Self-Assembled Monolayer-Tuned Growth of ZnO Nanorods for Organic Solar Cells

by

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Organic solar cells have the potential to meet the rising energy demand. They offer great prospects due to their inexpensive processing techniques. They can be fabricated from solution at low temperatures, which makes them compatible for flexible substrates and large area roll-to-roll printing techniques. Despite these attractive features, there is plenty of room for improvement of organic solar cells. Organic solar cells benefit from the high absorption coefficients of organic polymers. However, most of the incoming light is not absorbed by the photo active semiconductor layer. One of the ways to improve absorption is to use ZnO nanostructures. Vertical arrays of nanostructures or nanorods can act as scattering elements which scatter incoming light. They elongate the optical path length inside the active layer and enhance the absorption. Secondly, the ZnO nanorods can serve as pathways to the electrodes for efficient charge carrier collection.

For application in organic solar cells, it is critical to control the dimensions and the distribution of ZnO nanorods. In this thesis, a simple method is introduced to achieve controlled growth of ZnO nanorods via electrochemical deposition. Self-assembled monolayer (SAM) of alkanethiol molecule is applied on a conducting substrate to define the nucleation sites of ZnO. A growth model of ZnO on SAM-modified substrate is developed, which is supported by impedance measurements. The control of the dimensions and the nucleation density of ZnO nanorods are achieved by systematically varying the quality of SAM and the parameters of electrochemical deposition. Angle-resolved transmission measurements are performed to study the light scattering properties of the ZnO nanorods. Bulk heterojunction organic solar cells are successfully fabricated based on semiconductors poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and ZnO nanorods. Investigations are performed to study the influence of ZnO nanorods on the performance of solar cells.

Another aspect that plays a big role in organic semiconductors is the charge carrier mobility. The MIS-CELIV (metal-insulator-semiconductor charge carrier extraction by linearly increasing voltage) technique is effectively used to get selective mobility of holes and electrons in semiconductor blend of P3HT:PCBM. In this thesis, a simulation method based on 1-dimensional drift-diffusion equation is used to analyze the MIS-CELIV mea-
urements. The novelty of this method is that it includes doping and trapping effects, which have been ignored in traditional MIS-CELIV analysis. In addition, an analytical model is introduced which allows determination of the conductivity of semiconductor.
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Chapter 1

Introduction

1.1 Motivation

Due to growing concerns over climate change, there has been an increase in the demand of renewable energy resources in the last few decades. Photovoltaic is one of the main sustainable energy resources. Although inorganic solar cells such as Si cells dominate the photovoltaics industry, it is still not able to compete with other sources of electricity generation. The reasons being the high production costs and the use of toxic chemicals during manufacturing. In this regard, low cost organic solar cells are seen as good alternatives. Organic semiconductors can be synthesized and solution-processed at relatively cheaper cost. Unlike inorganic solar cells, the fabrication of organic solar cells can be done at low temperature. These aspects make organic solar cells compatible for lightweight and flexible substrates. In comparison with their inorganic counterparts, organic solar cells have low power conversion efficiency and poorer stability. However, these drawbacks of the organic solar cells can be compensated by their positive aspects. They have tremendous potential to seek for new markets where low cost and low power are required. Organic solar cells have piqued the interest of many. And in the last 15 years, the efficiency has risen from $2.5\%^1$ to $13.2\%^2$.

1.2 Goal of the thesis

The main focus of this thesis is to develop zinc oxide (ZnO) nanorods with tailored dimensions and distribution that can be used to enhance solar cell performance. The dissertation includes the fabrication, analysis, challenges and possible solutions applied
during the work. The outcome of this work is intended to give an understanding of the role of ZnO nanorods in organic solar cells. Besides characterization of solar cell performance, the scope of the thesis is to determine the charge transport properties of the semiconductor.

1.3 Outline of the thesis

Chapter 1 gives a brief motivation behind choosing organic solar cells for this dissertation. The following five chapters give the general overview and the basics of this work. In Chapter 2, the concept of organic semiconductor is introduced to the reader. The origin of conductivity and some charge transport models in organic semiconductors are explained. Chapter 3 explains the basics of organic bulk heterojunction solar cells. In Chapter 4, a review of recent developments in organic solar cells is presented. The applications of nanostructures in organic solar cells and the basics of light scattering are explained. Chapter 5 introduces the theory of electrochemical deposition of ZnO. In Chapter 6, the theory of self-assembled monolayer is highlighted.

In Chapter 7, a method is introduced to tailor the growth of ZnO nanorods. A simple model is developed to explain the growth mechanism of ZnO by self-assembled monolayer. Impedance analysis is used to study the self-assembled monolayer quality. Scanning electron microscopy (SEM) investigations are used to characterize the size and distribution of ZnO nanorods.

In Chapter 8, the tailored growth of ZnO nanorods via self-assembled monolayer is extended to transparent indium tin oxide (ITO) substrate, which is widely used as window electrode in organic solar cells. Angle-resolved diffusive transmission measurements are carried out to analyze the light scattering properties of ZnO nanorods. Bulk heterojunction solar cells with ZnO nanorods on ITO are fabricated. Investigations are carried out about the contribution of ZnO nanorods to light scattering effect.

Chapter 9 deals with the MIS-CELIV technique. Some basics of metal-insulator-semiconductor (MIS) devices and MIS-CELIV are presented. MIS-CELIV measurements are performed to estimate the mobility of charge carriers in bulk heterojunction semiconductor layer. An analytical model is developed to quantify the conductivity in the layer. A new approach to analysis of MIS-CELIV data is introduced where simulations are used to fit the MIS-CELIV data to extract the mobility and the doping concentration.
Chapter 2

Organic Semiconductors

2.1 Organic semiconductors

Organic semiconductor, as the name implies, are mostly made up by carbon and hydrogen atoms, including a few atoms of nitrogen, oxygen and sulphur. Organic semiconductors can be classified into three types based on the morphology.\(^3\)

- **Molecular crystals**: Molecular crystals can be characterized by a perfectly ordered point lattice and a basis. The basis is formed by molecules which are held together by van der Waals interactions. These crystals are formed by molecules which are flat, large and aromatic, such as naphthalene, anthracene, pentacene and perylene. Due to the high degree of order, these crystals exhibit high charge carrier mobilities and they are widely used in organic field-effect transistors.

- **Amorphous molecular films**: These films can be associated with molecules that form amorphous morphology and they have short range order. They are normally deposited via thermal evaporation or from solution-processed spin coating technique. Some good examples of molecules that come under this classification are fullerene C\(_{60}\) and 4, 4′-N, N′-dicarbazolylbiphenyl (CBP).

- **Polymer films**: Polymers consist of a chain of covalently coupled molecular units. The backbone of semiconducting polymer is formed by a chain of carbon atoms with alternating single and double bonds. They exhibit high degree of disorder. They are suitable for polymer blends since they are less likely to crystallize. They are solution-processable, which makes them compatible with a range of deposition techniques such as spin coating, doctor blading or roll-to-roll printing. Examples of
such polymers include poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and polyaniline.

Many of the materials widely used in organic solar cells are not crystalline, but they have amorphous and polymer-like morphology with high degree of disorder. Therefore, this chapter deals with the properties of conjugated polymers.

2.2 Conductivity in organic semiconductors

The backbone of semiconducting polymer is formed by a chain of carbon atoms with alternating single and double bonds. A carbon atom has in the ground state a $1s^22s^22p^2$ configuration. In organic semiconductors, sp$^2$ hybridization is present, i.e. the s and p orbitals form three sp$^2$ orbitals as shown in Figure 2.1. This in-plane overlapping gives rise to three $\sigma$ bonds. The fourth orbital $p_z$ lies perpendicular to the bond. When a $p_z$ orbital overlaps laterally with another $p_z$ orbital, a $\pi$ bond is formed. This gives rise to the presence of alternating single and double bonds in a molecule, which is coined as conjugation. The wavefunctions of $\pi$ orbitals in adjacent carbon atoms overlap and the electrons at these orbitals get delocalized. The delocalization along the backbone chain of conjugated polymer serves as pathway for charge carriers.

Unlike inorganic semiconductors, organic semiconductors have weak intermolecular orbital interaction typically by so-called van der Waals interaction and they do not form conduction band and valence band. The molecular orbitals split into bonding state (HOMO or highest occupied molecular orbital) and anti-bonding state (LUMO or lowest unoccupied molecular orbital). Due to the weak intermolecular interaction, the electronic properties of the organic semiconductors are largely dependent on the molecules themselves. In their pure state, organic semiconductors are insulating. Therefore, they are made conducting or semi-conducting by chemical doping, charge carrier injection from electrodes or by photoexcitation. Organic semiconductors can also be divided into n-type and p-type semiconductors. Depending on the HOMO (ionization potential) or the LUMO (electron affinity), the semiconductor molecules show preference to either transport holes or electrons.
2.3 Charge transport in organic semiconductors

The charge carriers in organic semiconductors are localized on individual molecules or chain segments. Delocalization of the charge carriers only occur along the $\pi$ conjugated segment of the backbone chain. Thus, hopping transport occurs from one localized state or $\pi$ conjugated segment to another (Fig. 2.2a). Due to the nature of organic semiconductors, there are many models on hopping transport. This section will cover only two models which are relevant to this thesis.

According to Bässler, charge carriers move via hopping between spatially and energetically distributed localized states with a Gaussian distribution of density of states.\(^5\)

\[
g(E) = \frac{N}{\sigma \sqrt{2\pi}} \exp\left(-\frac{E^2}{2\sigma^2}\right) \tag{2.1}\]

where $E$ is the energy, $g(E)$ is the density of states, $N$ is the number of randomly distributed localized states and $\sigma$ is the energy variance. The hopping rate $\nu_{ij}$ from an occupied site $i$ to an empty site $j$ can be expressed by the Miller-Abrahams expression.\(^6\)

\[
\nu_{ij} = \nu_0 e^{-2\alpha|\mathbf{r}_{ij}|} \begin{cases} 
\exp\left(-\frac{E_j - E_i}{kT}\right), & \text{if } E_j > E_i \\
1, & \text{else}
\end{cases} \tag{2.2}
\]

where $\nu_0$ is the attempt-to-jump frequency, $\alpha$ is the inverse localization radius (due to overlap integral of the wavefunctions assuming exponential decay with distance), $E_i$ and $E_j$ are respectively the energy levels of sites $i$ and $j$, $k$ is the Boltzmann’s constant and
Figure 2.2: Sketches showing (a) hopping transport mechanism from one localized state to another under the influence of electric field $F_x$ and (b) multiple trapping and release (MTR) model.

