component must:

1. Promote charge transfer; electrons must be able to transfer between the polymer and organic, to do so requires a band offset greater than the binding energy of the exciton within the polymer (typically 0.3 eV [35]).
2. Have n-type conductivity; materials for h-PV are acceptor materials and require n-type conductivity so that electrons transferred from organic species can be carried to the respective electrode.

These material requirements are satisfied by metal oxides, which have wide band gaps and n-type conductivity through intrinsic defects and impurity dopants. The energy of the conduction band of these materials is often below that of highest occupied molecular orbital (HOMO) of the organic donor materials leading to a sufficient energy offset for charge transfer to occur. The wide bandgap and low energy of the valence band is sufficient to block hole transport within these materials. Owing to these properties, metal oxides, specifically ZnO and TiO₂ are well suited for application in h-PV materials; the physical properties of these two oxides are compared in table 1.1.

Table 1.1: Comparison between the optoelectronic properties of ZnO and TiO₂.

	ZnO	Ref.	TiO ₂	Ref.
Crystal phase used for PV	wurtzite	[46]	anatase	[47]
Crystal packing	hexagonal	–	tetragonal	–
Band gap (eV)	~ 3.3	[48]	~ 3.2	[49]
Position of HOMO (eV)	4.2	[50]	4.2	[51]
Position of LUMO (eV)	7.4	[50]	7.4	[51]
Carrier concentration (cm ⁻³) ¹	6x10 ¹⁶	[52]	8x10 ¹⁶	[53]
Electron mobility (bulk) (cm ² v ⁻¹ s ⁻¹)	205	[52]	20	[54]
Electron mobility (nanostructure) (cm ² v ⁻¹ s ⁻¹)	75 nanorod	[55]	≈ 10 ⁻⁶ nanoparticles ²	[56]

¹ In ZnO carrier concentration can be varied many orders of magnitude by changing processing conditions. Values as high as 2x10¹⁹ cm⁻³ have been reported [57].

² Mobility values of TiO₂ nanorods are not reported in the literature. Growth of TiO₂ nanorods are possible [58] (4 nm in diameter, 20 – 40 nm in length), nevertheless, mobility values would be expected to be significantly less than the bulk values.

ZnO and TiO₂ are wide bandgap materials with high transparencies, in this respect the difference in band gap ZnO and TiO₂ is negligible. It is however, the electronic properties which differentiate these materials. Table 1.1 shows that ZnO

has superior n-type conduction, a result of higher electron mobility within the material. The electron mobility is an order of magnitude greater than that observed in TiO_2 . Mobility values for both materials in nanostructured forms are presented as an example of the materials properties for potential incorporation within devices. Here ZnO nanorods are seen to have higher mobilities than bulk TiO_2 , it is for these reasons and the ease at which nanostructures can be formed (section 1.2.2.5), that ZnO has been chosen in this work.

1.2.1.2 Crystalline structure

Zinc oxide is a group II-VI semiconductor with a hexagonal wurtzite crystal structure [46]. Here four oxygen ions co-ordinate a zinc ion at the corners of a tetrahedron (Fig. 1.3). The lattice parameters have been measured ($a = 3.2495 \text{ \AA}$ and $c = 5.2069 \text{ \AA}$) and the density of the oxide is 5.605 g cm^{-3} . Rock salt and zinc-blend crystal structures have also been shown to exist at high pressure [59].

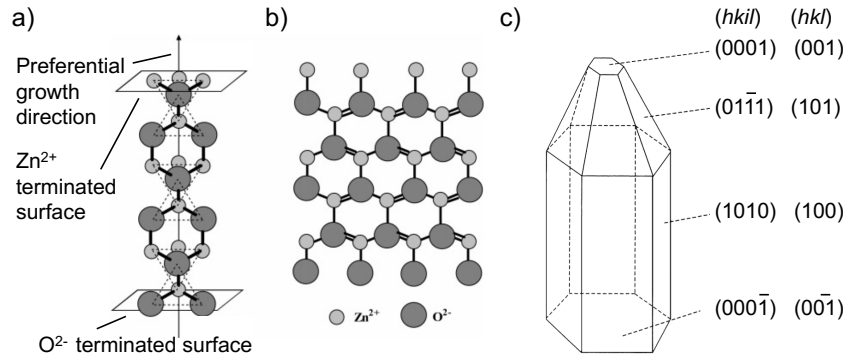


Figure 1.3: a) Schematic of hexagonal wurtzite crystal structure showing polar faces and preferential growth direction b) crystal structure – side-on orientation showing asymmetry of Zn^{2+} and O^{2-} layers, a,b) adapted from ref. [60]. c) Schematic representation of ZnO crystal showing crystal planes with both (hkl) and $(hkli)$ notation, adapted from ref. [61].

Figure 1.3 shows schematically the ZnO crystal structure. The alternating distance between closed packed oxygen and zinc layers is $0.69 \text{ \AA}$ and $1.99 \text{ \AA}$ respectively [62]. The lack of symmetry in the c-axis of the crystal leads to polarity within ZnO wurtzite crystals, the surface perpendicular to the c-axis is composed wholly of either O^{2-} or Zn^{2+} ions (Fig. 1.3a), this surface is termed the (002) plane. Planes that lie parallel to the c-axis ((100), Fig 1.3b) consist of Zn-O dimers that are charge neutral. The surface energies of the (100), (110) and (001) faces have been calculated by *ab initio*

methods (linear combination of atomic orbitals), finding the different energies to be 2.32 J m^{-2} , 4.1 J m^{-2} and 5.4 J m^{-2} respectively [63].

Bulk-truncated structures as shown in figure 1.3a,b are rarely seen on the surfaces of real crystals, which often reconstruct or relax to reduce their surface energy. The polar ZnO surface is known to reconstruct and does so to reduce $\sim \frac{1}{4}$ of the surface charge [64]. Three mechanisms have been proposed for this recombination, the creation of a metallic surface by introduction of surface states, removal of surface atoms and charged impurities on the surface (for example hydroxyl species). In contrast, the non-polar ZnO surfaces, containing the same number of zinc and oxygen atoms show no reconstruction [65].

Regardless of surface reconstruction, the polar ZnO surface has the highest surface energy and the formation of this surface is the least thermodynamically favourable. Growth, dissolution and etching all occur favourably in the $\langle 001 \rangle$ direction to minimise the formation of the polar face. Through this preferential growth, ZnO nanostructures form – nanorod growth is of interest and discussed in section 1.2.2. Growth of many other nanostructures is possible and these include; dendrites [66], tetrapods [67], helices [68], particles [39] and platelets [69].

1.2.1.3 Electronic properties

The electronic properties of ZnO are in part controlled by the extent which ZnO crystals deviate from stoichiometry [70]. Two types of impurity exist, those from intrinsic crystalline defects and impurities resulting from extrinsic dopants. Intrinsic defects may be further categorised into lattice vacancy (V_O , V_{Zn}), interstitial (O_i , Zn_i) or antisite (O_{Zn} , Zn_O) defects. Extrinsic dopants may be added to the material to purposefully change material properties or are incorporated unintentionally through the processing environment [71]. Defect formation, film properties and processing conditions are discussed below for both intrinsic and extrinsic dopants with a key interest given to the effect of defects on devices performance.

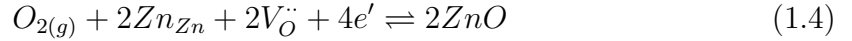
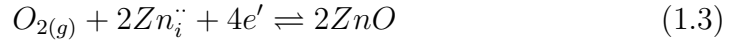
Intrinsic defects

Intrinsic defects within ZnO are donors and through ionisation contribute to free electrons within the solid. Formation of intrinsic defects is energetically favourable when the Gibbs free energy, ΔG_d (Eqn. 1.1) is negative [70]. The enthalpy of formation (ΔH_d) is positive due to the additional energy required to move or remove atoms from the lattice. This is balanced by the entropy of the system, ΔS , which promotes defect formation through the increase in the disorder of the solid.

$$\Delta G_d = \Delta H_d - T\Delta S \quad (1.1)$$

$$N_d = N \exp(-\Delta H_d/k_b T) \quad (1.2)$$

The equilibrium concentration of defects is described by equation 1.2 [70] and is dependent on the number of available sites (N) and the temperature (T) multiplied by the Boltzmann constant (k_b). In ZnO two types of defects are prevalent; the Frenkel reaction describes the formation of zinc interstitials (Eqn. 1.3), whilst oxygen vacancies occur via the Schottky reaction (Eqn. 1.4).



From the above equations, defect concentrations are dependent on the amount of gaseous oxygen in the system. Thus, within the rate equation defect formation will be dependent on oxygen partial pressure, this effect is well observed in the literature whereby differing growth conditions can dramatically change conductivity. Work by Fritsch reported in ref. [70] showed that ZnO conductivity can increase from 0.01 S cm^{-1} to 10 S cm^{-1} for samples annealed in oxygen atmosphere and those prepared without annealing. Determining the defect ($Zn_i^{\cdot\cdot}$ or $V_O^{\cdot\cdot}$) that contributes to the increased conductivity within ZnO is a source of active discussion in the literature [72, 73, 74].

Much research has been completed to find the energies of these defects to quantify defect formation and the contribution of each defect to conductivity in ZnO. Djuric et al. summarise computational defect data (Fig. 1.4) finding both $V_O^{\cdot\cdot}$ and $Zn_i^{\cdot\cdot}$ to be thermodynamically favourable and occupy similar energies [74]. Schmidt-Mende and MacManus-Driscoll also review reports in the literature which highlight the effect of processing conditions; at low pO_2 and high $pZnO$, it is likely that Zn_i dominates, whereas at low pO_2 and low $pZnO$, it is probable that V_O dominate [75].

The contribution of defects to ZnO conductivity is dependent on the position of defects within the band gap. Defects with low energies, often termed shallow donors, are positioned close to the conduction band and when charged will donate electrons to the conduction band. Defects with higher energies, termed deep donors, are less able to contribute free charges and less likely to increase conductivity.

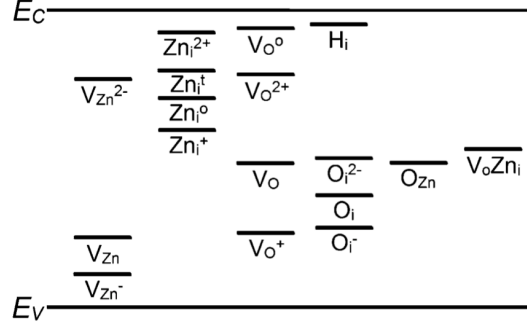


Figure 1.4: Calculated energy levels of different defects in ZnO from literature review by Djuricic et al. [74] modified from ref. [76]. The defects in this diagram, from left to right are zinc vacancies (V_{Zn}), zinc interstitials (Zn_i), oxygen vacancies (V_O), hydrogen interstitial (H_i), oxygen interstitials (O_i), oxygen atom on zinc site (O_{Zn}), oxygen vacancy zinc interstitial complex (V_OZn_i). Each defect is shown with their respective charge(s).

Extrinsic dopants

The most prevalent external dopant in ZnO is hydrogen, which has been shown theoretically by DFT calculations to reside in interstitial spaces within the ZnO crystal [77] and contributed to conductivity as a shallow donor (Fig. 1.4). Hydrogen is present in the majority of synthesis methods, experimentally hydrogen interstitials (H_i) are seen to occur in high concentrations $6 \times 10^{16} \text{ cm}^{-3}$ [78], and in some cases it is thought to be the dominant donor in ZnO [79]. Nitrogen has also been proposed as a dopant which may incorporate within the structure as a Zn_iN_O complex [80].

The optoelectronic properties can be further controlled by intentionally doping n-type ZnO crystals with donor group III elements (B [81], Al [82] [83], Ga [84]), to promote conductivity, or doping with acceptor group V elements (N [85], P [86], As [87], Ag [88]), which hinder electron conductivity. Donor dopants are readily incorporated into ZnO, leading to conductivities as high as $2 \times 10^4 \text{ S cm}^{-1}$ for films doped with 1 wt% alumina (Al_2O_3). Due to a high optical transmittance, 80 % in the range 400 – 800 nm, these films are of interest as transparent conducting oxide that may replace the well-used indium tin oxide (ITO) [83].

The inclusion of p-type dopants is of interest because of the possibility to create a p-n junction from ZnO, however, the p-type defect chemistry of ZnO is complex and while p-type doping is possible [88], conductivity is often only observed over short time periods of hours to weeks [89]. The difficulties in p-type doping are attributed to the low solubility of dopants [90] and intrinsic defect compensation [91].

This work does not investigate extrinsic dopants; however, it is important to note that dopants can be used to control film properties and in terms of processing dopants can be readily included into nanostructured films as easily as they are in planar films *i.e.* by low temperature solution based methods [82, 92].

The extent to which defects control material properties is increased in nanostructured ZnO, whereby a much higher interfacial area increases the inherent concentration of surface defects and allows for facile diffusion throughout the nanostructure. This is of key interest for h-PV devices, in which defect states may act as traps, hindering the flow of charge from organic to inorganic, a topic discussed in the section below.

ZnO defects chemistry in relation to nanorods and OPV devices

Defects within ZnO distort both the crystalline and the electronic structure of the material. As such they can be investigated by X-ray diffraction methods and also by spectroscopic methods such as electroluminescence (EL) or photoluminescence (PL). In practice spectroscopic methods have higher sensitivity and PL is often measured by exciting the crystal with a laser and observing emission by fluorescence from the various energy states present. Results are reported in terms of photon energy against PL intensity, here the near band edge (NBE) peak corresponds to emission from the band gap and peaks at lower energies are attributed to emission from defects within the bandgap. Many defects with similar energies result in complex spectra featuring numerous overlapping peaks; as understanding which defects contribute to conduction is a source of discussion, so too is assigning energies to these defects observed by experimental methods.

The NBE peak is observed in the range 3.27 – 3.36 eV and occurs due to exciton recombination from the conduction band [93]. Two other significant peaks at ~ 2.45 eV and ~ 2.15 eV have been observed corresponding to green and yellow respectively in PL experiments. Green emission is commonly attributed to oxygen vacancies [94, 95], while yellow emission attributed to surface hydroxyl groups [93]. The final peak of interest is a shoulder on the NBE peak, occurring at 3.3628 eV (I_4) and attributed to hydrogen doping [64, 74].

Qui et al. observe a large NBE peak width in the PL emission of hydrothermal nanorod samples and attribute it to a high defect concentration in these samples. The authors show a reduction in yellow emission on annealing (at temp. > 200 °C / 2 hr), attributing it to a reduction in OH^- defect concentrations [93]. A reduction in defect emission upon annealing is also observed in doped ZnO nanorods (Al, Cu, Co, Mn) grown by electrochemical methods [96]. Tam et al. observe emission from the

I₄ peak showing hydrogen dopants within ZnO nanorods [76]. The authors however, note that a reduction in PL intensity is not necessarily sufficient proof of a reduction in defect concentration as some defects may be non-radiative [76].

Conduction within ZnO is seen to be dependent on processing conditions and arise from the rich defect chemistry of the metal oxide. Defects have been observed by PL measurements in ZnO nanorods, with photoemission from defect states being seen to reduce upon annealing. Another method to remove surface defects is to passivate the surface with coating. For nanorod transistors an increase in electron mobility, from 75 to $> 1000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$, is observed when a polyamide coating is applied [55]. In h-PV, TiO₂ is often used as an interlayer [97, 98, 57] and is seen in devices to increase photocurrent and reduce the recombination rate [97], an optimised TiO₂ layer thickness (4 – 10 nm) can improve device efficiency by a factor of 5 [98]. Both observations are implicit of a reduction of defects at the interface leading to an increase in effective device operation.

1.2.1.4 Summary

ZnO has been compared to TiO₂ and it has been shown that the ZnO properties may be more applicable to optoelectronic applications than TiO₂. This is due to the high conductivity of ZnO and the ability to maintain electrical properties when processed on the nanoscale. The optical and electronic properties have been considered with particular attention to that of the defect chemistry of ZnO, which has a rich variety of intrinsic defects that contribute to the electrical properties and many suitable external dopants that can further enhance the conductivity. In the ultimate paragraph of this section it is suggested that defects can act as trap states hindering the function of devices that rely on the transfer of charge along or across a ZnO interface. This is discussed further in section 1.3.

The next section considers methods used to deposit ZnO thin films, and nanostructures of particular interest are methods that can create metal oxide films at low temperatures.

1.2.2 Low temperature ZnO deposition methods

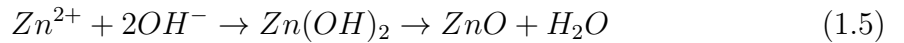
Numerous experimental methods are available to create ZnO thin films and nanostructures. The methods, in general can be divided into two groups; those that are based on high temperature ($> 500 \text{ }^\circ\text{C}$) and vacuum processing ($<< 1 \text{ atm}$) and those which can be completed without such processes. In the first group

methods such as pulsed laser deposition (PLD) [99], chemical vapour deposition (CVD) [100] and atomic layer deposition (ALD) [101] reaction conditions are controlled (oxygen partial pressure, temperature and reagent flow rate) to form films with specific conductivity or morphological properties. Equipment used in these deposition methods is in general, expensive involving a vacuum system and large sealed deposition chambers. In the same instance, films created by these methods are often only possible over small areas ($\approx 5 \text{ cm}^2$ for PLD [102]). While the controlled deposition of ZnO by these methods is good, the application of these methods to large scale processing required for large area PV-devices is poor.

Low temperature processing is thus desirable for scalability and for the low capital cost of equipment. The methods of solution processing, electrodeposition, spray pyrolysis and hydrothermal deposition are discussed below in terms of experimental conditions used to control the crystallinity, optoelectronic and morphological properties of ZnO films.

1.2.2.1 Colloidal methods

The formation of ZnO thin films can be achieved through the creation of ZnO particles in solution and their subsequent casting on a heated substrate. Several groups have produced ZnO thin films by this method and use these films for functional layers in devices [103, 104]. The synthesis of ZnO colloids proceeds through the hydrolysis and decomposition of Zn^{2+} ions in solution to ZnO (Eqn. 1.5).



Early work by Haase et al. and Kock et al. investigated colloidal synthesis using zinc perchlorate [105, 106]. Spectral methods have been used to observe the presence of nanoparticles. In more recent work Pacholski et al. created ZnO colloids from zinc acetate precursors [107]. Here, transmission electron microscopy (TEM) is used to observe particles with an average diameter of 3 nm, with the authors giving reference to a patent granted to Womelsdorf et al. [108]. It is noted that the $\text{Zn}^{2+}:\text{OH}^-$ ratio is seen to be important, values of 1:1.6 to 1:1.95 are reported to be preferable for colloidal growth. Sub-stoichiometric values are favoured because the degree of supersaturation controls the kinetic driving force for particle formation.

Hosono et al. have shown that ZnO colloids can be created in alcoholic solutions, without the addition of sodium hydroxide (NaOH) or other additives. Controlling the amount of H_2O present is the key to this synthesis method [109]. Chaing et al.

recommend limiting the water content to less than 10 times the molar amount of Zn precursor, the authors show this to be possible with zinc chloride (ZnCl_2) and NaOH reagents in a solution of ethylene glycol [110].

ZnO nanoparticle synthesis by colloidal methods allows for high density films with small crystalline grains (< 5 nm) to be created, due to the small particle size these films can be formed in thin films (< 20 nm). While grain boundaries arising from numerous grains will increase the sheet resistance of these films this may be compensated by the reduced thickness lowering series resistance. The morphology of these films is crystalline with mixed orientation analogous to the orientation of a powder diffraction pattern. Nanoparticles made in solution can be applied to a variety of substrates including flexible substrates, for example, polyethylene terephthalate (PET) ($T_m \sim 260$ °C), which cannot be used in higher temperature processing methods.

1.2.2.2 Sol-gel processing

A sol is a colloidal suspension of solid particles in a liquid [111]. Sol-gel processing is reliant on the stability of metal precursors and surrounding ligands, these typically being alkyl, alkoxy or acetate groups. The formation of inorganic films is dependent on sol-gel precursors, typically occurring through the hydrolysis and dehydration of the metal precursor.

The method for sol-gel film deposition of ZnO was first reported by Ohyama [112], where dip coating and thermal treatment is applied to build up coats of oxide to a dense film. It was observed that a high annealing temperature gives rise to preferential crystallographic growth in the (002) direction, although no increase in peak intensity was observed above 600 °C. In all cases, optical transparency was above 70 % with higher transparency observed at lower temperatures, 500 °C anneal gives transparency 75 – 80 %. A critical layer thickness of 100 nm was required for preferential growth, the authors attributed this to the substrate effects.

Spin coating provides a technique to deposit thin films on large substrates, the orientation of grains within sol-gel films is preferential for nanorod growth. Olson et al. have used this method for the creation of thin films used in h-PV devices [37].

1.2.2.3 Spray pyrolysis

Spray pyrolysis is a scalable deposition technique that allows for the rapid formation of ZnO thin film. Zinc salt solutions are emitted through a spray nozzle and the

carrier gas directs the aerosol towards a heated substrate, where solvent evaporation occurs and zinc ions oxidise to form ZnO crystals. Typical conditions involve solutions of zinc acetate in methanol, argon carrier gas and substrate temperatures of 450 °C [113]. Films are shown to be poly-crystalline and dopants (Al, In, Cu, Fe and Sn) can be incorporated into the solution to tailor film properties and are observed to vary grain morphology [114].

1.2.2.4 Electrodeposition

Electrodeposition of ZnO was first studied by Lincot [115]. The process employs a reference electrode to monitor the application of a current between two submerged electrodes, which drives the formation of ZnO from Zn^{2+} ions. This is more favourable when oxygen is present in solution [116]. In the presence of a current, charge on the surface of the working electrode increases hydroxyl precursors and the local solution pH so that equation 1.5 is thermodynamically favourable.

Electrodeposition is a well studied method with film morphologies reliant on zinc precursor [117], concentration [118], applied potential [119] and temperature [120, 116]. In contrast to the aforementioned processing methods, electrodeposition is able to create both thin films and nanorod morphologies. For the former, films are created by an island growth mode. At temperatures (> 34 °C) growth proceeds by the formation and dehydration of a $\text{Zn}(\text{OH})_2$ gel film. On dehydration, islands are seen to form and it is estimated that at 70 °C the dehydration step takes 1 – 2 s [120] with continuous films forming when isolated grains coalesce. A two step process of film formation is often used; firstly a high voltage is applied to drive nucleation of numerous zinc islands which are then oxidised *in-situ* to form ZnO and coalesce rapidly to form a thin film [121]. Dense films are grown in high precursor concentrations (> 10 mM), where lateral growth is favoured, initial pH values are observed to be between 5 and 6.

Nanorod growth by electrodeposition

In contrast to the growth of dense films, nanorod formation is observed at low zinc precursor concentrations. In this case the reduced consumption of hydroxide ions results in an excess generated at the surface of the electrode, at this interface the pH is > 9 and Zn^{2+} ions are stabilised in hydroxide complexes ($\text{Zn}(\text{OH})_3^-$, $\text{Zn}(\text{OH})_4^{2-}$) [122]. The electrostatic interaction between the negatively charged species and the electrode cause crystal growth to proceed strongly in the c-axis direction with very little growth in the lateral direction [122]. The experimental conditions for nanorod

growth have been investigated by Guo et al. who showed that; applied voltage reduces nanorod diameter and increases nanorod density, higher temperature result in longer nanorods with increased diameter consistent with increased reaction rates and that reducing the zinc ion concentration reduces nanorod diameter and density [118].

Electrodeposition must be completed on conducting substrates and while this limits the range of materials that can be used it is not a problem as devices generally require an electrical contact. The main issue is that these substrates must be electrically uniform so as to nucleate and grow films simultaneously at all points across the film. This however, is not often the case for ITO, where it has been observed that only 40 – 50 % of active sites are available for electron transfer [123]. The difficulty obtaining a clean surface and thus being able to deposit uniform films on ITO by electrodeposition ultimately limits the use of this technique for optoelectronic applications.

1.2.2.5 Hydrothermal deposition

Hydrothermal deposition, often termed chemical bath deposition, is an aqueous technique allowing for the formation of colloids, nanostructures and thin films by means of hydrolysis and/or condensation reaction from solution. Deposition can be conducted on any type of substrate and nominally on any area providing the solution conditions are uniform across the substrate. Growth typically occurs on suspended substrates in sealed containers at temperatures $< 100\text{ }^{\circ}\text{C}$, although some groups use autoclaves to reach higher temperature and pressures [124, 125].

Nanorod growth is readily observed in hydrothermal deposition. Formation of solid films can also be created by the coalescence of nanorods [126]. Nanorod growth by this method is presented in more detail in section 1.2.3.

1.2.2.6 Summary

The growth of ZnO thin films and nanostructures by low temperature deposition methods has been examined. These solution based techniques are of interest because they provide low cost low energy methods to produce functional substrates. Of most interest are electrodeposition and hydrothermal growth both which allow for nanorod growth. In particular the hydrothermal method is of interest for the ability to deposit ZnO on all types of substrate and across large areas. The method is presented in detail in the next section (1.2.3). The growth mechanisms are briefly discussed before

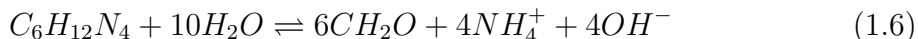
research in the literature is reviewed to determine the effect of substrate, temperature, solution concentration and also additive to ZnO nanorod growth.

1.2.3 ZnO nanorod growth by hydrothermal deposition

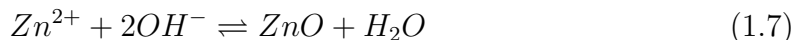
Hydrothermal deposition, in the simplest terms, is the forced hydrolysis of aqueous metal salts leading to the formation of solid colloidal metal oxide or hydroxide. Hydrolysis is possible in aqueous solutions at elevated temperatures (80 – 100 °C) and allows for the formation of numerous metal oxides, including ZnO, Co_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$ and CuO [127]. The shape, size and chemical structure of these particles is crucially dependent on the pH, concentration of the reactants, temperature, counter ion, method of mixing and concentration of additive included in growth solutions. ZnO particles are observed to nucleate in solution, and upon reaching a critical size, growth is seen to proceed along the length of the nucleate with little increase in the width of the particle [128] resulting in either prismatic or needle-like shapes.

Laudise and Ballman were the first to describe ZnO needle-like structures grown from hydrothermal methods, commenting on the need for NaOH to aid growth and observe that the maximum growth rate is in the $\langle 0001 \rangle$ crystal direction with minimal growth observed in the $\langle 1000 \rangle$ direction [124]. The mechanism to explain the variation in crystal growth is proposed by Li et al., who suggested that growth occurs by the addition and dehydration of $\text{Zn}(\text{OH})_4^{2-}$ units. The rate of growth on different planes occurs at a rate proportional to the ease that growth units can be incorporated into the lattice at the crystal interface [61]. This is dependent on the crystalline surface and specifically the composition of the surface that can be described in terms of the orientation of $\text{Zn}^{2+}\text{-O}_4^{6-}$ coordinated tetrahedra units. The corners of these tetrahedra may form additional bonds to growth units to enlarge the lattice; the amount of corners present on the crystal surface dictate the growth rate of that surface. On the $\{0001\}$ surface every coordinated tetrahedron has one corner present at the interface, on the orthogonal $\{1010\}$ surface half the coordination tetrahedrons have a corner present the other half, are tetrahedron faces. The pyramidal $\{01\bar{1}\bar{1}\}$ surface has half corners and half edge tetrahedrons present. This explains the differences in crystalline growth rates (R) where $R_{\langle 0001 \rangle} > R_{\langle 01\bar{1}\bar{1} \rangle} > R_{\langle 1010 \rangle}$. As previously discussed, these surfaces can be stabilised by atomic reconstruction (section 1.2.1.2), and their growth can be modified by solution additives as discussed in section 1.2.3.4.

The hydrothermal synthesis of ZnO nanorod arrays was first reported by Vayssieres et al. as a two-step process where a thin seed layer is deposited followed by nanorod growth [129, 130]. The novel steps in work by Vayssieres et al. was a) to include a ZnO seeded substrate in growth solutions which aids heterogeneous nucleation on the substrate surface, providing close to homoepitaxial growth [131, 132], and b) to include an oxygen precursor (hexamethylene tetramine, HMT) which slowly releases OH^- ions to solution on degradation at temperature (Eqn. 1.6). The increase in solution pH favours the formation of ZnO through the dehydration of $\text{Zn}(\text{OH})_2$ (Eqn. 1.5). Synthesis by this method allows for the formation of arrays of nanorods on conductive substrates suitable for device applications and does so in reasonable synthesis times compared to growth without HMT (2 hrs [103] vs. 24 hrs [61]).



The reaction kinetics of hydrothermal deposition have been investigated by studying the reaction between $\text{Zn}(\text{NO}_3)_2$ and HMT in an equimolar 50 mM concentration at 90 °C. It was found that HMT acts as a buffer; in the initial 2 hour period pH increases until a pH of ~ 5.64 is reached which is maintained for the next 7 hours until the end of the experiment [133]. The speciation of zinc ions is investigated and although ammonium (NH_4^+) and formaldehyde (CH_2O) are formed (Eqn. 1.6) the majority of zinc present remains in the form Zn^{2+} at the reaction pH [133]. It is clear that the reaction products from HMT degradation do not hinder the formation of ZnO from solution. Over longer time spans Ashfold et al. observe the emergence of nanotubes [133]. This can be explained through the preferential growth at the nanorod edge through a spiral column growth mode [134].



Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) have shown nanorods grown by the hydrothermal method to be single crystalline in nature [126]. Variables effecting array morphology are discussed in the sections below.

1.2.3.1 Effect of substrate

Hydrothermal deposition is possible on a variety of substrates, ZnO nanorod growth has been observed on ITO [38], gold [135], silicon [133], glass [104] and flexible

substrates [103, 136]. Control of nanorod growth and subsequent array morphology can be dramatically enhanced by depositing a thin ZnO film on the substrate prior to hydrothermal deposition (Fig. 1.5), these layers aid nucleation of ZnO nanorods. Guo et al. investigated the effect of seed layer morphology, considering films formed from colloidal ZnO particles, and by sol-gel and hydrothermal techniques [104]. Seed layer morphology was seen to control nanorod diameter and density; smaller grains in the seed layer (as present in colloidal nanoparticles) resulted in arrays with reduced diameters and increased nanorod densities [104, 137]. The importance of relative humidity on seed layer deposition is reported and shown to effect nanorod alignment [138].

Control of nanorod deposition is possible through the patterning of seed layers prior to growth, this is applicable to devices aiding in the creation of individually referenced cells [139].

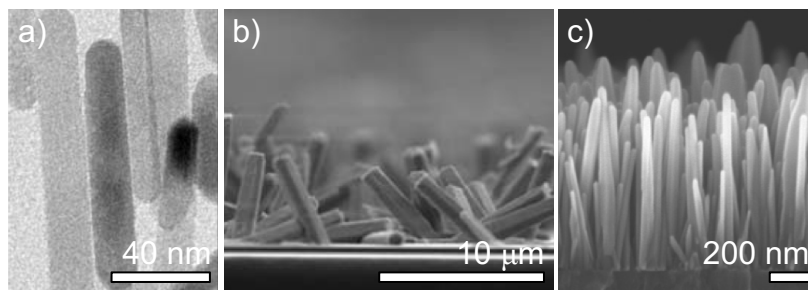


Figure 1.5: Scanning electron micrographs showing various ZnO morphologies produced by hydrothermal deposition; a) from solution precipitation, b) deposition on unmodified ITO-glass substrate, c) deposition on Si substrate with ZnO nanoparticle seed layer. a,b,c) adapted from refs. [107], [140] and [76] respectively.

1.2.3.2 Effect of temperature

High temperatures are required to activate the growth process, in accordance with the thermal degradation of HMT to yield OH^- ions (Eqn. 1.6). Reactions conducted at higher temperatures (80, 95 °C) for a given time period show an increase in nanorod length with little change in nanorod diameter [104]. An increase in NBE intensity is seen in PL measurements and attributed to a reduction in the defect density of nanorods grown at higher temperatures [104], however, as previously discussed (section 1.2.1.3) this may not be accurate due to non-radiative decay.

1.2.3.3 Effect of concentration

The reaction between $\text{Zn}(\text{NO}_3)_2$ and HMT is commonly completed at an equimolar concentration of 25 mM [130]. A reduction in the concentration of reactants (10 to 1 mM) is seen to reduce nanorod diameter [130]. At 2.5 mM, 88% of rod diameters are in the range 15 – 30 nm [104].

Upon mixing, ZnO forms as nanorods heterogeneously on the sample surface and homogeneously in the solution. The consumption of reagents leads to a reduction in concentration as growth time is increased. At very long growth times (> 10 hours) the emergence of tubular [133] or fine nanowire [141] morphologies is observed due to ZnO dissolution and re-precipitation.

The growth of long nanorods for DSSCs and also thin film transistors is possible by the re-immersion of nanorod substrates in new deposition baths resulting in continued nanorod growth [21]. Alternatively, chemical additives can be included to deposition baths to control morphology, this is discussed in the subsequent section (1.2.3.4).

1.2.3.4 Effect of additives

The inclusion of additive to growth solutions may influence the nanorod morphology by effecting the chemical kinetics of HMT degradation (Eqn. 1.6) and so controlling the supply of OH^- to solution, or by the addition of non-reactive additives that influence morphology through adsorption of ions to ZnO crystalline surfaces.

The addition of ammonia to growth solutions is seen to slow the degradation of HMT by altering the position of the chemical equilibrium. This leads to longer nanorods for a given initial growth concentration. Nanorod growth is seen to continue for periods up to 24 hours in solution yielding nanorod with lengths up to $\sim 22 \mu\text{m}$ – although significant nanorod thickness is also observed ($0.8 - 1 \mu\text{m}$) [142]. Re-immersion of nanorod substrates in baths with ammonia has been used to form arrays of $50 \mu\text{m}$ in length [143, 144]. Deposition without ammonia additive results in the termination of nanorod growth at ~ 2.5 hours with nanorod lengths $\sim 1 - 2 \mu\text{m}$ [21, 103].

For the inclusion of non-reactive additives there are two approaches; addition of surfactants and addition of inorganic ionic additives. In the first instance work by Law et al. [21] and Zhou et al. [145] concerning the addition of the surfactant polyethylenimine (PEI) is of interest; each report shows that surfactant addition hinders nanorod growth in the lateral direction, thus aiding in the growth of long

nanorod structures. It has been proposed that HMT also hinders lateral growth through the absorption to non-polar planes [146].

The study of ionic additives in hydrothermal deposition is sporadic in the literature. However, it is well known that ions are able to influence crystal growth. Several studies have reported the effect of Zn counter-ions on nanorod morphologies grown by hydrothermal deposition. Nanorods grown with chloride (Cl^-) and acetate ($\text{C}_2\text{H}_3\text{O}_2^-$) counter ions are seen to grow similar nanostructures. Nitrate counter ions (NO_3^{2-}) are observed to increase the length of nanorods, most likely due to the increase in rate resulting from dissociation of nitrate to nitrite in solution and accompanied hydroxide formation. Sulphate ions are seen to promote hexagonally terminated ZnO, likely due to the high charge density of the ion [147, 126].