$T$ is the absolute temperature. The energy difference between $E_i$ and $E_j$ is compensated by absorption or emission of phonons. From Equation 2.2, it can be interpreted that charge transport at low temperatures is dominated by more distant transitions than at higher temperatures. Thus, charge transport takes place in the variable range hopping (VRH). Unlike delocalized transport that occurs in metals and inorganic semiconductors, this transport is not limited by phonon scattering, but phonons assist in the hopping transport. Therefore, mobility is known to increase with rising temperature.

According to the multiple trap and release (MTR) model, charge transport occurs in a narrow delocalized band in combination with a high concentration of localized levels that act as traps as shown in Figure 2.2b. As the charge carriers travel through a delocalized level, they can interact with the localized states. The mobility edge is defined as the energy level which separates localized and non-localized states. If the localized state is separated from the mobility edge by more than a few $kT$, the localized state acts as a deep trap. If the charge carriers are trapped inside deep traps, they essentially cannot get out by thermal activation. On the other hand, localized states with energies within a few $kT$ of the mobility edge are called shallow traps. They have a finite trapping time, after which the charge carriers can be released by thermal activation. The exponential density of states $N(E)$ is given by:

$$N(E) = \frac{N_t}{kT_0} \exp\left(\frac{E}{kT_0}\right)$$

(2.3)

where $N_t$ is the density of traps and $T_0$ is the distribution width parameter. The number
of occupied traps $n_t$ can be expressed as:

$$n_t = \int_{-\infty}^{E_F} N(E) dE = N_t \exp\left(\frac{E_F}{kT_0}\right)$$  \hspace{1cm} (2.4)

where $f(E) = \frac{1}{\exp\left(\frac{E-E_F}{kT}\right)+1}$ is the Fermi-Dirac distribution function.

Due to the trapping process, the resulting mobility $\mu_e$ is effectively reduced compared to the mobility $\mu_0$ in the delocalized band and it can be given by:\textsuperscript{8}

$$\mu_e = \mu_0 s \exp\left(-\frac{E_t}{kT}\right)$$  \hspace{1cm} (2.5)

where $s$ is the ratio of effective density of states at delocalized band edge to the concentration of traps, $E_t$ is the energetical distance between the trap level and the delocalized band edge.
Chapter 3

Organic Bulk Heterojunction Solar Cell

3.1 Brief history of organic solar cell

The first organic cells were based on single organic layer and they exhibited efficiencies below 1%.\(^{11}\) In a solar cell, after light absorption by semiconductor electrons get excited to higher energy level and holes are created. An electron–hole pair or an exciton is created. For exciton separation, the excitons should possess sufficient thermal energy to overcome the Coulomb binding energy or they have to dissociate at the contacts before recombination. The low dielectric constant of organic semiconductors result in a large Coulomb binding energy in the range of 0.5 – 1 eV.\(^{12}\) The excitons do not have enough thermal energy (\(kT\)) to overcome this binding energy. Secondly, the distance travelled by the electron and the hole before recombination (or so called diffusion length) is very short with values less than 20 nm.\(^{13}\) Thus, the semiconductor thickness has to be very small to prevent exciton recombination and to allow exciton separation. Tang et al. introduced the bilayer structure where a second semiconductor layer was applied on top of the existing semiconductor layer.\(^{14}\) Such bilayer solar cell with an efficiency of 1% served as a benchmark for many years. Some years later, the concept of electron transfer from conjugated polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) to buckminster fullerene (\(C_{60}\)) was discovered.\(^{15,16}\) This was a breakthrough in the field of organic photovoltaics (OPV) as this introduced the usage of conjugated polymers as electron donors and fullerene derivatives as electron acceptors. The conjugated polymer absorbs light and donates electron to the electronegative fullerene derivative semiconductor which accepts the electron.

In the 1990s, Yu et al. introduced the bulk heterojunction (BHJ) concept, where an
interpenetrating network of acceptor and donor semiconductors was used to enhance the solar cell performance.\textsuperscript{17} The diffusion length limits the the thickness of the semiconductor layer to allow efficient charge separation. This created a dilemma as decreasing the semiconductor layer thickness would compromise the absorption. The BHJ structure increased the interfacial areas between acceptor and donor and improved exciton dissociation. On the other hand, if the donor and acceptor intermixing is very fine, then the percolation pathways to the electrodes are absent and the charge transport suffers. Thus, morphology plays an important role in the performance of organic solar cells. Several studies have been performed to achieve optimum phase segregation of acceptor and donor. This has been done by optimizing the processing parameters,\textsuperscript{18} choice of solvent,\textsuperscript{1} by putting additives to the semiconductor solution\textsuperscript{19} or by novel semiconductor alternatives.\textsuperscript{20} Significant progress has been made in the field of bulk heterojunction organic solar cells and the efficiency has reached over 9\%.\textsuperscript{21}

### 3.2 Working principle of BHJ solar cell

Figure 3.1a shows the structure of bulk heterojunction (BHJ) solar cell where a blend layer of donor and acceptor type semiconductors is placed between two electrodes. The organic solar cell works in the following consecutive steps (Fig.3.1):\textsuperscript{22}

- **Absorption**: In the first step, photons with energy $E_p$ greater than the band gap of the semiconductor ($E_g$) are absorbed. The unabsorbed photons are simply transmitted. The excess energy $E_p - E_g$ is lost as thermal energy. The absorption process excites the electron in the donor (which is usually the absorbing semiconductor) from the lower HOMO level to the LUMO level. The absence of electron in the HOMO level creates a hole. An exciton pair is formed where the excited electron and the hole are bound by Coulomb energy.

- **Exciton diffusion**: The exciton has to diffuse to a donor–acceptor (D-A) interface to overcome the exciton binding energy and separate. At this point there are two competing processes. The first one is the diffusion process of the exciton with the exciton diffusion length $L_D$ given by:

$$L_D = \sqrt{D\tau} \hspace{1cm} (3.1)$$

where $D$ is the diffusion coefficient and $\tau$ is the lifetime of exciton. For organic
Figure 3.1: (a) Structure of bulk heterojunction (BHJ) organic solar cell. (b) Illustrations of working principle of BHJ solar cell showing (1) absorption and exciton creation (2) exciton diffusion, (3) charge transfer, (4) polaron pair dissociation, (5) charge transport and (6) charge extraction. (Adapted from Deibel et al.\textsuperscript{22}) (c) Energy band diagram of BHJ solar cell.

semiconductors \( L_D < 20 \text{ nm} \).\textsuperscript{13} The second process is relaxation which happens if the exciton travels a distance larger than its diffusion length. This results in a so called geminate recombination where the excess energy is emitted as a photon with lower energy (photoluminescence). Therefore, the excitons should be generated within a distance of \( L_d \) from the D-A interface.

- Charge transfer: At the D-A interface, the exciton is still bound by Coulomb energy. Charge transfer of electron occurs from the donor to the electronegative acceptor, i.e. the electron moves from donor LUMO to the acceptor LUMO. The prerequisite of efficient charge transfer is that the energy offset between the LUMO of the donor and the LUMO of the acceptor has to be larger than the exciton binding energy. The hole and electron are on different semiconductor molecules, but still bound by Coulomb energy. This complex is called a polaron pair or charge transfer complex (CTC).\textsuperscript{22} The charge transfer process is known to be very quick (within hundreds of femtoseconds) for several D-A blends.\textsuperscript{23}
• Polaron pair dissociation: The dissociation of the charges in the polaron pair can be described by the Braun–Onsager model.\textsuperscript{24,25} According to this model, the probability of dissociation of Coulomb-bound pair of polaron depends on the external electric field and the lifetime of the initial bound state.

\[ p(F) = \frac{k_d(F)}{k_d(F) + k_r} \]  

where \( F \) is the electric field, \( p(F) \) is the dissociation probability, \( k_d(F) \) is the field dependent rate of dissociation and \( k_r = \tau^{-1} \) is the rate of recombination which depends on the lifetime of the bound exciton state \( \tau \). This means that after separation, the polaron pair can either recombine or dissociate into free charges.

• Charge transport and extraction: After dissociation, the charges have to travel through the organic semiconductor materials to the electrodes. The charge transport takes place via a hopping process between two neighbouring localized energy states. At this point, loss mechanism in the form of recombination can happen. In a bulk heterojunction the acceptor and donor materials form an interpenetrating network. So, electrons and holes can meet each other during extraction and recombine. The recombination can happen between a polaron pair or between a mobile charge carrier and a carrier in the trap. The recombination process is called non-geminate recombination. For the final charge extraction, the work function of the electrodes has to be matched appropriately with respect to the energy levels of the acceptor and donor. In addition, surface recombination mechanism at the organic-electrode interface can occur.\textsuperscript{26} Due to localized charge transport, the charge carrier mobility in disordered semiconductor and in this case of BHJ solar cells, is very low with values < 10\textsuperscript{-3}cm\textsuperscript{2}/Vs,\textsuperscript{27} which is very small compared to the mobility of inorganic semiconductors (upto 10\textsuperscript{3}cm\textsuperscript{2}/Vs).\textsuperscript{28} If the charges are not extracted quickly, which is the case with organic semiconductors due to low charge carrier mobility, then the charge carriers pile up at the electrode. This creates a space charge region and the extraction process becomes worse.