Morphological changes can result from ionic additives altering the growth environment. Govender et al. report on the influence of addition of KCl to solution. Granular films, not nanorod films are observed and it is suggested that KCl adsorption may occur on the (100) surface to promote indirect c-axis growth and alter grain morphology [126]. In other work the ratio of $\text{Cd}^{2+}/\text{Zn}^{2+}$ is controlled to produce pyramidal structures [148], however, these films are grown without seed layers; the resulting array morphology and the effect of solution additives will be considerably different for seeded substrates.

Joo et al. investigate a variety of ionic salts and their influence on ZnO nanorod array formation using an alkaline (pH 11) deposition bath method [149]. Although differing from the hydrothermal method which is conducted at pH 5.5 – 6 [133], changes in nanorod aspect ratio are observed and the report provides a good comparison with hydrothermal HMT-based growth.

1.2.3.5 Nanorod array formation

The nucleation and growth of nanorod arrays is dependent on the width, length, shape and density of columnar ZnO growth. This in turn depends on the deposition conditions (substrate, reaction temperature, reagent and additive concentration and growth time). Dense films form when nanorod growth in the lateral direction is high, leading to coalescence. Nanorod arrays are formed when lateral growth is reduced.

Nanorod nucleation can be initiated by ZnO seed layers [104] and is also possible, at least on glass, by surface treatment with potassium permanganate (KMnO_4) [147]. These studies, however, do little to describe the method by which growth takes place in terms of the number of nuclei, growth rate and the resulting morphology at any given time period.

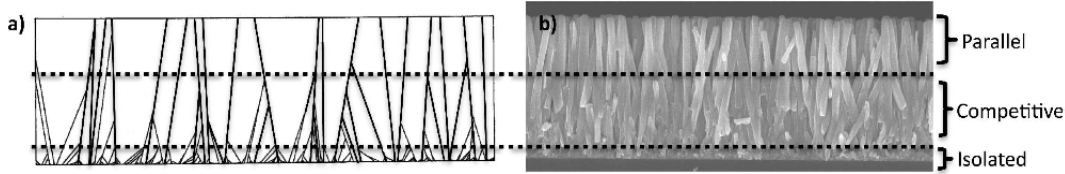


Figure 1.6: a) 2D simulation of randomly oriented crystal growth. b) SEM image of nanorod growth with dashed lines marking isolated, competitive, and parallel regions. Reproduced from ref. [150].

Recent work investigates the nucleation and growth by validation of a geometrical selection model [150]. Here, nanorod density is plotted as a function of time finding that as nanorod length, L , increases nanorod density is convergent to $L^{-0.8}$. This fits well with computational work that estimates that the relationship varies with L^{-1} . The authors attribute the density convergence to the nanorod growth process; on nucleation nanorods are isolated (high nanorod density), as growth proceeds nanorods interact and impinge resulting in a reduction in nanorod density. After this competitive regime, non-interacting or highly aligned nanorods are favoured, an array with low nanorod density and high alignment to the substrate is now observed (Fig. 1.6).

1.2.3.6 Summary

The variables of substrate, growth temperature, reagent concentration and solution additives outlined above have been used to control nanorod array morphology. Of these, substrate and solution additives are dominant and are of interest for further work with the aim to precisely tailor nanorod density, width and length. Additionally, through the understanding of array formation, with time the opportunity to control nanorod alignment by low temperature methods is possible. However, within this large variable space published data is sporadic and there is a difficulty in discerning clear trends, due to a number of factors:

- Nanorod growth conditions by different techniques are not comparable due to variation in the mechanism by which growth takes place. For instance, the addition of 60 mM KCl in electrochemical deposition is seen to be sufficient to stabilise the (002) surface and change the morphology from rods to platelets [60]. In contrast, ionic addition by hydrothermal methods is only shown to vary nanorod shape and size [126]; platelet growth by the hydrothermal method has not been reported in the literature. Additionally, although growth by deposition

bath methods is similar (heterogeneous nucleation from solution), different reaction conditions and reagent methods (for example HMT based hydrothermal deposition vs. NaOH based alkaline deposition) will give different results owing to the different chemical environments of reagents.

- Comparison of different experimental additives is difficult. Due to differing charge densities, ionic species have varying solubility in solution. In addition, reports are presented with differing concentration ranges which often do not overlap.
- Nanorod dimensions and orientation are dependent on substrate. Growth on seeded substrates allows for the formation of arrays with a high nanorod density owing to many initial nucleates [104]. In contrast, growth conducted on glass or silicon substrates is initiated at random nucleates and so morphologies are disordered and not subject to the same growth mechanisms as observed in seeded nanorod growth.

These factors highlight some of the interesting challenges to understanding the growth, and control of growth of ZnO nanorods by hydrothermal deposition. The control of nanorod growth is thought to dramatically improve the performance of ZnO nanorod devices (discussed below) and aid the use of the novel properties of these crystals in optical and electronic devices.

1.2.4 Nanorod device applications

ZnO has been used in numerous applications (rubber manufacture, concrete production, food additive, pigments and coatings) with $\sim 10^5$ tonnes produced each year. The development of nanoscience and significant research in the past 20 years has lead to the inclusion of ZnO into many novel and interesting applications, which may exploit the properties of ZnO in the form of thin films, for use in transparent conducting electrodes [151], transparent thin film field effect transistors [152] and as a doped semiconductor, in spintronic applications [153]. Other applications seek to exploit the novel properties of ZnO nanostructures; these applications are discussed below.

1.2.4.1 Photovoltaics

Considerable applications of ZnO thin films are found in photovoltaics (PV), particularly in the use of ZnO layers as electron transporting, hole blocking layers (HBL) [154] or optical spacer layers [155].

ZnO nanorods are a much discussed topic for application in hybrid photovoltaics (Fig. 1.7) and these devices are discussed further in section 1.3. In other PV areas, nanorods have been applied to BHJ solar cells and in DSSCs. To date, each of these devices have been seen to perform with efficiencies of 3.9 % [156] and 5.65 % [144] respectively. In the first instance, ZnO nanorods add little to increase BHJ device performances, which are typically reported without nanorods as having efficiencies of $\sim 4 - 5$ % [28]. Achieving efficient BHJ devices in this architecture is difficult as P3HT must be infiltrated into the nanorod array. In doing so the controlled formation of intermixed BHJ morphologies may be lost.

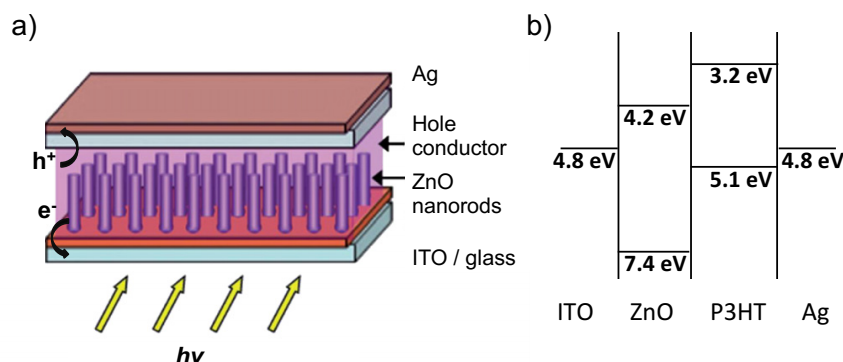


Figure 1.7: a) Schematic of hybrid device with structure: fluorine doped tin oxide (FTO) / ZnO nanorods / hole conducting polymer / metal top contact. Electron transfer occurs from polymer to ZnO nanorods and ITO, hole transfer from polymer to metal. Figure adapted from ref. [157]. b) Band diagram for typical h-PV device.

Nanorod DSSCs operate with good efficiencies, those reported in ref. [144] are comparable to other solid state BHJ devices. In a DSSC configuration there is no need to form specific polymer morphologies; nanorods have been grown, coated with absorber and infiltrated with hole conducting polymer numerous times to build well functioning devices.

1.2.4.2 Light emitting diodes

Light emitting diodes (LEDs) are semiconducting devices which convert electrical energy to light energy. The application of a voltage in the forward bias across the

device directs the recombination of electrons and holes, which releases photons with energy corresponding to the band gap of the semiconductor. The production of high quality LEDs is reliant on the ability to create p- and n-type materials with high charge carrier concentrations. It is possible to form these junctions with As-doped p-type and Al-doped n-type ZnO layers [158] and more recently UV LEDs have been produced by band gap engineering use beryllium oxide (BeO)-ZnO active layers [41].

In combination with p-type polymers, ZnO thin films have been used to create hybrid devices often termed HyLEDs. Here, ZnO is used as an injection layer with device performance seen to vary with film processing conditions. Sessolo et al. report that the best devices employ nanoparticles created at room temperature, these have larger band gaps which are better aligned to polymer LUMO levels, increasing charge injection [159].

ZnO nanorods have been applied to HyLED devices, in an initial report Könenkamp et al. show a junction between nanorods and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) resulting in excitonic and defect emission from ZnO (Fig 1.8a) [40]. These device architectures have been extended further by addition of organic polymers to create HyLED devices that emit blue, red and white light [160]. In addition, creation of LED devices is seen to be possible on flexible substrate (Fig. 1.8b,c) [160, 161].

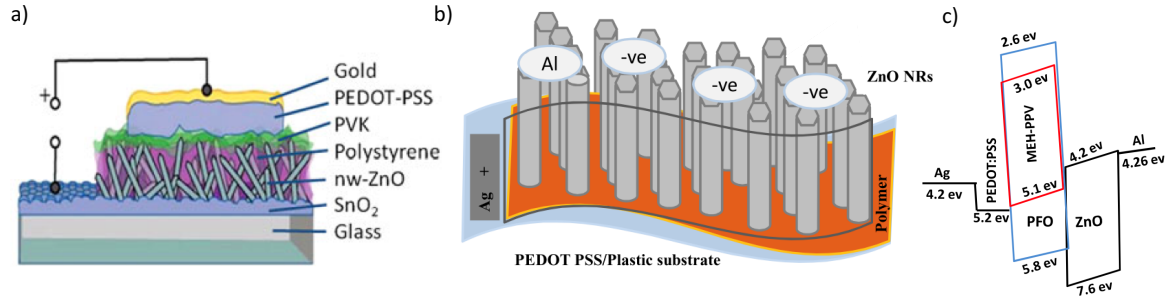


Figure 1.8: a) Schematic of nanowire LED grown on glass, reproduced from ref. [96]. b) Schematic diagram for inverse nanowire LED device used by Zaman et al., nanorods are grown on flexible substrates coated with functional polymers. (c) The bandgap diagram is shown these devices use a blend of poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and polyfluorene (PFO). b,c) Reproduced from ref. [160].

1.2.4.3 Piezoelectric devices

Charges within ZnO can be displaced on the application of a force causing macroscopic dipoles on the crystal. ZnO exhibits the best piezoelectric property of the tetrahedrally bonded semiconductors [162] and the piezoelectric properties have been used in several devices including force sensors, surface acoustic wave (SAW) devices and electromechanical generators [163, 164].

Electromechanical generators have been created from ZnO nanorods, which are displaced by movement of a flexible substrate, creating a voltage and current within an external circuit. One such device employs ZnO nanorods which have been grown radially around Kevlar fibres, the power density of a fabric made from these fibres is $4 - 16 \text{ mW m}^{-2}$ [165]. Higher outputs were seen to be possible for nanorods grown in a lateral direction and integrated between two metal contacts. These devices had a peak output density of 2.7 mW cm^3 [166].

1.2.4.4 Gas sensors

High surface sensitivity to gas molecules in ZnO is attributed to the filling of defect states at the crystalline surface, these are suggested to be oxygen vacancies [167]. ZnO nanorods have high surface to volume ratios, increasing their sensitivity to chemical sensing. Often, nanoparticles are made into sensors by pressing porous pellets and metal contacts are applied, the resistivity of these samples is seen to reduce by exposure to numerous gases, including alcohol, ammonia, carbon monoxide and hydrogen sulfide [168]. The gas sensitivity is of interest for the potential to create low cost sensors however, there is currently little reported data on methods to allow for individual gas sensing specificity using ZnO.

1.2.5 Poly 3-hexylthiophene (P3HT)

Poly 3-hexylthiophene (Fig. 1.9a,b), was used in this study. P3HT has a small band gap, 1.9 eV [169], high hole mobility, up to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [170] and additionally the polymer is commercially available in a variety of molecular weights. The excellent properties of P3HT have been applied to field effect transistors (FET) [171] and organic photovoltaic (OPV) devices [172], it is because of these applications that the polymer is perhaps the best characterised conjugated polymer in the literature. Polymer properties are discussed below, foremost with an overview of conduction within conjugated polymers and P3HT (section 1.2.5.1). An in depth review of literature on the structural characterisation of P3HT is presented (section 1.2.5.2)

along with a discussion of optical absorption and charge generation of the polymer (section 1.2.5.5). The properties discussed in each section, are correlated to polymer processing conditions and polymer crystallinity which often dominates the behaviour of organic materials.

1.2.5.1 Conduction in conjugated polymers

The conductivity of conjugated polymers is inherently linked to the monomer repeat units from which polymer chains are formed. If these units allow for π -orbital delocalisation, charges may be mobile in the backbone direction. Additionally, if the monomer units can pack together and form crystallites, charges are able to move between chains and freely throughout the material. In general, mobility and conductivity are highly dependent on inter-chain charge transport and so the microstructure of the polymer is fundamental in determining polymer properties [173].

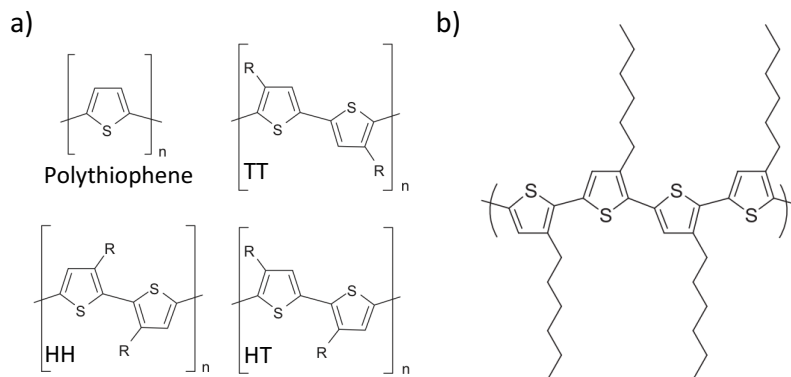


Figure 1.9: a) Polythiophene monomer repeat unit and different substituted derivatives showing tail-to-tail (TT), head-to-head (HH) and head-to-tail (HT) couplings. Reproduced from ref. [169]. b) Portion of head-to-tail regioregular P3HT chain. Reproduced from ref. [174].

The first conjugated polymer to be studied, polyacetylene, had a simple structure being formed of a carbon backbone with alternating single and double bonds between the carbon atoms. This structure allowed for a high crystallinity with few packing defects and with it the ability to process films with high conductivities in the region $\sim 10^5 \text{ S cm}^{-1}$ [175]. Polyacetylene is one of the most conductive conjugated polymers with other electroactive polymers including polypyrrole (600 S cm^{-1}) and polythiophene (100 S cm^{-1}) [176] (Fig. 1.9a). In contrast to these polymers the bulk

conductivity of P3HT is considerably lower, initially observed to be $\approx 5 \times 10^{-2} \text{ S cm}^{-1}$ [177]. The hexyl side chains added to thiophene rings do not contribute to the movement of charge within P3HT and so reduce conductivity in the bulk crystal. The addition of side chains, however, does increase the solubility of the polymer in organic solvents allowing for ease of processing that distinguishes organic from traditional silicon-based electronics.

1.2.5.2 Crystalline packing in P3HT

The introduction of insulating side groups may severely impair polymer properties through disruption of inter-chain packing and the creation of amorphous films. However, increases in structural order are possible by ordering the side chain position within each polymer chain (Fig. 1.9a). The increase in the polymer chain regioregularity reduces packing defects and allows polymers to obtain higher degrees of crystallinity. The synthesis of regioregular (RR) P3HT and specifically the formation of head-to-tail (HT) coupling (Fig. 1.9a,b) is out of the scope of this thesis and reported elsewhere [178, 169]. The use and advantages of using HT-coupled RR P3HT are well reported; a high regioregularity is seen to increase OPV device performance owing to enhanced film packing [179]. The self-assembly of polymer crystals from solution is an inherent characteristic of P3HT; needles several hundred micrometers long have been reported [180, 181] and allow for the study of polymer crystalline packing. Tashiro et al. refined the P3HT packing structure by combining X-ray diffraction of polymer films with computational modelling [182]. They found strong diffraction in the alkyl stacking, $\langle 100 \rangle$ direction (Fig. 1.10a), corresponding to an inter-chain packing distance of 16.6 Å. Packing in the orthogonal π - π stacking $\langle 020 \rangle$ direction has an inter-plane packing distance of 3.8 Å. Although not seen in experimental data, modelling experiments conducted at 0 K indicate that P3HT chains pack with some degree of tilt to allow for closer packing of the thiophene rings. It is notable that side chain inter-digitation packing structures are not favoured, likely due to the significant reduction in entropy required for such a configuration. Further work by Sugiyama et al. determine the structure and orientation of P3HT thin films by X-ray diffraction and electron spin resonance [183]. They find chains in P3HT thin films to be orientated perpendicular to substrate ($\langle 100 \rangle$ direction) also with a distance of 16.0 Å (XRD peak $5.5^\circ 2\theta$). Powder samples displayed an additional peak at $23^\circ 2\theta$ indicating the inter-chain spacing between thiophene rings (lattice spacing 3.9 Å). This is not observed in XRD of thin film polymer samples due to the preferential out-of-plane packing of the crystals with respect to the substrate

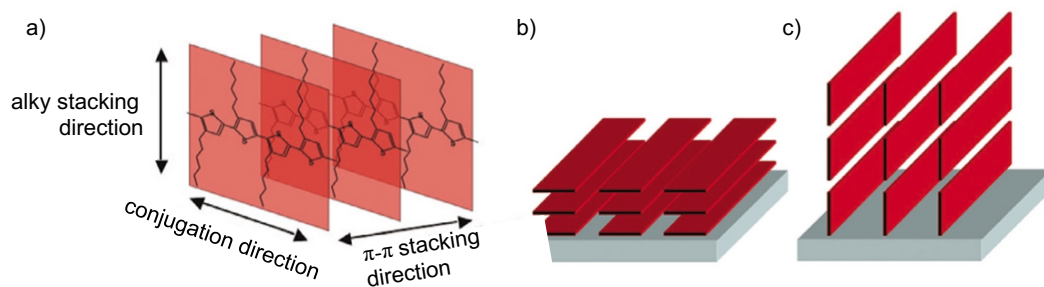


Figure 1.10: a) Crystal structure and crystalline directions for P3HT. Alkyl stacking direction and π - π stacking direction correspond to the (001) and (020) lattice plane respectively. Fast charge transfer occurs in the conjugation and π - π stacking directions, resulting in differing electrical properties for polymer crystallites in the in-plane (b) and out-of-plane (edge-on) (c) orientations. a,b,c) Adapted from ref. [173].

surface. Figure 1.10 schematically shows the packing observed experimentally in P3HT crystallites.

1.2.5.3 P3HT crystallite orientation

Variations in crystal orientation, resulting from differing chain packing with respect to the substrate, is of crucial importance to obtaining the desired properties from conjugated polymer materials in optoelectronic applications. Kline et al. investigate orientation by application of different self assembled molecules (SAMs) to vary P3HT crystallite orientation at the buried interface within thin film transistor (TFT) devices [184]. In their study, octadecyltrichlorosilane (OTS) and hexamethyldisiloxane (HMDS) were used to modify silicon TFT substrates. X-ray diffraction rocking curves and FET measurements of hole mobility were used to quantify the degree to which P3HT crystallites were orientated with respect to the sample surface. OTS modified substrates were seen to have an increased number of highly $\langle 100 \rangle$ -oriented crystals, resulting in an 100-fold increase in mobility over that of films deposited on HMDS modified substrates. The increase in mobility is attributed to a change in crystal orientation at crystallite grain boundaries. OTS grains orientated in the [100] direction feature alkyl chain terminated (010) and thiophene ring terminated (001) faces at the grain boundaries. Such grain boundaries have a higher electronic overlap owing to numerous π -stacking planes in close proximity. Conversely, P3HT orientated in the $\langle 010 \rangle$ direction on HMDS modified substrates have predominately alkyl terminated grain boundaries; hindering charge transfer in the in-plane direction.

In these studies, hole mobility was measured by transistor techniques, only giving information on mobility in the in-plane direction. If increased hole mobility in the out-of-plane direction is desired, as is the case for OPV, then π - π stacking such as on HMDS modified substrates may be beneficial.

In addition to surface modification, crystal re-orientation can be observed on melt annealing of thin films [185]. Lilliu et al. have used grazing incidence X-ray diffraction (GI-XRD) to study crystallite orientation in the P3HT:PCBM system [186]. On melt annealing the orientation of P3HT thin films (22 nm in thickness) were seen to move from a poly crystalline orientation to textured films whereby the majority of crystallites are in an edge-on orientation.

X-ray techniques are able to probe polymer orientation and morphology quantitatively and over a range of length scales. Rivnay et al. present an extensive review on X-ray techniques [187], many of which have been pioneered by the Salleo group in collaboration with the Stanford Synchrotron Radiation Lightsource (SSRL). Of interest is recent work by the Salleo group [188] and Macdonald group [189] concerning crystalline disorder. Both groups have built on work by Hindeleh et al. who describe the paracrystalline distortion parameter, g_{hkl} [190]. This term describes the deviation of the crystal from perfect ordering. Values $< 1\%$ are indicative of highly ordered crystals, between 1 – 10 % represents paracrystalline materials, and 10 – 15 % is considered to be a glass or melt. Thin films of P3HT were found to have a paracrystallinity of 5 % [189].

Paracrystallinity is calculated from the width of P3HT (100) and subsequent high order diffraction peaks, the amount these peaks deviate from the (100) peak is an indication of how much the crystal is perturbed by lattice defects. Diffraction peak widths are modified by these lattice defects, because of which Rivnay asserts that; ‘the width of a first order peak cannot provide a grain size’ and that paracrystallinity must be accounted for when applying the Scherrer equation to calculate polymer crystallite size.

1.2.5.4 Effect of molecular weight

The last and perhaps most important factor to consider is the molecular weight of the polymer. Molecular weight is known to dramatically affect polymer properties, including melting temperature [191], density and mechanical properties [192]. Concerning conjugated polymers, Kline et al. observe; ‘Molecular weight...has a tremendous effect on both the polymer morphology and charge-carrier mobility’ [184].

Increases in polymer chain length effect material properties through changes in macroscopic polymer morphology. Within thin films, small chain molecules are more able to find crystalline configurations, longer chain polymers, which are extensively entangled within the film must form morphologies with a much larger mixture of amorphous and crystalline regions. Entangled chains may traverse many crystalline domains [193] and increase the melting point because all crystallite packing must be disrupted for the material to enter the liquid phase. Mechanical properties may also improve, entangled chain morphology are much tougher because chains can be sheered in response to physical deformation [194].

Despite higher amorphous content, improvement in polymer electronic properties are correlated with the point at which chain entanglement occurs. In the case of films made from low molecular weight P3HT ($M_n \approx 4$), short nanorod shaped crystallites, on the scale of 100 nm in length and 5 nm in width, are observed [195]. Mobility, from TFT measurements, increases if crystallites have increased local order [196]; consistent with AFM images showing longer crystallites which have a higher connectivity to neighbouring grains in low molecular weight films [197]. High molecular weight P3HT films ($M_n > 30$) have mobilities a 100 times greater than low molecular weight films. Characterisation by UV-Vis and GI-XRD show that morphologies of these films do not have a significant increases in π - π stacking over low molecular weight films. Instead the increase in mobility is attributed to an increase in the inter-connectivity of aggregates through chain entanglement. Work by Koch et al. supports this model for mobility; collated hole mobility values are seen to reach a maximum around the entanglement threshold and plateau at higher molecular weights [198].

The mobility dependence on molecular weight is often overlooked in the literature, with many authors concerned solely with processing conditions for thin films. In general processing techniques which allow polymer morphologies to obtain high crystallinity with a degree of interconnectivity, either through fine low molecular weight morphologies or of polymer films above the entanglement threshold will give the best device performances. Polymer processing is discussed further in section 1.2.5.6.

1.2.5.5 Optical absorption and charge generation

The optical properties of P3HT are strongly dependent on the processing routes by which films are made and the macromolecular polymer properties (RR , M_n). In solution, P3HT exhibits a broad absorption with onset at ~ 550 nm. The properties of P3HT film are very different, the absorption band is red shifted with an onset at ~ 650

nm [169]. Crystalline films show two distinct absorption peaks at 520 nm and 560 nm with a shoulder at 620 nm. Initial reports attempted to describe spectra in terms of photonic absorption within single planar P3HT chains. It is now more fully understood that the presence of neighbouring chains must be taken in to account [199]. Brown et al. ascribe the three absorption peaks of regioregular P3HT to 0-0 transition (520 nm), 0-1 transition (560 nm) and π - π^* transition (620 nm). Spectra for regiorandom P3HT seem to be blue shifted, the amorphous nature of the film causes exciton localisation, increasing absorption energies. While there is a large shift in 0-0 and 0-1 transitions, there is little change in the energy of the π - π^* transition (620 nm shoulder); the authors assign this peak to absorption from intrachain excitons [199]. It should be noted that while the intensity of this peak is higher for the regioregular crystalline film, it is also observed for the regiorandom amorphous film and so care must be taken in concluding a high film crystallinity from the presence of the π - π transition.

No data concerning the absorption co-efficient of P3HT is seen in the literature. The maximum absorbance, however, is presented and seen to occur in films of 250 nm at a wavelength of 520 nm [200]. This strong absorption is advantageous for solar applications, where active layers can be made with low thickness.

1.2.5.6 P3HT processing and deposition methods

One key advantage of organic electronics is that they can be processed rapidly from solution to functional thin films. The ultimate goal of processing in this manner is to create films at high speed in high quantity by roll to roll (R2R) processing methods. This nascent technology is already being developed for creation of large area OPV devices by Krebs et al. at the Technical University of Denmark [201]. R2R processing can also be used in device development, the many experimental variables in optimising devices architecture makes creation of efficient devices labour intensive. A differential pumped slot-die coater within a R2R set up can be used to aid in the rapid combinatorial screening of donor-acceptor blends [154].

Processing by R2R requires a large amount of space and capital investment, making it unfeasible for many laboratories. Small scale methods such as spin coating and wire bar coating are preferred and discussed below. In addition, melt pressing is presented as a possible method to make thin films, the results of such efforts being discussed in section 4.3.

For polymer films produced from solution methods polymer dissolution must occur, which is possible if a polymer has more affinity for a solvent than it has in

the solid state. Empirical solubility parameters δ_{Solvent} , δ_{Polymer} are used to predict dissolution, which is expected if there is a difference of 3.5 – 4.0 between the parameters [202]. P3HT is highly soluble and will dissolve easily in all benzene based solvents. The morphology of thin films is closely linked to polymer-solvent interactions. Slow drying of P3HT films in high vapour pressure atmospheres promotes crystalline ordering which increases TFT measured hole mobility by an order of magnitude [203]. Slow drying can be assisted by using high boiling point solvents [204] and recent work has been published concerning the use of surfactant additives such as 1,8-octanedithiol (ODT) with high boiling points ($T_b = 270$ °C) to control polymer and BHJ morphologies [205].

Spin coating

Film formation by spin coating involves a substrate placed on a stage or chuck which undergoes rapid rotation. Layer deposition is controlled by many factors including concentration, spin speed, spin time, substrate properties, temperature, volatility of solvent, polymer-solvent interactions and solvent exhaust rate (partial pressure of solvent). Of these factors concentration is the most important in controlling film thickness, with spin speed being the secondary controlling factor. At higher speeds (> 2000 rpm) film thicknesses are reduced, as material is quickly lost from the substrate. Experimental results of these factors are presented by Mellbring et al. in their detailed work on spin coating of polyethylene [206].

Wire bar coating

Wire bar coating involves drawing a wire-wound bar over a heated substrate to control the amount of solution deposited on the substrate. This is similar to the blade doctor technique employed in R2R coating systems. Again, solution concentration is key in wire bar coating and film thickness is in theory, the product of concentration and wire diameter. In practice 25 % of the solution is lost coating the bar. Nevertheless, wire bar coating is a highly scalable method, often used with continuous rolls for coating of large area flexible substrates.

Solid state processing

Solid state processing enables the use of polymers which otherwise might be insoluble due to high molecular weight or low solvent affinity. Films processed by a hot compression method are seen to have anisotropic crystal orientation and texture resulting from polymer shear on the application of external pressure [207].

Higher crystallinity of polymer films is advantageous to conduction properties and in addition, solid state techniques remove solvent trapping and surface wetting issues inherent with solution processing. Without the need for organic solvents, processing methods are environmentally safe if up-scaling by this method can be achieved.

Despite these advantages, solid state processing has not received wide attention in the optoelectronic device community as thin films produced by these methods are typically too thick ($10 - 100 \mu\text{m}$) for the required applications. Some work however, has been completed on the use of lamination in device processing, which is shown to work as well or better than solution casting numerous layers [208].

Post processing

Once films have been created by either solution or solid methods, post processing is often used to enhance polymer properties. Annealing is used in BHJ formation to create desired polymer-small molecule morphologies [209]. This is completed at temperatures higher than the glass transition temperature (T_g) of P3HT, typically 140°C and allows for alkyl chain movement which improves packing and transport within polymer crystallites [210].

1.2.6 Metal oxide-polymer composites

The creation of ordered metal oxide polymer composites and their optoelectronic properties are of interest in this thesis. Numerous articles from a range of scientific fields report on methods to create such functional materials. The most reported method is the formation of oxide nanostructure and infiltration of polymer. Work has also been completed on the *in-situ* formation of both the organic [211] and oxide species [212]. These methods are novel and may result in a finer degree of mixing, although this does not significantly enhance photovoltaics performance ($\eta = < 0.1\%$ for MEH-PPV TiO_2 pairing [213]), perhaps due to a large disruption in polymer packing leading to reduced mobility within the polymer.

The filling and properties of two types of porous substrates are examined below.

1.2.6.1 Ideal metal oxide-polymer composited

Having regular and controllable pores, anodic alumina (AAO) presents an ideal structure for filling studies. Coakley et al. completed such studies to investigate the optimum pore size for filling of P3HT with respect to hole mobility and in comparison with planar P3HT films [200]. They found that for 75 nm pores hole

mobility increases from $3 \times 10^{-4} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ for planar films to $6 \times 10^{-3} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ for ordered films. This order of magnitude increase was explained by an aligning of the polymer chains at the pore walls and this effect is seen predominately at hole diameters of 75 nm. At 120 nm diameters the hole mobility was observed to reduce to $2 \times 10^{-4} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$.

AAO porous arrays of 50 nm diameter and 150 nm depth have been used to synthesis ordered P3HT arrays. The creation of a BHJ by evaporation of C_{60} on to the P3HT has shown to dramatically increase the performance of ordered devices ($\eta = 1.12 \%$) over devices made from planar films ($\eta = 0.17 \%$) [214]. The authors attribute this in part to increased surface area and increased hole mobility of polymer crystallites with in-plane orientation to the substrate.

Further information regarding confined polymer crystallisation can be found in non-conjugated polymer literature. For polyvinylidene fluoride (PVDF), it is observed that two techniques are available to control the crystalline orientations; crystallisation of infiltrated AAO with or without a polymer over layer (Fig. 1.11a-c). In the latter case, AAO pores are interconnected with crystallite nucleation occurring in the bulk polymer reservoir leading to the predominately one crystallite orientation along AAO pores. In the case where pores are not connected, crystallites are in numerous orientations as shown by additional XRD peaks [215].

Pore width has been further studied to investigate crystallisation. The heat of fusion of isotactic polypropylene (iPP) is measured for various pore diameters, a reduction in enthalpy is observed as pore size decreases and through extrapolation at AAO pores sizes $< 20 \text{ nm}$ no nucleation is observed. Pore volume is used to described the observed onset of heterogeneous nucleation at pore sizes $< 65 \text{ nm}$. In larger pores there is a greater likelihood that impurities will exist from which nucleation can occur, this is observed in differential scanning calorimetry (DSC) where a small degree of under-cooling is required for pores sizes $> 65 \text{ nm}$ [216].

The confinement of polymer crystallites results in the suppression of spherulitic superstructures and can enhance polymer properties, specifically hole mobility in conjugated polymers. This is dependent not only on polymer orientation but also pore size and processing methods. The filling of nanostructures, in which pores are interconnected is a more complex topic and discussed below.

1.2.6.2 Filling of ZnO nanorod arrays

To date, little work has been completed concerning polymer crystallite size within nanorod arrays. An interconnected porous network will allow polymer crystallites

to obtain larger sizes than the confined pores within AAO templates and these crystallites will have some degree of orientation as the nanorod array hinders polymer crystallisation in the lateral direction. The formation of such morphologies may be advantageous as excitons must be able to travel small distances laterally from polymer to ZnO and holes to travel larger distances vertically to the top contact. There are no current reports investigating polymer morphology within nanorod arrays. Although, some information can be gained from the creation and optimisation of h-PV devices. Polymer processing and review of h-PV device performance is discussed in the next section (1.3).

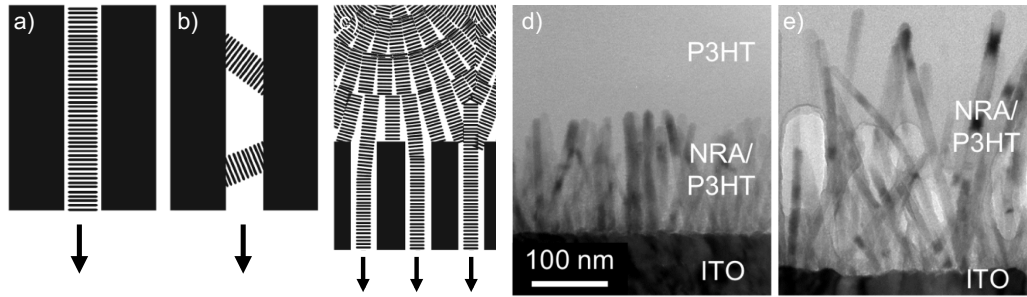


Figure 1.11: Schematic of crystallite growth in AAO arrays, a) lamellae with growth direction parallel to pore axis, b) growth that impinges on pore walls, c) crystallite growth whereby nucleation occurs in the bulk, lamellae impinge on template and growth is directed into aligned pores. Adapted from ref. [215]. d) 180 nm and e) 380 nm TiO_2 coated ZnO nanorod arrays (NRA) infiltrated with P3HT by spin coating and melt processing method [217]. e) Shows voids in polymer infiltration typical of difficulty in filling disordered nanorod arrays.

The filling of nanostructures for h-PV was first examined by Olson et al. [218]. Nanorod infiltration was achieved by spin coating a thick polymer layer and then annealing at a temperature above the melting temperature (T_m) of the polymer. Polymer in the liquid phase is able to flow within the nanostructure and filling is crucially dependent on polymer viscosity, molecular weight, temperature and annealing time. SEM images and X-ray photoelectron spectroscopy (XPS) [38] show polymer filling to the bottom of the arrays, however, in some cases incomplete filling is observed due to volumes of trapped gas within the nanostructure (Fig. 1.11e [217]). The inability to fill these volumes is attributed not to poor polymer processing methods but to poor array formation where nanorod misalignment is high.