As stated earlier, the work function of the electrodes is critical to extract the charges. In the conventional architecture of solar cell (Fig. 3.1a), a transparent conducting oxide (TCO) with high work function is used as the window electrode for incoming light and for hole collection. Another metal electrode with low work function is assigned to collect electrons. Metal aluminium (Al) with its low work function is commonly used as the
cathode. However, Al is known to oxidize in air and degrade solar cell performance.\textsuperscript{12} In the conventional solar cell (Fig. 3.1a), there is an anode buffer layer (ABL). The role of ABL is to provide an intermediate energy level between the HOMO of donor and anode for hole collection. In some cases, ABL can have a higher LUMO level than the LUMO of acceptor and block the electrons from going towards the anode. With the concept of buffer layer in mind, another solar cell configuration has been developed. This is the so called inverted structure of solar cell as shown in Figure 3.2. In this structure, the configuration is inverted and another buffer layer analogous to ABL for the case of electrons can be used, i.e. cathode buffer layer (CBL). Since the charge extraction is controlled by the energy levels of the buffer layers, this configuration allows more stable and high work function metals such as Ag and Au to be applied on top of the solar cell as anode. Thus, the inverted configuration of BHJ solar cell is less prone to degradation and displays good stability.\textsuperscript{29}

### 3.3 Solar cell device parameters

Figure 3.3a shows the current-voltage ($I-V$) characteristics of a solar cell in the dark and under illumination (in light). Initially, no current is flowing in the dark as there is no photogenerated charge carrier. At high forward bias, anode and cathode inject holes and electrons respectively into the solar cell and current flow occurs. In light, charge carriers are generated due to photon absorption. Based on the applied voltage, the $I-V$ curve can be divided into different regimes.

- **Open-circuit condition:** This condition occurs when the charge carriers generated under illumination accumulate at the respective electrodes. This results in a potential difference which reduces the built-in potential. Carrier generation and recombination balance each other out and no net current exists inside the device. The voltage at which this condition occurs is defined as open-circuit voltage ($V_{oc}$).
Figure 3.3: (a) $I - V$ curves of solar cell in the dark and in the light. (b) Circuit of the solar cell with the parasitic resistances $R_s$ and $R_{sh}$.

• Short circuit condition: This condition is achieved when $V = 0$ V. Upon illumination, photogeneration of charge carriers occur and they are collected at the respective electrodes. This generates a maximum current in the 4th quadrant which is termed as the short circuit current ($I_{sc}$).

• Power output regime: This occurs between the two regimes that are stated above. In this regime, the solar cell generates power ($P = IV$). At a certain point, the power output is maximum ($P_{max}$). This point is called the maximum power point ($M_{PP}$). With this parameter, the efficiency of solar cell ($\eta$) can be expressed as:

$$\eta = \frac{P_{max}}{P_{in}}$$  \hspace{1cm} (3.3)

where $P_{in}$ is the power of the incoming light. Another performance parameter called the fill factor ($FF$) can also be defined and it gives the ratio between $P_{max}$ and the product of $V_{oc}$ and $I_{sc}$. Now the $\eta$ in Equation 3.3 can be rewritten as:

$$\eta = \frac{FF \cdot I_{sc} \cdot V_{oc}}{P_{in}}$$  \hspace{1cm} (3.4)

In non-ideal solar cells, parasitic resistances like series resistance ($R_s$) and shunt resistance ($R_{sh}$) are present. Figure 3.3b shows the circuit of solar cell. The $I - V$ curve of solar cell can be expressed by the equation:

$$I(V) = I_0 \left\{ \exp \left( \frac{e}{nkT} (V - IR_s) \right) - 1 \right\} + \frac{V - IR_s}{R_{sh}} - I_{ph}$$  \hspace{1cm} (3.5)
where $I_0$ is the dark saturation current, $e = 1.602 \times 10^{-19}$ C is the elementary charge, $n$ is the diode ideality factor, $k = 1.3086 \times 10^{-23}\text{JK}^{-1}$ is Boltzmann’s constant and $T$ is the absolute temperature.

Series resistance in solar cell arises due to resistance from bulk, interfaces and electrode contacts during charge transport. For a good $FF$, it is desirable to have low series resistance. Shunt resistance should be high to prevent leakage current which is caused by impurities and defects in morphology of semiconductor layer. $R_s$ and $R_{sh}$ can be estimated by taking inverse of linear slope of the $I − V$ curve around $V_{oc}$ and $I_{sc}$, respectively.

### 3.4 Quantum Efficiency

The device parameters illustrated in the previous section describe the solar cell performance based on the electrical I-V measurement. Another quantity that describes the solar cell performance is the quantum efficiency. The external quantum efficiency ($EQE$) is defined as the ratio of the number of charge carriers collected to the number of incident photons at a particular wavelength.

$$EQE(\lambda) = \frac{N_c}{N_p} = \frac{j_p}{e \cdot N_p}$$

(3.6)

where $N_c$ is the number of extracted charge carriers per time per unit area, $N_p$ is the number of incoming photons per time per unit area and $j_p$ is the measured photocurrent per unit area at a specific wavelength. Under short-circuit condition ($V=0$), the short-circuit current density $j_{sc}$ can be obtained.

$$j_{sc} = q \int EQE(\lambda) \phi_\lambda d\lambda$$

(3.7)

where $\phi_\lambda$ is the photon flux, which is the number of incident photons per time per unit area per wavelength.

Unlike EQE, the internal quantum efficiency ($IQE$) considers the absorption of photons by the semiconductor. It gives the ratio of the collected carriers to the number of photons that are absorbed by the solar cell. Thus, $IQE$ can be expressed as:

$$IQE(\lambda) = \frac{EQE(\lambda)}{1 – R(\lambda)}$$

(3.8)
where $R(\lambda)$ is the wavelength dependent reflectance of the solar cell and $1 - R(\lambda)$ quantifies the amount of light absorbed by the solar cell.
Chapter 4

Nanostructures in Organic Solar Cells

4.1 Recent progress in organic solar cell

The record performance of organic solar cells stands at 13.2% for multi-junction structures\(^2\) and at 11.84% for single junction\(^30\) devices. The performance of organic solar cells is mainly limited due to the charge carrier recombination processes and the limited absorption in the photo active layer. Organic semiconductors have high absorption coefficients. However, the absorption width is narrow. Figure 4.1 shows the absorption spectrum for the bulk heterojunction mixture of semiconductor donor Poly(3-hexylthiophene-2,5-diyl) (P3HT) and acceptor [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). The first peak at 500 nm corresponds to the maximum absorption of P3HT and the second peak at 330 nm, which is beyond the visible spectrum (400-700 nm) is the absorption peak of PCBM. Based on this spectrum, the band gap of the photo active semiconductor P3HT is calculated to be 1.85 eV, which is at 670 nm wavelength. Within the absorption range which starts at 670 nm, not all incoming photons are absorbed and beyond that, photons are lost to transmission. The amount of light that can be absorbed by the semiconductor layer depends on the thickness and the absorption coefficient. The absorbance \(A\) of a semiconductor with thickness \(d_s\) can be expressed as:

\[
A = 1 - \frac{I(d_s)}{I_0} = 1 - e^{-\alpha d_s}
\]

(4.1)

where \(I_0\) is the intensity of the incoming light, \(I(d_s)\) is the intensity of light at semiconductor thickness \(d_s\) and \(\alpha\) is the absorption coefficient of semiconductor.

The absorption can be enhanced by increasing the semiconductor thickness. However,
Nanostructures in Organic Solar Cells

Figure 4.1: Irradiance of the sun at air mass index of 1.5 (AM 1.5)\textsuperscript{31} and measured absorption coefficient of bulk heterojunction mixture of P3HT:PCBM plotted as a function of wavelength $\lambda$.

due to the short diffusion length of excitons, the thickness cannot be scaled up to accommodate optimum absorption. According to Gilot et al., the optimum thickness for organic semiconductors considering the recombination losses and the optical interference effects is 100 nm.\textsuperscript{32} However, not all incoming photons within the absorption range is absorbed due to reflection from electrodes and transmission for semi-transparent organic solar cells.\textsuperscript{33} For single-junction organic solar cells, where there is only one junction type between acceptor and donor semiconductors, Miyadera et al. estimated the efficiency limit to be in the range of 17\textendash 22\%.\textsuperscript{34}

The concept of multi-junction or tandem structure has been extended to organic solar cells.\textsuperscript{35} In tandem solar cells, multiple junctions of semiconductors with different band gaps are used to optimize absorption by covering wide part of the solar spectrum. Optical losses can also be reduced by using low band gap polymers\textsuperscript{36} to improve absorption and optical spacer\textsuperscript{32} to redistribute the electric field inside the solar cell. Further work has been done to improve charge transport and collection in organic solar cells by optimizing the processing parameters,\textsuperscript{18} choosing proper solvent,\textsuperscript{1} alternative acceptors,\textsuperscript{20} matching interlayers\textsuperscript{37} and electrodes.\textsuperscript{38}

Nanostructures based on metal oxides such as titanium oxide ($\text{TiO}_2$) or zinc oxide ($\text{ZnO}$) are commonly employed to improve organic solar cell performance. Due to their n-type semiconducting nature, they are incorporated as electron acceptor in hybrid-polymer solar cells.\textsuperscript{39} However, due to the poor phase separation between the polymers and the nanostructures such solar cells exhibit sub-par performance. There-
Figure 4.2: Organic solar cell with nanostructures used for (a) efficient charge collection and (b) light trapping effect.

Therefore, nanostructures are embedded into the bulk-heterojunction mixture of acceptor and donor semiconductors. In this manner, the nanostructures increase the interfacial area for exciton dissociation and they serve as electron transport pathways to the cathode as shown in Figure 4.2a. Several groups have reported optimum performance of such solar cells based on ZnO nanostructures in bulk heterojunction solar cells.\textsuperscript{40--42} Light trapping management in solar cells is crucial to enhance the absorption of active semiconductor layer. Nanostructures can act as scattering elements to couple light (Fig. 4.2b). In this manner, the optical pathway of incoming light is elongated and ZnO nanostructures are used to improve absorption of photoactive semiconductor in solar cells.\textsuperscript{43,44}

### 4.2 Light Scattering theory

In optics, light is often treated as a plane wave, in which the waves have constant frequency and the wavefronts of the waves are infinite parallel planes. The propagation of such a plane wave $\bar{E}(z, t)$ in z-direction and at time $t$ is expressed by:

$$\bar{E}(z, t) = E_0 e^{i(kz - \omega t)} = E_0 e^{i\phi}$$

(4.2)

where $E_0$ is the amplitude of the wave, $k$ is the wavevector, $\omega$ is the angular frequency and $\phi$ defines the phase of the wave.

The wavevector $k$ is defined as:

$$k = \frac{2\pi n}{\lambda_0}$$

(4.3)

where $n$ is the refractive index of propagating medium and $\lambda_0$ is the wavelength of light.
Nanostructures in Organic Solar Cells

in vacuum. Figure 4.3 shows the propagation of light rays through nanorod and through a medium in which the nanorod is placed. A phase shift occurs between the light waves as they travel through media with different refractive indices. The phase shift $\Delta \phi$ is given by:

$$\Delta \phi = \frac{2\pi}{\lambda_0} h_{nr} (n_{nr} - n_a)$$

(4.4)

where $h_{nr}$ and $n_{nr}$ are the height and the refractive index of the nanorod and $n_a$ corresponds to the refractive index of the medium in which the nanorod is embedded.

If the phase shift is $\pi$, the outgoing waves from the nanorod and the medium interfere destructively. The direct transmission or specular transmission of light rays gets cancelled out allowing light to scatter at different angles and the optical path length is increased. However, for a phase difference of $2\pi$, constructive interference occurs and more light is transmitted in the specular direction and the optical path length gets reduced. The optimum effect of light trapping is seen for solar cells for a phase shift of $\pi$. The crucial parameter phase shift depends on the refractive indices of the propagating media and on the height of the nanorod.

The intensity of light $I$ is given by:

$$I \propto |E(z, t)|^2$$

(4.5)

Based on the approach of Battaglia et al., Schwarz et al. developed a relation to express the intensity of specular transmission $I_{\text{specular}}$ as:

$$I_{\text{specular}} \propto |p_{nr} + p_a e^{i \Delta \phi}|^2 = 1 - 4p_{nr}(1 - p_{nr}) \cdot \sin^2\left(\frac{\pi(n_{nr} - n_a) h_{nr}}{\lambda_0}\right)$$

(4.6)

where $p_{nr}$ is the fraction of areal coverage of nanorods on the surface and the coverage corresponding to nanorod devoid region is assigned as $p_a = 1 - p_{nr}$.
4.3 Angle-resolved diffusive transmission

Spectrometers can be used to measure the reflectance, absorbance and transmittance at normal direction. However, to measure the light scattered in several directions angle-resolved techniques are required. Figure 4.4 shows the set up of angle-resolved diffusive transmission measurement. In this technique, the intensity of light due to scattering and specular transmission is measured by a photodetector which can revolve around the sample.

The normalized solid angle intensity $I_{sa}$ is expressed by:

$$ I_{sa} = \frac{I_{\text{meas}} \sin \theta}{I_0 \Delta \Omega} $$

(4.7)

where $I_{\text{meas}}$ is the measured intensity, $\theta$ is the scattering angle and $I_0$ is the incoming main beam intensity measured without sample. $I_0$ can be measured directly using the detector if the width of the incoming laser spot is much smaller than the width of the detector.

The solid angle of photodetector $\Delta \Omega$ is given by:

$$ \Delta \Omega = \frac{A_d}{R_d^2} $$

(4.8)

where $A_d$ is the active area of photodetector and $R_d$ is the distance between centre of rotation and photodetector.

Assuming same scattering distribution horizontally and vertically, the fraction of scattered light intensity $q_{\text{scatter}}$ can be expressed as a function of polar angle (or scattering
Figure 4.4: Set up of angle-resolved transmission measurement, in which incoming light from laser diode is transmitted and measured by revolving detector at different angles.

angle) $\theta$, azimuthal angle $\psi$ and solid angle $\Omega$.

$$ q_{scatter}(\theta_1 \ldots \theta_2) = \int_{\theta_1}^{\theta_2} \int_{0}^{2\pi} \frac{1}{I_0} \frac{\partial I_{meas}}{\partial \Omega} \sin \theta \, d\psi \, d\theta $$

$$ = 2\pi \int_{\theta_1}^{\theta_2} \frac{1}{I_0} \frac{\partial I_{meas}}{\partial \Omega} \sin \theta \, d\theta $$

$$ = 2\pi \sum_{i=1}^{i_2} \frac{1}{I_0} \frac{I_{meas}(\theta_i)}{\Delta \Omega} \sin \theta_i \cdot \Delta \theta_i $$

(4.9)

where $\Delta \theta_i = \frac{\theta_{i+1} - \theta_{i-1}}{2}$ is the angular step size.

The main beam interferes with the scattered light at small angles in the range $-3^\circ \leq \theta \leq 3^\circ$. Therefore, the scattered light intensity is assigned to other angles, i.e. $-90^\circ < \theta < -3^\circ$ and $3^\circ < \theta < 90^\circ$. 
Chapter 5

ZnO Basics

5.1 Brief review

Nanostructures of ZnO has received widespread attention due to the versatile properties of ZnO. ZnO is a semiconductor with hexagonal wurtzite crystal structure. It has a wide and direct band gap of 3.37-3.44 eV, which is appropriate for short wavelength opto-electronic applications.\(^{47}\) ZnO is primarily an n-type semiconductor due to the presence of impurities such as hydrogen that act as shallow donor.\(^{48}\) Intentional p-type doping of ZnO is widely pursued, but it is unstable. Owing to its high electron mobility with values up to 205 cm\(^2\)/Vs,\(^{49}\) it is commonly used in thin film transistors. Due to its transparency in the visible spectrum, it is used in light-emitting diodes and solar cells. ZnO can be doped by group-III impurities such as B, Al, Ga and In. Al-doped ZnO (AZO) can be employed as a transparent conductive oxide replacement to the expensive indium tin oxide (ITO).

The applications and properties of ZnO nanostructures depend on the distribution, morphology and size.\(^{47}\) It is challenging to achieve aligned and controlled growth of ZnO nanostructures. There are several methods to deposit ZnO nanostructures. Kong et al. deposited ZnO nanostructures by using the vapour-solid (VS) method, where ZnO nanorods are obtained from decomposition process of ZnO powder at high temperatures of 1350°C.\(^{50}\) Reportedly they obtained complex ZnO nanostructures such as nanohelixes and nanobelts by using this method. There are other methods such as vapour-liquid-solid (VLS),\(^{51}\) pulsed-laser deposition (PLD),\(^{52}\) metal organic chemical vapor deposition (MOCVD),\(^{53}\) and molecular beam epitaxy (MBE).\(^{54}\) Some of these methods such as MBE and MOCVD yield highly crystalline ZnO with less impurities, thereby making them pre-
ferred techniques for electronic devices. However, these methods require high temperature and expensive equipments.

ZnO can also be deposited via the wet-chemical route. In the hydrothermal method, ZnO is formed due to chemical reaction in a heated aqueous solution. Prior to the deposition, this technique requires a seed layer of nanoparticles. However, the deposition is very slow and it can take up to several hours. The spray pyrolysis method results in a fine distribution of particles which are deposited by spraying a precursor solution onto a heated substrate. The constituents of the precursor react on the hot surface and they decompose into ZnO. However, it is difficult to obtain 1-D nanostructures using this method.

ZnO nanostructures can also be obtained from aqueous solution by electrochemical deposition. Electrochemical deposition provides a controlled and scalable way to grow ZnO nanostructures. This technique enables control of the morphology by changing the parameters of deposition. It allows high deposition rate and since it can be done at low temperature, it is compatible with flexible substrates. According to Izaki et al. and Peulon et al., the pH has to be increased in the immediate vicinity of the substrate (cathode) for ZnO to deposit. Peulon et al. used the reduction of oxygen to increase the pH, while Izaki et al. used nitrate (NO$_3^-$). Due to the high solubility of NO$_3^-$ in water, electrochemical deposition with NO$_3^-$ is reported to be much faster. Thus, in this thesis electrochemical of ZnO was done using nitrate salt.

### 5.2 Electrochemical deposition of ZnO

Figure 5.1 shows the electrochemical deposition set up of ZnO. The set up requires three electrodes, which are cathode, reference electrode and counter electrode. In this work, Ag/AgCl has been used as reference electrode, Pt as the counter electrode and the conductive substrate on which ZnO is to be deposited is assigned as the cathode. The electrodes are dipped inside an electrolyte solution which is an aqueous solution of zinc nitrate (Zn(NO$_3$)$_2$) and potassium chloride (KCl). KCl is used as supporting electrolyte to improve conductivity of the electrolyte solution. Zn(NO$_3$)$_2$ dissociates into zinc ion Zn$^{2+}$ and nitrate ion (NO$_3^-$) inside the bulk solution. The reaction mechanism leading to formation of ZnO is explained below.

- Nitrate reduction: When a driving voltage is applied, reduction of (NO$_3^-$) occurs at
Electrochemical deposition of ZnO

the cathode.

\[ \text{NO}_3^- + 2e^- + H_2O \rightarrow \text{NO}_2^- + 2OH^- \quad (5.1) \]

- Formation of Zn(OH)$_2$: The hydroxide ion combines with Zn$^{2+}$ to form Zn(OH)$_2$ at the cathode surface (Fig. 5.2).

\[ 2OH^- + Zn^{2+} \rightarrow Zn(OH)_2 \quad (5.2) \]

- Formation of ZnO: At a certain temperature, Zn(OH)$_2$ dehydrates to form ZnO nuclei.

\[ Zn(OH)_2 \rightarrow ZnO + H_2O \quad (5.3) \]

These nuclei serve as seed layer for ZnO growth. The minimum temperature required for dehydration of Zn(OH)$_2$ is estimated to be 34°C.$^{59}$

Figure 5.1: Illustration of electrochemical growth set up with three electrodes.

Figure 5.2: Formation of ZnO via electrochemical deposition process.
Chapter 6

Self-Assembled Monolayer

6.1 Introduction

The term self-assembled monolayer was coined by Zisman et al. in 1946 when they made a self-assembly of monolayer on a metal surface. The major breakthrough came 40 years later when Allara and Nuzzo prepared a well assembled layer of functional organic molecules from solution onto noble metal Au. Self-assembled monolayer (SAM) is a monolayer of regularly oriented molecules adsorbed onto a surface. The thickness of SAM is in the range of 1-3 nm. Therefore, SAMs can generally adsorb onto objects of all sizes ranging down to nanostructures. Depending on the functional group of the SAM molecule, the surface properties of materials can be tuned. Preparation of SAMs are done from liquid phase or from gas phase methods which do not require complex deposition techniques. All these characteristics make SAM attractive for a wide range of applications as protection layer, for bio-chemical sensors and to pattern arrays. Self-assembled monolayers have been used to modify the interfacial properties in many organic electronics and in thin film transistors as a very thin gate insulator.