Others have employed methods to aid complete infiltration, including soaking nanostructures in a low polymer concentration solution prior to spin coating at a higher concentration [50], and the application of UV light to increase the

hydrophilicity of the surface [219], although in general nanostructure wetting is favourable through capillary action within the nanostructure. Little improvement in device data is seen with these polymer processing methods, spin coating and melt annealing are the dominant polymer processing methods for these devices.

1.3 Overview of hybrid photovoltaics (h-PV)

The respective properties and processing conditions for ZnO (section 1.2.1) and P3HT (section 1.2.5) as well as the formation of composite structures (section 1.2.6) have been discussed. In the final section of the literature review h-PV devices composed of ZnO and P3HT are discussed in terms of mechanism of operation, device architecture and device performance.

1.4 Hybrid photovoltaic devices

Typical hybrid devices have ‘inverse’ architectures, in the form ITO/ZnO/P3HT/Ag. In contrast to BHJ devices, holes are transported to the metal contact and electrons to the ITO, a band diagram for such a device has previously been presented in figure 1.7. Device operation in this configuration is much more stable than BHJ devices created with low work function electrodes (Ca, Al) [29]. A typical hybrid morphology attempts to maximise polymer donor and metal oxide acceptor interface through nanostructuring (Fig. 1.12a) or blending the two components. A nanorod h-PV device with ‘inter-digitated’ structure was often proposed as an optimum morphology for BHJ cells owing to the short exciton pathways between the digits in the lateral direction and the increased charge conductivity in the vertical direction along the digits. It was proposed that such structures had the potential to reduce charge recombination and increase device efficiency by increasing mobility of each component [218]. However, it is now accepted that the intermixing within BHJ morphologies form much finer microstructures than can be realised in h-PV composites and in addition, the complex routes of charge generation in BHJ morphologies (section 1.1.2) are not observed in h-PV devices. As such, arguments for the creation of ‘inter-digitated’ morphologies to improve BHJ efficiencies are generally flawed.

Concerning the operation of h-PV devices, photoexcitation occurs within the polymer to create a mobile electron-hole pair, which may dissociate in the region of the metal oxide-polymer interface. The exact exciton dynamics are a source of discussion in the literature, with some authors reporting that excitons do not dissociate at metal

oxide interface and instead dissociate within disordered polymer near the interface (Fig. 1.12b) [220, 221]. Others conclude that dissociation must occur at the interface owing to transient absorption spectroscopy (TAS) experiments showing no change in absorption for pristine P3HT films, consistent with no increase in free charge carriers without a heterojunction [222]. Despite the lack of a detailed mechanism, it is clear that a heterojunction is required for charge collection and operation. Both p- and n-type materials conduct respective charges to anode (ITO) and cathode (Ag) electrodes, resulting in a voltage being formed across the device.

The testing and performance of h-PV devices is described below.

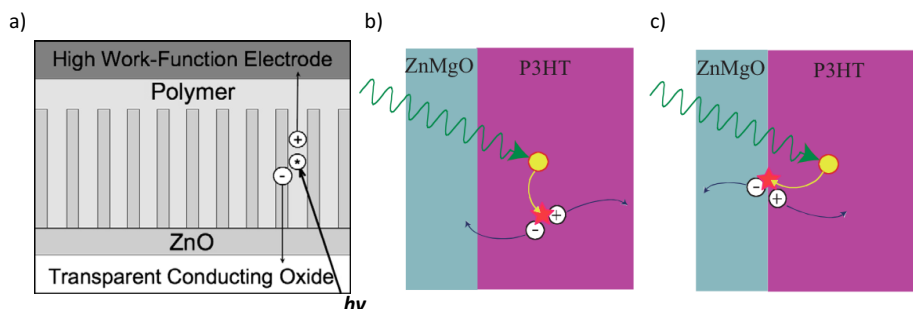


Figure 1.12: a) Schematic showing architecture of nanorod based h-PV device. Photoexcitation occurs in the polymer, holes are conducted to the top electrode and electrons through the metal-oxide to the bottom electrode. Adapted from ref. [218]. b) Schematic diagram of photoexcitation and charge dissociation in h-PV bilayers occurring close to the interface and c) at the metal oxide-polymer interface. b,c) Reproduced from ref. [221].

1.4.1 Solar cell performance

A photovoltaic device can be considered as an electrical or photophysical device. As an electrical component photons are absorbed to create a photocurrent (I_{ph}), the voltage generated across the device is dependent on the ability for the device to function as a diode. This performance is hindered by loss pathways attributed to the series resistance (R_s) and the shunt resistance (R_{sh}) of the device (Fig 1.13). Typically devices are tested in the dark to examine diode characteristics and then under illumination to characterise photoresponse. Illumination spectra and intensity is standardised to American Society for Testing and Materials (ASTM) criteria, which approximate terrestrial conditions [223].

Complementary investigation of photovoltaics concerns the photophysical treatment of devices. In this case the operation of the absorber material and

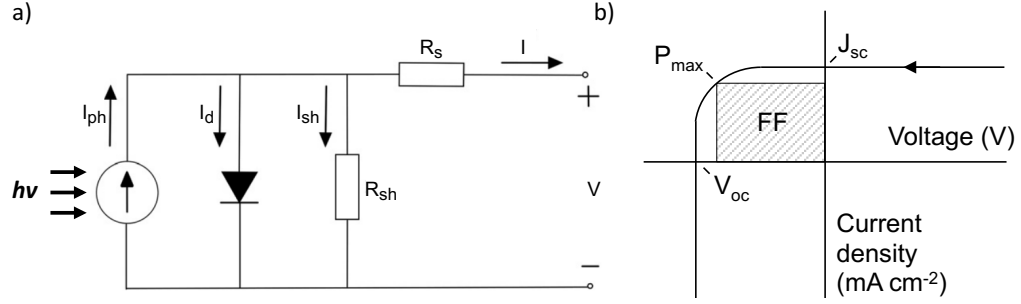


Figure 1.13: a) Comparative circuit diagram of photovoltaic device. Adapted from ref. [224]. b) Typical current density-voltage (JV) curve for a h-PV device showing short circuit current density (J_{SC}), maximum power point (P_{max}), open circuit voltage (V_{OC}) and the fill factor (FF).

method by which photon intensity is converted to electrical energy is considered. The overall efficiency of the device, termed power conversion efficiency (PCE) (Eqn. 1.8) is equal to the combined efficiency of each step in the device operation; absorption (η_{abs}), exciton diffusion (η_{diff}), exciton dissociation (η_{diss}), charge transfer (η_{tr}) and charge collection (η_{cc}) (Eqn. 1.8). Loss mechanisms reduce efficiency at each step these include; reflection / poor band gap matching to the solar spectrum, exciton decay, geminate recombination at the heterojunction interface and charge transfer to wrong electrode (short circuit current) [225].

$$PCE = \eta_{abs} + \eta_{diff} + \eta_{diss} + \eta_{tr} + \eta_{cc} \quad (1.8)$$

$$PCE = \frac{V_{OC} J_{SC} FF}{P_{in}} \quad (1.9)$$

Comparative electrical circuits and knowledge of the photophysical mechanisms of charge generation in PV materials allows for meaningful electrical characterisation (Fig. 1.13b). External quantum efficiency, often abbreviated simply to η , is calculated from the ratio of electrical power generation to power supplied by illumination (Eqn. 1.8). The power generated is calculated from the product of open circuit voltage, V_{OC} , short circuit current, J_{SC} and an ideality variable, the fill factor FF (Eqn. 1.9). Further analysis of each factor is explained below.

$$FF = \frac{V_{MP}J_{MP}}{V_{OC}J_{SC}} \quad (1.10)$$

$$J_{SC} = J_0 \exp(qV/k_bT - 1) \quad (1.11)$$

$$V_{OC} = \frac{1}{q}(|E_{HOMO,D}| - |E_{LUMO,A}|) - 0.3 \text{ V} \quad (1.12)$$

$$qV_{OC} = \Delta E_{DA} - \frac{\sigma^2}{k_bT} - k_bT \ln \left(\frac{N_A N_D}{np} \right) \quad (1.13)$$

The fill factor is the fraction of power generated by the cell at the maximum power point ($V_{MP}.J_{MP}$), over that of the theoretical available power from the product $V_{OC}.J_{SC}$. The fill factor in part describes the losses apparent in device operation. Fill factors for Si solar cells are high, typically above 80 % [5], in general those for h-PV and OPV devices are lower (between 55 – 60 % [226, 227]) due to the inability to fulfil criteria for efficient devices as outlined in equation 1.8 or by non-optimised device architecture or active layer morphology [228].

Cell operation occurs at J_{SC} when there is an equilibrium flow of both positive and negative charge to drive an external load. In an ideal cell where effects of R_s and R_{sh} are omitted, the movement of charge is balanced by the external load which negates the formation of any voltage between the contacts. In this case J_{SC} is given by equation 1.11, where J_0 is the current density of minority carriers, q unit charge, V the applied voltage or load on the cell, k_b Boltzmann constant and T the temperature [229]. In the operation of real devices J_{SC} is reduced by the difference in charge carrier mobility of holes and electrons. The extraction of opposite charges from the device is not equal, leading to the creation of space charge layers at the electrodes, often hindering large J_{SC} values.

Open circuit voltage represents the maximum voltage that a solar cell can provide to an external circuit. This is a quasi-equilibrium state where a potential difference is built up between the two electrodes. For OPV devices it has been shown that V_{OC} is proportional to the difference between the HOMO level of the donor ($E_{HOMO,D}$) and the LUMO level of the acceptor ($E_{LUMO,A}$) minus 0.3 V (Eqn. 1.12) [35]. The empirically found loss of 0.3 V is attributed to recombination losses causing energy loss and reduced voltage. Further work has been completed to quantify V_{OC} which

can be expressed in three terms as shown in equation 1.13. Here, ΔE_{DA} refers to the band energy offset, $E_{HOMO,D}-E_{LUMO,A}$, the second term represents disorder-induced loss and the third term represents recombination induced loss, where σ characterises the density of HOMO-LUMO states, $N_{A,D}$ the total density of hole or electron states and np the product of electron and hole trap concentrations [229]. V_{OC} has been correlated with measurement of temperature, light intensity, work function of the electrode and material microstructure [229].

1.4.2 h-PV device performance

The architecture and construction of h-PV devices have been in development since 2007 and have been created in three architectures; those having bilayer, nanorod and nanoparticle morphologies. To date, these architectures have performed with efficiencies of 0.05 % [57], 0.82 % [226] and 2.00 % [39] respectively. Device performance and properties are summarised in table 1.2.

The surface area of nanorod and nanoparticle devices can be estimated as 10^1 and 135^2 times that of a bilayer junction. When considering h-PV performances nanorod efficiencies show an increased performance per surface area, whereas for nanoparticles efficiency does not scale well with surface area. Both these observations imply that photovoltaic performance is reliant on factors other than the intermixing of donor-acceptor materials in h-PV systems. Through control of materials properties by various processing methods that h-PV systems can be better understood and devices enhanced. Of specific interest is the optimisation and function of nanorod devices which may increase polymer functionality through polymer confinement and orientation in nanostructures as discussed in section 1.2.6.2. Preferable nanorods morphologies are discussed below.

Nanorod density, while perhaps unimportant in terms of increases in surface area is important for controlling the interconnected pore size within the array morphology. Density is predominately controlled by nanorod width, nanorods having large diameters in general, have reduced densities [226]. Conduction in nanorods is seen to be dependent in part on the width of nanorods; those with larger diameters have reduced resistances due to a reduced geometric surface/volume ratio and it is

¹For a hexagonal array of nanorods with 50 nm diameter, 500 nm length and 50 nm spacing between each nanorod

²Estimated for spherical nanoparticles with diameters of 5 nm and 50 % volume fraction and in a 225 nm thick film comparable with experimental data from ref. [39]

suggested that surface defects dominate conduction in nanorods with diameters < 50 nm [230].

Perhaps the most important variable is nanorod length, which defines the amount of polymer within the composite and optical absorption and charge generation respectively. Interestingly, there are mixed results reported by the same group on the topic; 0.76 % is observed for optimised nanorods of 600 nm in length [38], whereas shorter 300 nm nanorods grown from a different seed layer perform with efficiencies of 0.82 % [226]. The contrast in results for nanorod length may be due to differences in the age of test cells. The formation of Ag_2O with time is seen to increase the work function of Ag and so increase the driving force for charge collection in these h-PV devices [29]. The efficiency of bilayer devices more than doubles to 0.04 % over a period of 10 days before becoming stable.

The effect of prolonged exposure to UV also has an effect on device performance. UV absorption by ZnO promotes additional charge carriers to the ZnO conduction band. This has the effect of increasing the conductivity of the layer and to improve electron selectivity which leads to increased device performance [231]. It is possible to create the same effect by brief application of reverse bias treatment (20 V, 2 s). Here, injected holes in the ZnO layer passivate defects leading to increased electronic conduction [232].

In terms of the polymer component in h-PV devices, relatively little work has been completed regarding the optimisation of polymer morphologies. Processing from the melt and subsequent slow cooling allows polymer chains to find equilibrium positions. When annealing times are increased from 1 – 30 minutes, device performance degrades, an effect not observed in bilayer devices [233], suggesting that a non-equilibrium polymer morphology is favourable. The authors show reduced hole mobility for P3HT infiltrated into ZnO nanorod arrays when compared with bilayer and bulk films and reason that polymers in these nanostructures are predominately orientated in the $\langle 100 \rangle$ direction which has reduced conductivity due to the presence of alkyl side chains. As discussed in section 1.4.1, one factor limiting device performance is the vastly different mobilities of the electrons in the n-type and holes in the p-type material. Achieving high hole mobility through control of polymers in nanostructured arrays is key to increased device performance.

Table 1.2: Summary of data for performance of ZnO-P3HT h-PV devices.

Bilayer devices

P3HT thickness (nm) ¹	ZnO thickness (nm) ¹	Efficiency (%)	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF (%)	Ref.
50	45 (HC)	0.027	217	0.338	37	[57]
50	30 (LC)	0.050	421	0.278	43	[57]

¹ Estimated from data in ref. [234] ² LC and HC stand for low and high conductivity samples respectively.

Nanorod devices

Seed layer type	Nanorod diameter (nm)	Length (nm)	Efficiency (%)	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF (%)	Ref.
Sol-gel	45	200	0.28	443	1.33	48	[235]
Sol-gel	-	400	0.53	440	2.17	56	[37]
Aqueous sol-gel (20 nm) [236]	-	600	0.76	543	2.67	53	[38]
Sol-gel (130 nm)	50	300	0.82	565	2.64	55	[226]

NB: Nanorod density not reported in any of the above h-PV device studies.

Nanoparticle devices

Active layer thickness (nm)	NP diameter (nm)	Efficiency (%)	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF (%)	Ref.
225	< 5	2.0	750	5.2	52	[39]

1.4.3 Summary

The performance of nanorod h-PV devices depends on numerous variables including; nanorod width, length and density, as well as polymer processing conditions, age of device and testing conditions. Recently published data shows that the best nanorods h-PV devices operate with an efficiency of 0.82 % [226], although this contradicts previously published work concerning optimum nanorod length. Such work is typical of the current literature where there is still discussion regarding the optimum h-PV structure and the mechanisms by which these devices operate.

1.5 Thesis Structure

Hybrid photovoltaic devices composed of metal oxide-organic pairings are currently limited by ineffective charge transfer between the materials and by poor transport of free charge out of the active layer; control of interfacial properties, and the structure and morphology of each component is key to device optimisation. In work presented as part of this thesis, ZnO nanorods are paired with the photoactive polymer, poly 3-hexylthiophene (P3HT) – two areas have been studied, i) nanorod alignment to aid polymer infiltration and ii) elucidating optimum polymer processing conditions to prepare efficient devices.

Chapter 3 investigates aligned nanorods synthesised from ZnO coated substrates by a hydrothermal method. To understand the influence of ionic additives on morphological control the addition of potassium chloride (KCl) to growth solutions is investigated.

Chapter 4 investigates effective nanorod infiltration by spin coating and annealing above the polymer melting point. Small angle X-ray scattering and X-ray diffraction during heating and cooling was conducted to investigate polymer orientation and crystallite structure within nanostructured films. In chapter 5 these results are combined with device and optical absorption measurements to investigate the relationship between morphological characteristics of the constituent materials and h-PV performance.

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Chapter 2

Characterisation Techniques

This chapter contains a detailed explanation of methods used to characterise oxide, polymer and composite thin films. The characterisation techniques used most frequently, scanning electron microscopy (SEM) and X-ray diffraction (XRD), for investigation of film morphology and film crystallinity respectively are presented first and in most detail. Other techniques are presented in the latter sections (2.3 – 2.8) and in each case relevant equations and information pertinent to subsequent analysis are included.

Characterisation technique sections are written so as to give a full overview of the methods used. Additional experimental details relevant to these techniques are supplied in latter results chapters and accompanied by experimental methods for the growth of nanorods (chapter 3), polymer processing (chapter 4) and device creation (chapter 5).

2.1 Electron microscopy

Scanning electron microscopy (SEM) has been used to probe ZnO surface morphologies and transition electron microscopy (TEM) used to investigate individual ZnO nanorods.

The ability to resolve surface features is directly proportional to the wavelength of radiation incident on the surface. The often used analogue of classical Rayleigh criterion for light microscopy (Eqn. 2.1) [1] can be used to describe the wavelength-resolution relationship and shows that imaging with electrons is advantageous due to their small wavelengths. The smallest distance that can be resolved, δ , is given by the wavelength of the radiation, λ , the refractive index of the viewing medium, μ , and the semi-angle of collection of the magnifying lens β .

$$\delta = \frac{0.61\lambda}{\mu \sin \beta} \quad (2.1)$$

The resolution of a light microscopy in the visible range (400 – 800 nm) is around 500 nm; using electrons, with wavelengths much less than 0.1 nm the ability to resolve surface features can be greatly improved [2]. In addition, increased control of electron beams is advantageous, in SEM a greater depth of field and depth of focus is achievable than possible with light microscopy. Additionally, for both electron microscopy methods the complex process of electron interaction with matter may yield a variety of useful signals including secondary electrons, characteristic X-rays, visible light and elastically or inelastically scattered primary electrons. The instrumental setup and imaging method for each technique is described below (section 2.1.1 and 2.1.2).

2.1.1 Scanning electron microscopy

ZnO thin films, nanorod and hybrid organic-inorganic morphologies were examined using SEM. A Zeiss Gemini SEM fitted with a field emission gun (FEG) was used at an accelerating voltage of 5 kV. To create an electron beam, electromagnets in the field lens narrow the source, which is then focused by the objective lenses and rastered over the surface by scanning coils further down the instrument column. Focusing on to the surface is then completed by adjusting the working distance (focal length) and by alignment of imaging aperture and lens astigmatism. Figure 2.1 shows a schematic ray diagram for the SEM used. Here, the gun is held at a vacuum of $\sim 10^{-7}$ Pa, while the sample chamber is vented to atmospheric pressure for loading and pumped to $\sim 10^{-3}$ Pa for imaging.

Images are obtained by recording secondary electrons (SE) that are emitted from the surface, these have typically energies of < 50 eV [4]. Their low energy and thus small mean free path within the sample ensures a high surface sensitivity. The SEM used has two detectors, a secondary electron positioned at a low angle to the substrate surface and an annular detector positioned ‘in-lens’ [5]. The position of in-lens detector enables 70 – 80 % of SE generated at the surface to be captured resulting in high resolution microscopy images [3]. This detector was used for imaging.

Contrast in SEM arises from variation in the morphology of the sample surface. As the beam rasters over the surface secondary electrons are emitted, points which have a greater exposed surface receive a higher electron irradiation, emit more electrons and appear brighter in the SEM image. This is the source of the apparent shadowing

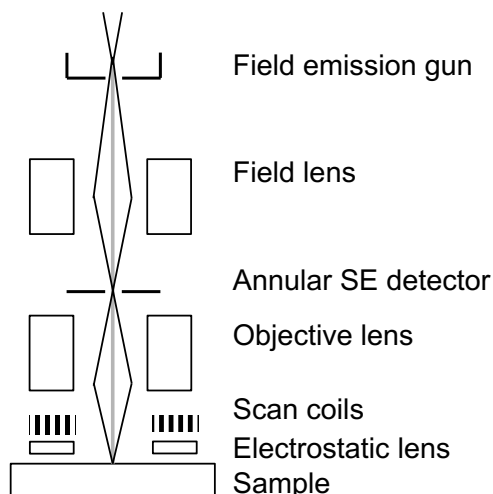


Figure 2.1: Schematic ray diagram for a typical SEM with annular ‘in-lens’ secondary electron detector. Adapted from ref. [3].

in the imaged nanorod morphologies (Fig. 2.2). When focusing the microscope there is a compromise between depth of field and resolution. This is dependent on the working distance of the beam. A large working distance allows for a large depth of field, the beam is narrow at the focal point and much more of the surface topology can be imaged. A small working distance reduces the depth of field but increases the resolution as the sample is closer to the detector and a greater number of electrons can be captured for each scan. A compromise also exists between magnification and resolution, low magnification allows for large areas to be imaged, however only a high magnification can obtain sufficient resolution for fine surface detail to be observed. This is an intrinsic problem of electron microscopy, small areas are observed and used to make generalisation about large areas. The solution is imaging many areas of different samples and using them to collect large data sets to reduce error in the observation of surface morphologies.

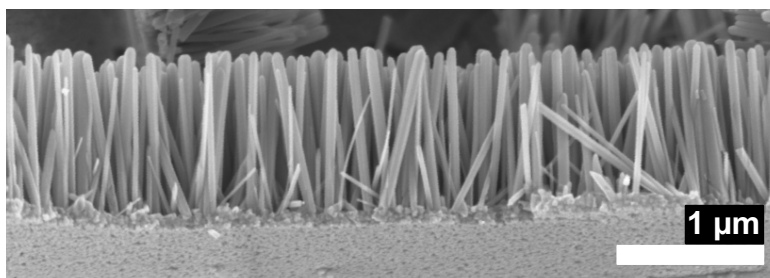


Figure 2.2: Micrograph showing a cross-section image of a ZnO nanorod film.

Scanning electron microscopy is a valuable tool allowing for investigation of large sample areas, in particular it is suitable to feature sizes and substrate areas of films prepared in this project. Studies of microscopy images have been used to quantify nanorod density, length and diameter as growth conditions were varied (section 3.4, 3.5). Nanorod morphology and infiltration has been qualitatively examined by imaging samples in cross section. Two methods were used to prepare cross sectional samples; lifting the film from the substrate by scratching the surface with a diamond scribe (Fig. 2.2), or by cooling the sample with liquid nitrogen cracking it and then tilting to view films in cross section. The latter is especially suited for investigating devices as all layers can be imaged at once and the integrity of the composite can be preserved.

2.1.2 Transmission electron microscopy

A JEOL2010 TEM was used to image and characterise nanorod films. In a similar method to the SEM, an electron beam is created by applying an accelerating voltage between a tungsten tip and anode. TEM differs from SEM as the sample is positioned in the instrument column and the transmitted beam is collected for imaging. Three sets of lenses are used, the condenser lens which controls the size and intensity of the beam, the objective lens, which sits after the sample and controls the magnification of the image for the first intermediate image or diffraction pattern and the final projector lens which enlarges the beam to create an image suitable for viewing on a phosphorous plate or charge-coupled device (CCD) for the formation of digital images [2].

In this thesis, image contrast is due to mass-thickness contrast resulting from the varying degrees of elastic electron scattering by differing amounts of material. Thicker samples scatter the beam more resulting in fewer electron being transmitted, such areas appear darker on the image plate.

Selected area electron diffraction (SAED) was used to investigate the crystalline nature of nanorods at differing positions. ZnO nanorods were prepared by scratched a film and dispersing nanorods by sonicating in methanol, which evaporates without residue. The solutions were further diluted by a factor of ten and a drop of each was deposited on a copper TEM grid, which was dried thoroughly prior to imaging.

2.2 X-ray methods

Through observation of diffraction and scattering from lattice planes, X-rays were used to probe the crystalline ordering of oxide, polymer and composite samples. X-ray diffraction is firstly presented, with an in depth description of the criteria for diffraction, subsequently the analysis of X-ray patterns that allow for determination of crystallite grain size as well as the origin of diffraction intensity is discussed. In the final section, X-ray scattering and the key differences between this technique and XRD are described.

2.2.1 X-ray diffraction

X-ray diffraction was used to characterise crystallinity and orientation of ZnO nanorod morphologies. In latter work, XRD is used to investigate the crystallinity of polymer on oxide layers and provide in-situ measurement during heating and infiltration of polymer into nanostructured arrays.

Diffraction occurs when incident X-rays interact with a scattering medium so as to interfere constructively. This is only possible when the difference between the distance travelled by two points on the incident wave front is an integer multiple of the wavelength. Figure 2.3 illustrates this point, showing two parallel rays forming the wave front AC and interacting with a regular array of scattering centres. After scattering, if rays are to constructively interfere the second wave must return to being in phase with the first. As such it must travel an integer multiple of the wavelength equal to $n2CB$. This describes the Braggs equation (Eqn. 2.2). Here, n is an integer, λ the X-ray wavelength in nm, θ the Bragg angle ($^\circ$) and d the lattice spacing ($\text{\AA}$) [6].

Diffraction may occur from large lattice spacings such as the regular spacing between polymer chains ($> 10 \text{ \AA}$) or from the spacing between atomic planes present within unit cells which have much smaller spacings (in general $\leq 10 \text{ \AA}$). Incident rays that do not satisfy the Bragg equation interfere destructively. Parallel rays that are partially in phase at the surface will also interfere destructively due to interaction with rays scatter from planes further within the solid which will be wholly out of phase with the surface rays.

$$n\lambda = 2d \sin \theta \quad (2.2)$$

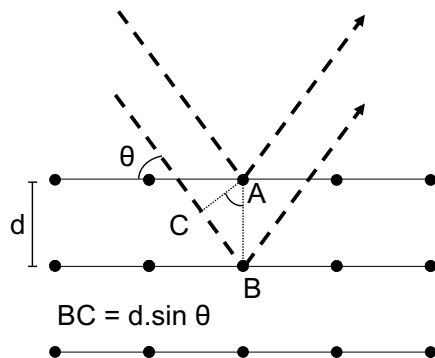


Figure 2.3: Schematic illustration of conditions for Bragg diffraction. Scattering of incident X-rays must be in phase for diffraction to occur.

Diffraction measurements were conducted in the 2θ configuration, where by an X-ray beam and detector move in unison with the same angle (θ) to the sample to measure diffraction peaks. Data were collected from a Panalytical X'Pert Pro diffractometer in which a copper target is used to generate characteristic K_α X-rays (K to L state transition with wavelength 0.15405 nm). The X-ray tube was operated with accelerating voltage and beam current of 40 kV and 40 mA respectively. An X'Celerator detector, able to record diffraction data from multiple 2θ angles simultaneously, is employed. This reduces scan time as acquisition rate is increased. For polymer samples, where investigation of low angle peaks leads to a diffuse X-ray beam across the sample, the program 'Auto-slits' is used to maintain a uniform beam area incident on the sample. This allows for fair comparison between polymer peaks as there is no X-ray intensity variation with angle.

Temperature resolved X-ray diffraction work was completed on an identical diffractometer with the addition of an Anton Paar XRK-900 sample stage; these experiments were completed with tube conditions of 45 kV and 40 mA. Nitrogen was bled in to the sample chamber to provide an inert atmosphere.

In both cases a nickel filter is used to remove K_β (K to M state transition) radiation and additional signal from the doublet $K_{\alpha 2}$ is removed after measurement in the program HighScore Plus.

In this thesis the morphology of thin films of a constant phase (or two-phase heterojunction) is of interest. XRD analysis concerns peak position, width and intensity to understand the crystal structure of thin films. To do so Scherrer analysis and peak fitting are applied; the details of which are discussed below.

2.2.1.1 Scherrer analysis

In a perfect diffractometer, when diffraction occurs at the Bragg angle a sharp peak with negligible line width would be observed. In practice, destructive interference of the incident X-ray beam is not wholly complete due to the finite thickness of the film being examined. For this reason signal from X-ray interference by a lattice can be collected over a range of angles close to the Bragg angle, leading to a broadening of diffraction peaks. This is of use and provides additional information about the structure of the material; the width of diffraction peaks can be related to the size of crystallites as shown in the Scherrer formula (Eqn. 2.3). Broadening of diffraction peaks can also be attributed to strain in the materials, this is discussed in the next section (2.2.1.2).

Peak width is measured by determining the angular $^{\circ}2\theta$ value of the peak at halve the maximum of the peak, this quantity is termed the full-width half maximum (FWHM). For analysis of crystallite size by this method, it should be noted that only FWHM values that are significantly larger than the instrumental broadening of the machine can be used. This limits the use of the Scherrer formula to crystallite sizes typically below ≈ 100 nm. The calculated size of these crystallites are observed for crystals in the out of plane direction of the sample due to diffraction only occurring from these planes. Generally crystals in unordered thin films can be assumed to be in equal dispersion in all directions and so the Scherrer formula can be applied to calculate the average crystal size for all grains within a sample.

$$\tau = \frac{K\lambda}{(B - B_0)\cos\theta} \quad (2.3)$$

Equation 2.3 shows the Scherrer formula where τ is the mean crystallite size, λ the X-ray wavelength, B the peak FWHM, B_0 the instrumental broadening ($0.08^{\circ}2\theta$, measured from the (111) silicon single crystal standard at diffraction peak at $28.5^{\circ}2\theta$ close to the peak of interest; ZnO (002)), K is a dimensionless shape factor, typically 0.9, which assumes a distribution of spherical crystallites and θ the Bragg angle for the selected peak. τ and λ are measured in nanometers, B and B_0 in radians and θ in degrees. More details regarding the derivation of the Scherrer formula can be found in ‘Thin Film Analysis by X-ray Scattering’ by Birkholz [7].

2.2.1.2 Strain

There are many sources of strain in thin films, including defects, dopants within the crystal, recrystallisation processes, differences between the substrate and thin film

resulting in strain through mismatching of epitaxy in growth or thermal expansion coefficient [8]. Strain causes a variation in the lattice spacing of the sample and shifts XRD peak position according to $(d_0 \pm d_{Strain})$. The analysis of strain is possible by comparison of peak positions between strained and unstrained (normally powder) samples.

2.2.1.3 Intensity of diffracted X-ray beams

The intensity of diffraction that occurs as an incident X-ray beam interacts with a sample is in part dependent on the crystalline plane from which diffraction is observed. The structural factor (F) describes the contribution to the diffracted signal by summing scattering from all atoms of the unit cell (Eqn. 2.4). Here f is the amplitude of the wave and the complex exponential term correlates the hkl reflection with the uvw coordinates of the atom. The structure factor has been correlated directly with intensity to provide a means to quantify the relative peak intensity from different planes in a unit cell [6]. The development of the X-ray diffraction technique has prompted further investigation in to the factors that effect peak intensity [9]. These factors are summarised below in equation 2.5. For comparison between the integrated areal diffraction intensity (used in this thesis synonymously with integrated intensity) of different samples key factors to take in to account are, the structure factor, Bragg angle (θ) and sample volume (ν). Due to factors being inter-related, it is clear that diffraction intensity from differing crystalline planes at differing incident angles is not directly comparable and that because intensity increases linearly with sample volume a direct comparison between intensity values is not possible unless sample volume is known or can be estimated.

$$F_{hkl} = \sum_1^N f_n e^{2\pi i(hu_n + kv_n + lw_n)} \quad (2.4)$$

$$I_{(hkl)} = \frac{I_0 \lambda^3}{64\pi r} \left(\frac{e^2}{m_e c^2} \right)^2 \frac{M_{(hkl)}}{V^2} |F_{(hkl)}|^2 \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \frac{\nu}{\mu_s} \quad (2.5)$$

Where, $I_{(hkl)}$ is the integrated intensity (arbitrary units), I_0 is the intensity of the incident beam, λ the X-ray wavelength, r the distance from the specimen to the detector, $(e^2/m_e c^2)^2$ the square of the classical electron radius, F , the structure factor, $M_{(hkl)}$ the multiplicity for reflection hkl , V the volume of the unit cell, θ the Bragg angle, μ_s the linear attenuation coefficient of the specimen and ν the volume of

material diffracting [9]. For a given diffractometer, diffracting material and diffraction angle all factors apart from the last listed here, ν , are constant at any given time.

2.2.1.4 Texture analysis through X-ray diffraction

Texture in a thin film is apparent when crystals are not distributed in a random manner but display some degree of orientation. The resulting diffraction pattern is one where peak intensities deviate in their ratio from that predicted in equation 2.4. In the case of ZnO thin films grown in this work, preferential orientation is always observed in the $\langle 002 \rangle$ direction. Quantification of texturing is possible by comparing the ratio of peak intensities, which is expected to differ from that of an isotropic powder standard¹, in this standard the peaks (100):(002):(101) are recorded to be in the ratio 5:3:10. An alternative method to investigate texture is the comparison of peak intensities between a sample and that of a control.

2.2.2 Small angle X-ray scattering

Small angle X-ray scattering (SAXS) is a powerful technique that can be used to measure particle shape in solution and crystallite orientation in thin films. Here, experiments have been completed by recording the X-ray scatter from a beam incident to the sample surface at grazing angles ($\approx 1^\circ$). Scattering experiments are completed at a fixed angle, X-ray interaction with the differing lattice spacing within the sample gives rise to out of plane (q_z) scatter. If crystalline planes are orientated in-plane scatter also occurs in-plane along the q_y direction. A 2D detector allows for the collection of signal from q_z and q_y directions and angles in between these axis. Scatter from these angles would not be observed in a standard 2θ scan from an X-ray diffractometer, for this reason SAXS is a key complementary characterisation technique and highly applicable to polymer films which can readily change crystallite orientation on heating and cooling.

SAXS measurements were conducted on an Anton Paar SAXSess mc^2 instrument using a copper target X-ray tube operating at accelerating voltage of 40 kV and beam current of 50 mA. A point mode configuration was used with sample height being adjusted so as to align samples within the incident beam and sample tilt adjusted to scatter the beam; typical tilts were $\approx 1^\circ$. The program SAXSquant was used to analysis data collected from the imaging plate. Typical SAXS images, as shown in figure 2.4, are composed of a primary beam and beam stop at the bottom of the

¹ICDD PDF 00-001-1136, Appenix 1 table A.4

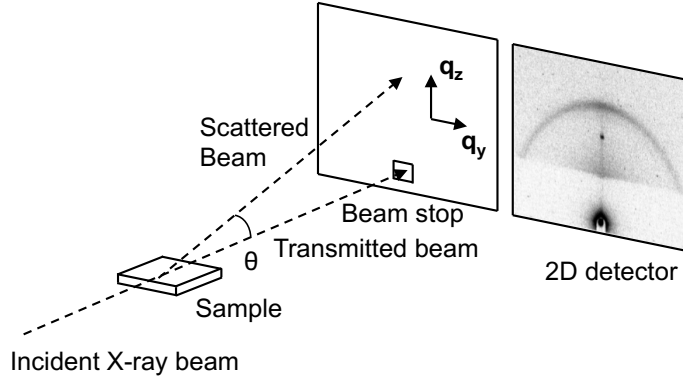


Figure 2.4: Schematic illustration of small angle X-ray scattering of a thin film sample, showing incident X-rays glancing the film and being scattered through angle θ . The scattered image is collected on a 2D detector, here a representative image showing scattering from the P3HT (100) peak is shown as an example.

image, scatter from the sample surface, a high intensity spot corresponding to X-ray reflection from the sample surface and subsequently a series bands corresponding to the scattering from crystals within the film. Bands form due to the polycrystalline nature of the examined samples. Variation in scattering intensity at points along the band correspond to preferential alignment of the crystalline planes in that plane. The scattering patterns, which capture an image from reciprocal space, display scattering from large lattice spacings obtained at small angles and *vice versa*. Scattering on the Anton Paar SAXSess mc^2 is possible for angles up to 40° , this corresponds to q_z -values in the range $0 - 0.25 \text{ \AA}^{-1}$ resulting in possible lattice spacing to be measured between $0.25 - 25 \text{ \AA}$, consistent with equation 2.6.

$$q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d} \quad (2.6)$$

2.3 Optical spectroscopy

Optical absorption was measured by ultra-violet visible spectrophotometry (UV-Vis) (Bentham 2000 Series Spectrophotometer). In operation, white light from a halogen lamp passes through a pair of diffraction gratings to provide a monochromated beam. The beam is then collimated to create a uniform spot size, which is incident on the sample. At a point past the sample, a silicon photodiode is used to convert the intensity of light transmitted at each wavelength to an electrical signal, this transmitted signal (T) (Eqn. 2.7) is amplified and recorded by windows based software

(BenWin+). Samples are compared against an air reference to give an absolute measurement of absorption for all layers in the sample.

Further analysis of absorption spectra can be completed by correlating the magnitude of the absorption peak to the film thickness. Application of the Beer-Lambert law (Eqn. 2.8) [10] allows the magnitude of the intensity of the transmitted beam (I) to be correlated with the absorption coefficient (α) and the distance the light travels through the absorbing medium (l). For thin films, the magnitude of the transmitted beam is dependant on the initial intensity minus the losses of absorption, scattering and reflectance of the sample. The loss contribution from the latter two factors are negligible for bilayer films allowing only absorption to be considered and α may be calculated. Unfortunately this technique cannot be applied to nanorod samples due to a higher degree of scatter arising from nanostructured films.

$$T = \frac{I}{I_0} \quad (2.7)$$

$$I = I_0 10^{-\alpha l} \quad (2.8)$$

The band gap of a material can be found by investigation of the absorption edge of the optical spectra. This corresponds to the minimum photon energy required to promote an electron from the valence band edge to the conduction band edge. While the proof of equation 2.9 [11] is out of the scope of this thesis it is useful to display the origin of Tauc plots presented later in this work. Having an exponent of 2, equation 2.9 can be applied to ZnO and P3HT as both are direct band gap semiconductors [12, 13].

$$(\alpha \hbar \omega)^2 = A(\hbar \omega - E_{og}) \quad (2.9)$$

Where, A is a constant, $\hbar \omega$ the photon energy, α the absorption coefficient, E_{og} the optical band gap of the sample. The optical band gap can be estimated by extrapolating the straight portion of a curve displayed on the axis, $(\alpha \hbar \omega)^2$ against $\hbar \omega$.

2.4 Line profilometry

Layer thickness was measured using a Dektak 150 profilometer. Profilometry involves a tip contacting and being drawn across the sample surface, vertical displacement is

measured as a function of distance, with this instrument 1 nm accuracy in step height is possible [14].

To examine oxide samples, layers were scratched to expose glass or indium tin oxide (ITO) substrates and provide a step for measurement. Polymer samples were scratched and coated with 10 nm of gold to protect the surface from the pressure of the Dektak head which is configured for measurements of hard materials. In each case thickness was averaged over 10 measurements to ensure a representative average of the sample thickness.

2.5 Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) was used to investigate the temperature at which polymer phase transitions occur (Mettler Toledo DSC1) and to investigate the thermal decomposition of sol-gel solutions (Stanton Redcroft STA-780). For polymer samples ≈ 5 mg of material were loaded into an aluminium pan and run through three heating and cooling cycles at a constant rate, the temperature difference between sample and inert reference is recorded as a function of temperature. When exothermic processes occur, crystallisation for example, a positive difference is observed between reference and sample and a peak in the DSC trace is observed; the reverse is true for endothermic processes.

For sol-gel solutions ≈ 10 mg was loaded in to an open platinum boat and heated to allow for removal of precursor species. Both experiments were completed between room temperature and 300 °C.

2.6 Gel permeation chromatography

Gel permeation chromatography (GPC) or exclusion chromatography is one method to determine molecular weight and the polydispersity (PD) of polymer samples [15]. GPC is a separation technique, which relies on the flow of a polymer solution through a porous gel having a pore size on the order of macromolecular coil radius in solution. The flow of polymer through the column is dependant on the size of polymer chains; both short and very long chain polymer molecules are able to flow through the column easily. In the former case, flow of sufficiently short chains is not hindered by the pores, in the latter case long chains, which form bulky macromolecules, are unable to enter small pore sizes these are equally not hindered. Modest molecular weights will be

retained to a larger extent in the pores and their flow hindered in proportion to length of polymer chains [16].

Retention times of polymers are recorded by spectroscopy methods (UV-Vis) to estimate the proportion for each fraction. Retention time for the sample is then corrected against a calibration chart of known molecular weight to obtain molecular weight for the sample.

2.7 Contact angle analysis

The surface energy of a solid governs the degree to which a liquid will wet and form an interface; droplets with a high contact angle (Fig. 2.5a), indicate the formation of a solid-liquid interface is unfavourable, describing a low surface energy; where as a low contact angle (Fig. 2.5b) indicates a high surface energy with the liquid wetting the surface. In this study, new solid-solid interfaces are formed from polymer solutions, good wetting and thus low contact angles are desirable.

The contact angle of distilled water droplets ($\approx 3 \mu\text{L}$) on thin film surfaces were measured using an optical microscope (Veho Discovery VMS-004). Although, polymer solutions made with organic solvents are used for film deposition, water is chosen because it has a low evaporation rate and high surface tension allowing measurements to be made on a reasonable time scale and providing droplets that have a large variation in contact angle between different substrates. In contrast, due to high vapour pressures, organic solvents evaporate quickly and readily wet most substrates. Data analysis is conducted using the program ImageJ to accurately fit droplet radius and measure contact angle between drop and substrate [17].

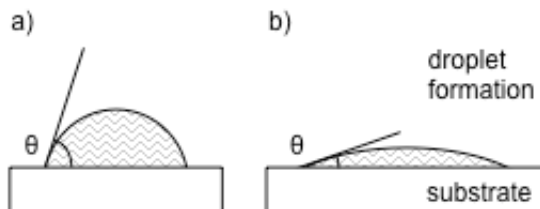


Figure 2.5: Schematic showing contact angle (θ) measurements for substrates that (a) favour droplet formation, and (b) droplet wetting.

2.8 Viscosity measurements

The characteristics of polymer-polymer chain interactions in solution can be investigated by measuring polymer viscosity. Using dilute solutions of polymer with varying molecular weight it is possible to observe a distinct increase in viscosity due to chain entanglement when polymer chains become of sufficient length to interact [18]. This threshold is of interest because entanglement dominates drying and crystallisation behaviour of films made from solution.

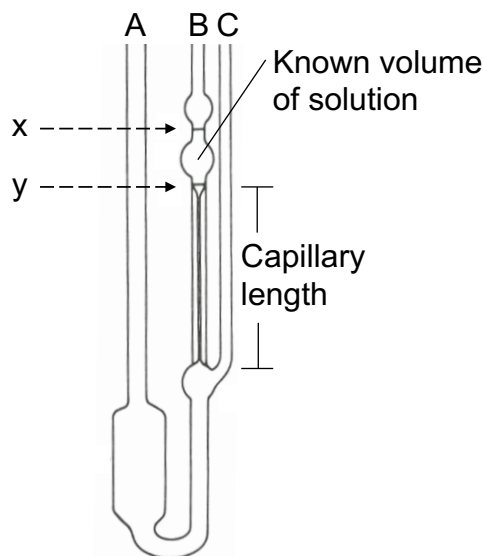


Figure 2.6: Schematic of a suspended level dilution viscometer (Ubbelohde) adapted from [19].

In operation polymer viscosity is measured using a suspended level dilution viscometer or ubbelohde, figure 2.6. Measurements are taken by blocking tubes A and C and a pipette bulb is used to fill the volume of the chamber and above. The time taken for solution to drain between lines x and y is measured, with tubes A and C unblocked there is no pressure build up thus flow time is independent of the volume of solution in the system.

Ubbelohde measurements were taken for P3HT samples using a solution of 0.1 wt% P3HT in chlorobenzene. For the each measurement six readings are taken; glassware is washed with chlorobenzene and repeat measurements of pure solvent are taken in between P3HT samples to confirm glassware is clean. Measurements were conducted over the period of a week with the temperature stabilised to 21 °C by submerging the ubbelhode glassware in a water bath.

The specific viscosity (Eqn. 2.10) of the solution can be found by comparison of know values of flow time for solvent to solvent viscosity η_0 , then to work out increases in solvent due to polymer addition to the solution [16].

$$\eta_{SP} = \frac{\eta - \eta_0}{\eta_0} \simeq \frac{t - t_0}{t_0} \quad (2.10)$$

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Chapter 3

Nanorod Growth

3.1 Introduction

This chapter contains a systematic investigation into conditions required to control nanorod growth. The first section (3.3) focuses on seed layer creation and characterisation; electron microscopy and X-ray diffraction data are presented. The second section (3.4), compares nanorod films grown without additives to those with the addition of ionic and surfactant additive. The morphology of nanorods is characterised by optical spectroscopy, X-ray diffraction and contact angle measurements.

The final section (3.5) shows work concerning the addition of ionic additive, potassium chloride (KCl), the premise of this work being that ionic additives can interact with the polar growth faces of ZnO crystal structures and in doing so control morphology. Films have been characterised by a range of techniques to investigate the crystal and morphological properties of the films. Analysis of data on nanorod height, width and density from SEM micrographs are combined with XRD data to present a measurement of nanorod alignment. The effect of the ionic additive on morphology, alignment and rod termination are discussed. The study of a wide range of additive concentrations has aided in the understanding of growth mechanisms, which are proposed.

3.2 Experimental methods

3.2.1 Planar ZnO

The majority of thin ZnO films were deposited by spin coating (Chemat Technology KW-4A) from a sol-gel solution of zinc acetate onto indium tin oxide (ITO)-coated glass substrates (PsiOteC UK Ltd; 12-16 Ω/sq). Prior to spin coating substrates were cleaned by sonicating sequentially in acetone, methanol, and distilled water for 15 minutes, before drying with compressed air. The final cleaning step was a UV-ozone treatment (UVOCS) for 10 minutes. Planar films were also deposited by electrodeposition and spray pyrolysis. All reagents unless otherwise stated were obtained from Sigma Aldrich.

Sol-gel Processing

Solutions were prepared by mixing zinc acetate dihydrate ($\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2(\text{H}_2\text{O})$) and 2-aminoethanol ($\text{H}_2\text{N}(\text{CH}_2)_2\text{OH}$) in 2-methoxyethanol ($\text{HO}(\text{CH}_2)_2\text{OCH}_3$) [1]. A 0.75 M sol-gel concentration was used. Dense layers were prepared by loading the solution at 500 rpm and spinning at 2000 rpm for 30 s. The process was repeated three times with the substrates briefly heated (8 minutes, VWR Hotplate) to 300 °C between coats. A final 60 minute anneal (Carbolite 5L RWF) at 450 °C was carried out following deposition and heat treatment of the last coating step.

Electrodeposition

A computer controlled potentiostat (Autolab PGSTAT 12 with GPES software) was used in a three electrode configuration to create films by electrodeposition. In this system a Pt mesh is used as a counter electrode, a pre-cleaned ITO substrate as the working electrode and an Ag / AgCl reference electrode. Thin films were made as reported in the literature, with experiment conditions taken from Wei et al. [2]. Prior to deposition O_2 gas was bubbled through solution for a period of 20 minutes. Electrodeposition was carried out galvanostatically up to a charge of 1.68 mA cm^{-2} at a temperature of 65 °C in 0.05 M zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) solutions.

Spray Pyrolysis

Films deposited by spray pyrolysis were made by spraying a precursor solution through an air gun on to a heated substrate, according to Bashir et al. [3]. A precursor solution of 0.2 M zinc acetate dihydrate ($\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot 2(\text{H}_2\text{O})$) in methanol was

used. The substrate temperature was 400 °C and distance from air brush nozzle to hot plate was 30 cm. Films were made by a circular process of coating the substrate with aerosol for a period of 12 s followed by 45 s rest to allow for vapour to evaporate before repetition.

3.2.2 ZnO nanorods

Aqueous solutions of $\text{Zn}(\text{NO}_3)_2$ were heated ($95\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$) in a water bath. Substrates, attached by wire on the rear side, were suspended at a fixed position 15 mm below the full level of a sealed 1 L glass reagent bottle (Fig. 3.1). Growth was initiated by adding a 20 mL aliquot of hexamethylene tetramine (HMT, $\text{C}_6\text{H}_{12}\text{N}_4$) and to the reaction vessel, making the total volume to 1 L and the concentration of both reagents 25 mM. When included, additives were mixed prior to initiation of the reaction; the ionic additive (KCl) was dissolved along with the zinc nitrate, while the surfactant additive (polyethyleneimine (PEI), low-molecular weight, average 25 kg mol⁻¹) was dissolved with the HMT.

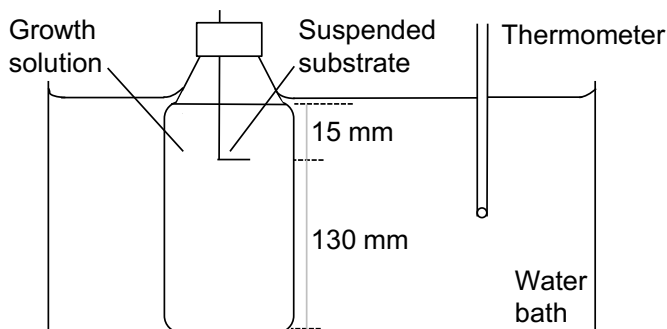


Figure 3.1: Schematic of experimental set up for nanorod growth by hydrothermal technique.

3.3 Seed layer formation by spin coating

There are numerous methods to create thin oxide layers, many of which have been outlined in Chapter 1 (1.2.2), of particular interest are methods that allow for the formation of thin layers over large area at low cost and low temperature. These include electrodeposition [4], spray pyrolysis [3] and spin coating [1]. Initial experiments were conducted by all three methods finding spin coating to be the most applicable for the formation of subsequent nanorod seed layers owing to the ability to form continuous

layers with a good uniformity in grain size. Spin coating was continued in further experiments for seed layer formation.

3.3.1 Results and discussion

The morphology of films deposited by electrodeposition, spray pyrolysis and spin coating are shown in figure 3.2. Comparison between these images shows variation in film uniformity and grain size, resulting from different processing methods. Films made by electrodeposition (Fig. 3.2a) are seen to be non-continuous with large independent grains of ZnO observed on the ITO surface. Film formation by this method is dependent on the reaction between Zn^{2+} and OH^- ions at the substrate surface. To form a continuous film, ZnO must nucleate and then grow on the surface. It is only when grains become large enough to coalesce that a dense film will be formed. In this experiment growth was not conducted for sufficient time for film formation and it may not be possible to form dense films by electrodeposition without films being of considerable thickness (> 500 nm). In contrast, the non-aqueous growth methods, spray pyrolysis and spin coating, form thin layers by the ready oxidation of zinc precursors at temperature. The morphologies of these films (Fig. 3.2b,c) are seen to be dense and have an increased uniformity in ZnO grain size when compared to processing by electrodeposition. Of the two films processing by spin coating give the smallest grain size. For seed layer films a small grain size is advantageous, work completed by Guo et al. show that reducing the grain size of the seed layer yield greatly reduced nanorod diameters, as such the spin coating process was chosen to be the most suitable seed layers for the potential to produce densely populated ZnO nanorod arrays [5].

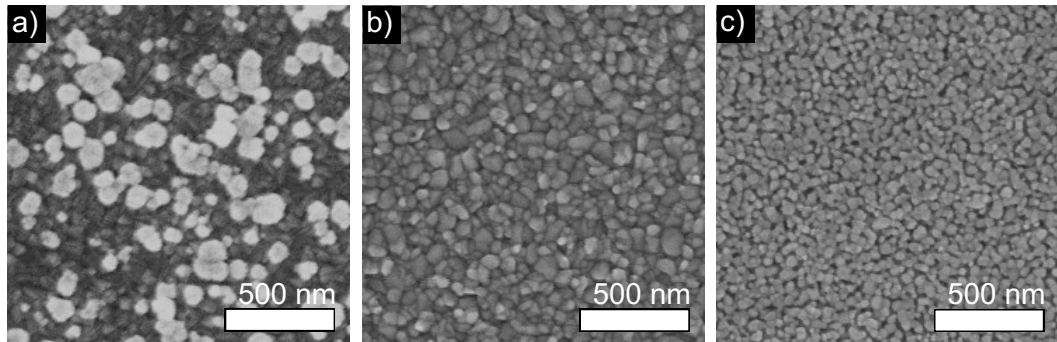


Figure 3.2: Scanning electron microscopy images showing ZnO thin films prepared by a) electrodeposition b) spray pyrolysis and c) spin coating.

Thin seed layers of ZnO were deposited on ITO substrates by spin coating, ZnO films with a thickness of 130 ± 27 nm were made from three coating cycles at a 0.75 M concentration. Differential scanning calorimetry (DSC) measurements carried out on the zinc acetate precursor showing two distinct endothermic regions (Fig. 3.3), corresponding to the energy required to remove water and acetate molecules during the drying of the sol-gel. A sharp peak on cooling at ~ 200 °C corresponds to an increase in energy of the sample compared to the reference. This is attributed to the crystallisation of ZnO from the sol-gel solution, in order to obtain crystallised ZnO thin films, annealing was completed at 300 °C between between coats. The films produced are poly-crystalline in nature. It was found that layers are formed by subsequent coating and heating steps with a minimum of three coats is required to form a continuous dense film. After coating, films are annealed to fully remove any trapped solvent and to increase the crystallinity of the film. The annealing temperature was investigated and found that crystallisation (and subsequent rod growth) will occur from films annealed at a temperature lower (450 °C vs 600 °C) than stated by authors who pioneered this method, Ohyama et al. [1]. The motivation for such an experiment is to reduce the oxidation of tin in ITO, which is favoured at high temperatures and degrades the conductivity of the substrate. Recent work concerning ZnO growth on ITO shows 450 °C to be the onset temperature above which degradation may occur [6]. This temperature was chosen to promote the greatest degree of crystallinity in the shortest annealing time.

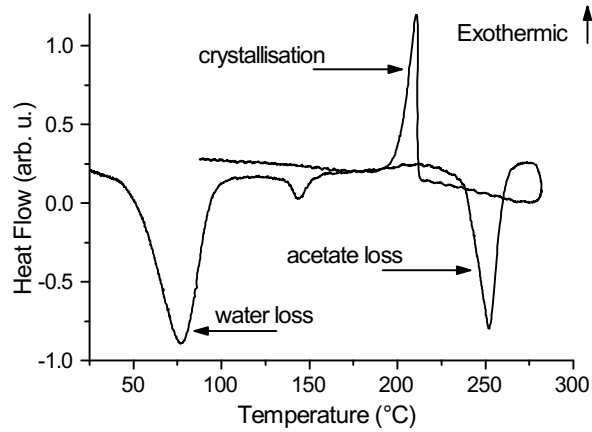


Figure 3.3: Differential scanning calorimetry of zinc acetate sol-gel solution show two regions of heat loss corresponding to the loss of water and acetate molecules from the sample and one region of heat gain corresponding to the crystallisation of ZnO from the sol-gel precursor.

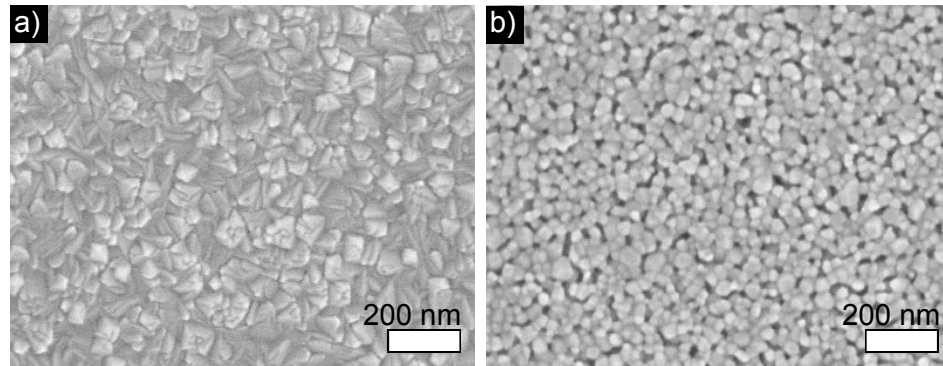


Figure 3.4: Scanning electron microscopy images showing a) ITO substrate and b) ZnO sol-gel seed layer prepared under conditions described in section 3.2.1.

SEM images of an ITO substrate and a thin ZnO seed layer are shown under high magnification in figure 3.4. The ITO film (Fig. 3.4a) has distinct faceted grains with approximate size < 50 nm, in contrast grains of ZnO (Fig. 3.4b) are smaller (< 30) nm and more rounded in shape. At lower magnifications seed layer films are seen to be continuous and uniform on the millimetre scale.

Figure 3.5 shows X-ray diffraction patterns for samples coated for three times *via* the spin coating process, samples were investigated with (Fig. 3.5c) and without

(Fig. 3.5b) a 60 minute anneal at 450 °C. The pattern for a bare ITO coated glass substrate is shown as a control (Fig. 3.5a), substrate peaks have been identified by asterisk marks on the uppermost pattern; the remaining peaks of the ZnO have been labelled with their corresponding hkl indices. On annealing, as the film becomes more crystalline, an increase in the peak intensity of all ZnO peaks is observed. The most intense diffraction peak occurs from the (002) plane and is a result of significant texturing in the thin film. The preferential orientation of ZnO crystallites is due to the hexagonal crystal structure of ZnO, which is previously discussed in section 1.2.1.2. For the purpose of nanorod growth a high proportion of (002) planes within the crystalline seed is desirable because the (002) plane acts as a nucleation point from where subsequent growth of nanorods may occur.

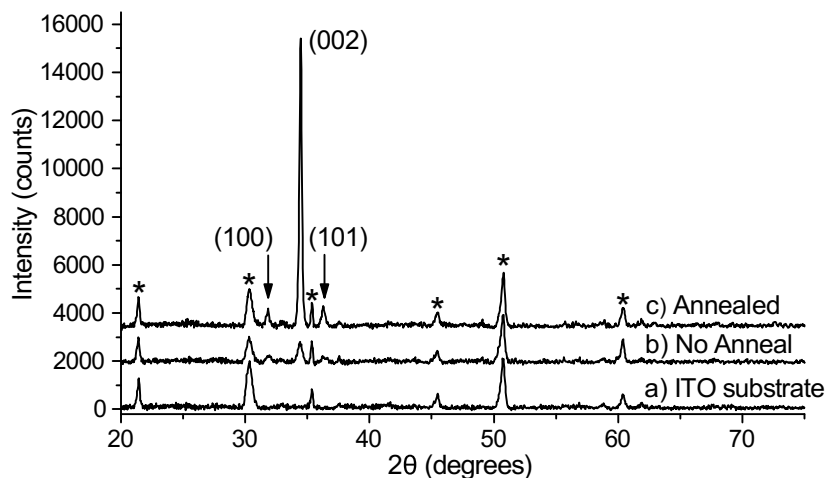


Figure 3.5: X-ray diffraction patterns of a) ITO substrate, b) sol-gel film without 60 minute anneal and c) sol-gel film annealed for 60 minutes at 450 °C. Prominent zinc oxide peaks are labelled, * mark ITO substrate peaks.

3.4 Nanorod growth by hydrothermal deposition

As previously described (section 1.2.2), nanorod growth by the hydrothermal deposition is dependent on the solution temperature, volume, concentration, precursors and substrate. Here, these variables are not changed, instead the effect of additives to solution are investigated as a method to control nanorod morphologies. Two additives are investigated; polyethylenimine (PEI) and potassium chloride

(KCl). These give insight to the effect of surfactant and ionic additives to nanorod growth.

Four growth conditions were investigated and are shown in table 3.1. Nanorods have been grown for 200 minutes, corresponding to a time period where the reaction has been driven to near completion and the maximum possible volume of ZnO in the reaction vessel deposited on to the substrate [7].

Table 3.1: Growth conditions for investigation of addition to nanorod growth, in each case reactant concentrations are 25 mM $\text{Zn}(\text{NO}_3)_2$, 25 mM HMT.

	Concentration of additive	
	KCl	PEI
a	-	-
b	-	10 mM
c	100 mM	-
d	100 mM	10 mM

3.4.1 Results and discussion

Initial investigation of the pH of precursor solutions was completed to determine the chemical environment of these species. Prior to mixing, the salt solution pH was 5.7, the pH of the HMT aliquot was 11.3. Upon completion of the reaction a pH of the products in solution of around 6 was observed and this is consistent with values observed in the literature [8].

3.4.1.1 Scanning electron microscopy

The morphology of nanorod arrays are investigated by scanning electron microscopy (Fig. 3.6). From images presented in the figure alone, various observations can be made; firstly, the termination of nanorods is seen to differ between those grown with and without ionic additives. In figure 3.6a sharp tips are observed, when growth is completed with ionic additives (Fig. 3.6c) nanorods are terminated by hexagonal facets. Qualitatively variations in nanorod length, width and uniformity can also be observed. To further investigate these structures, the dimensions of nanorod arrays were quantified by measuring areal density, nanorod length and width, measurements are shown in table 3.2.

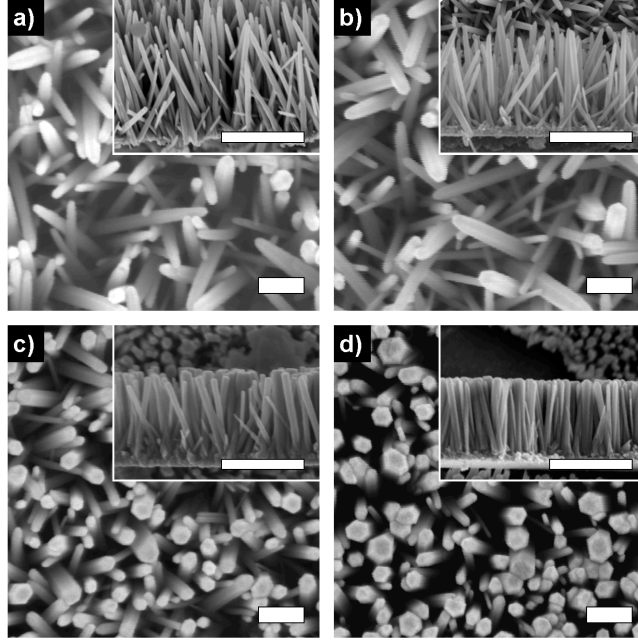


Figure 3.6: SEM micrographs showing top-surface rod morphology and cleaved cross sections (in- sets) for ZnO rods grown by hydrothermal method under the conditions, (a) additive free growth, (b) addition of PEI (10 mM), (c) addition of KCl (100 mM), and (d) combined addition of PEI (10 mM) and KCl (100 mM). Main scale markers 100 nm, inset 1000 nm

Table 3.2: Nanorod dimensions and areal density obtained on various nanorod films. Values in brackets display standard deviation.

	Average rod diameter (nm)	Average rod length (nm)	Areal density (μm^2)
No additives	78 (29)	1280 (390)	45
Surfactant (10 mM PEI)	58 (12)	860 (210)	47
Ionic additive (100 mM KCl)	81 (27)	900 (160)	35
Ionic and surfactant additives	51 (22)	840 (20)	86

As previously reported in the literature, surfactant addition is seen to reduce nanorod diameter [7]. For nanorods grown in these experiments diameter is reduced by 25 % (78 ± 29 nm without surfactant, 58 ± 12 nm with surfactant), importantly this effect is continued to be observed when KCl is added (average diameter 51 ± 22 nm). It is seen that, KCl addition alone does nothing to control the lateral growth, but interestingly a decrease in the standard deviation of nanorod length is observed,

suggesting that KCl hinders c-axis nanorod growth. When both additives are present an increase in nanorod areal density is seen. Such changes are characteristic of nanorod formation and subject to further discussion in section 3.5.2.

3.4.1.2 X-ray diffraction

The formation of crystalline ZnO by hydrothermal deposition was confirmed using XRD (Fig. 3.7). Analysis of the XRD data is possible by characterisation of peak position, peak width and intensity, the details of which are discussed in section 2.2. Nanorod films are seen to be highly crystalline with an intense (002) peak this is attributed to the preferential growth of ZnO crystal on the basal plane and consistent with previous reports [1, 9]. Diffraction from this plane occurs in the region $34.4^\circ 2\theta$ is of interest in this study to determine the crystalline nature of the thin film. To ensure a fair comparison between peak angles, diffraction patterns are aligned to peaks arising from the substrate. These peaks occur at known fixed angles and allow any small errors in sample loading to be corrected. Diffraction patterns have been aligned to the invariant (222) ITO peak at $30.31^\circ 2\theta$. Figure 3.7 inset shows the aligned ITO peak for this data set, alignment gives confidence in the position of crystalline ZnO peaks and allows for further discussion.

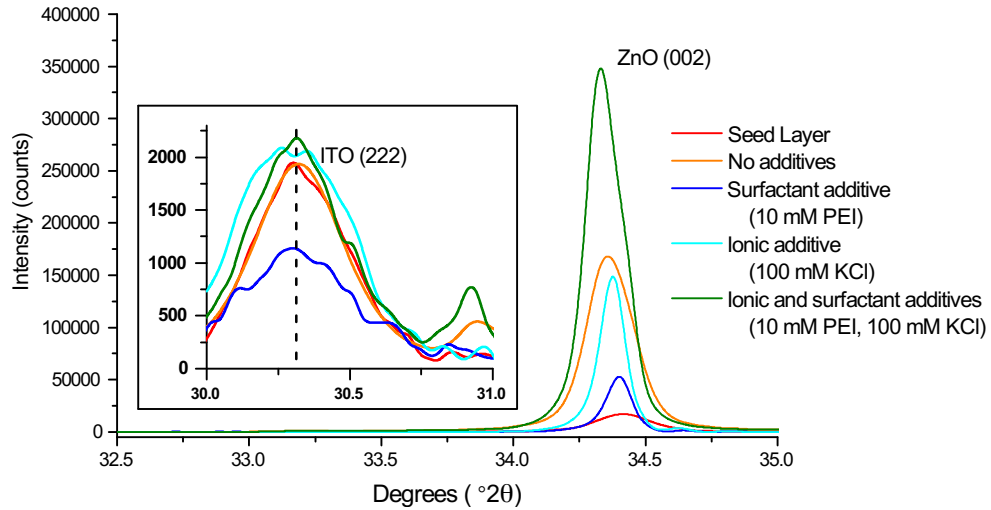


Figure 3.7: X-ray diffraction showing intensity of the (002) peak for samples grown with various additives. Inset shows alignment of diffraction patterns to ITO peak at $30.31^\circ 2\theta$.

Overall there is a $0.06^\circ 2\theta$ difference between the position of the highest (seed layer, $34.40^\circ 2\theta$) and lowest (nanorods growth with both additives, $34.34^\circ 2\theta$) ZnO

(002) diffraction peaks. This is attributed to strain within the film resulting from varying amounts of defects present. All sample peaks are at a lower position than that of bulk single crystal ZnO, $34.55^\circ 2\theta$ [6], corresponding to an increase ($\sim 0.2\%$) in the c-axis lattice spacing for nanorods grown by the hydrothermal method.

The shift is attributed to the position of zinc interstitial species (Zn_i), which are seen in density-function calculations to occupy the octahedral site and shift the c-axis to higher lattice spacings [10, 11]. Increases in c-axis lattice spacing is observed in thin films growth by pulse laser deposition [12] and attributed to a low oxygen partial pressure, which promotes Zn_i formation. The presence of zinc interstitials has been measured in nanorod samples using photoluminescence, however, lattice spacings were not correlated to defect concentrations [13].

The Scherrer equation was used to calculate crystallite size from the (002) and (101) diffraction peaks; data are shown in table 3.3. The Scherrer equation is reliant on the FWHM of diffraction peaks, as peak width (B) approaches that of instrumental broadening (B_0) the relationship between FWHM and grain size fails to hold as $B - B_0$ tends to 0. The intense and narrow diffraction from the (002) plane for nanorod samples correspond to large crystal sizes ($\gg 100$ nm) which cannot be calculated by the Scherrer equation; thus crystallite size were extracted from the (101) peak. This provides information, not on the size of grains in the preferential $\langle 002 \rangle$ growth direction which is known to be > 100 nm, but instead on a plane that lies perpendicular to the direction of growth. From such analysis a comparison of nanorod width can be made providing that nanorods are in such an orientation so that diffraction can occur from the (101) plane.

Of the $d_{(101)}$ shown in Table 3.3, the largest difference in grain size is observed between seed layers and nanorod arrays grown without additives. This is consistent with disordered nanorod films having large diameters as previously imaged using SEM (Fig. 3.6). Overall, the similarity of these values to that of the seed layer, is indicative of little diffraction from the nanorod (101) crystalline plane.

In the final column of table 3.3, the relative intensities of the (002) and (101) peaks are shown with the purpose of quantifying the film texture. The relative intensity of a ZnO powder standard (00-001-1136) for the ratio (002):(101) is 0.3. Here films are seen to be highly textured with the highest value corresponding to nanorods growth with KCl and PEI additives. This high intensity diffraction can be explained by a combination of either increased nanorod volume (higher areal density) or increased vertical nanorod alignment to the substrate.

Table 3.3: Calculated crystallite sizes for seed layer and nanorod films prepared under the conditions described. The addition of KCl is seen to significantly increase the intensity of the 002 diffraction peaks.

	Crystallite size (nm) ¹		(002)/(101)
	d ₍₀₀₂₎	d ₍₁₀₁₎	Peak Intensity ²
Seed layer	71	56	10
No additives	-	105	58
Surfactant (10 mM PEI)	-	60	11
Ionic additive (100 mM KCl)	-	46	83
Ionic and surfactant additives	-	70	141

¹Crystallite sizes that exceed Scherrer analysis are not shown.

²Nanorod samples include contribution from seed-layer.

3.4.1.3 Optical spectroscopy

For many applications including that in this work high optical transparency is required. To investigate the optical properties, transmission spectra of the films were measured against an air background; spectra are shown in figure 3.8a and divided in to two groups, substrates and nanorod films. The ITO/glass substrate shows a strong absorption at < 320 nm that rises sharply to give the substrate a transparency of > 90 % over the 400 – 900 nm range. A ZnO seed layer on the ITO substrate shows the characteristic ZnO absorption band onset at 360 nm.