6.2 Basics of self-assembled monolayer

Self-assembled monolayer is formed by chemisorption of a molecule onto a surface which has an affinity for the head group. Figure 6.1 shows the constituents of self-assembled monolayer on a surface. They are head group, backbone chain and end group. The stability of the SAMs depends on the interaction of head group with substrate surface and the interactions between the neighbouring molecules. The head group binds to the sur-
face with ionic or covalent bonds.\textsuperscript{68} Between molecules, the interactions are weaker with van der Waals interactions\textsuperscript{69} and hydrogen bonds.\textsuperscript{70} The orientation of SAM molecules on the surface can be described by the tilt of the backbone with respect to the surface and the angle of rotation about the long axis of the molecule.\textsuperscript{63} There are different types of molecules that form SAMs as shown in Figure 6.2. The head group determines the surface on which the molecules bind and form SAM. Thiol (-SH) and sulphide groups show affinity for transition metals such as Au, Ag, Cu and Pt and inorganic semiconductors such as GaAs and CdSe. Silane groups prefer to form SAM on silicon oxide (SiO\textsubscript{2}) and carboxylic (-COOH) groups bind on metal oxides such as Al\textsubscript{2}O\textsubscript{3}, ITO and ZnO.\textsuperscript{71} The surface property is tuned by the end group. Adsorption of molecules with end groups –CH\textsubscript{3} and –CF\textsubscript{3} make the surface hydrophobic and anti-adherent, while –COOH, –NH\textsubscript{2} or –OH groups result in hydrophilic surfaces with good metal ion and protein binding properties.\textsuperscript{64}

SAMs can be prepared by adsorption process from gas and liquid phase. Gas phase adsorption requires high vacuum and it is suitable for short molecules (alkyl chain with less than 10 C-atoms) since they are volatile.\textsuperscript{72} The most common way to prepare SAMs is via adsorption process from solution. For thiols, commonly used solvents are ethanol and methanol and for very long molecules with low solubility toluene and hexane are used.\textsuperscript{68} On Au, the adsorption of thiol molecules takes place in two steps. In the first step, the thiol is physisorbed onto the Au surface. In the second step, cleavage of S-H bond occurs leading to chemisorption with a strong covalent bond between thiol and Au (40 kcal mol\textsuperscript{−1}).\textsuperscript{73} This adsorption process is as follows:\textsuperscript{74,75}

\begin{equation}
CH_3(CH_2)_nSH + Au \rightarrow (CH_3(CH_2)_nSH)_{phys}Au
\end{equation}

\begin{equation}
(CH_3(CH_2)_nSH)_{phys}Au \rightarrow CH_3(CH_2)_nS - Au + \frac{1}{2}H_2
\end{equation}
According to Vericat et al., there are two distinct adsorption kinetics leading to SAM formation (as shown in Figure 6.3). The first step happens from a few seconds to a few minutes depending on the concentration of the precursor molecules. In this step, up to $\sim 85\%$ of maximum coverage of SAM is achieved and the molecules are in disordered state. The second step is self-assembling step, where interactions take place between molecules so as to organize the molecules or ions in a state where the thermodynamic energy is minimum. This is a slow process which can take hours until the SAM coverage reaches its maximum. The adsorption rate also depends on the reactivity of head group. Wang et al. observed that Trichloro(octadecyl) silane (OTS) molecules formed complete SAM on silicon nitride after 5 minutes, whereas octadecyltrimethoxysilane SAMs took 120 minutes. This was attributed to the more reactive head group of OTS, which required less bond dissociation energy to replace the groups attached to the silicon atom.

For thiols, the adsorption process takes place in four steps. The first step is physisorption (Equation 6.1). In the second step, the thiol molecule covalently binds to substrate surface (Equation 6.2) and the molecules are lying flat on the surface. During the third step, more molecules adsorb onto the surface and the thiol molecules start standing up. In the final step, more molecules adsorb and self-assemble leading to complete SAM formation. On Au, the thiol molecules prefer to chemisorb at defective sites of the Au surface such as step edges, where the molecules nucleate. Due to the van der
Self-Assembled Monolayer

Figure 6.3: Illustrations highlighting the two-step mechanism of SAM formation: (a) disordered state and (b) ordered state forming self-assembled monolayer.

Waals interactions between alkyl chains, SAM on alkanethiol molecules are tilted with an angle of $\sim 26^\circ$ from the surface normal and a packing distance of $\sim 0.5$ nm between neighbouring thiol molecules is achieved. In case of Ag, the packing distance is reduced to $\sim 0.46$ nm since alkyl chains on Ag are almost perpendicular.

In addition to the molecule type, the characteristics of SAM depend on substrate surface preparation, concentration of molecules in solution, immersion time, humidity, temperature, substrate orientation, etc.\textsuperscript{75,76} Dirt and chemical residues on the substrate surface can be detrimental to SAM quality. Therefore, substrates are cleaned with plasma treatment, solvent cleaning and UV-ozone cleaning etc. For long immersion duration, complete SAM can be achieved.\textsuperscript{79} Higher concentration of molecules in solution are used to reduce the immersion time required for complete SAM formation. However, if the concentration is too high, then multilayer can be formed.\textsuperscript{80}

According to some studies, in addition to the adsorption mechanism desorption processes of thiol can also occur.\textsuperscript{81,82} The desorption process occurs by a reduction process as follows:

$$R - S - M + e^- \rightarrow R - S^- + M$$

where $R$ corresponds to alkyl chain, $S$ is sulphur atom and $M$ denotes metal. Oyamatsu et al. reported that the voltage at which desorption occurs depends on the thiol type and the ions in the ionic solution.\textsuperscript{83}

6.3 Microcontact printing

Microcontact printing was introduced by Whitesides et al. to replicate patterns of self-assembled monolayer with spatial resolution down to the sub-$\mu$m range.\textsuperscript{84} In this thesis, microcontact printing is used in Chapter 7 for patterning self-assembled monolayer. This soft lithography technique needs a master template based on Si, which is prepared by
Microcontact printing

Figure 6.4: Schematics of microcontact printing starting from UV exposure on negative photoresist layer, development process, fabrication of PDMS stamp, inking PDMS with molecules and stamping process resulting in patterned SAM formation.

using photolithography. Si wafer is coated with a photoresist (photo sensitive resist) and exposed to UV light through a shadow mask. Depending on the type of photoresist, the UV exposure has different effects. On a positive photoresist, parts which are exposed to UV radiation become soluble during development process. On the other hand, for negative photoresist the polymers in exposed regions cross-link and they become insoluble. During development, the photoresist layer is immersed into a developing solution and only the cross-linked patterns are left behind as shown in Figure 6.4. Usually after development step is the etching process. The photoresist is used as an etch resist to form a patterned Si master. In case of negative photoresist SU8, it is difficult to remove the cross-linked SU8 photoresist from the Si substrate. Therefore, the SU8 features remain as part of the master. An elastomer of poly(dimethylsiloxane) (PDMS) is poured over the master and it inherits the complementary features of the master. After the PDMS is cured (annealed to harden it), the PDMS is inked. Prior to stamping, the solvent in ink is evaporated so that the liquid ink does not spread. Finally, the PDMS stamp inked with molecules is stamped on a substrate. The formation of SAM on the substrate occurs as ink molecules diffuse from the PDMS bulk to the surface of substrate.\textsuperscript{85}

The quality of microcontact printing is affected by factors such as contamination and stamp deformation. Stamp deformation can occur during stamping or removal. This happens if the aspect ratio of the features is high or too low.\textsuperscript{86} Due to the mobility of ink molecules, the ink can spread laterally towards areas where no ink is desired as the printing time and the ink concentration increases.\textsuperscript{87} Other factors affecting the quality of microcontact printing are temperature and humidity.\textsuperscript{88}
Chapter 7

Self-Assembled Monolayer-Tuned Growth of ZnO Nanorods

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7.1 Introduction

Due to its wide band gap, high thermal stability and high electron mobility, ZnO is widely used in transparent electronics. Arrays of ZnO nanostructures or nanorods have been used in hybrid-polymer solar cells as n-type semiconductor, light trapping structures in solar cells and as biosensors. For these applications, precise control of morphology, distribution and size of ZnO nanorods is critical. Electrochemical deposition of ZnO offers the advantages of control and low temperature processing technique. Several works have been reported on the tailored growth of ZnO nanorods by changing the pH, using buffer layer, varying electrochemical deposition parameters and pulsed voltage method. However, the ZnO nanorods obtained by some of these methods cannot control the density of ZnO nanorods.

In this chapter, a simple method has been introduced to tune the density and size of ZnO nanorods. Self-assembled monolayer (SAM) of alkanethiol has been used to tailor the growth of ZnO nanorods. SAM has been applied on metal surface to passivate the surface. The SAM is not perfect as there are defects or pinholes in the monolayer. During electrochemical deposition, the ZnO nanorods nucleate and grow through the pinholes in SAM, whilst creating gaps between ZnO nanorods. The size and density of the ZnO nanorods has been varied by changing the parameters of electrochemical deposition. Further, microcontact printing of SAM has been used to pattern the growth of ZnO nanorods. Impedance measurements have been carried out to analyze the blocking behaviour of SAM. Topographical characterization of the ZnO nanorods has been investigated by using scanning electron microscopy (SEM).

7.2 Experimental procedure

Polyethylene terephthalate (PET) substrates were cleaned with acetone, de-ionized water and dried with nitrogen gas. Two types of metal/PET substrates were investigated in this work. 100 nm Au was sputter coated on PET substrate at rate of 25 nm/s and chamber pressure of $5 \cdot 10^{-5}$ mbar. The same sputter coating parameters were used to get 100 nm Ag on PET substrates. To get rid of organic residue, the substrates were placed inside UV-ozone chamber for 5 minutes.