Nanorod films all show a large amount of scattering, corresponding to the broad peak ranging from a maxima at the band gap to minima at 900 nm in UV-Vis spectra. The nanorod films appear translucent to the eye, with the most scatter observed in nanorods growth without additives. This is attributed to the misalignment and large variation in the length and width of nanorods. Consistent with data from SEM images an increase in the homogeneity of nanorods is seen in the least scattering film, that was grown with KCl and PEI additives. At higher wavelengths a weak oscillation in the UV-Vis signal can be observed. These peaks arise from light trapping within the sample and occur due to two reflecting interfaces, resulting in (Fabry-Perot) interference. The observation of such peaks signifies a non-scattering film with good uniform in thickness.

The band gap (E_g) of sol-gel seed layers and nanorod arrays are shown in the Tauc plot presented in figure 3.8b. The measured band gaps of these films are 3.25 eV and 3.10 eV for the sol-gel and nanorod samples respectively. The value for bulk ZnO is

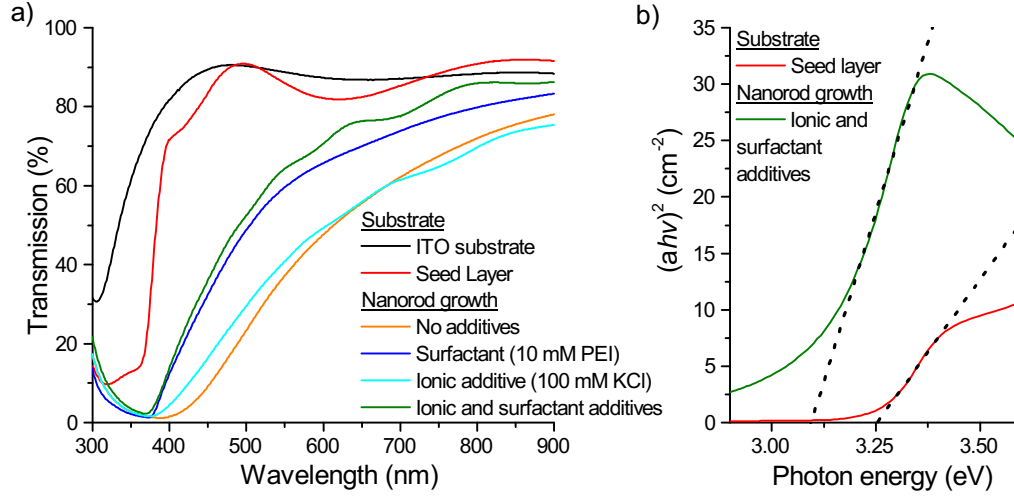


Figure 3.8: a) UV-visible spectra for ITO substrate, seed layer, and nanorod arrays. b) Tauc plots showing optical band gap for seed layer and nanorod samples.

often quoted in the region ~ 3.3 eV [14, 15, 16]. Both films have values below this; the narrowing of the band gap is attributed in the literature to the presence of n-type defects [17, 14] that have energies within the electronic band gap, the measured E_g is that of the transition from the valance band to the n-type donor level. It is likely defects lower the band gap in the measured films. In addition, and especially for the nanorod film, there is significant scatter, this hinders investigation of the on set of E_g and so may result in the under or over estimation of the E_g by this technique.

3.4.1.4 Contact angle

The degree that a liquid wets a surface provides an indication to the extent a polymer solution may wet and fill a nanostructured substrate. For this purpose, a low wetting angle corresponding to the formation of a liquid-solid interface is desired. Contact angles measured for water droplets on flat substrates (ITO and ZnO seed layers) and nanostructured films are shown in table 3.4.

The wetting angle is significantly decreased in the majority of nanorod samples compared to planar substrates. Interestingly samples grown with just PEI additive exhibit a degree of hydrophobicity. Importantly, superhydrophobic (contact angle $> 150^\circ$) behaviour shown in some ZnO nanorod arrays [18, 19] is not observed and samples grown with both additives in solution are seen to have favourable wetting properties.

Table 3.4: Measured contact angle of water for substrate and seed layer (top), and ZnO nanorod samples (bottom).

Substrate	Contact angle (°)
ITO substrate	55
ZnO seed layer	51
Nanorod growth	Contact angle (°)
No additives	15
Surfactant (10 mM PEI)	88
Ionic additive (100 mM KCl)	7
Ionic and surfactant additive	6

3.4.2 Conclusions

The morphology and crystal structure of ZnO thin films deposited by spin coating have been characterised. From these seed layers, zinc oxide nanorods were successfully grown under a four different experimental conditions. For a growth time of 200 minutes, nanorods $\sim 800 - 1200$ nm in length and $50 - 80$ nm in width were created. In the case of surfactant addition, results were consistent with the literature [7]. Ionic additives were seen to have a significant effect on the nanorod morphology, X-ray diffraction patterns and optical properties of the thin films. Discussion linking nanorod morphology to XRD peak intensity, width and position is presented. In addition, morphology is correlated with optical scattering in UV-Vis data and contact angle measurements.

3.5 Control of nanorod growth by addition of ionic additives

Nanorod growth is observed from sol-gel seed layers and variation in nanorod morphologies are seen with the inclusion of additives to hydrothermal growth solutions. Further studies to investigate the effect of ionic additives on nanorod morphology is of interest. The creation of tailored nanorod morphologies allowing for enhanced nanorod alignment, increased uniformity in nanorod length and interfacial area, will aid the filling of nanostructures, as well as increase device performance by reducing short circuit currents and increasing charge collection. Ultimately the ability

to control the fine structure of nanorod morphologies will enhance the processing and performance of hybrid photovoltaic and optoelectronic devices.

Experiments undertaken in this section are a logical continuation from previously presented work (section 3.4). Here, nanorod morphology as a function of KCl concentration is examined. Samples were grown for two time periods and characterisation of their morphology completed by SEM and XRD. Analysis of morphology by SEM shows a systematic change in nanorod length, width, and density with KCl concentration. This data is combined with integrated peak intensity XRD data and used to estimate nanorod alignment. Morphological changes are discussed in terms of the ability of ionic species to stabilise the polar (002) ZnO surface and the effect this has on physical nanorod-nanorod interactions.

3.5.1 Film morphology and crystalline structure

Nanorod growth was carried out at equimolar (25 mM) concentrations of $\text{Zn}(\text{NO}_3)_2$ and HMT and 10 mM PEI, whilst the KCl concentration was systematically varied (0 – 500 mM). The influence of growth time on rod length is shown in figure 3.9, a linear increase in rod length is observed (25 – 120 minutes) after which time the overall growth rate is reduced due to consumption of the reactants. Linear growth is a result of the steady decomposition of HMT in solution, which acts as a buffer to provide hydroxide ions (Eqn. 1.6) that are subsequently consumed to produce ZnO (Eqn. 1.7) [20].

Nanorod growth times presented in this section differ from the previous section (3.4) where growth reactions were allowed to proceed for 200 minutes. Here growth was investigated for times of 40 and 120 minutes. The range of times presented in this section cover length scales that are applicable for efficient hybrid photovoltaic devices (500 – 600 nm) [21], as well as investigating growth early and late in the linear regime.

Figure 3.10 shows cross-sectional and surface SEM images of ZnO nanorod structures grown for 120 minutes over the 0 – 500 mM KCl concentration range. A similar figure showing growth from 40 minutes is presented in Appendix 1, page 156 (Fig. A.1). Variation in KCl concentration is shown to influence the nanorod length, vertical alignment, aspect ratio and tip termination for 120 minutes growth. The introduction of KCl (10 mM) results in a significant increase in rod length (860 ± 250 nm) compared with growth in the absence of KCl (370 ± 130 nm). Increasing the concentration of KCl to 50 mM results in a further increase in rod length (1050 ± 180

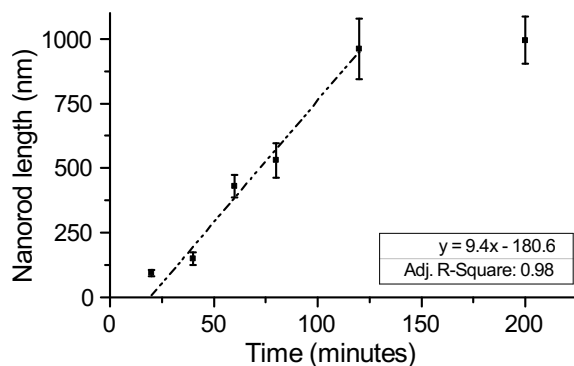


Figure 3.9: Average length on ZnO nanorods as a function of growth time from hydrothermal baths consisting of equimolar (25 mM) $\text{Zn}(\text{NO}_3)_2$ / HMT solutions containing 10 mM PEI and 100 mM KCl. Error bars show standard deviation.

nm), at higher KCl concentrations a gradual reduction in nanorod length is observed (Fig. 3.10d-f). At KCl concentrations (< 200 mM) the nanorods are terminated with sharp points, above this concentration nanorods are terminated by flat surfaces and show clear hexagonal faceting.

The crystallographic nature of ZnO nanorods grown under different conditions was examined by transition electron microscopy (Fig. 3.10i,j). No grain boundaries are observed in these micrographs, indicating nanorods of single grains of ZnO. This is consistent with SEM micrographs where nanorods are not seen to deviate from their growth direction, only individual crystalline facets are observed. Selected area diffraction (Appendix 1 page 157, Fig. A.2) was conducted on both samples and seen to give a diffraction pattern consistent with a single crystal, showing diffraction from (002) and (010) planes.

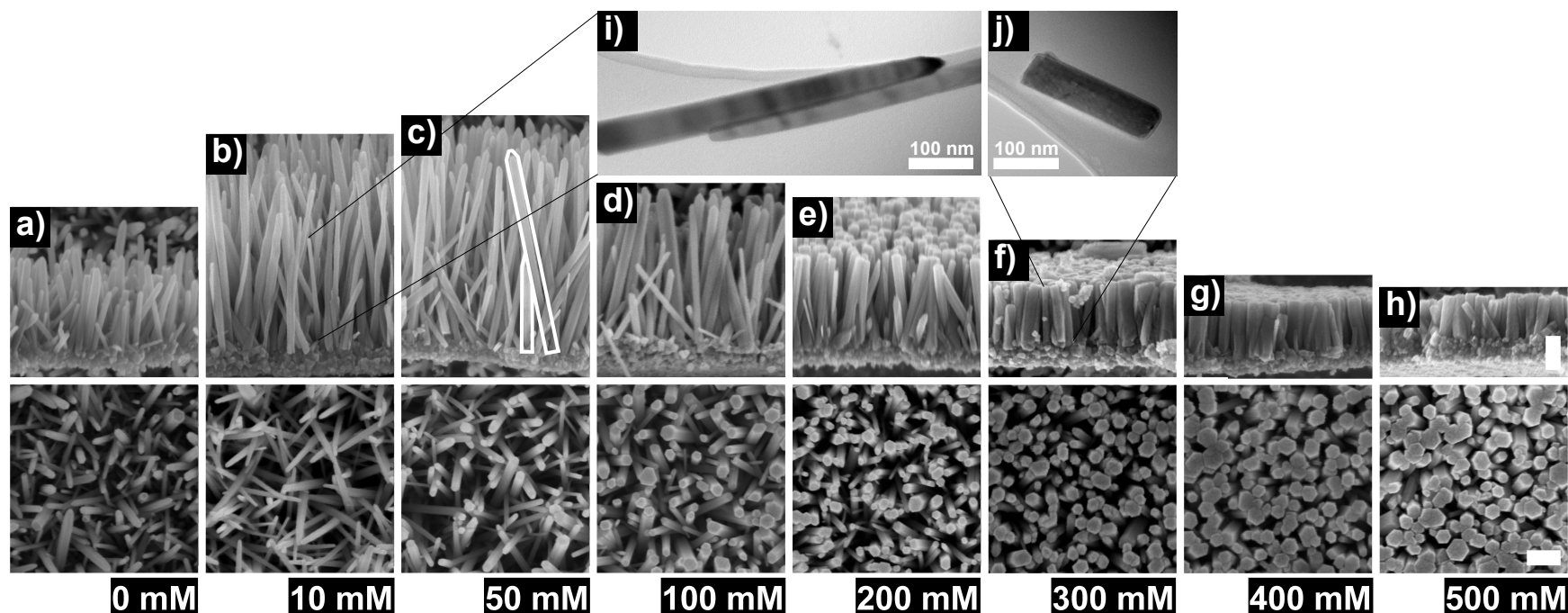


Figure 3.10: Cross-section (upper) and surface (lower) SEM images of ZnO nanorods grown from hydrothermal baths containing equimolar (25 mM) $\text{Zn}(\text{NO}_3)_2$ / HMT and 10 mM PEI. The influence on nanorod morphology with the addition of a) 0, b) 10, c) 50, d) 100, e) 200, f) 300, g) 400, h) 500 mM KCl at a growth time of 120 min is illustrated. Scale markers are 200 nm with nanorod-nanorod interaction highlighted in c). TEM images for 10 mM (i) and 300 mM (j) KCl additive are shown to highlight variation in nanorod termination.

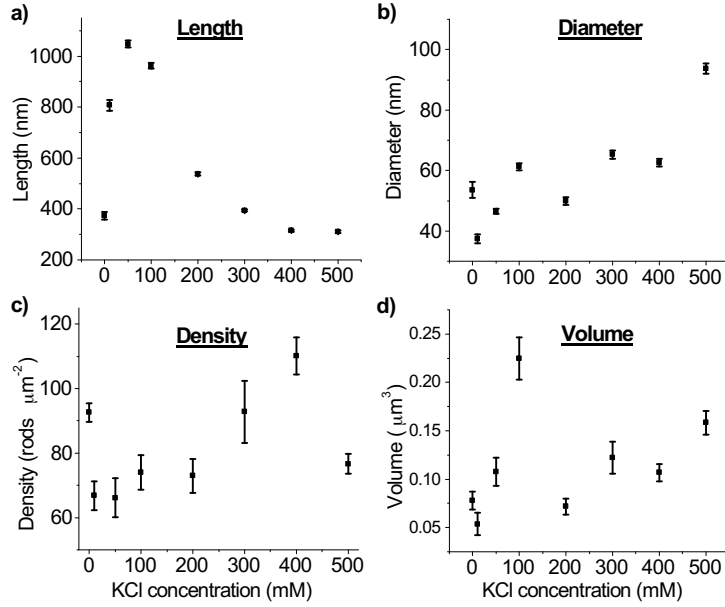


Figure 3.11: Morphological data obtained from SEM micrographs, showing a) length, b) diameter, c) areal density and d) volume of ZnO nanorods grown for 120 min with varying concentrations of KCl. Error bars show standard error.

To further quantify the influence of KCl on nanorod growth detailed analysis of films grown under each set of growth conditions was carried out using SEM images. Figure 3.11 shows the processed results obtained from image analysis (120 minute growth) for measured rod length, diameter, areal density and calculated deposition volume as KCl concentration is varied, calculated averages are plotted and accompanied by the standard error of the mean. It should be noted that such errors are small due to the large measured sample size (Appendix 1, Table A.1), the display of standard error over standard deviation has been chosen to reflect the significant data set behind each measurement. The variation in standard deviation of nanorod length is discussed later in section 3.5.2. A minimum of two samples at each KCl concentration were analysed at a number of locations on each substrate.

In summary, and consistent with the trends shown in figure 3.10, nanorod length increases on addition of KCl, reaching a maximum at 50 mM (1050 nm (13.3)); above this concentration nanorod length is gradually reduced. The measured rod diameter increases across the concentration series to a maximum of 94 nm (1.7) at 500 mM KCl. The areal density is reduced on addition of small amounts of KCl but increases with increasing KCl concentration, until the final film where a decrease in density is observed due to nanorod coalescence (Fig. 3.11).

Films grown over the entire KCl concentration range were characterised using X-ray diffraction. Diffraction patterns for KCl concentrations (0 – 500 mM) and growth times of 40 and 120 minutes are shown in figure 3.12a. Data is presented in the 30 – 40 °2 θ range, showing the (002) ZnO diffraction peak (~ 34.4 °2 θ); to highlight distribution of peak intensities for nanorod films, data were normalised to highest intensity peak (400 mM, 120 minutes). The ITO (400) substrate peak has been used here to align X-ray patterns on the 2 θ axis and is shown for reference. The integrated intensity of ZnO (002) peak has been used to quantify rod alignment.

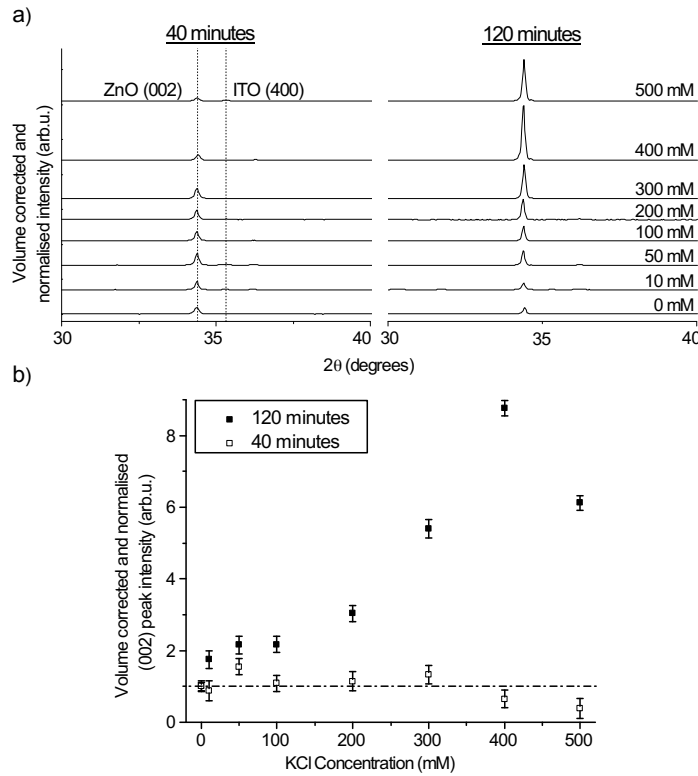


Figure 3.12: XRD patterns and calculated diffraction data for ZnO nanorods films grown with varying KCl concentrations, a) volume corrected and normalised ZnO (002) peaks for growth times of 40 (left) and 120 minutes (right), b) integrated (002) peak intensity corrected for volume and normalised to 0 mM KCl sample. Values above 1 show increased diffraction as a result of nanorod alignment compared to the control (0 mM KCl).

Variation in diffraction intensity occurs due to the quantity and orientation of nanorods on the substrate (*cf.* diffraction intensity, Eqn. 2.5). To deconvolute the orientation and volume effects the integrated (002) peak areas are corrected for the

sample volume (Fig. 3.11d, Table A.1). Finally to quantify rod alignment, data were normalised to the (002) peak intensity of the 0 mM KCl sample, providing a direct comparison of KCl addition on vertical alignment, figure 3.12b. Samples grown for 40 minutes show little variation in vertical alignment as the KCl concentration is varied. In contrast those grown for 120 minutes all show improvements in alignment that reaches a maximum at around 400 mM KCl.

3.5.2 Role of KCl in nanostructure formation

A simple method for controlling ZnO nanorod morphology through addition of KCl to the hydrothermal growth bath is presented. The subject of the following discussion regards the physical interaction between ionic additives and nanorod crystals during growth to provide an explanation for morphological changes as a function of KCl concentration.

3.5.2.1 Solution chemistry

It is first necessary to consider the free energy of hydration for each of the ionic species present in the hydrothermal bath *i.e.* NH_4^+ , K^+ , NO_3^- , NO_2^- , Cl^- , OH^- . These typically lie between -285 and -430 kJ mol⁻¹ [22], indicating that these species will be heavily solvated during nanorod growth hence reactions *between* these species in solution are unlikely. Furthermore all ionic species are in low concentrations, the maximum ([KCl] 500 mM), is significantly lower than the solubility limit at 100 °C (7.6 M). As such, KCl is thought to directly effect nanorod growth through adsorption to growth planes and not by any effect in solution chemistry of the deposition baths.

In the presence of KCl the observed nanorod growth behavior can be explained by considering nanorod surface termination. In order to minimize the area of high energy (002) surfaces nanorod growth proceeds primarily along the <002> direction with slow growth in the <100> directions. Figure 3.10 shows that at KCl concentrations < 100 mM the nanorods are terminated by (101) faceted points, and as the KCl concentration increases a planar (002) surface is stabilised. It is proposed that the observed increase in nanorod length at 10 mM KCl *i.e.* rapid <002> growth, is due to the partial stabilisation of a small (002) surface at the tip of the growing rod and not lateral (100) adsorption as previously speculated [20]. The proposed morphology of the growing rods is shown schematically in figure 3.13. In the absence of KCl, nanorods are terminated by sharp points and the (002) surface is fully minimized figure 3.13a. Addition of small amounts of KCl, results in the partial stabilisation of

the (002) surface (Fig. 3.13b), which promotes rapid $\langle 002 \rangle$ growth and explains the observed increase in nanorod length and accompanying reduction in diameter. Further increases in KCl concentration completely stabilise the (002) surface resulting in a promotion of lateral growth and formation of planar faceted rods shown schematically in figure 3.13. This is consistent with micrographs presented in the previous section (section 3.4.1.1, Fig. 3.6).

Under alkaline deposition conditions (pH 11) where it has been proposed that changes in nanorod aspect ratio are attributed to cation adsorption to the lateral (100) surfaces [23], in the hydrothermal method used growth occurs at pH 5.5 - 6.0 [24]; under these conditions the non-polar (100) surface is thought to remain neutral, with any charging of the (100) surface negligible in comparison to the effect of additive stabilisation to the (002) growth surface, growth rates on the relative planes.

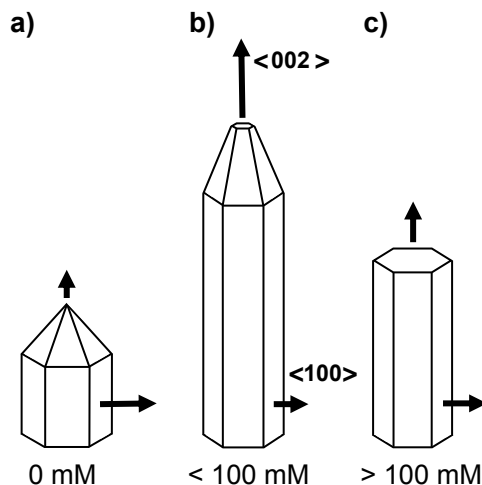


Figure 3.13: Schematic illustration showing comparative directional growth rates as KCl concentration is varied a) 0 mM, b) < 100 mM, c) > 100 mM.

3.5.2.2 Physical nanorod interaction

As the growth time is extended from 40 to 120 minutes there is a distinct reduction in areal density of nanorods (*cf.* Fig 3.11, Table A.1), indicating that many of the nucleated nanorods observed early in the linear growth regime, do not continue to grow. We propose that this phenomenon results from the interaction of growing nanorods, figure 3.10c, which is supported by the observed increase in (002) diffraction intensity at longer growth times (*cf.* 40 vs. 120 minutes, Fig. 3.12b). Very recent work

shows the validation of this theory by application of the geometrical selection model [25], which outlines three distinct growth regimes. Here, nucleates are first isolated in their growth and as growth progresses nanorod interaction increases. In this stage growth is competitive; assuming a fixed growth rate, those that have nucleated first or those that are more aligned are not hindered in their growth. Once termination of misaligned nanorods is complete, growth continues in a regime where nanorods are aligned to neighbouring crystals.

The observed increase in alignment with addition of KCl to growth solution is thought to increase the transition from isolated to aligned nanorod regimes. The addition of different KCl concentrations is seen to alter the growth rate between lateral and vertical directions. In concentration regimes where c-axis growth is hindered (> 100 mM KCl), nanorod diameters are increased; hence rod-to-rod interactions occur at an earlier growth stage. Under these conditions (> 100 mM KCl), misaligned nanorods are more likely to interact early in the growth process and terminate, i.e. growth in the competitive regime is reduced, resulting in the highly orientated films at lower time periods. The XRD data support this hypothesis; diffraction intensity per unit volume is at a maximum at 400 mM KCl for 120 minute growth, showing increased alignment despite the reduced nanorod length (315 nm) of these films. Above 400 mM KCl growth in the $\langle 002 \rangle$ direction is hindered to the extent that nucleates coalesce before aligned nanorods form.

3.5.2.3 Nanorod uniformity

Increasing the KCl concentration results in a marked reduction in the standard deviation of rod length, showing improved uniformity as KCl concentration is increased (Table 3.5).

An increase in nanorod uniformity is possible by two methods: reduction in nucleation time and increased nanorod interaction. The first method increases uniformity by reducing the time between each nucleate and thus individual nanorod lengths would have a much smaller distribution. Analysis of the SEM micrographs of short (40 min) growth time samples yields some information about nanorod nucleation and early-stage growth behaviour. In these experiments similar areal densities were measured without KCl and across the whole KCl concentration series (Table A.1), showing a small range of nucleates $132 - 179 \mu\text{m}^{-2}$, with the majority between $140 - 155 \mu\text{m}^{-2}$. If KCl effected nucleation, this value would change dramatically as a function of concentration; thus it is thought that the nucleation step is not dependent on KCl concentration.

Table 3.5: Length and standard deviation values of ZnO nanorods grown for 120 min with varying concentrations of KCl additive.

KCl Concentration (mM)	Length (nm)	Standard Deviation (nm)	Sample Size (n)	Standard Deviation \ Length
0	370	130	70	0.35
10	860	250	150	0.30
50	1050	180	191	0.18
100	960	120	106	0.12
200	540	80	147	0.15
300	390	40	134	0.10
400	310	30	97	0.11
500	310	20	28	0.08

Alternatively, and in line with arguments presented in section 3.5.2.2, an increase in uniformity can be explained through nanorod interaction. The increase in nanorod width with KCl concentration, increases rod-to-rod interaction reducing shorter nanorods at earlier points in their growth and thus narrowing the distribution in nanorod length.

3.5.3 Conclusions

A reproducible method for preparing tailored ZnO nanorods from aqueous solutions has been developed through incorporation of KCl into the hydrothermal growth bath. KCl acts as a growth modifier through stabilisation of the polar (002) nanorod surfaces. The range of KCl concentrations investigated (0 – 500 mM) spans growth modes where partial adsorption results in the formation of high aspect ratio nanorods and complete adsorption results in the formation of near-coalesced rods.

At high KCl concentrations (> 100 mM) the growth of shorter and wider ZnO nanorods is observed, consistent with reduced <002> growth due to stabilisation of the (002) surfaces by KCl. The incorporation of simple ionic additives into the hydrothermal growth bath provides a convenient method affording control of the nanorod dimensions, area density and surface termination. This represents a significant step in the controlled and reproducible low-cost solution processing of tailored nanostructures and should facilitate the uptake of these structures into relevant device architectures.

3.6 Summary

The formation of ZnO seed layers, growth of nanorods and investigation of the effect of ionic additives on nanorod growth has been presented. Thin ZnO film formation was shown to be possible by spin coating of sol-gel solutions, crystalline films were formed by annealing and these films used as seed layer for growth of nanorod arrays.

ZnO nanorod arrays were grown for 200 minutes by the hydrothermal method, growth was modified by addition of surfactant (PEI) and ionic salt (KCl). The effect of additives on film properties was investigated by electron microscopy, X-ray diffraction, UV-Vis spectroscopy and contact angle measurements. These experiments found interesting initial results concerning rod uniformity and the effect of ionic additives on morphology. Further work investigated ionic additive addition in a large concentration range, morphologies were quantified from SEM images in terms of nanorod length, width, density and calculated volume. X-ray diffraction from thin films was recorded and used in conjunction with sample volume to investigate nanorod alignment. Here alignment is a function of nanorod growth time and KCl concentration; a maximum was observed at [400 mM] KCl in nanorods grown for 120 minutes.

The nanorod formation process is explained through a geometrical selection argument; at low growth times nanorods are isolated, as nanorod length increases interaction between nanorods results in the termination of misaligned nanorods, an increase in nanorod alignment and a reduction in nanorod density. This argument for alignment through growth has recently been described in the literature [25]. The degree to which geometrical selection occurs is dependant on nanorod length, width and growth rate on each plane, which has not previously been observed experimentally. These factors are considered when explaining the highly aligned nanorods observed in samples grown with [400 mM] KCl.

The transition from disordered nuclei to ordered nanorods is an interesting phenomena. Such effects are not often observed in the physical world, where systems are often driven to the lowest energy and highest entropic state. These nanostructures are used in the creation of hybrid photovoltaics devices, data of which is presented in the final results chapter (Chapter 5). The following chapter characterises the morphology of photoactive polymer infiltrated within nanorod arrays.

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Chapter 4

Polymer Infiltration and Morphology

4.1 Introduction

To create h-PV devices from ZnO nanorod arrays, a photo-active polymer must be infiltrated to fill the voids between nanorods and form a two phase composite. This chapter investigates processing requirements for polymer infiltration and the subsequent polymer morphology once infiltration has been completed. Two key aims are apparent for the infiltration of nanorod arrays; a) the formation of an interface between the polymer acceptor and metal oxide donor materials, the interface and physical contact between the two species being necessary for charge transfer from acceptor to donor to occur, and b) the formation of a polymer morphology that allows for high hole mobility within the polymer layer, so as to aid conduction of holes away from the interface and towards the electrode. Variations in polymer crystallinity and orientation, as previously discussed in section 1.2.5, are seen to effect the hole mobility [1, 2] and optical absorption [3, 4] of P3HT thin films. The method of polymer infiltration and resulting polymer morphology is crucial to device performance.

Numerous techniques are available for processing polymer towards the aforementioned aims. These include spin coating, wire bar coating, solid state processing and post processes and have been presented in section 1.2.5.6.

In the first of two sections of work presented in this chapter, the topic of infiltration is investigated (section 4.3). This is completed by comparison of spin coating and solid state processing. Further analysis of infiltrated samples is presented in section 4.4. Here, the ability for polymers to flow into nanostructures is related to

the topic of polymer chain entanglement and polymer viscosity. Data are presented for viscosity of P3HT solutions as a function of molecular weight. Subsequent work investigates polymer crystallite size and orientation using X-ray scattering and diffraction techniques (section 4.4).

4.2 Experimental methods

4.2.1 ZnO growth conditions

Standard bilayer and ZnO nanorod arrays were used in the investigation of polymer morphology. ZnO bilayers were created from a 0.75 M sol gel solution (thickness 130 nm) and spin coated following the procedure described in section 3.2.1. ZnO nanorods were grown following the procedure described in section 3.2.2, the additives 100 mM KCl and 10 mM PEI were included in growth baths to control nanorod morphology. Growth was conducted for 85 minutes to obtain nanorods $\approx$ 500 nm in length.

4.2.2 Polymer deposition

Experimental techniques were presented in section 2; further details pertaining to experiments conducted in this chapter are included below.

For the filling of nanorod arrays presented in section 4.3, poly(3-dodecylthiophene-2,5-diyl) (P3DDT, M_w 60 kg mol⁻¹, Merck) was used. Polymer films were made by spin coating (Spin 150, CPK Industries) using a polymer concentration of 40 mg mL⁻¹ P3DDT in xylene heated to 100 °C and spin coated using a three step program; 200 rpm / 60 s, 1000 rpm / 5 s followed by 200 rpm / 300 s. Additionally films were made from the solid state using a heated press (Rondol Technology). Here, polymer was sandwiched between a nanorod substrate and top glass slide applying heat (190 °C) and pressure (1 kN) so as to melt and thin the film over the substrate. Melt pressing was completed in an air environment for a period of 5 minutes melting and a further 5 minutes pressing the films.

For viscosity measurements, five P3HT samples with number average molecular weights (M_n) in the range 6 – 94 kg mol⁻¹ were used. These samples were characterised by gel permeation chromatography (GPC) and seen to have the following molecular number average, molecular weight average and polydispersity values (Table 4.1).

Table 4.1: Macromolecular parameters of RR-P3HT used in viscosity experiment.

Number average molecular weight (M_n) (kg mol ⁻¹)	Weight average molecular weight (M_w) (kg mol ⁻¹)	Polydispersity (PD)
6.4	12.4	1.9
18.3	31.5	1.7
26.2	47.8	1.8
81.3	208.2	2.6
93.9	347.7	3.7

Subsequent work investigated polymer processing with commercially available P3HT from two batches with molecular weights M_n 29.6 kg mol⁻¹, 46.2 kg mol⁻¹ (Merck) (Table 4.2). These were used without further characterisation. For ease of reading the two polymers are referred to with reference to the M_n as 30 K and 50 K in sections 4.4.2, 4.4.3. In order to examine melting points for P3HT DSC measurements were conducted (Fig. B.1) showing that complete melting occurs at temperatures above 250 °C for both low and high molecular weight P3HT.

Table 4.2: Macromolecular parameters of RR-P3HT used for investigation of polymer films on ZnO planar films and in ZnO nanorods.

Number average molecular weight (M_n) (kg mol ⁻¹)	Weight average molecular weight (M_w) (kg mol ⁻¹)	Polydispersity (PD)
29.6	65.2	2.2
46.2	124.8	2.7

Films were made by spin coating (Chemat Technology KW-4A) from xylene polymer solutions at 100 °C. Unless otherwise stated the solution was left on the substrate for 10 s prior to spin coating at 2000 rpm for 30 s. Polymer film thickness was varied by changing polymer concentration and was examined between 10 - 40 mg mL⁻¹.

4.2.3 X-ray diffraction experiments

For samples examined by small angle X-ray scattering (SAXS) sample tilts ranged from $0.8 - 1^\circ$ in order to maximise scatter from each individual sample. Scattering experiments were conducted for 30 minutes in an evacuated chamber (~ 1 mbar).

XRD experiments carried out under heating and cooling were conducted between $25 - 250^\circ\text{C}$ in order to examine polymer ordering prior to and after melting. In the region $25 - 200^\circ\text{C}$ temperature was increased in steps of 25°C , between $200 - 250^\circ\text{C}$, 10°C steps were used with the motivation to gain increased resolution in the elevated temperature region prior to melting. At each temperature point, scans were run between $3 - 40^\circ 2\theta$ to investigate the P3HT (100) peak (at $\sim 5.5^\circ 2\theta$) and to include the ZnO (002) peak at $34.4^\circ 2\theta$, individual XRD scans took approximately 10 minutes, total annealing run-time for heating and cooling was ≈ 5 hours. To ensure polymer degradation did not occur, thermal annealing was completed in a sealed hot stage with under flowing nitrogen.

4.3 Nanorod infiltration

In this section of work poly(3-dodecylthiophene-2,5-diyl) (P3DDT) is used to investigate the filling of nanorod morphologies. P3DDT has a lower melting point than P3HT ($T_{m,P3DDT} \approx 190^\circ\text{C}$ vs $T_{m,P3HT} \approx 250^\circ\text{C}$), thus enabling melt processing to be completed at a lower temperature.