For self-assembled monolayer preparation, 5 mM concentration of 1-octadecanethiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$) was prepared in ethanol (from Sigma Aldrich with 99% ethanol and
The PET substrates were immersed into the alkanethiol solution to allow adsorption of thiol molecules. To remove the unbound molecules of the organic self-assembled monolayer (SAM), the substrates were washed with ethanol. To characterize the surface property, contact angle measurements were performed by putting a 10 µl volume droplet of water on the samples.

Impedance measurements were carried out to analyze the blocking property of self-assembled monolayer. Figure 7.1 shows the impedance measurement set up of the SAM substrates. The electrolyte was an aqueous solution of tris-buffer (obtained from Sigma Aldrich) with 10 mM concentration and adjusted pH of 7.4. The electrolyte was contained inside a polydimethylsiloxane (PDMS) block which has cylindrical hole with 5 mm diameter and 1 cm height. The impedance data were acquired by using a lock-in amplifier (SR830DSP, Stanford Research).

For electrochemical deposition of ZnO, a three-electrode set up was used as shown earlier in Chapter 5 (Fig.5.1). The counter electrode was Pt and the reference electrode was Ag/AgCl. Electrochemical deposition of ZnO was carried out on metal/PET substrates and SAM modified metal/PET substrates. Aqueous solution of zinc nitrate (Zn(NO₃)₂) and potassium chloride (KCl) was used as electrolyte. To analyze the distribution and the morphology of the ZnO nanostructures, scanning electron micrographs of the electrodeposited ZnO nanostructures were recorded. To get the size and the distribution of ZnO nanorods, the SEM images were analyzed using ImageJ software.

For microcontact printing, the first step was fabrication of master. A Si wafer was spin coated with 1.5 µm thick SU8 photoresist (from Microchemicals). The photoresist was baked on a hotplate at 95°C for 1 min. The photoresist was exposed to UV light for 30 s through a shadow mask. Post exposure the photoresist was baked at 95°C for 1 min. The photoresist was immersed inside the SU8 developer for 5 min. After development, the structured SU8 was baked at 150°C for 3 min to make the SU8 patterns hard. In order to prepare PDMS stamp, a degassed mixture of 10:1 weight ratio of Sylgard 184 silicone elastomer (obtained from Dow Corning) and curing agent was poured over the master template. The PDMS was cured inside an oven at 70°C for 90 min. Once it cooled down, the 3 mm thick PDMS was peeled off from the master. The PDMS was cut into dimensions of 1x1 cm. The stamp was inked with thiol solution. It was dried by using nitrogen before applying it on the substrate. In addition to the structured PDMS stamp, another PDMS stamp with no pattern was also prepared.
7.3 **Theory on impedance analysis**

To quantify the blocking property of SAM, impedance spectroscopy has been employed. Based on the impedance measurement set up (Fig. 7.1), the electrical impedance of the self-assembled monolayer (SAM) can be modelled into an equivalent circuit consisting of the SAM resistance $R_{\text{SAM}}$, the SAM capacitance $C_{\text{SAM}}$ and the electrolyte resistance $R_e$. As the impedance is measured across the electrolyte and the SAM of alkanethiol on the metal surface, the system can be described by an $RRC$ circuit as shown in Figure 7.2a. For the sake of simplicity this model assumes that there is no diffusion of ions from electrolyte into SAM. The impedance of the RRC circuit can be expressed as:

$$Z(\omega) = R_e + \frac{1}{R_{\text{SAM}}} + \frac{1}{i\omega C_{\text{SAM}}}$$  \hspace{1cm} (7.1)

where $Z$ is the impedance and $(\omega)$ is the angular frequency.

If $R_{\text{SAM}}$ is very large at low frequencies, the $RRC$ circuit gets simplified to the $RC$ circuit (Fig. 7.2b). For the $RC$ circuit, the impedance can be written as:

$$Z(\omega) = R_e + \frac{1}{i\omega C_{\text{SAM}}}$$  \hspace{1cm} (7.2)

The corresponding absolute value of impedance is:

$$|Z(\omega)| = R_e \sqrt{1 + \frac{1}{(\omega R_e C_{\text{SAM}})^2}}$$  \hspace{1cm} (7.3)

At low frequencies, $(\omega) \to 0$, $|Z(\omega)|$ is dominated by the SAM capacitance.

$$|Z(\omega)| \approx \frac{1}{\omega C_{\text{SAM}}}$$  \hspace{1cm} (7.4)
Results and Discussion

At high frequencies, \((\omega) \to \infty\), \(|Z(\omega)|\) is dominated by the electrolyte resistance.

\[
|Z(\omega)| \approx R_e
\]  

(7.5)

The RC model has been used to obtain the SAM capacitance and the RRC model has been used to determine the SAM resistance. The thickness of the capacitive SAM can be calculated by assuming a parallel plate capacitor with electrolyte and metal as plate conductors and SAM as the dielectric.

\[
C_{SAM} = \frac{\varepsilon_0 \varepsilon_{SAM} A}{d_{SAM}}
\]  

(7.6)

where \(\varepsilon_0 = 8.8542 \times 10^{-12} \text{Fm}^{-1}\) is the vacuum permittivity, \(\varepsilon_{SAM}\) is the dielectric constant of SAM, \(A\) is the cross-sectional area of the SAM exposed to electrolyte and \(d_{SAM}\) is the thickness of SAM.

7.4 Results and Discussion

7.4.1 Impedance measurement on SAM samples

Contact angle measurements confirmed the presence of self-assembled monolayer (SAM) as the contact angle changed from 17° for bare Au to 92° for Au samples immersed in alkanethiol solution for 30 s. Due to –CH\(_3\) end group of the thiol, the Au surface switched from hydrophillic to hydrophobic. To quantify the surface coverage and the packing density property of SAM, impedance measurements were carried out on SAM samples.\(^{95}\)
The density of alkanethiol molecules was tuned by varying the adsorption time of the alkanethiol molecules on Au, i.e. different immersion time of Au in alkanethiol solution. Figure 7.3 shows the impedance measurements and the corresponding theoretical fits. The phase curves confirm that at high frequencies the absolute impedance is resistive with a phase shift of 0° due to the electrolyte resistance. At frequencies > 100 Hz, the phase shifts towards -90°, which corresponds to the capacitive behaviour of SAM. The contribution of the SAM resistance ($R_{SAM}$) is seen at low frequency (< 20 Hz) as the phase shifts from -90° towards 0°. Since $R_{SAM}$ is very high, the theoretical fitting was done using the $RC$ model. It can be seen that for increasing adsorption time, the contribution of $R_{SAM}$ increases (as shown in Figures 7.3a and 7.4a).

For 30 s adsorption time on Au, $R_{SAM}$ is 90 kΩ and it increases to 260 kΩ for 10 min adsorption time. The increasing resistance confirms that the alkanethiol molecules are more packed for longer adsorption time. For 1 hour and 24 hour adsorption times, it increases to 780 kΩ and 800 kΩ, respectively. This observation corresponds to the two-step mechanism of SAM formation mentioned earlier. SAM formed on Au after 30 s adsorption time are in a disorganized state as the molecules have just started to attach to the metal surface. Thus, $R_{SAM}$ is low. At 10 minutes, the SAM molecules are getting out of the disordered state and they start to self-assemble. After 10 min adsorption time, $R_{SAM}$ increases gradually as more alkanethiol molecules attach and assemble with time.

![Figure 7.3: (a) Absolute impedance plots of SAM on Au for different alkanethiol adsorption time and their theoretical fits. (b) Corresponding phase plots of impedance measurement.](image)

On Ag, $R_{SAM}$ also increases as the alkanethiol adsorption time is increased. The alkyl chains are almost perpendicular to the Ag surface and the packing density of SAM
molecules on Ag is high. Thus, $R_{SAM}$ is higher on Ag. Using alkanethiol SAM dielectric constant of 2.55, the corresponding thickness of SAM on Au and Ag was determined. On Au, the SAM thickness values are in agreement with literature findings for alkanethiols. For lower adsorption time, the SAM thickness is slightly small as the SAM molecules are disordered and they are not aligned properly on Au. After 10 min adsorption time, the SAM molecules arrange themselves into a regularly packed structure. This results in an increase in thickness at higher adsorption times. For Ag, the SAM thickness is higher as they align more perpendicularly to the surface. At longer adsorption times starting from 10 min, the thickness values are much higher than a monolayer thickness of $\sim 2$ nm. The reason for this finding can be attributed to formation of silver oxide ($Ag_2O$) during UV-Ozone process. The presence of $Ag_2O$ would decrease the capacitance and hence give higher $d_{SAM}$ values. The reason for higher $R_{SAM}$ values on Ag can also be traced back to $Ag_2O$ formation.

### 7.4.2 Electrochemical growth of ZnO on SAM modified Au surface

The electrochemical growth of ZnO on Au surface produces a dense layer of ZnO nanorods (Fig.7.5a). For organic solar cells, there has to be gaps between the nanorods to allow proper infiltration of the semiconductor polymer. This is achieved by modifying the metal surface using SAM. Figures 7.5b-e show the SEM images of ZnO nanorods on SAM modified Au. ZnO nanorods have been electrodeposited on Au samples which have been immersed in thiol solution for different time durations. Table 7.1 lists the ZnO nanorod
coverage and size distribution. For the bare Au sample, the coverage of nanorods is 71.6%. Once the Au sample is treated with alkanethiol for 30 s, the coverage of ZnO nanorods decreases to 52.4%. This less sparse coverage of nanorods can be attributed to the presence of SAM on Au.

![SEM image](image)

(a)

![SEM image](image)

(b)

![SEM image](image)

(c)

![SEM image](image)

(d)

![SEM image](image)

(e)

Figure 7.5: (a) SEM image of electrodeposited ZnO nanorods on Au substrate. SEM images of ZnO grown on Au samples with SAM formed during adsorption time durations of (b) 30 s, (c) 1 minute, (d) 1 hour and (e) 24 hours. The insets show the side-view SEM images. For sample with highly dense coverage of ZnO (b), the sample was scratched to get the height of ZnO nanorod. Parameters of electrochemical deposition are 10 minutes deposition time, 5 mM (Zn(NO$_3$)$_2$) and 0.1 M KCl concentration, -0.975 V against Ag/AgCl and temperature of 55°C.

Figure 7.6 shows the growth model of ZnO on Au and SAM modified Au surfaces. As seen from the impedance measurements, the SAM of alkanethiol molecules exhibits high resistance. Unlike bare Au, where ZnO grows everywhere, the SAM acts as a blocking layer that impedes ZnO nuclei to grow on the Au surface. Since the packing of alkanethiol molecules in SAM is not perfect, there are bound to be defects or pinholes in the SAM.
Results and Discussion

Table 7.1: Size and distribution data of ZnO nanorods on Au substrates with varying thiol adsorption time extracted from SEM images in Figure 7.5.

<table>
<thead>
<tr>
<th>Thiol adsorption time</th>
<th>ZnO coverage (%)</th>
<th>Nanorod height (nm)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 s</td>
<td>71.6</td>
<td>135 ± 15</td>
<td>72 ± 10</td>
</tr>
<tr>
<td>30 s</td>
<td>52.4</td>
<td>131 ± 17</td>
<td>84 ± 16</td>
</tr>
<tr>
<td>1 min</td>
<td>50.4</td>
<td>126 ± 12</td>
<td>82 ± 10</td>
</tr>
<tr>
<td>1 hour</td>
<td>35.1</td>
<td>164 ± 21</td>
<td>98 ± 11</td>
</tr>
<tr>
<td>24 hour</td>
<td>10.8</td>
<td>266 ± 13</td>
<td>134 ± 49</td>
</tr>
</tbody>
</table>

Figure 7.6: Schematic illustration of the growth of ZnO on (a) bare Au and (b) SAM modified Au surface where the ZnO nanorods nucleates through the pinholes of SAM.

This allows the ZnO to nucleate and grow through these pinholes. This theory can be proved by observing the SEM images for varying adsorption times. As the adsorption time of alkanethiol on Au increases, the alkanethiol molecules become more organized and are densely packed. There are less pinholes in the SAM from where ZnO can nucleate. Thus, the coverage of ZnO decreases as the adsorption time increases. The ZnO nanorods grown on SAM/Au resulting in larger diameter and height compared to the ZnO grown on bare Au. Initially, ZnO nucleates at few sites on SAM/Au. For the same electrolyte concentration, this leaves more Zn\(^{2+}\) which can further react and grow on the ZnO nuclei. Thus, the nanorods are bigger and longer on SAM/Au samples. As the adsorption time increases, the ZnO nanorods are fewer, but their sizes are bigger.

The density of alkanethiol in SAM can also be changed by thermal activation. Electrochemical deposition of ZnO was performed on Au samples which were immersed inside alkanethiol solution at temperatures of 25°C, 50°C and 75°C (Fig. 7.7). There is no significant trend in the coverage of ZnO. At room temperature, the ZnO coverage is 42.8%, which increases to 65.1% and 54.2% for adsorption temperatures of 50°C and 75°C, respectively. What is noteworthy is that as the temperature increases, the ZnO nanorods coalesce. At 75°C, the ZnO nanorods have merged to form islands with large empty space in between. Thermal processes can induce lateral movement of SAM molecules.
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Figure 7.7: SEM images of ZnO nanorods for samples with SAM adsorbed on Au at alkanethiol solution temperature of (a) 25°C, (b) 50°C and (c) 75°C deposition temperatures. The insets show the side-view SEM images. Electrochemical deposition was carried out using the same parameters of the reference sample with 10 minutes deposition time, 5 mM \(\text{Zn(NO}_3\text{)}_2\) and 0.1 M KCl concentration, -0.975 V against Ag/AgCl and temperature of 65°C.

on the surface, thereby influencing the formation of ordered SAM domains. STM measurements done by Yamada et al. on thiol/Au (111) surface highlighted that there are domains and pits with depths of 0.24 nm, which is approximately equal to the step height of monoatomic Au(111).\(^9\) The pits were assigned to be vacancy islands corresponding to the top surface of Au, which were created due to the missing Au atoms during Au-thiol formation. With increasing temperature, the pit size increases and the size of the alkanethiol domain size also increases. Thus, with increasing SAM domain size the ZnO nanorods are forced to merge together.

The distribution and the size of ZnO nanorods can also be tuned by changing the parameters of ZnO electrochemical deposition such as deposition or growth time, electrolyte concentration, deposition temperature and overvoltage. Figure 7.8 shows the SEM images of ZnO nanorods grown on SAM/Au obtained by varying the ZnO growth time, while keeping the thiol adsorption time of 30 s the same for all samples. The first noticeable trend is the increasing surface coverage of ZnO as the growth time increases. For 1 min ZnO growth, there are few ZnO nanorods with 28.9% coverage. The nanorods or in this case to be more appropriate, nanospheres have height of 45 nm and lateral diameter of 66 nm. For 5 minutes growth time, the ZnO nanorods begin to merge resulting in a higher ZnO coverage. The lateral diameter remains the same, but the height has increased to 128 nm. The same increasing trend is observed for 10 minutes and 20 minutes growth times. As the growth time increases the ZnO nanorods start to grow vertically and laterally and they overcome the blocking effect of SAM. The distributions and sizes of these samples are listed in Table 7.2.
Results and Discussion

Figure 7.8: SEM images of ZnO grown on 30 s SAM/Au for (a) 1 minute, (b) 5 minutes, (c) 10 minutes, (d) 20 minutes and (e) 8 mM Zn(NO₃)₂ and 0.16 M KCl aqueous concentration. The insets show the side-view SEM images. Electrochemical deposition parameters of the reference sample as shown in (c) are 10 minutes deposition time, 5 mM (Zn(NO₃)₂) and 0.1 M KCl concentration, -0.975 V against Ag/AgCl and temperature of 55°C.

Using the parameters of 10 min growth time as reference (Fig. 7.8c), only one parameter was changed at a time for comparison. For increased electrolyte concentration of 8 mM (Fig. 7.8e), it can be seen that the ZnO nanorods have coalesced to form bigger island with high ZnO coverage of 63.4%. In comparison to the 5 mM sample (Fig. 7.8c), the nanorod diameter has increased by factor of 1.3, while the height remains almost the same. This is due to the fact that at higher electrolyte concentration, more Zn²⁺ ions are present to enlarge the ZnO size.

In the next step, the deposition temperature is varied. Figures 7.9a and 7.9b show the SEM micrographs of ZnO nanorods grown at deposition temperatures of 45°C and 65°C, respectively. It can be seen that at low temperature of 45°C, the coverage of ZnO nanorods is less with 26.7%. As the temperature increases to 55°C, the coverage increases to 52.4%. However, at 65°C the ZnO coverage decreases to 42.7%. The number density of ZnO nanorods can be determined from the ZnO coverage and the nanorod diameter. For the 45°C sample, the average nanorod number density is 36 µm⁻². For 55°C and 65°C samples, the number density increases to 94 µm⁻² and 108 µm⁻², respectively. As the deposition temperature increases, more Zn²⁺ can overcome the activation energy
Table 7.2: Size and distribution data of ZnO nanorods obtained by varying electrochemical deposition parameters on Au with 30 s SAM adsorption time. The highlighted bold text corresponds to the electrochemical deposition parameter that is varied in reference to the parameters used in the third entry row.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coverage (%)</th>
<th>Diameter (nm)</th>
<th>Height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min, 55°C, 5 mM, -0.975 V</td>
<td>28.9</td>
<td>66 ± 23</td>
<td>45 ± 13</td>
</tr>
<tr>
<td>5 min, 55°C, 5 mM, -0.975 V</td>
<td>41.1</td>
<td>67 ± 11</td>
<td>128 ± 15</td>
</tr>
<tr>
<td>10 min, 55°C, 5 mM, -0.975 V</td>
<td>52.4</td>
<td>84 ± 17</td>
<td>131 ± 17</td>
</tr>
<tr>
<td>20 min, 55°C, 5 mM, -0.975 V</td>
<td>54.2</td>
<td>95 ± 18</td>
<td>213 ± 18</td>
</tr>
<tr>
<td>10 min, 55°C, 8 mM, -0.975 V</td>
<td>63.4</td>
<td>137 ± 8</td>
<td>109 ± 23</td>
</tr>
<tr>
<td>10 min, 45°C, 5 mM, -0.975 V</td>
<td>26.7</td>
<td>97 ± 23</td>
<td>125 ± 14</td>
</tr>
<tr>
<td>10 min, 65°C, 5 mM, -0.975 V</td>
<td>42.7</td>
<td>71 ± 8</td>
<td>189 ± 22</td>
</tr>
<tr>
<td>10 min, 55°C, 5 mM, -0.775 V</td>
<td>34.8</td>
<td>81 ± 7</td>
<td>137 ± 7</td>
</tr>
<tr>
<td>10 min, 55°C, 5 mM, -1.075 V</td>
<td>51.2</td>
<td>78 ± 11</td>
<td>122 ± 14</td>
</tr>
</tbody>
</table>

barrier and diffuse towards the Au surface. This means more ZnO nucleation takes place and thus, the number density of ZnO is high at higher temperatures. In addition, the ZnO nanorods are expected to grow as temperature increases and this trend is observed experimentally as the nanorod height increases at higher deposition temperatures.

In Figures 7.9c, 7.8c and 7.9d, the driving overvoltage has been varied to -0.775 V, -0.975 V and -1.075 V, respectively. The nanorod diameter decreases for higher driving voltage. The number density of the ZnO nanorods also increases from 68 µm\(^{-2}\) to 108 µm\(^{-2}\) at -0.775 V and -1.075 V, respectively. As the voltage increases, more OH\(^-\) ions are generated, which increases the pH of the Au surface. Electrochemical growth of ZnO in an alkaline solution is known to result in smaller rod diameters.\(^ {99}\) According to Khajavi et al. higher ratio of OH\(^-\)/Zn\(^{2+}\) results in smaller nanorod diameter as the Zn\(^{2+}\) cannot diffuse along the ZnO nanorods.\(^ {100}\) At this point another factor needs to be taken into account, i.e. the desorption of SAM molecules from the Au surface. Oyamatsu et al. revealed that desorption of thiol can happen in ionic liquids when a driving voltage is applied. Although the exact voltage at which desorption occurs depends on the type of electrolyte and alkanethiol, their findings indicate that desorption happens around -1 V for many alkanethiols.\(^ {83}\) Thus, the reason for the high coverage of ZnO nanorods can also be attributed to the desorption of thiols from the SAM layer.
Results and Discussion

Figure 7.9: SEM images of ZnO grown on 30 s SAM/Au at (a) 45°C, (b) 65°C deposition temperatures, (c) -0.775 V and (d) -1.075 V overvoltages. The insets show the side-view SEM images. Electrochemical deposition parameters of the reference sample (Fig.7.8c) are 10 minutes deposition time, 5 mM (Zn(NO$_3$)$_2$) and 0.1 M KCl concentration, -0.975 V against Ag/AgCl and temperature of 55°C.