Three polymer processing methods were investigated; spin coating, spin coating and annealing at T_m for 10 minutes, and melt pressing at T_m . Figure 4.1 shows a difference in the measured thickness of the P3DDT films when deposited by spin coating and spin coating followed by melt annealing. The difference ≈ 200 nm, is attributed to infiltration of the polymer into the nanorod array. Polymer infiltration is also shown to be possible by pressing (Fig. 4.1c). Control of film thickness by melt pressing was difficult, being related closely to the amount of dry polymer placed on the substrate. For spin coated films, thickness values are large ($> 2\ \mu\text{m}$) and due mainly to the prolonged spinning program used. Polymer thickness can easily be controlled in spin coating by varying solution concentration and spin program.

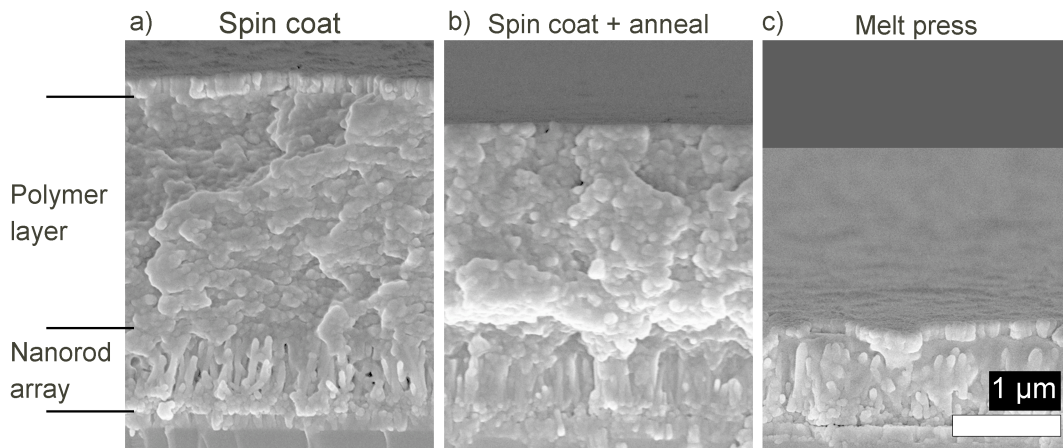


Figure 4.1: Scanning electron micrographs of cross sections for nanorod infiltration by a) spin coating, b) spin coating and annealing, and c) melt pressing. a,c) Show evaporated silver top contacts on top of polymer films owing to the use of these substrates as test cells.

These and other results obtained show the two step process of spin coating and annealing to be the most reproducible method for forming nanorod-polymer composites. Furthermore the possibility of controlling the polymer morphology by thermal annealing is an attractive prospect; for these reasons this method was selected for further infiltration studies.

4.4 P3HT morphology in nanorod arrays

The filling of nanorod arrays is dependent on polymer processing from the liquid phase. The ability for a polymer to flow is closely linked to polymer viscosity and molecular weight (M_n); at a critical molecular weight, $M_{n,E}$ chain entanglement occurs leading to an increase in the viscosity. Work on this topic is presented in section 4.4.1.

In addition to polymer infiltration, the morphology of polymer crystallites within the nanostructure will control the optoelectronic properties of the composite. The extent which polymer crystallites can nucleate and grow are defined by the width, length and density of nanorods. In the experiments conducted in sections 4.4.2 and 4.4.3 nanorod arrays are grown under fixed conditions to allow for the investigation of polymer morphology. Crystallite orientation and grain size within nanorod arrays are investigated and compared to similar polymer layers on planar ZnO thin films. Finally

results are discussed in terms of h-PV devices and the effect of polymer morphology on performance.

4.4.1 Determination of chain entanglement threshold

There are many reports considering polymer viscoelasticity [5], crystallinity [6] and polymer dynamics in solution [7]. The latter topic is of interest when considering the methods by which polymer processing leads to nanorod infiltration. Here, polymer chains must be considered both in a solvated liquid phase (spin coating), then in the melt phase (annealing). The model used to describe chain interactions in both phases is the ‘reptation’ or tube model [8, 9].

This model defines a polymer chain of length N , the polymer chain is surrounded by a theoretical tube of radius a , which constrains the contour of the chain. The radius of tube, a , is sufficiently small to strongly constrain only polymers with high chain lengths. These polymers are termed as having chain lengths or molecular weights above the entanglement chain length (N_E) or entanglement molecular weight ($M_{n,E}$). Either side of this value polymer properties are vastly different, of specific importance are changes in hole mobility [10, 11] and polymer morphology [1, 12]. Polymer viscosity also varies as a function of molecular weight, at low chain lengths ($M_n < M_{n,E}$) a linear relationships holds, whereas at higher chain lengths ($M_n > M_{n,E}$) viscosity values increase as a power law, where M_n is raised to the index b [13].

$$\eta \propto \begin{cases} M & M_n < M_{n,E} \\ M^b & M_n > M_{n,E} \end{cases} \quad (4.1)$$

In the tube model, the movement of polymer chains in solution and melt phase are considered as free chains whereby groups of monomer units are free to rotate around the polymer backbone. In P3HT, chains segments are linear [14] and due to the synthesis and chemical structure are assumed to lack cross linking or back biting that might complicate viscosity measurements.

Figure 4.2 shows the specific viscosity for P3HT samples with molecular average number weights in the range 6 – 94 kg mol⁻¹. Standard deviation for each sample from the measurement of solution flow time, t , and solvent, t_0 , is included in the displayed error bars. These are small due to the good repeatability of the experimental procedure in the samples shown. On increasing M_n a rapid change in viscosity is observed. This is displayed by plotting the log of molecular weight; two linear regions are observed corresponding to free chains in solution at low molecular weights and

chain entanglement leading to increased viscosity at high molecular weights. The entanglement threshold ($M_{n,E}$) for P3HT measurement by this method was estimated to be around 48 kg mol⁻¹.

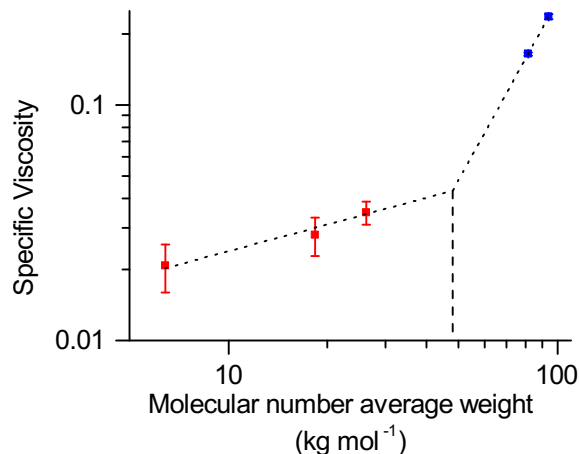


Figure 4.2: Specific viscosity for P3HT with molecular average number weight in the range 6 – 94 kg mol⁻¹. Dotted lines show trend in viscosity and dashed line entanglement threshold ($M_{n,E}$).

No error value has yet been attached to that of $M_{n,E}$ found above by the suspended capillary method. The calculation of error for $M_{n,E}$ is more difficult than application of experimental error resulting from variations in polymer flow time. In the first instance, the independent variable, M_n , calculated here by GPC measurements may have significant undertermined error. GPC measurements are completed by measurement of the elution time for a specific polymer and calibration of known molecular weights to flow times. Typical calibration curves are formed from characterisation of the column with polystyrene of known M_n . P3HT conformation and ordering in solution, however, are different from that of polystyrene; due to regular ordering of side chains RR-P3HT macromolecules organise in a variety of rod-like to helical conformations dependent on the anti-syn orientation of monomers units [14]. Thus, the flow dynamics of P3HT coils within the pores of a GPC column are within a different regime than those for polystyrene; experimental work by Holdcroft estimates that GPC overestimates regiorandom-P3HT M_n by a factor of 1.8 – 2.0 [15], which may distort the calculation of $M_{n,E}$.

Another topic to consider in polymer based experiments is the variation in polymer chain length within a sample. This is termed the polydispersity (PD) and easily calculated by the division of molecular number and molecular weight averages

(M_w/M_n). Values of PD for the samples used are shown in table 4.1 and range from 1.7 – 3.7, these are typical of those in the literature for P3HT samples [12]. PD values are often misleading; while a higher polydispersity implies a wider molecular weight distribution, a wide molecular weight distribution may not necessary be characterised by high PD values due to the different weightings of narrow or diffuse molecular distributions [16]. High PD values may skew results owing to partial entanglement effecting flow times.

The overestimation of P3HT by M_n does not present a problem for comparison between different samples, providing that P3HT polymer samples are compared relatively and M_n determined by similar polystyrene calibrated GPC measurements. Although, it may along with uncertainty in PD, explain in part why viscosities for longer chain lengths in figure 4.2 fail to conform with equation 4.1., whereby accumulated data from a variety of polymer samples has shown empirically that $b = 3.4$ [13]. For P3HT samples examined here, a value of 2.5 is observed.

In summary, discerning $M_{n,E}$ of P3HT is a complex problem, closely linked with experimental inaccuracies in measurement of M_n and the dispersion of molecular weights in a particular sample. The data presented are the best possible with regards to P3HT samples available and show clear dependence of viscosity with molecular weight.

Interestingly, no value for P3HT entanglement threshold has been proposed in the literature. Others have reported molecular weight dependence on hole mobility and this gives some indication of chain entanglement, which leads to increased mobility through interaction of longer chains within the material. Collated hole mobilities are reported in ref. [17]; values are seen to plateau at $M_n \approx 30 \text{ kg mol}^{-1}$, in some agreement with the $M_{n,E}$ value found here by viscometry.

The entanglement of polymer chains and resulting variation in polymer properties stems from polymer morphology of chain extended ($M \leq M_{n,E}$) and folded conformations ($M \geq M_{n,E}$). In the next sections (4.4.2, 4.4.3) two commercially available P3HT samples are used to investigate the polymer crystallite properties on ZnO planar and nanorod films. P3HT samples used in this work were chosen to investigate one sample below and one in the region of the entanglement threshold.

4.4.2 Small angle X-ray scattering

In preparation of samples for SAXS and XRD experiments, it was important to tailor the thickness of polymer films such that, on annealing, nanorods were completely filled

without an additional polymer surface layer. In doing so scattering and diffraction signals were able to be related directly to the polymer within nanorod structures and not from any additional polymer present in a capping layer.

A P3HT concentration of 40 mg mL^{-1} P3HT (M_n 30 K) was used to fill ZnO nanorod arrays with lengths $\approx 500 \text{ nm}$. A thin film on glass made from the same concentration had a measured thickness of 180 nm . A polymer volume fraction of 0.36 can be estimated from the difference in film heights of the two materials, while this gives no information of surface area it does give insight to polymer loading and pore volume.

The dependence of film thickness on solution concentration was investigated in the range $10 - 40 \text{ mg mL}^{-1}$ (Fig. B.2). The high molecular weight sample (M_n 50 K) for the same concentrations produced thicker films likely due to increased entanglement and viscosity during the spin coating process. To obtain a film thickness of 180 nm , 29.5 mg mL^{-1} was used on planar ZnO and for polymer infiltration (M_n 50 K). Using polymer films of the same thickness coated on planar substrates and nanorod arrays gave a comparison between nanorod and bilayer data. Uncoated nanorods and the various degrees of coating are shown in figure 4.3.

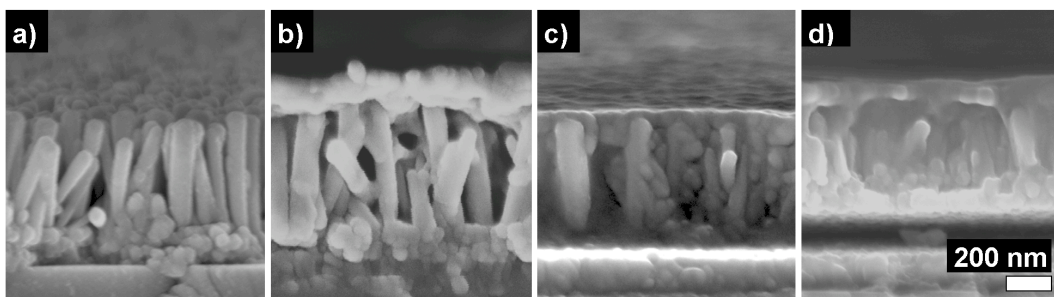


Figure 4.3: Cross sectional scanning electron micrographs showing ZnO nanorods a) as prepared, b) coated without anneal (M_n 50 K) c) coated with anneal (M_n 30 K) d) coated with anneal (M_n 50 K)

SAXS was used to investigate the orientation of P3HT crystallites for polymer on planar ZnO films and for polymer infiltrated into ZnO nanorod arrays. Data were collected on film which was subsequently developed. Complete scattering patterns for all films are included in the appendix (Fig. B.3 and B.4), a typical scattering pattern is shown in figure 4.4. Dark bands are formed on the film due to exposure from X-rays that have been scattered by the sample. The central spot is from the primary beam and observed at the bottom of the film. Above this there are two exposed areas resulting from X-ray scatter and reflection from the sample surface. Here, spots not

lines are present because the system was configured in point mode with the primary beam narrowed to a small incident point that interacts with the sample.

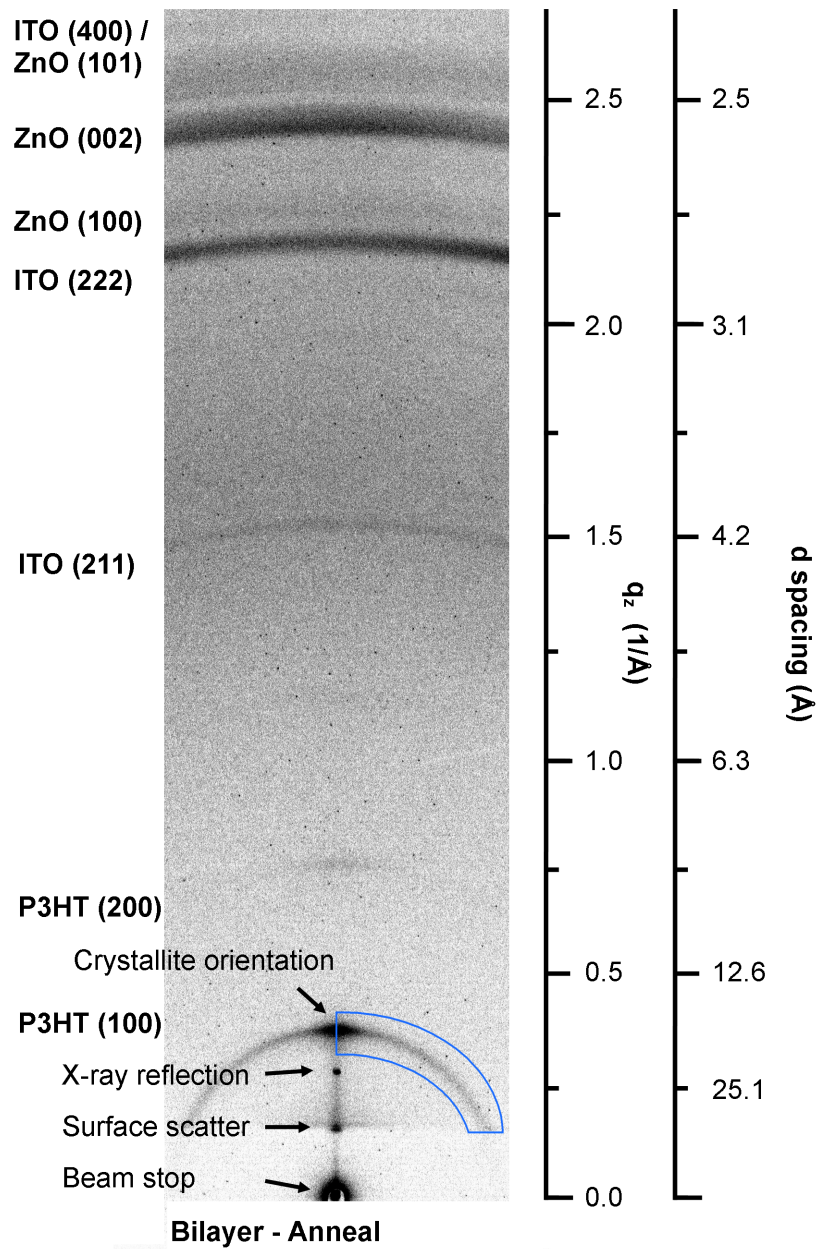


Figure 4.4: SAXS pattern for P3HT (30 K) on planar ZnO, showing characteristic scattering arcs for ZnO:P3HT samples. Labelled on the pattern are points of high scattering intensity resulting from direct transmission, surface and reflection from the surface and P3HT crystallite orientation perpendicular to the substrate. The blue box overlaid on the pattern shows the boundaries of integration for quantifying crystallite orientation from the P3HT (100) plane. Other peaks labelled for material and Miller indices, d-spacing calculated from equation 2.6.

Results are reported in terms of d-spacing and also the reciprocal vector q , the two being linked by equation 2.6. At higher q values and small d-spacings broad arcs are observed due to scattering from the individual sets of crystalline planes. The majority of arcs are broad and of uniform intensity indicating a uniform distribution of crystals in each direction. In this work, scattering that occurs from polymer chains is of interest and can be observed in the first arc present in figure 4.4, which corresponds to an interchain distance ~ 16 Å. This spacing is from the P3HT interchain distance in the [100] direction [18]. Planes formed from packing between thiophene rings (the [010] direction) are not observed in the vertical, q_z , direction of these scans due to the relatively low incidence of these peaks in this direction, it was also not possible to observe the (010) scattering peak in the horizontal q_y direction due to the small q distance on the detector in this direction. For this reason, the (100) plane was used in this work to quantify crystallite orientation of polymers on ZnO bilayers and within ZnO nanorod arrays.

Crystallite orientation can be observed by increases in intensity at points around the arc, this can be quantified by integrating the area around the arc to measure the degree of scattering as a function of angle. The boundaries of an integral are shown in the blue box in figure 4.4. Integrals have only been calculated from $0 - 90^\circ$ because scattering is symmetrical around the mid-point of the film.

Figure 4.5 shows the complete SAXS data set for the scattering arc from the P3HT (100) plane. For pristine polymer films on planar substrates (Fig. 4.5a,e) the P3HT arc is diffuse with the majority of scattering in the out-of-plane [100] direction. After annealing (Fig. 4.5 b,f) the arc becomes narrower; indicating increased uniformity in the distance between polymer chains, due to improvements in polymer crystallinity. For both molecular weights intensity is at a maximum perpendicular to the substrate, showing that the majority of crystallite (100) planes are orientated in this direction. While this is the preferred orientation for P3HT [10, 11], it is also worth noting that intensity at all points along the arc are increased, showing that many crystallites have an orientation between the vertical and horizontal; this will be termed mixed orientation.

For pristine polymer on nanorod films a larger degree of mixed orientation is observed than for on bilayers samples. This is due to the disruption of the crystalline packing of polymer chains when films are formed from spin coating and also indicates some degree of infiltration of polymer within the nanorod array prior to annealing, in agreement with scanning electron micrographs (Fig. 4.3b). For annealed polymer films on nanorod substrates a reduction in band-width similar to that of polymer films

on planar substrates is observed (Fig 4.5c,g-d,h). It is likely, however, that overall there is more amorphous content in polymers within nanorod arrays as the nanorod morphology will hinder crystallisation. Polymer orientation within nanorod arrays is seen to have less out-of-plane character with only a small increase in intensity observed perpendicular to the substrate for the 30 K P3HT and a completely mixed orientation for molecular weight 50 K. This gives some comparison for different molecular weight samples within nanorod structures. Polymer chains in the extended case (30 K) may crystallise in their preferred (out-of-plane) orientation, whereas longer entangled chains (50 K) are hindered in their crystallisation and adopt a mixed orientation within the nanorod structure.

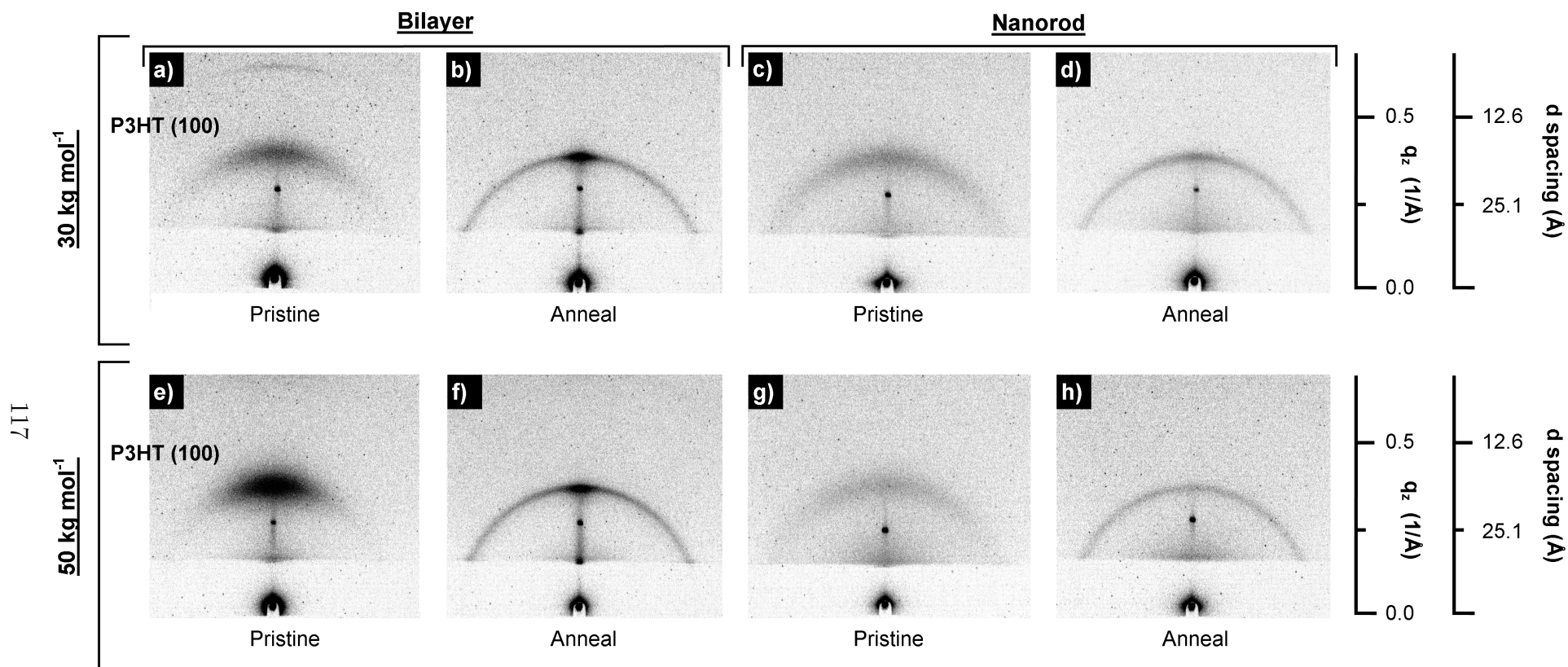


Figure 4.5: SAXS patterns for P3HT of two molecular weights (60 kg mol⁻¹ (a-d), 120 kg mol⁻¹ (e-h)) for polymer films on planar sol-gel ZnO and ZnO nanorod substrates. Polymer films are examine after spin coating with no further treatment (pristine) or after a slow heating and cooling program (anneal) as described in section 4.2.3.

The position of scattering peaks in the q_y and q_z directions are easily compared in figure 4.5. However, due to differences in sample tilt and height which has been varied to improve scattering between samples, the exact peak intensity of individual arcs are not directly comparable between scans. SAXS by this method is not quantitative as it was not possible to count scattered X-rays. Normalising for contrast allows for further analysis and a fair comparison between scans. Scattering arcs are integrated over the area encompassing half of the arc (as shown in Fig. 4.4) to give information on the relative intensity of scattering as a function of angle. Data from these integrations are plotted as normalised intensity against azimuthal angle in figure 4.6.

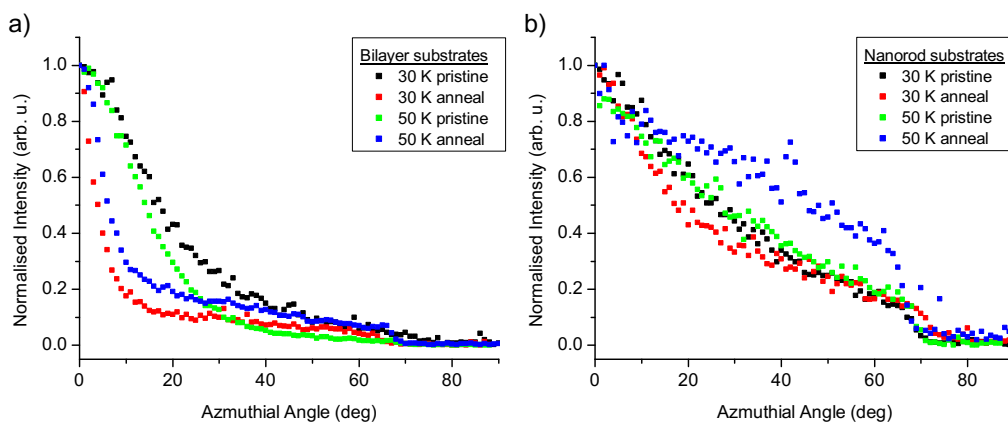


Figure 4.6: Plots showing distribution of crystallites as a function of azimuthal angle for polymer films on a) bilayer and b) nanorod substrates. Data from integration of half P3HT (100) scattering arcs (illustrated in Fig. 4.4).

For polymers on planar and nanorod substrates polymer crystallite orientation is seen to be perpendicular to the substrate, shown in these plots as a maxima at 0° . The distribution of crystallites is shown by comparing how the plots tail to zero at higher angles. For planar substrates curves rapidly reduce to zero showing that the majority of crystallites are in the out-of-plane orientation, scattering intensity from these crystals is seen to increase with annealing, resulting in highly orientated crystalline films. This trend is not observed for polymer films on nanorod substrates, where a higher degree of mixed orientation is observed on annealing. While there is an increase in crystallinity (as seen from the reduced arc width in Fig. 4.5), there is little change in the orientation between pristine and annealed samples. In the planar study, P3HT on ZnO planar layers are seen to orientate with a strong in plane character. Nanorod arrays provide a template for this orientation in 2-dimensions allowing for

both in-plane orientation to the seed layer and in plane orientation to the nanorod walls. This may result in a higher degree of mixed orientation in nanorod samples.

As described above, SAXS can only give qualitative information on the degree of polymer crystallinity. Investigation of crystallite size will enable a more complete understanding of the polymer behaviour within nanorod arrays. This is studied by temperature resolved X-ray diffraction in the subsequent section.

4.4.3 Temperature resolved X-ray diffraction

Figure 4.7 shows diffraction from a ZnO:P3HT bilayer (130 nm ZnO, 173 nm P3HT) on ITO. Two distinct 2θ regions are present from diffraction data. The first, at low angles, $< 20^\circ 2\theta$, correspond to diffraction from the large P3HT inter-chain distances. Diffraction from ZnO and ITO substrate corresponds to atomic spacings in these crystals and is observed at high angles, $> 20^\circ 2\theta$.

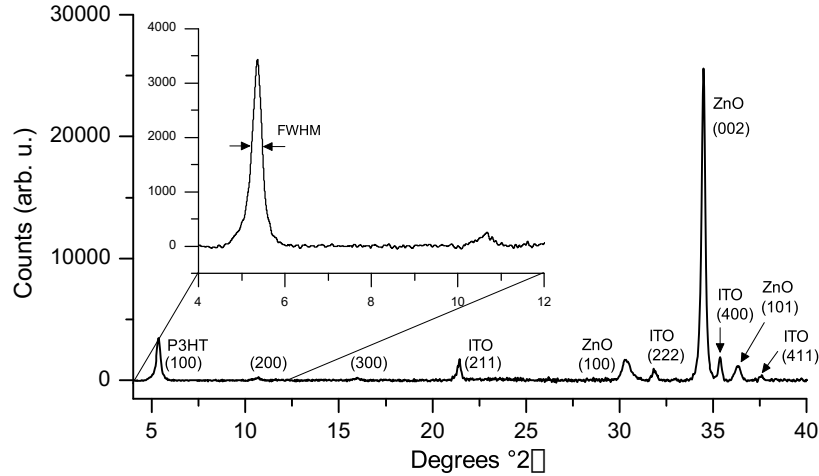


Figure 4.7: XRD of ZnO:P3HT bilayer (130 nm:173nm M_n 30 K), inter-chain P3HT peaks present at low angles ($3 - 20^\circ 2\theta$), ZnO and ITO peaks are present at higher angles ($20 - 40^\circ 2\theta$). Inset shows FWHM of P3HT (100) peak used here to estimate crystallite size.

The aim of this study was to examine crystallite growth on heating, polymer infiltration into nanorod arrays near melting and crystallisation once infiltration had occurred. Large angular ranges ($3 - 40^\circ 2\theta$) allowed change in both materials to be studied, however, no significant change in the ZnO/ITO peaks were anticipated at these low temperatures. Diffraction data showing heating and cooling of a bilayer ZnO:P3HT (M_n 30 K) sample is presented in figure 4.8a, data has been formatted

into contour plots (Fig. 4.8b,c) to show the variation in the P3HT (100) and ZnO (002) peak position and intensity as a function of heating. On heating, the polymer peaks are seen to move to lower angles as thermal energy increases inter-chain spacing. Polymer chains are mobile close to T_m – peak intensity increases as the material seeks an energetically favourable, crystalline morphology. Similar analysis is shown for the ZnO (002) peak (Fig 4.8c) and as expected little variation in peak parameters is observed over the heating range.

Consistent with SAXS experiments described in the previous section, annealing experiments were conducted on planar and nanorod substrates with thin polymer films of two molecular weights (M_n 30 K and 50 K). To manage the large data sets created by XRD experiments a batch processing script presented in section B.4 was written for HighScore Plus. In validating this procedure it was found that there were significant differences between the curve fitting algorithm in HighScore Plus and alternative program, Data Viewer, as such data were fitted manually in Data Viewer.

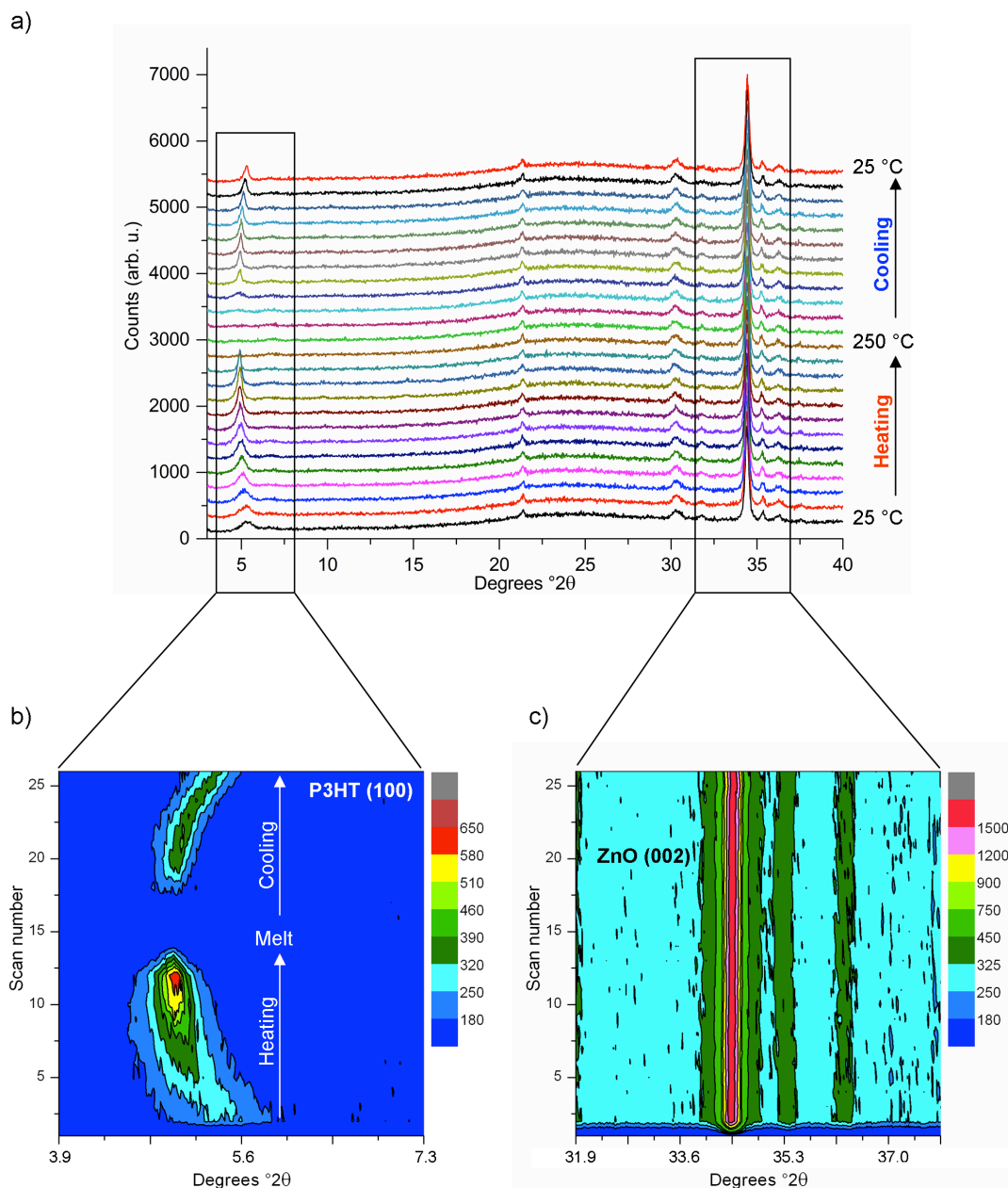


Figure 4.8: a) Diffraction patterns for a ZnO:P3HT (M_n 30 K) bilayer on heating and cooling, in total 25 patterns are shown. b,c) Contour plots showing the variation in the P3HT (100) and ZnO (002) peak during the heating cycle. Colour scale bars refer to X-ray counts.

Polymer crystallite size is approximated by applying the Scherrer equation from the FWHM of the P3HT (100) peak (Fig. 4.7 inset). To provide an accurate estimation, the paracrystallinity of the films should be calculated [19]. Calculation

of paracrystallinity is possible by determining the deviation in d-spacing within the material at higher order reflections, the variation of d_{norm} to $d_{observed}$ will give the apparent disorder within the crystal [20]. Unfortunately, achieving higher order diffraction peaks (P3HT ($h00$), where $h = 2, 3$), was not possible in this experiment. Three inter-related factors hinder the detection of these peaks; low film thickness, reduced polymer crystallite orientation (especially in nanorod samples) and low X-ray intensity, resulting from relatively quick XRD scans on laboratory based diffractometers. For determination of paracrystallinity synchrotron sources are often used [19].

It has previously been reported that P3HT (M_n 20.1 kg mol⁻¹, PD 1.7) has a paracrystallinity of 5 %, which results in 14.5 % reduction in the calculated grain size measurement than from Sherrer alone [21]. Due to the inability to study polymer paracrystallinity with lab based X-ray techniques, grain sizes shown in figure 4.9 have been adjusted by -14.5 % to account for the estimated paracrystallinity of P3HT.

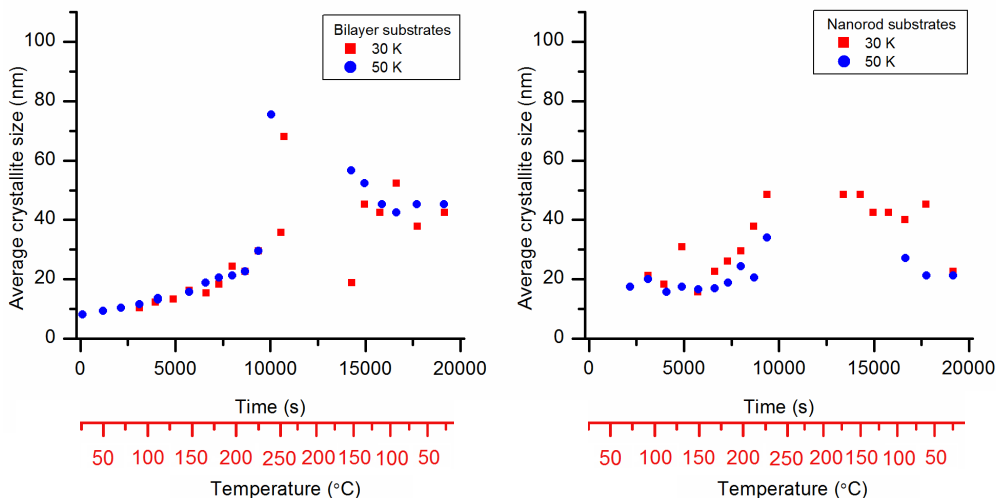


Figure 4.9: Plots showing polymer crystallite size from FWHM of XRD data as a function of temperature. Data for polymer thin films on a) planar and b) nanorod substrates are shown.

Temperature resolved X-ray diffraction (Fig. 4.9) shows the slow heating of thin polymer films through the liquid phase and then subsequent polymer re-crystallitation on cooling. For both molecular weights as temperature is increased crystallite size is seen to increase, this effect is due in part to some polymer chains becoming more ordered, although perhaps a more prominent effect is due to the melting of small crystallites. As the temperature approaches the melting range of the polymer these

are the first to melt and no longer dominate the XRD signal. At higher temperatures diffraction arises solely from large crystallites within the film. The opposite process occurs for polymer films as they cool. Diffraction is initially observed from larger crystallites and with a greater degree of under cooling many more crystallites nucleate, however, crystallite growth is now hindered by the previous crystallites present in the film. The later formed crystallites are smaller and being more numerous, dominate the X-ray signal leading to an increase in FWHM and reduction in measured crystallite size.

This technique is able to give some information on the range on crystallite sizes within a polymer film. In the case of P3HT on planar films crystallites vary from 10 – 80 nm with little difference observed between molecular weights. On annealing the average crystallite size is seen to increase in size and reduce in range between 50 – 70 nm. Polymer films on nanorod substrates prior to melting are seen to have a smaller distribution, in the range 20 – 60 nm. On cooling from the melt, the 30 K polymer were observed to have a grain size range of 50 – 60 nm and polymer with molecular weight 50 K a grain size range of 20 - 30 nm. A significant delay between melting and the formation of polymer peaks for 50 K polymer in nanorod films was observed; indicating that a large driving force is necessary to nucleate crystallite growth for high chain length polymers. A similar effect is observed in DSC data (Fig. B.1) where the crystallisation peak for the high molecular weight is apparent at lower temperature. Based on the XRD data, the grain sizes for polymers in nanorod arrays is seen to be slightly smaller than on planar films; this is perhaps due to the nanorods confining grain growth to a certain size.

In-situ XRD for polymer samples is useful for the ability to observe microscopic variations in crystallite size during heating. The experiment conducted show the variation in bilayer and nanorod samples leading to useful comparative information between the two substrates. It should be noted that the calculation of grain size has prominent errors for experiments on laboratory based X-ray sources. The main difficulty is the determination of FWHM from low intensity diffraction peaks. This is due to both nature of polymer samples (semi-crystalline) and due to both the relatively short time period used for $^{\circ}2\theta$ scans and the low intensity of X-rays used. Integrated peak intensities observed for polymer samples were in the hundreds of counts, in contrast intensities for ZnO samples, examined in chapter 3 were observed to yield intensities a hundred or more times greater. Low signal increases uncertainty in peak fitting leading to higher uncertainty in estimated grain size.

An absolute limitation of using XRD is that it examines the crystallite portion of the film and of this only the out-of-plane crystallites contribute to diffraction. Earlier SAXS data showed that P3HT crystallites tend to orientate out-of-plane, which is useful for this characterisation, however, there may be a significant amount of crystallites in the sample that do not contribute to XRD signal. Lastly the amorphous content of the film must be considered. Temperature resolved experiments are able to estimate crystallite sizes but overall calculation of film crystallinity is lacking. From the data, it is clear that polymer within nanorod arrays had a lower (100) peak intensity but this can be attributed to either out-of-plane crystallites or higher amorphous content.

This work can be directly applied to that completed in ref. [22], whereby the effect of melt annealing treatment is considered in the performance of h-PV (ZnO:P3HT) devices. The authors show that melt annealing does little to effect bilayer performance and if completed for 1 minute annealing can increase nanorod devices performance, however at longer time periods heating is observed to degrade performance. While no details of P3HT (M_n , PD) are presented; it is likely the work uses low molecular weight polymers where $M_n \ll M_{n,E}$. The authors propose that polymer reorientation occurs and show reduced hole mobilities within annealed composite structures. The reorientation on heating is directly observed in this work (Fig. 4.2.3) and indeed is likely to hinder conductivity in the vertical direction, due to alkyl chain stacking. For larger molecular weight polymers, however, such defined reorientation is not observed despite the good filling of nanorods. It can be thought that polymers with higher molecular weights, where $M_n \geq M_{n,E}$ can improve conduction in nanorod arrays due to a higher mixed orientation that allows for increased interaction between crystallites. The difference between these melt annealed polymer morphologies can be considered as the difference between polymer lamellae with growth direction parallel to pore axis and those with crystallite growth that impinges on pore walls, as shown schematically in figure 1.11 (section 1.2.6.2).

4.4.4 Conclusions

The viscosity of P3HT in solution was studied and the chain entanglement threshold estimated to be around 48 kg mol^{-1} ($M_{n,E}$). The orientation, crystallite size and effect of melt annealing has been investigated for two P3HT samples, made as films on planar ZnO layers and ZnO nanorod arrays. On annealing, polymer films on planar substrates have a predominately out-of-plane orientation with crystallites aligning

perpendicular to the substrate. Polymer films on nanorod substrates are seen to have a larger mixed orientation. The crystallite size of these films is dependent on molecular weight; extended chains ($M_n < M_{n,E}$) within nanorod arrays are able to form crystallites of similar dimensions to those in planar films (≈ 50 nm), while entangled chains of higher molecular weights ($M_n \approx M_{n,E}$) cannot obtain the same conformation in nanorod arrays (≈ 25 nm).

The errors of investigating polymer morphology by these methods as well as the applicability of this work to that completed in the literature has been discussed. Of particular importance is how these results can give insight into the working of h-PV devices and allow for device performance to be enhanced through optimised polymer processing.

4.5 Summary

Significant work was completed on polymer morphology within ZnO nanostructured films. Filling was possible by spin coating and annealing, importantly void spaces were not observed within nanorod arrays – this being attributed to increased nanorod alignment from previous work. P3HT viscosity was measured and used to determine the chain entanglement threshold. Two P3HT samples, having nominally extended and entangled chains, were used to examine the polymer morphology on ZnO bilayers and within nanorod arrays. From characterisation by SAXS and XRD methods the orientation and polymer crystallite size were found. These differed between planar and nanostructured substrates and between the two molecular weights investigated. Polymers within nanostructures had reduction of crystallite sizes and an increased mixed orientation was observed. While both molecular weights had similar crystallite sizes on planar substrates, the higher molecular weight polymer had both a reduced crystallite size within the nanorod array and less re-orientation after annealing in the melt. This may prove to be advantageous; increasing the hole conduction pathway out of nanorod pores.

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Chapter 5

Device Measurements

5.1 Introduction

The study of hybrid photovoltaic devices formed from ZnO and P3HT is presented in this chapter. Results are divided into two sections, concerning planar bilayer devices (section 5.3) and devices created from nanorod substrates (section 5.4). In each section polymer processing conditions are investigated, specifically the effect of annealing and the effect of molecular weight on device performance.

5.2 Experimental methods

5.2.1 Device formation

Devices were made in the configuration ITO/ZnO/P3HT/Ag as shown schematically in figure 5.1. Here ITO, functions as an anode and the metal top contact as the cathode, the so-called inverse architecture. ZnO and P3HT deposition was completed as previously described (sections 3.2, 4.2).

Nanorod growth was completed with additives 10 mM PEI and 100 mM KCl to control nanorod width and alignment, respectively. Growth was conducted for a period of 85 minutes resulting in nanorods of ≈ 500 nm in length. At the end of growth nanorods were washed in distilled water and dried at 95 °C. Prior to polymer deposition nanorod substrates were heated at 150 °C for 5 minutes to remove surface adsorbed water.

The same P3HT samples used in previous work (section 4.4) are applied to device studies. Macromolecular parameters are presented in section 4.2. In keeping with previous work the two molecular weights (M_n) used are termed 30 K and 50 K.

Polymer annealing was conducted on a hot plate (VWR) in a sealed container with flowing nitrogen, or for latter work (section 5.4.2) in a glove box using a programmable hot plate (Dataplate PMC 730 series). Silver contacts were evaporated (Emitech K975X) through a shadow mask to create three contacts each with an area of 0.08 cm^2 . To enhance electrical contact between the device and sample holder silver paint was applied on the edge of evaporated contacts. Contact to ITO was made by removing the polymer with a scalpel and ZnO with concentrated sodium hydroxide. Silver paint was also used to provide a good electrical contact to ITO.

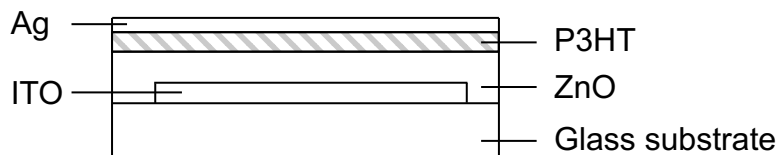


Figure 5.1: Schematic diagram of device layers.

5.2.2 Solar cell testing

Device performance is examined on a commercial system (Newport Solar Simulator 91159) which replicates solar irradiance and spectrum. Collimated light from a xenon arc source passes through a filter to approximate the air mass 1.5G (AM1.5G) spectral standard [1]. A calibrated silicon photodiode is used to measure light intensity at the sample plane and the load on the bulb is adjusted to produce 100 mW cm^{-2} (1 sun) in line with the standard for photovoltaic testing as described in American Society for Testing and Materials E927 (ASTM E927) [2].

Devices were tested in the range 0.5 V to -0.5 V (Keithley 2420 SourceMeter, Measure IV v2.04). As appropriate for devices with inverse architectures, current density-voltage (J-V) curves are presented in the inverse, and tested to reach diode breakdown in the third quadrant of the J-V curve, as shown in figure 1.13b. From the measured J-V curves values for short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (η) are calculated. All devices are stored and tested in air.

To ensure ageing effects [3] did not influence device efficiency, unless otherwise stated, all devices were tested within 24 hours of the deposition of polymer layers. Devices were made and tested in sets which causes some variation in devices age between sets.

In general, each plotted point results from the measurement of two samples, each with three contacts making a total of six J-V curves per point. Results are presented with accompanying standard deviation errors.

5.3 Bilayer devices

Investigation of bilayer h-PV devices is presented in this section. Layer thickness is of interest and is characterised by the absorption of P3HT layers and effect on device performance.

5.3.1 P3HT absorption

Absorption curves of P3HT on ZnO layers are shown in figure 5.2. The absorption of ZnO is in the region ~ 360 nm, consistent with a band gap of 3.25 eV as shown in section 3.4.1.3. The absorption spectra of P3HT has a band onset at ~ 450 nm and extends to 650 nm. Of the three peaks discussed in ref. [4], only two can be distinguished here; the 0-0 transition (520 nm) and 0-1 transition (560 nm) appear in almost equal measure giving a flat peak in the range 520 – 560 nm. The π - π^* transition at 620 nm is observed to be well defined here and although not an absolute measurement of crystallinity shows the close proximity of polymer chains.

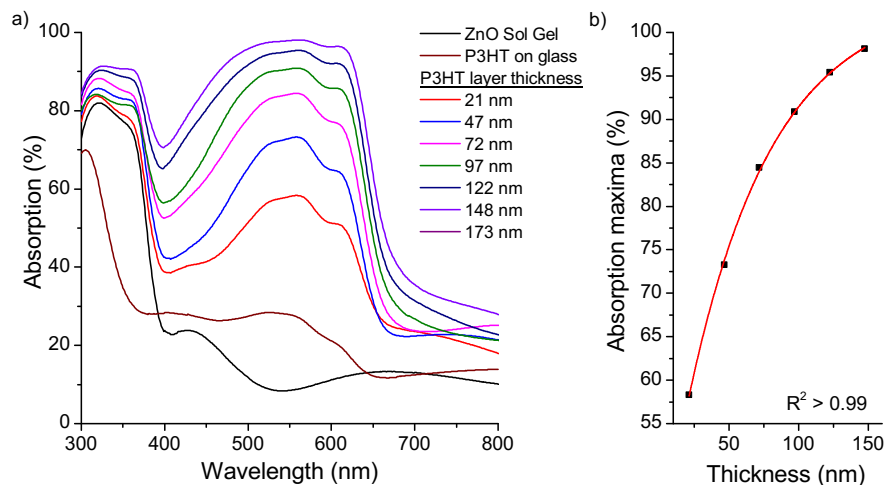


Figure 5.2: a) UV-Vis absorption spectra for varying thickness of P3HT on ZnO sol-gel thin films. ZnO layer on glass (130 nm) and P3HT layer on glass (10 nm) are shown as a comparison. b) Absorption maxima at 560 nm against P3HT thickness; an exponential curve is fitted.

Increasing P3HT thickness increases absorption (Fig. 5.2), until at the highest thickness measured, 173 nm, all optical transitions are saturated leading to an absorption of nearly all incident photons in the region 500 – 650 nm.

The correlation between absorption maxima and film thickness is shown in figure 5.2b and can be fitted with an exponential function, consistent with the Beer-Lambert law (Eqn. 2.8). An R^2 value of < 0.99 is found, indicating a good fit between these parameters.

5.3.2 Layer thickness studies

ZnO layer thickness was investigated in the range 20 – 130 nm, corresponding to sol-gel concentration of 0.1, 0.2, 0.3 and 0.75 M (3 coats). At low thickness values (< 50 nm) there was no photovoltaic response due to short circuits between the anode and cathode. This suggests that dense continuous ZnO films are not formed at low thickness values. While thinner layers may be preferable in order to reduce series resistance in the device, the use of thin layers created by this method are not suitable. In this research, a sol-gel concentration of 0.75 M (130 nm) was used.

The effect of polymer thickness was investigated using M_n 30 K P3HT with data from J-V curves being shown in figure 5.3. The data are divided into four graphs showing the effect of thickness on J_{SC} , V_{OC} , FF and η (Fig. 5.3a-d respectively). The decay of J_{SC} and increase in V_{OC} with film thickness can be observed. J_{SC} decreases due to charge collection only being possible in the region of the ZnO:P3HT interface. As film thickness increases the effect of reflection from the back metallic contact is less pronounced, more excitons are created in the bulk and fewer in the region of the interface. This double absorption pathway is completely lost at thickness values > 75 nm with J_{SC} reducing to half the initial value, showing only charge generation from the incident light.

Increase in thickness and the resulting improvement in V_{OC} are attributed to a reduction in charge loss pathways allowing for a higher potential between the top and bottom contacts. In this case shunt resistance is increased, a thicker layer leads to lower parasitic losses through film pinholes effects and series resistance decreased owing to increased polymer ordering in the bulk polymer films aiding charge transfer [5, 6].

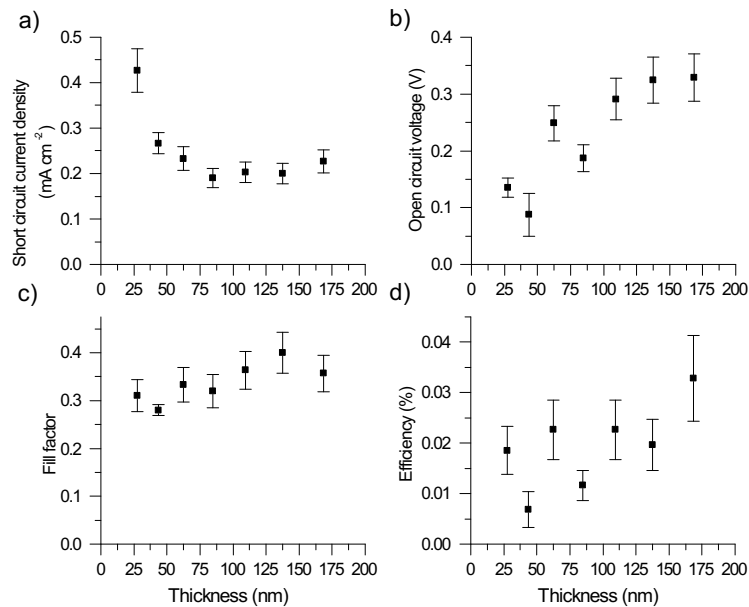


Figure 5.3: Bilayer device performance as a function of P3HT thickness (21 – 173 nm, M_n 30 K). Data from J-V curves are shown for a) short circuit current density, b) open circuit voltage, c) fill factor and d) efficiency. Error bars show standard deviation.

Overall efficiency values are comparable to those reported for bilayer devices in the literature. Interestingly, thickness values found for the best comparable literature devices (P3HT 50 nm, ZnO 45 nm) [7] differ greatly from the those found here (P3HT 175 nm: ZnO 130 nm). While there is indeed increased absorption in thicker films (75 % at 50 nm and near 100 % at 173 nm for the peak at 560 nm), it is only absorption in the interfacial region that contributes to charge generation. Here, the increase in layer thickness results in increased efficiency.

5.3.3 Polymer processing conditions

The previous study investigated films and devices with P3HT layers that were deposited without further processing. Melt annealing, as previously discussed, is of interest for nanorod films (chapter 4) as the study of polymer annealing on bilayers provides a comparison between the effect of polymer processing conditions on planar and nanostructured thin films.

Films were annealed at 250 °C for 0, 30, 60, 180 and 300 s and results are again plotted as J_{SC} , V_{OC} , FF and η (Fig. 5.4a-d). Unlike previous bilayer devices (section 5.3.2) those in this study were subject to a post process heat treatment (150 °C, 20

minutes) to allow for alkyl chain motion, which improves polymer morphology [8]. An increase in J_{SC} is seen with melting time - this is likely due to the polymer forming a closer contact with the inorganic and is especially valid if the surface is considered to be rough and have some degree of porosity.

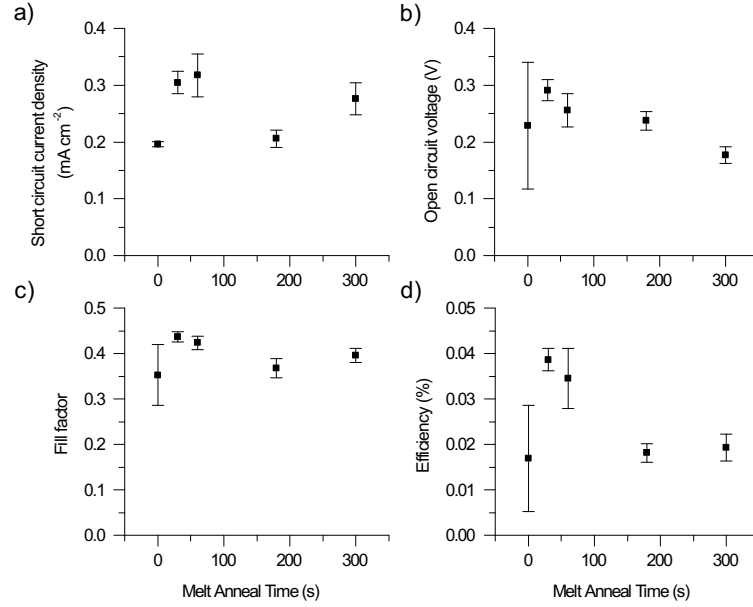


Figure 5.4: Bilayer device performance as a function of melt annealing time (0 – 300 s, M_n 30 K, film thickness 173 nm) Data from J-V curves are shown for a) short circuit current density, b) open circuit voltage, c) fill factor and d) efficiency. Error bars show standard deviation.

The decrease in V_{OC} with annealing is evident. Given that layer thickness and architecture of these devices is constant, the explanation of variation in photovoltaic performance is attributed to the morphology and electrical properties of the active layer. The series resistance was calculated from the resistive component of J-V scans conducted in the dark (linear positive x-axis region, Fig. C.2), the results of which are shown in table 5.1. Here, as series resistance increases V_{OC} decreases; characteristic of the loss in energy when moving charge through a more resistive annealed film.

$$J_{dark} = J_0(e^{qV/k_bT} - 1) \quad (5.1)$$

$$V_{OC} = \frac{k_bT}{q} \ln \left(\frac{J_{SC}}{J_0} + 1 \right) \quad (5.2)$$

Table 5.1: Device data for best performing bilayers in melt annealing study. Table shows correlation between open circuit voltage and series resistance.

Melt annealing time (s)	Open circuit voltage (V)	Series Resistance (Ω)
0	0.35	161
30	0.29	678
60	0.28	603
180	0.22	478
300	0.19	648

V_{OC} can be further discussed in terms of the relationship between an ideal diode (Eqn. 5.1) and the creation of photovoltage (Eqn. 5.2) [9]. The diode characteristics of the dark current J_{dark} are a function of applied voltage (V), charge on an electron (q), Boltzmann’s constant (k_b), temperature in kelvin (T) and J_0 , a constant linked to the barrier for charge injection [10]. The photovoltage results from the amount of photocharge generated, J_{SC} , divided by the ability for charge to be collected, J_0 . In this case, an increase in J_{SC} , is outweighed by the increase in J_0 resulting in an overall reduction in V_{OC} .

Lastly, reductions in V_{OC} have also been linked to interfacial recombination. The application of a thin TiO_2 layers in h-PV devices has been reported to increase V_{OC} from 0.2 to 0.5 V [12]. While a good interface between donor and acceptor is preferable in terms of J_{SC} , recombination is increased due to the increased proximity of free electrons and holes.

For the 50 K case (Appendix C, Fig. C.1) an increase in J_{SC} is observed until melt times of 300 s. This is perhaps due to an increase in energy required to order longer chains to a preferable conformation on the ZnO surface. Despite higher J_{SC} values, the loss in V_{OC} reduces η to maintain an efficiency of ~ 0.02 %. It should be noted that the 30 K and the 50 K data set are not directly comparable as P3HT films are of different thicknesses (170 nm vs 290 nm), the photophysical processes underlying the operation of these devices, however, are the same.

The morphology of bilayer films as a function of melt annealing has previously been characterised (section 4.4), showing an increase in out-of-plane crystallite orientation. The devices presented here differ from the aforementioned film as a result of the shorter annealing times and rapid quenching.

During these experiments melting is examined at short time scales by annealing at high temperature and removing the substrate from the hot plate after a given time. The rapid change in temperature results in a significant degree of undercooling and solidification time is short. Compared to samples which have undergone slow

cooling, the polymer morphologies produced here will have an increased amorphous content. Data on melt annealing on bilayer films has recently been published [11]. Little variation in device performance is observed and perhaps were due to a finer control of polymer crystallisation resulting in more uniform film morphology between samples.

5.3.4 Conclusions

The absorption of P3HT and characterisation of ZnO:P3HT bilayer devices has been investigated. Polymer film thickness was examined and higher efficiencies were found for thicker films. This was attributed to a reduction in series resistance and an increase in shunt resistance of these devices. To provide a comparison with nanorod samples, melt annealing of polymers on bilayer samples was conducted. A reduction in device performance was observed, primarily due to a loss of V_{OC} for these devices, and has been discussed in terms of polymer morphology, electrical properties and recombination current.

5.4 Nanorod devices

Results from the formation of nanorod h-PV devices are discussed in this section. Despite a fine control of nanorod morphologies as shown in chapter 3, conditions for nanorod growth were fixed for all experiments (section 5.2.1). The aim of this section of work was to determine optimum polymer processing conditions as it is thought to be a key factor hindering h-PV device performance.

5.4.1 Effect of annealing

The effect of heat treatment on nanorod device performance was investigated. The general trend in device data is that a short amount of annealing (~ 60 s) above the melting point increases the efficiency of the device. This is consistent with reports in the literature [13, 14, 15]. Longer annealing times reduce efficiency values due to a reduction in both V_{OC} and J_{SC} .

Results shown here present similar findings; on melt annealing efficiency, is increased over that of a bilayer (Fig. 5.5). The large increase in J_{SC} is attributed to nanorod filling, with increases observed in time periods as short as 10 s. At an annealing time of 60 s nanorod filling is complete. Melt annealing over longer time causes device performance to degrade. In a similar result as annealing experiments

conducted on bilayer films V_{OC} is seen to decrease with annealing time. The aforementioned arguments pertaining to polymer morphology, electronic properties and recombination are applicable also to nanorod devices.

Devices have been tested at 2, 43 and 63 hours and show increasing performance. This is attributed to the oxidation of the silver electrode resulting in an increased built in voltage [3].

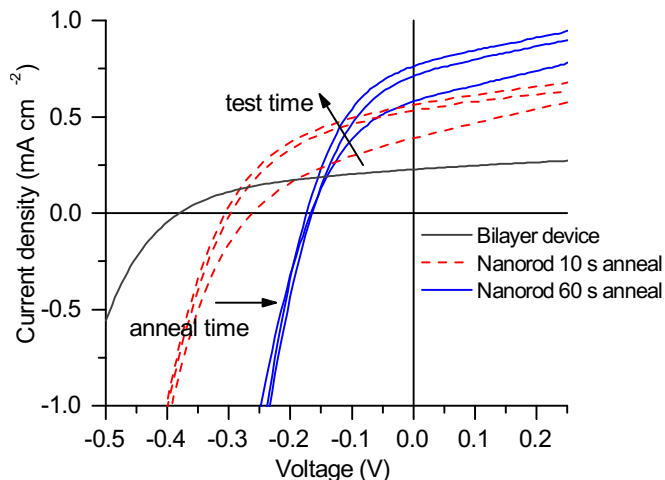


Figure 5.5: J-V curves showing the difference in melt annealing time (10 s vs 60 s) for nanorod h-PV devices (NR) (M_n 30 K, polymer thickness 173 nm, 150 °C 20 minute post anneal). Devices have been tested at 2, 43 and 63 hours and show increasing performance. Bilayer device shown as control (M_n 30 K, polymer thickness 173 nm, no anneal).

5.4.2 Effect of molecular weight

To increase control of polymer morphology, devices were subject to melt annealing and slow cooling using a programmable hot plate starting at a temperature of 250 °C before reducing to a temperature of 170 °C over a period of 90 minutes. The temperature for annealing was chosen to coincide with a point close to the crystallisation peak observed in DSC data (Fig. B.1). The slow cooling and one step process from melt to anneal aims to provide polymer infiltration and crystallisation from melt to allow for the maximum crystallinity of polymer films within nanorod arrays. Devices created by this process are comparable to samples studied in section 4.4.

Polymer processing in this manner has been completed for 30 K and 50 K P3HT with the data shown in figure 5.6. Consistent with previous bilayer studies, results

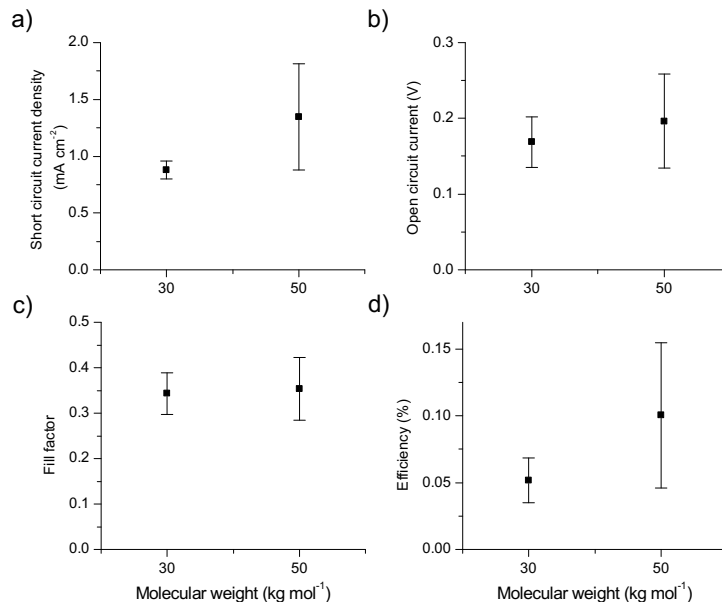


Figure 5.6: Slow cooled nanorod samples from the melt phase (polymer thickness 173 nm). a) short circuit current density, b) open circuit voltage, c) fill factor and d) efficiency. Error bars show standard deviation.

are shown with standard deviation and show some variation among measurements. The V_{OC} in these devices is similar to that observed in previous nanorod work and is also comparable to bilayer devices. This is indicative of a loss mechanism that occurs to all devices made here. Overall, the data shows an increase in performance for devices made with 50 K over 30 K owing to an enhancement in J_{SC} of these films. The use of a standard ZnO template ensures that the interfacial area between oxide and polymer is nominally the same, thus an increase in J_{SC} can be attributed to an increase in hole mobility resulting from the higher molecular weight polymer. On annealing, as shown in SAXS data (section 4.4) the entangled polymer occupies a more mixed conformation within the nanorod array allowing for continuous pathway towards the silver electrode.

Low V_{OC} values hinder the performance of these devices. The band offset (Eqn. 1.12) describes V_{OC} in terms of the difference between $E_{HOMO,D}$ and $E_{LUMO,A}$). For ZnO:P3HT devices a value of 0.9 V is apparent and by subtracting the loss term an ideal device can be expected to operate at V_{OC} to be 0.6 V; reported h-PV devices obtain values very close to this maximum (≈ 0.56 V) [16, 15]. High values are obtained by optimising not only polymer processing but also nanorod morphology and device architecture.

5.4.3 Conclusions

Nanorod devices are characterised in terms of annealing time, showing an increase in short circuit current density with increased annealing. At times greater than 60 s, nanorod performance is reduced. The dependence on characterisation time is shown to affect observed performance and is attributed to oxidation of contacts as is reported in the literature. Slow cooling of nanorod samples from the melt is observed to increase device performance over those that have been quenched. From this work a higher molecular weight P3HT is observed to give increased device performance owing primarily to an increase in J_{SC} current within nanorod devices. This is attributed to a higher hole mobility due to the mixed orientation of the polymer with the nanorod array.

5.5 Summary

The effect of polymer processing on the performance of bilayer and nanorod h-PV devices has been investigated. Polymer melting, shown to be a requirement for increased device performance due to nanorod infiltration, was completed on planar and nanorod substrates. In each case a reduction in device V_{OC} is observed. The dependence of V_{OC} on annealing is discussed in terms of polymer morphology, electrical properties and exciton recombination. Melt annealing in bilayer devices increases performance through a closer oxide-polymer interface, in nanorod devices J_{SC} increases significantly due to polymer infiltration.

The best nanorod devices were created from the slow cooling of polymers from the melt phase. The greater of the two molecular weights studied, gave higher device efficiencies. This has been discussed in terms of the resulting polymer morphology that allows for increased hole mobility out of the nanorod array and towards the top contact.

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Chapter 6

Summary and Future Work

6.1 Summary of work

The design, construction and operation of functional photovoltaic devices is of continued interest to the scientific community. Devices created from metal oxide-polymer composites combine high electron conductivity of oxide with photoactivity of the polymer species to create functional and stable devices. The goal of this thesis has been to extend and contribute to the understanding of such hybrid devices through investigation of low temperature processing methods.

Chapter 3 described the formation of ZnO nanorods by hydrothermal methods. SEM images have been used to quantify nanorod dimensions under varying growth conditions, this data are used with XRD data to correlate nanorod alignment with growth time and additive concentration. Changes in nanorod morphologies are observed and related to the stabilisation of the nanorod growth surface and ordering mechanism, providing an insight into methods by which nanorod growth occurs and can be controlled by hydrothermal deposition.

Of the range of nanorod morphologies created, a set of fixed growth conditions were chosen to study polymer infiltration (chapter 4). Complete infiltration was possible by processing using molten polymer. To characterise composites further, the polymer entanglement threshold was found by viscometry and the crystallite orientation and size of two molecular weights, one in the region of and one below the entanglement threshold were investigated by SAXS and temperature resolved XRD. Significant crystallite re-orientation is observed on annealing for both ZnO bilayer and nanorod substrates with the higher polymer molecular weight being found to hinder re-orientation and crystallite growth. To the author's knowledge, this is the first time orientation and crystallite size of h-PV films has been investigated.

Chapter 5 described the formation of hybrid devices and the effect of polymer processing conditions were considered. Initial studies of bilayer devices were completed to optimise and understand performance with respect to polymer thickness and melt annealing conditions. Nanorod devices were also optimised by considering melt annealing time. In both cases devices were quenched after annealing and significant open circuit voltage losses are seen to hinder device performance. The final section of work considers the performance difference between the two molecular weight samples, the higher molecular weight is observed to increase device performance and this was attributed to an increase in hole mobility out of the nanorod array.

The construction and characterisation of ZnO-P3HT h-PV devices has been investigated considering the formation of ZnO thin films and nanostructures, polymer processing techniques and investigation of the morphology of polymer thin films, finally PV devices were created. Overall, the work presented in this thesis develops general principles behind the creation of h-PV devices and aids understanding of the relationship between their processing, materials properties and performance.

6.2 Future work

Further work in this field can be divided into three topics concerning hybrid photovoltaics (section 6.2.1), organic photovoltaics (section 6.2.2) and processing and measurement of functional optoelectronic devices (section 6.2.3). In each section relevant topics are briefly discussed and novel research areas highlighted by recent literature publications.

6.2.1 Hybrid photovoltaics

There is much speculation as to the validity of h-PV device research, owing primarily to poor charge transport and poor charge transfer between polymer and metal oxide. Because of this device performances will always be poor. The topic, however, is of interest and befitting multi-disciplinary, device oriented approaches are applicable to a variety of topics. These are listed below detailing future research questions.

ZnO morphology

The optimum morphology of nanorod arrays and the effect on h-PV performance is one area that has yet to be fully understood. This is linked both to the growth conditions of nanorod effecting electron conduction and to the variation in polymer

pack from different nanorod morphologies. As shown in the research completed in this thesis, much can be done to vary both factors and in particular controlling growth by solution additives is one useful method. The use of novel conjugated polymers within nanostructures is of interest and it is possible that a single optimised nanostructure morphology may not be standard for all polymers

ZnO defects and devices

Increased understanding of ZnO optoelectronic properties has lead to improvements in devices incorporating the material. Specifically, control of defect states and thus conductivity is of interest. In nanostructures, this is possible by conformal coating of surface with n-type (TiO_2 , MgO) or insulating films (Al_2O_3) thin films. Such coatings may be created by chemical techniques or by physical deposition methods. Much work has been completed using TiO_2 [1, 2]. The investigation of other metal oxides (MgO , SnO) and perhaps functional materials or thin layers (ferroelectrics, surface assembled molecules) that could aid in charge collection and are be of interest.

In addition, the interaction of ZnO with organic species is a topic worth studying. The use of ZnO as a scaffold in solid state dye sensitised solar cells (ss-DSSC) is seen to increase efficiencies ($\eta > 5\%$) and allow thick films ($> 50\ \mu\text{m}$) to be created [1].

Polymer processing and architecture

Crystallite orientation and grain size in nanorod arrays have been observed in this thesis. Additional work in this field could further quantify both factors this is possible by conducting temperature-resolved grazing incidence XRD experiments at a synchrotron source. In addition, it has not yet been shown specifically how the degree of polymer crystallinity affects h-PV performance, this could be completed through polymer annealing experiments or with a secondary component that disrupts polymer backing.

One limitation of h-PV devices having inverse architectures as created in this thesis is the low hole conductivity compared to electron conductivity. This leads to space charged effects which limit device performance through increased exciton recombination. To increase conductivity different polymers or doped polymers could be used. One idea would also be to change the cell architecture and coat nanorod arrays with donor polymer on top of which a high conductivity, non absorbing organic material could be used.

New technologies

The recent introduction of meso-superstructured solar cells (MSSCs), based on mixed halide perovskites coating an aluminium oxide porous scaffold, is of some interest to the h-PV community [3]. These devices operate well ($\eta \approx 11\%$) and have long lifetimes. However, little is understood about the lead-based absorber, in particular of the high absorbance *and* high electron conductivity that is present in these films. Owing to such properties no n-type acceptor is needed, the porous scaffold creates a high surface area and highly scattering functional layer. In these devices organic hole conductors are still used and so understanding the interface between metal oxide and organic materials is of interest.

The lack of understanding in MSSC devices is characteristic of a nascent field but is also in part due to empirical research that aims solely to improve device efficiency. The recent spin-out of MSSC research in a venture backed by Oxford University supports such an industrialised view of PV research. The privatisation of early research presents a false economy as experiments which concern materials, properties and processing are completed with only a narrow view which hinders overall development of the field as there is a lack of valuable comments from the wider research community. Research with the sole aim of improving device efficiency, in many cases, contributes little to the field and perhaps this focus has been the source of many extraneous publications in the OPV and other PV fields.

6.2.2 Organic photovoltaics

Increased understanding in the field of organic photovoltaics is beginning to yield important results in defining the criteria required for the functioning of BHJ devices and why the P3HT:PCBM pairing works so well. The current theory supporting BHJ device operation suggests that three phases; a finely mixed fullerene-polymer, crystalline fullerene and crystalline polymer occur, creating energy sinks for electrons and holes in the latter two phases respectively. The energy variation of these two phases, provide pathways for the favourable transfer of charge from the active layer [4]. Further work should continue to develop understanding of the function of BHJ devices.

Following this theme, many new polymers with increased hole mobilities, lower band gaps and novel structures have been developed. These include new semi-crystalline polymers such as poly[2,5-bis(3-alkylthiophen-2-yl)]

-thieno(3,2-b)thiophene] (pBTTT) that allow for the intercalation of PCBM within side chain groups [5] aiding in finer intermixed morphologies.

Experiments to investigate the variation in BHJ morphologies within ZnO nanostructures may be of interest and crucial understanding toward charge transfer between organic and inorganic materials is still a key topic in the literature. As well as inducing some degree of control in polymer packing the use of nanostructures in BHJ could increase optical density and light trapping provided that both components are able to support charge transport through the layers. The difficulty in processing such a device is that melt annealing to fill nanostructures will destroy the intermixing of fullerene and polymer. As fullerenes are seen to be highly mobile in polymer films [6] and are also seen to rapidly segregate to interfaces [7].

The synthesis of fullerene species and specifically PCBM is fairly standardised and more recently groups are looking into controlling the absolute properties of conjugated polymers. This is reliant on both novel polymer repeat units and subsequent polymer synthesis methods. The reduction of polydispersity is a key topic and seen to be possible providing the correct starting reagents and catalyst are chosen [8]. The ability to produce monodisperse conjugated polymers is of significant interest due to the reduction in packing defects. Chains with the same length can form single crystal, not semi-crystalline phases. Monodisperse polymers would allow for much finer investigation of BHJ morphology and the absolute investigation of the function of different phases within OPV and h-PV thin films.

In terms of polymer science, the move towards higher molecular weight polymers, having increased hole mobilities is desirable. Processing methods required to make thin films of these polymer samples will need to be advanced, especially relating to increased solution viscosity and surface roughness due to high M_w . It is possible that with increased mechanical properties resulting from entanglement, sheering and other deformation methods could be employed to increase polymer crystallinity prior to their use in devices. Whether high molecular weight polymers can be synthesised with low PD is yet to be seen.

6.2.3 Processing methods and large area devices

Perhaps the most important topic from a material science perspective is the ability to process OPV devices and the subsequent measurement of film properties. In terms of processing, the inherent motivation of large area OPV devices by solution methods has yet to be realised. Devices made by rapid processing R2R methods only operate with

4 % efficiency [9], compared to state of the art laboratory devices OPV devices that exceed efficiencies of 7 % [10]. The significant difference in performance is attributed to the lack of morphology control over large areas (m vs. mm) in dramatically reduced time frames (seconds vs. minutes).

Understanding desirable donor properties, and the knowledge to synthesise these molecules is available within the chemistry community. However, difficulties currently lie in the creation of optimised devices using new materials. Device performance relies on many factors, including the composition of donor and acceptor [11], solvent [12, 13], annealing conditions [14, 15, 6], drying rate [16], chemical properties of donor [17], layer thickness [18] and more recently the incorporation of additives [19]. Developing morphology control through a deeper understanding of the interplay between chemical structures and processing conditions will be key to achieving high performance devices.

Unfortunately, while control of processing variables in the laboratory environment is understood, thin film formation by laboratory techniques is often inappropriate for large area deposition [9, 20, 21]. Further complications arise as modern R2R methods have even more processing variables and less is understood about their control. Consequently, it is timely that a novel technique is created with the ability to measure BHJ morphology during device fabrication.

A system that would allow in-situ characterisation of BHJ morphologies during fabrication would provide a versatile measurement, primarily to provide quality control data (process control). With further development this would allow for a feedback loop between morphology and processing conditions for dynamic control (process design) of thickness, composition, web speed, annealing and drying time. In either case, the ability to determine cell performance without the necessity to test cells will expedite progress in the field of organic photovoltaics. Such a measurement system is possible with contactless frequency-dependent impedance spectroscopy (Fig. 6.1).

The capacitance measurements of OPV devices where device doping density, carrier mobility [22] and deep trap states [23] have recently been reported. Impedance techniques also have been applied to OPV devices, investigating interfacial properties in hybrid cells [24] and in probing of the density of states and recombination dynamics in P3HT:PCBM cells [25]. The latter report being the first in the literature to conduct impedance spectroscopy measurements under illumination at open circuit voltage. Very recent work clarifies currents impedance models (for contact based methods)

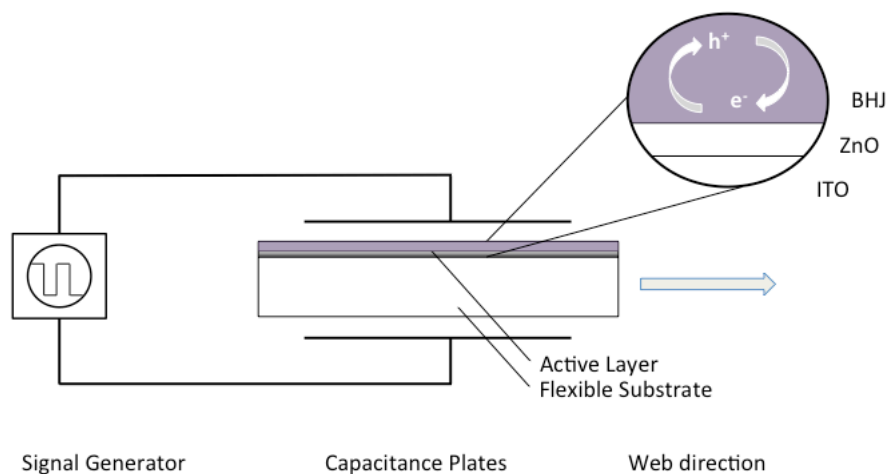


Figure 6.1: Schematic equipment set up of in-situ impedance measurement within R2R processing system. Applying a controlled alternating voltage to the plates causes movement of charge throughout the device. Charges within the active layer are highlighted.

concerning understanding of the origin of V_{OC} and electronic operation of BHJ morphologies [26].

The development of in-situ techniques will further understanding of optimised polymer processing conditions, increase device performance and aid in the rapid screening of polymer blends. Furthermore, such screening techniques will be invaluable in developing a wide range of organic electronic technologies that employ R2R methods. Contactless impedance spectroscopy of organic thin films is the topic of my National Research Council postdoctoral fellowship which has been accepted for further research at the National Institute of Standards and Technology, Gaithersburg, Washington D.C.

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Appendix A

Nanorod Growth

A.1 Statistical data on nanorod growth

Table A.1: Numerical data from analysis of nanorod micrographs on metrics, rod length, width and density for 120 minute growth time.

120 minute growth: Rod Length

KCl concentration (mM)	Rod Length (nm)	Standard Deviation (nm)	Standard Error	Physical Samples (n)	Images (n)	Sample size (n)
0	373	131.8	15.8	2	5	70
10	856	253.5	20.7	2	10	150
50	1048	184.4	13.3	2	18	191
100	962	116.6	11.3	6	14	106
200	538	82.1	6.8	2	13	147
300	394	40.7	3.5	2	16	134
400	315	33.3	3.4	2	12	97
500	311	23.6	4.5	2	5	28

120 minute growth: Rod Diameter

KCl concentration (mM)	Rod Width (nm)	Standard Deviation (nm)	Standard Error	Physical Samples (n)	Images (n)	Sample size (n)
0	54	17.3	2.6	2	2	44
10	45	16.9	1.5	2	7	131
50	47	13.1	0.9	2	13	228
100	61	25.0	1.2	4	4	417
200	50	15.0	1.2	2	10	151
300	65	19.2	1.4	2	8	200
400	63	18.7	1.3	2	4	200
500	94	23.5	1.7	2	5	187

120 minute growth: Areal Density

KCl concentration (mM)	Density (rods μm^{-2})	Physical Samples (n)	Images (n)	Sample Size (n)
0	93	2	3	1037
10	67	2	5	1247
50	66	2	4	987
100	75	5	5	1324
200	73	2	4	1090
300	93	2	4	1385
400	110	2	4	1644
500	77	2	3	858

Table A.2: Numerical data from analysis of nanorod micrographs on metrics, rod length, width and density for 40 minute growth time.

40 minute growth: Nanorod Length						
KCl concentration (mM)	Rod Length (nm)	Standard Deviation (nm)	Standard Error	Physical Samples (n)	Images (n)	Sample size (n)
0	166	39.5	7.0	1	4	32
10	315	67.0	6.7	1	6	100
50	266	52.1	5.2	1	6	99
100	149	25.0	3.6	1	4	49
200	104	18.2	3.2	1	4	32
300	135	12.9	1.1	1	5	40
400	114	17.1	2.1	1	6	68
500	100	19.0	7.8	1	1	6

40 minute growth: Nanorod Diameter						
KCl concentration (mM)	Rod Width (nm)	Standard Deviation (nm)	Standard Error	Physical Samples (n)	Images (n)	Sample size (n)
0	39	12.6	1.6	1	4	63
10	35	14.2	1.2	1	6	130
50	32	12.7	1.0	1	6	151
100	47	18.8	2.3	1	4	69
200	43	14.5	1.4	1	5	112
300	46	14.8	2.3	1	6	40
400	51	23.8	1.7	1	4	200
500	52	14.0	1.6	1	1	79

40 minute growth: Rod Density				
KCl concentration (mM)	Density (rods μm^{-2})	Physical Samples (n)	Images (n)	Sample Size (n)
0	141	1	3	1577
10	143	1	3	1602
50	141	1	3	1575
100	141	1	3	1575
200	154	1	3	1374
300	150	1	3	1681
400	132	1	3	1480
500	179	1	3	2006

Table A.3: Calculated deposition volume for 120 and 40 minute growth over the KCl concentration range 0 – 500 mM.

120 minute growth: Calculated Volume		
KCl concentration (mM)	Volume ($\mu m^3 \mu m^{-2}$)	Cumulative standard error (as fraction)
0	0.0779	0.12
10	0.0925	0.12
50	0.1181	0.12
100	0.2097	0.10
200	0.0766	0.11
300	0.1224	0.13
400	0.1068	0.08
500	0.1643	0.07

40 minute growth: Calculated Volume		
KCl concentration (mM)	Volume ($\mu m^3 \mu m^{-2}$)	Cumulative standard error (as fraction)
0	0.0282	0.15
10	0.0441	0.12
50	0.0309	0.08
100	0.0360	0.08
200	0.0236	0.12
300	0.0343	0.11
400	0.0303	0.10
500	0.0382	0.12

Table A.4: Zinc oxide powder diffraction pattern from ICDD PDF 00-001-1136. Peak is ordered by position, showing miller index (hkl), lattice spacing (d) and relative intensity of diffraction peaks (I).

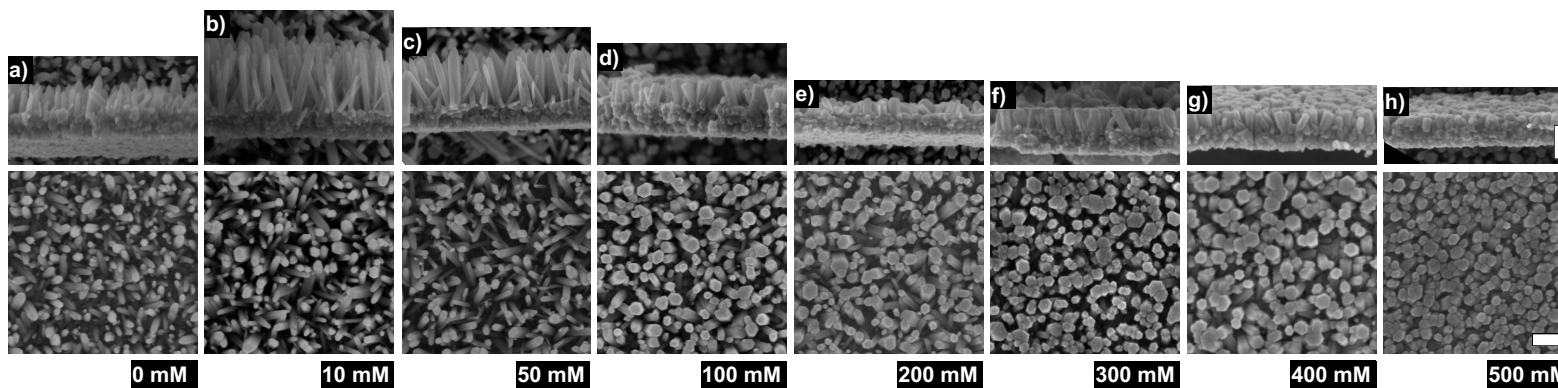
No.	h	k	l	d (Å)	$^{\circ}2\theta$	I (%)
1	1	0	0	2.81	31.820	50.0
2	0	0	2	2.61	34.331	30.0
3	1	0	1	2.46	36.496	100.0
4	1	0	2	1.91	47.569	16.0
5	1	1	0	1.61	57.168	30.0
6	1	0	3	1.47	63.204	30.0
7	2	0	0	1.40	66.763	2.0
8	1	1	2	1.38	67.861	20.0
9	2	0	1	1.36	68.999	8.0
10	0	0	4	1.30	72.675	2.0
11	2	0	2	1.24	76.809	2.0
12	1	0	4	1.18	81.506	2.0
13	2	0	3	1.09	89.934	4.0
14	2	1	0	1.06	93.221	2.0
15	2	1	1	1.04	95.578	4.0
16	1	1	4	1.02	98.085	2.0
17	2	1	2	0.98	103.630	2.0
18	2	0	4	0.96	106.719	2.0
19	3	0	0	0.94	110.063	2.0
20	2	1	3	0.91	115.662	2.0

Table A.5: Data from analysis of (002) diffraction peaks for 40 and 120 minute samples

XRD analysis 120 minutes				
KCl concentration (mM)	(002) Integrated Intensity	Volume (μm^{-3} per square μm)	Integrated intensity corrected for volume	Values normalised to 0 mM KCl sample
0	1152	0.078	14724	1.00
10	1469	0.060	24604	1.67
50	3660	0.118	31047	2.11
100	6450	0.212	30369	2.06
200	3358	0.077	43842	2.98
300	9333	0.122	76258	5.18
400	13231	0.107	123912	8.42
500	14291	0.165	86527	6.12

XRD analysis 40 minutes				
KCl concentration (mM)	(002) Integrated Intensity	Volume (μm^{-3} per square μm)	Integrated intensity corrected for volume	Values normalised to 0 mM KCl sample
0	1844	0.0287	64188	1.00
10	2585	0.0467	55344	0.86
50	2736	0.0307	89227	1.39
100	2663	0.0361	73711	1.15
200	1700	0.0228	74720	1.16
300	3900	0.0343	113660	1.74
400	1287	0.0303	42449	0.65
500	1009	0.0385	26422	0.39

A.2 Scanning electron microscopy



156 Figure A.1: ZnO nanorods grown from standard solutions, equimolar (25 mM) $\text{Zn}(\text{NO}_3)_2$ / HMT and 10 mM PEI. KCl concentration varied from left to right, a) 0, b) 10, c) 50, d) 100, e) 200, f) 300, g) 400, h) 500 mM. Cleaved cross sections are shown above and top-surface rod morphology below. Growth time 40 minutes. Scale marker for all images 200 nm.

A.3 Selected area electron diffraction

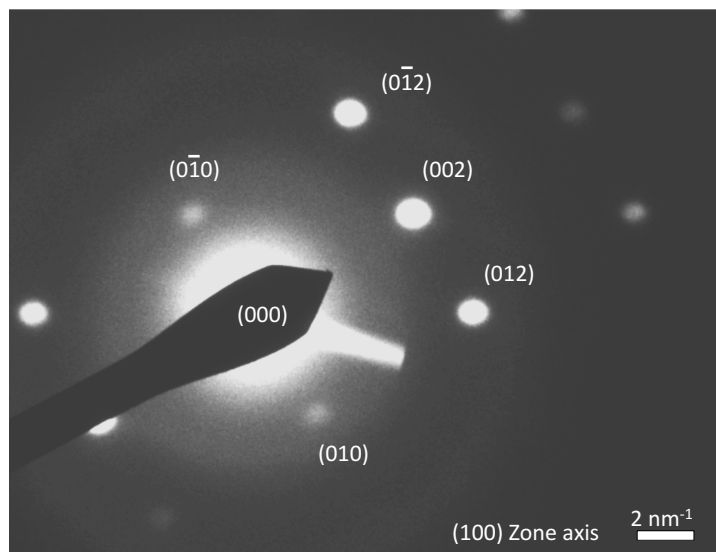


Figure A.2: Selected area electron diffraction of a singular ZnO nanorod examined on the (100) plane. Diffraction pattern indexed so as to show diffraction from the (002) and (010) planes.

Appendix B

Polymer Infiltration and Morphology

B.1 Differential scanning calorimetry

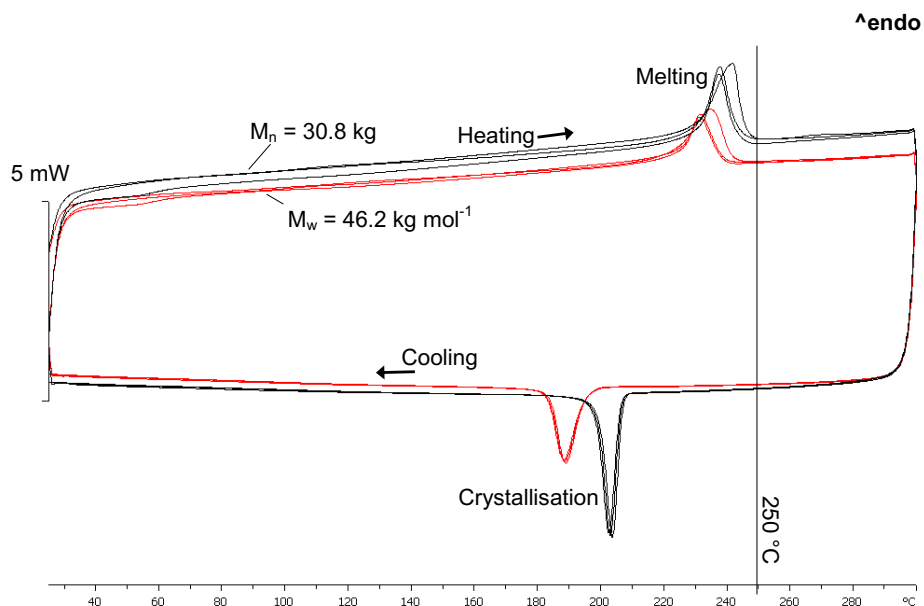


Figure B.1: Differential scanning calorimetry for low (30.8 kg mol⁻¹) and high (46.2 kg mol⁻¹) molecular weight (M_n) P3HT samples. Data shows melting is complete at temperatures above 250 °C.

B.2 Thickness study

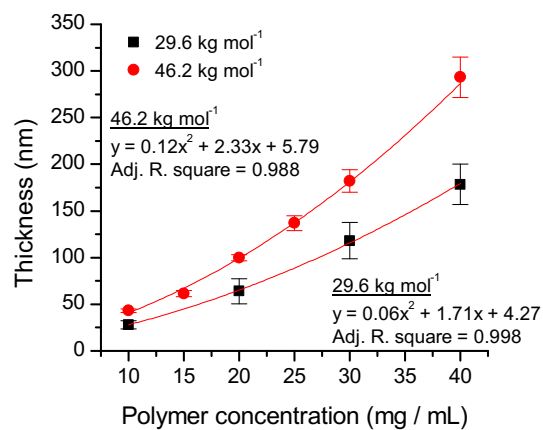


Figure B.2: Film thickness correlation with molecular weight for M_n 29.6 kg mol⁻¹ (30 K) and 46.2 kg mol⁻¹ (50 K). High molecular weight samples lead increased films thickness due to increase viscosity.

B.3 Small angle X-ray scattering data

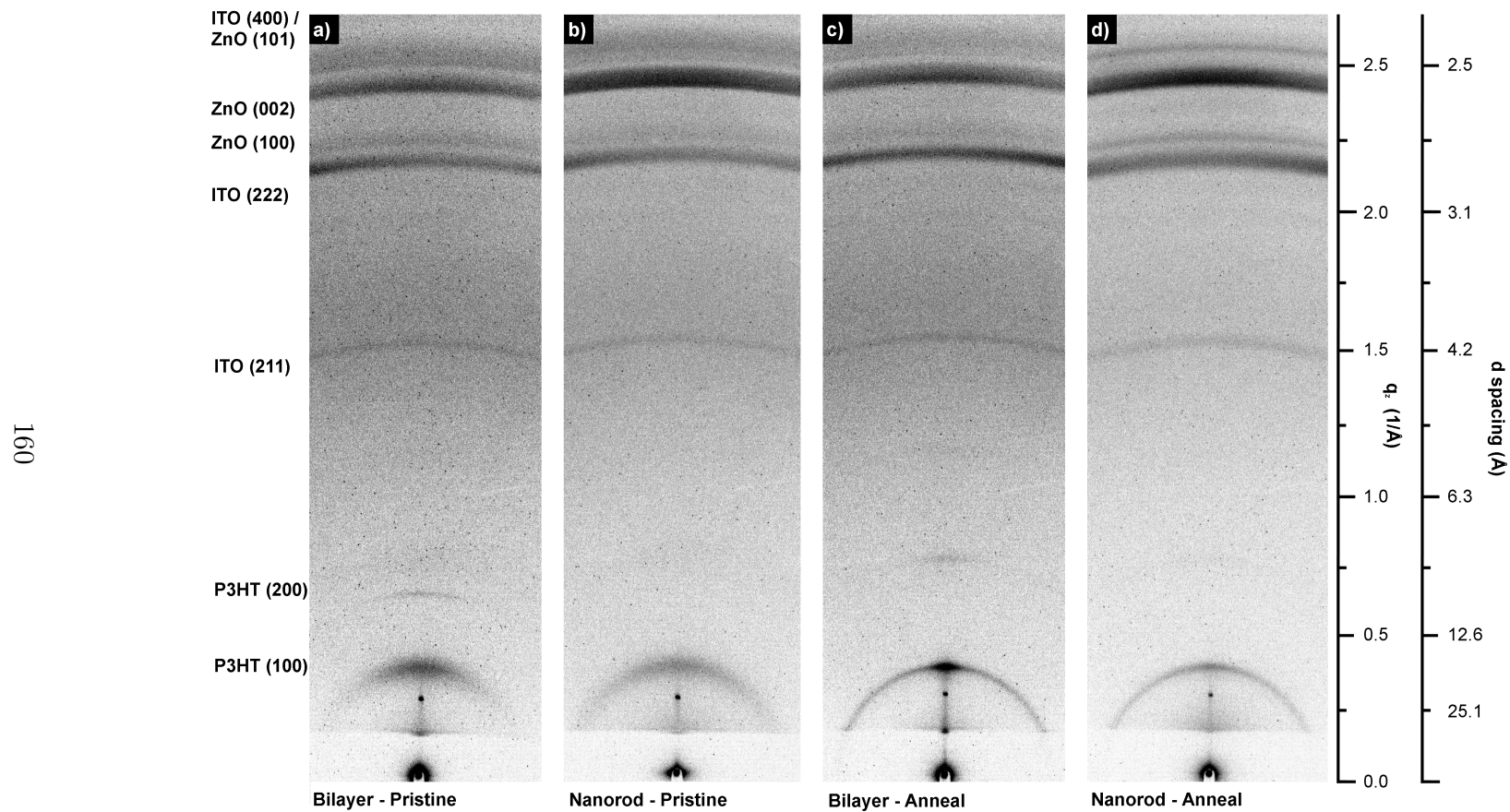


Figure B.3: Small angle X-ray scattering patterns for pristine and annealed P3HT (M_n 30 K) films on ZnO bilayer (a, b) and nanorod (c, d) substrates.

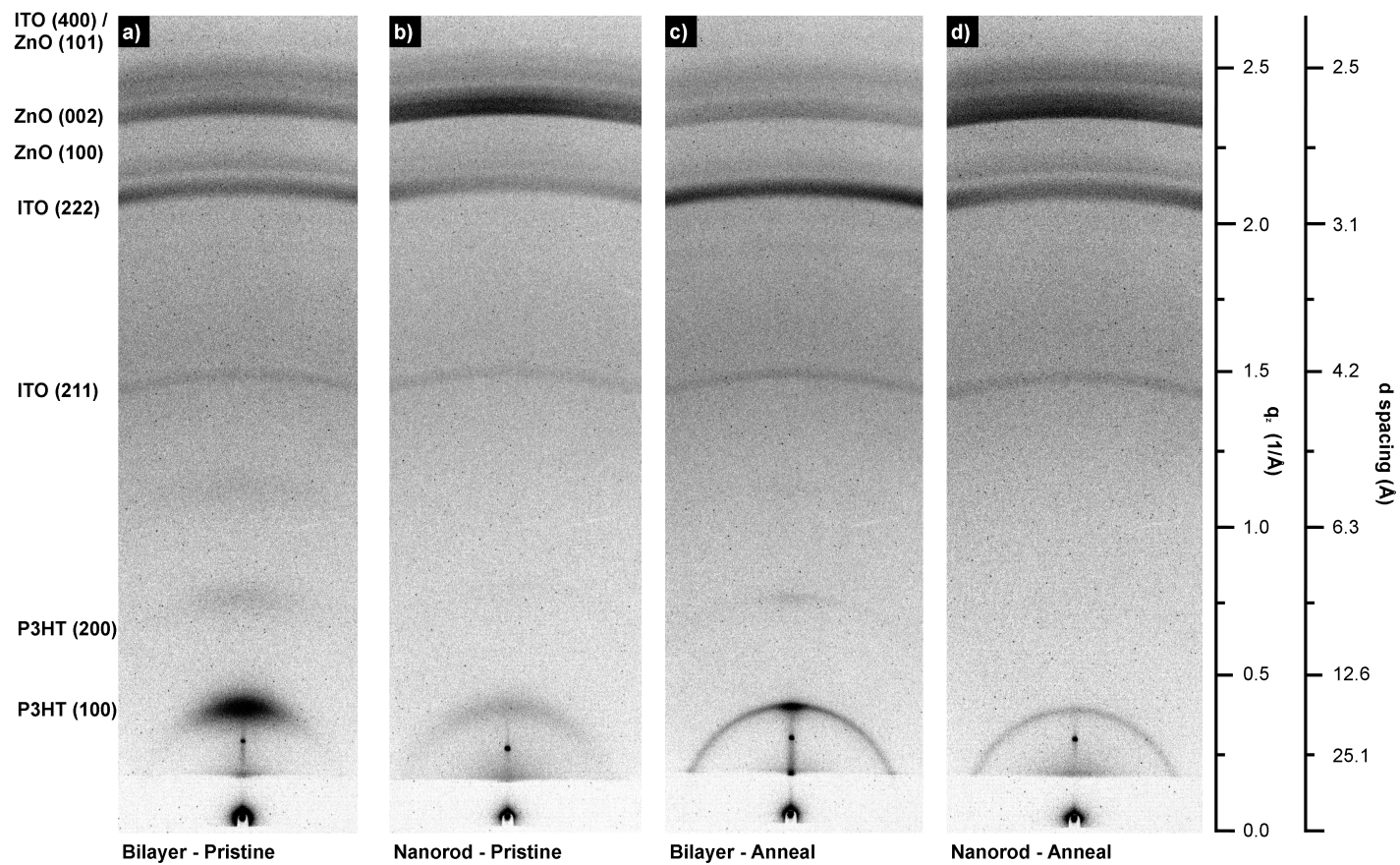


Figure B.4: Small angle X-ray scattering patterns for pristine and annealed P3HT (M_n 50 K) films on ZnO bilayer (a, b) and nanorod (c, d) substrates.

B.4 Batch processing of in-situ XRD data (HighScore Plus)

The following Pascal script was written and implemented in HighScore Plus with the purpose to process XRD patterns from in-situ measurements.

```
program DynamicFileNames;
var
// Define variables for peaks and meta data
  List: TStringList;
  i: Integer;
  Line, ColSeparator: string;
  Temperature: double;
  Length1: integer;
  Length2: integer;
  FileName: String;
  NewFileName: String;
begin
// Create data that is readable by MS Excel
  ColSeparator := Chr(9);
// Add filename and temperature to test variable
  FileName := Document.AnchorDataSet.Scan.ScanProperties.FileName;
  Temperature := Document.AnchorDataSet.Scan.ScanProperties.Temperature;
// Create the string list
  List := TStringList.Create;

try
// Add header line
  List.Add('Position' + ColSeparator + 'Height' + ColSeparator +
    'FWHM' + ColSeparator + 'Area' + ColSeparator + 'Temperature'
    + ColSeparator + 'FilePathName');
// Add all peaks
  for i := 0 to Document.AnchorDataset.Peaks.Count - 1 do

begin
Line := FloatToStr(Document.AnchorDataset.Peaks.Items[i].Position.Value) +
  ColSeparator +
  FloatToStr(Document.AnchorDataset.Peaks.Items[i].Height) +
  ColSeparator +
  FloatToStr(Document.AnchorDataset.Peaks.Items[i].FWHM.Value) +
  ColSeparator +
  FloatToStr(Document.AnchorDataset.Peaks.Items[i].Area.Value) +
  ColSeparator +
```

```

        FloatToStr(Temperature)+
        ColSeparator +
        FileName;
List.Add(Line);
end;

// Find the length of the array
    Length1 := Length(FileName);
// Copy all of the array minus the last few characters, corresponding to the .xrxml
    Length2 := Length1 - 11;
    SetLength(FileName, Length2);
// add to the address 4 characters - .txt
    NewFileName := FileName + 'PeakParameters.txt';
// Save list to an external ASCII file
    List.SaveToFile(NewFileName);

finally
// Finally free the string list
    List.Free;
end;
end

```

Appendix C

Device Measurements

C.1 Bilayer devices

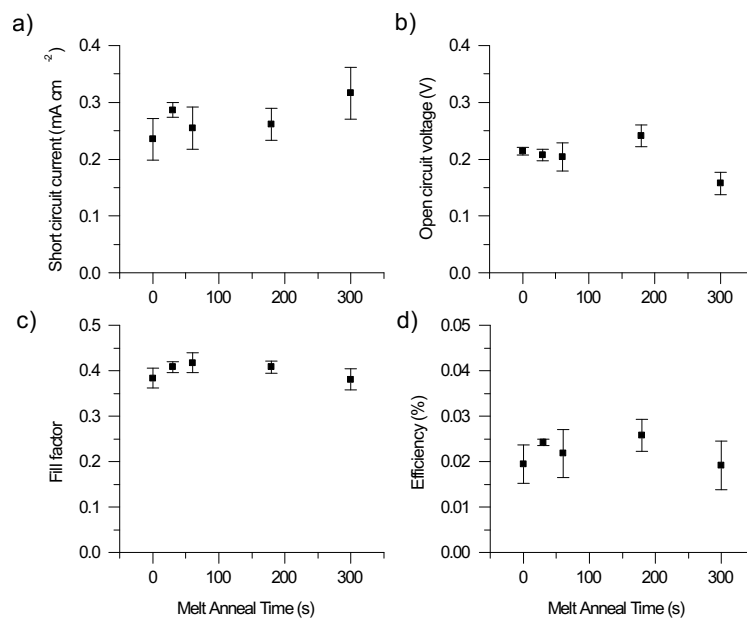


Figure C.1: Bilayer device performance as a function of melt annealing time (0 – 300 s, M_n 50 K, film thickness 290 nm) Data from J-V curves are shown for a) short circuit current density, b) open circuit voltage, c) fill factor and d) efficiency. Error bars show standard deviation.

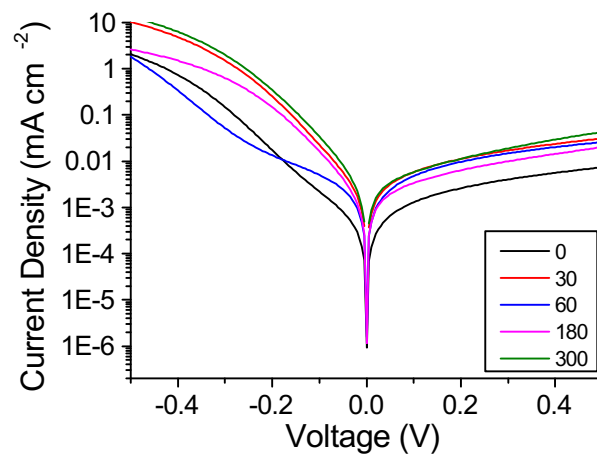


Figure C.2: Dark scans melt processed bilayer devices (0 – 300 s, M_n 30 K, film thickness 173 nm)