7.4.3 Electrochemical growth of ZnO on SAM modified Ag surface

Due to its stability and appropriate work function, Ag is widely used as a metal electrode in organic solar cells. Figure 7.10a shows the SEM image of ZnO electrodeposited on SAM modified Ag surface. The result is very different from the case of SAM/Au samples. Instead of nanorods, the morphology of ZnO on SAM/Au exhibits flower-like structures with petals. The size of the petals are also large with average width and average length of 136 nm and 248 nm, respectively. When exposed to air, silver is known to form a thin layer of native silver oxide (Ag$_2$O). Prior to SAM modification, Ag was treated with UV-ozone (UVO), which could have resulted in a thick layer of Ag$_2$O. According to Heideri et al. the change in morphology can be attributed to an increased pH $> 9$. During electrochemical deposition, the pH must have increased resulting in the flower patterns of ZnO. Thus, electrochemical deposition was carried out on Ag samples without UVO treatment. (Figures 7.10c and 7.10c). It can be seen from the SEM images that for the non-UVO Ag samples, the ZnO has nanorod morphology. On bare Ag, the ZnO is more tightly packed with a large coverage of 80.4% and smaller average diameter of 66 nm compared to the nanorods on Au (Fig. 7.5a). With 30 s SAM modification on Ag, the
ZnO coverage decreases to 59.7% with similar nanorod diameter of 65 nm. Thus, SAM can be used to tune the ZnO nanorod distribution on Ag as well. For the SAM/Ag sample, it can be observed that there are large defect structures on top of the nanorods. During electrochemical deposition, some Ag would frequently peel off from the PET substrate, probably due to poor adhesion. These defects may be the peeled off Ag or ZnO nanorods. Due to these highlighted issues, further investigation on electrochemical deposition of Ag was not carried out.

![SEM images](image)

**Figure 7.10:** SEM images of ZnO nanostructures on (a) SAM with adsorption time of 30 s on UV-ozone treated Ag, (b) bare Ag and (c) 30 s SAM/Ag with no prior UV-ozone treatment. The red circles on (c) highlight the defect structures. Electrochemical deposition was carried out with 10 minutes deposition time, 5 mM \(\text{Zn(NO}_3\text{)}_2\) and 0.1 M KCl concentration, -0.975 V against Ag/AgCl and temperature of 55°C.

### 7.4.4 Patterned growth of ZnO via microcontact printing

Microcontact printing can be used to apply alkanaethiol SAM on Au surface. In this subsection, microcontact printing was carried out using unpatterned PDMS stamp and patterned PDMS stamp. A PDMS stamp was inked with 1-hexadecanethiol solution, and it was brought into contact with Au surface. During contact the alkanethiol molecules from the stamp are transferred to the substrate. After microcontact printing was done for 30 s, ZnO was electrochemically deposited on the SAM/Au surface. For the unpatterned
Results and Discussion

Microcontact printing, Figure 7.11 shows the ZnO nanorods obtained after microcontact printing. The distribution of ZnO nanorods on Au sample is 63%, while on SAM/Au the coverage is higher with value of 66%. This means that the SAM is not properly formed during 30 s microcontact printing. The thiol molecule in SAM are in disordered phase (Fig. 6.3a) and they cannot block the nucleation of ZnO. The size of the nanorods for both samples is also small with average diameter of 35 nm for both samples since electrochemical deposition was carried out for shorter time period. This sample with electrochemical deposition time 5 min was chosen as reference for comparison with the ZnO grown on PDMS patterned SAM/Au samples later.

![Figure 7.11: (a) Top-view SEM image of ZnO grown on (a) bare Au and (b) on SAM modified Au done by 30 s microcontact printing with unstructured PDMS stamp. Electrochemical deposition was carried out with 5 minutes deposition time, 5 mM (Zn(NO₃)₂) and 0.1 M KCl concentration, -0.975 V against Ag/AgCl and temperature of 65°C.](image)

The patterned microcontact printing was done based on the structures of the master as shown in Figure 7.12. The patterned PDMS will have the complementary structures of the master. After microcontact printing, the thiol groups self-assemble on the substrate according to the patterns of the relief structures on stamp. The goal is to tune the density of ZnO based on the SAM patterns. The stamping time was varied and electrochemical deposition of ZnO was carried out. The corresponding SEM images are shown in Figure 7.13. It can be observed that ZnO nanorods grow everywhere on bare Au and SAM/Au regions. Since the SAM is leaky complete suppression of ZnO nanorod growth is not seen on SAM covered regions. The distribution of ZnO nanorods varies according to the region. The coverage of ZnO on Au for all three samples should be the same as shown in Figure 7.11a. This implies that the microcontact printing of alkanethiol has an impact on the ZnO formation on the Au region. For short microcontact printing time of 30 s, the coverage of ZnO on Au region is 49.2%. On SAM/Au region, the coverage increases to 60.5%. This is similar to the case of Figure 7.11, where the blocking behaviour of SAM
Figure 7.12: (a) AFM image of Si/SiO$_2$ master with SU8 photoresist used to fabricate PDMS stamp for microcontact printing. (b) Profile of the master structure obtained from (a) showing height, width of master and width of stamp structures $h_s$, $w_m$ and $w_s$, respectively.

is not seen. The SAM is in disordered phase, where many alkanethiol molecules are not aligned properly on Au. During electrochemical deposition, these disordered molecules create many defects which are preferable for nucleation of ZnO. As faster ZnO nucleation takes place at these sites, the Zn$^{2+}$ ions are depleted and less ZnO nucleation takes place on the Au region. Therefore, the coverage of ZnO on Au region is less compared to the ZnO on SAM/Au.

As the printing time is further increased, more alkanethiols can diffuse from the PDMS stamp to the Au surface. The thiol molecules have more time to organize and self-assemble into well-packed layer (Fig.6.3b). At this stage, the SAM can block the growth of ZnO. Therefore, after electrochemical deposition less coverage of ZnO is seen on SAM/Au regions. For microcontact printing time of 1 min, the coverage of ZnO on Au is 65.6%, whereas on SAM/Au region the coverage is 41.9%. The same trend is seen for the sample with 5 min microcontact printing time. ZnO coverage on Au is 42.60% and on SAM/Au it decreased to 22.7%.

Table 7.3 shows the widths of the ZnO growth on SAM and SAM/Au regions. It can be seen that the periods of the structures are comparable to the Si master within the error range. Usually longer microcontact printing time leads to more lateral diffusion of SAM molecules and the width of the printed SAM pattern increases. In this case, a systematic decrease of the width of ZnO on SAM/Au region is seen. This results in an increase in the width of ZnO on Au region. For longer printing times of 1 min and 5 min, it can be observed that there is gradual increase in the ZnO coverage distributions extending from SAM/Au region towards Au region. After microcontact printing, alkanethiol molecules
Results and Discussion

Figure 7.13: SEM images of ZnO nanorods obtained by PDMS stamping time of (a) 30 seconds, (b) 1 minute and (c) 5 minutes with 5 mM 1-hexadecanethiol ink on Au. (d), (e) and (f) show the corresponding zoomed-in images of (a), (b) and (c). Electrochemical deposition was carried out with 5 minutes deposition time, 5 mM (Zn(NO₃)₂) and 0.1 M KCl concentration, -0.975 V against Ag/AgCl and temperature of 65°C.

are adsorbed on the Au surface. However, during electrochemical deposition, the printed sample is under influence of applied voltage, higher temperature and conductive ions. Therefore, the thiol molecules can diffuse from the concentrated SAM region to the bare Au region. For longer printing time, the concentration of thiol in SAM is higher. Hence, the diffusion gradient is higher and more thiols diffuse towards bare Au region. This results in decreased width of ZnO on SAM/Au region.
Table 7.3: Widths of patterned regions $w_m$ (Au region) and $w_s$ (SAM region) as illustrated in Figure 7.12b. The data are extracted from SEM images in Figure 7.13 and AFM image in Figure 7.12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$w_s$ ($\mu$m)</th>
<th>$w_m$ ($\mu$m)</th>
<th>Period ($\mu$m) $w_m + w_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si master</td>
<td>18.7 ± 2.0</td>
<td>5.0 ± 1.8</td>
<td>23.7 ± 2.7</td>
</tr>
<tr>
<td>ZnO on 30 s SAM printed sample</td>
<td>19.5 ± 0.2</td>
<td>4.4 ± 0.1</td>
<td>23.9 ± 0.2</td>
</tr>
<tr>
<td>ZnO on 1 min SAM printed sample</td>
<td>17.8 ± 0.4</td>
<td>5.5 ± 0.3</td>
<td>23.3 ± 0.5</td>
</tr>
<tr>
<td>ZnO on 5 min SAM printed sample</td>
<td>16.3 ± 0.5</td>
<td>6.8 ± 0.4</td>
<td>23.1 ± 0.6</td>
</tr>
</tbody>
</table>

### 7.5 Conclusion

The distribution and the size of ZnO nanorods were tuned by applying self-assembled monolayer of 1-hexadecanethiol. Electrochemical deposition of ZnO on bare metal results in a dense distribution of ZnO. After application of self-assembled monolayer, the coverage of ZnO nanorod decreases. The alkanethiol adsorption time on Au was varied to analyze the role of SAM. The outcome confirms that the SAM acts as a blocking layer. During electrochemical deposition, ZnO nanorods nucleate and grow through the defects or pinholes in SAM. Impedance measurements were performed to quantify the blocking property of self-assembled monolayer. The parameters of electrochemical growth were systematically varied to control the ZnO nanorod growth. Patterned growth of ZnO nanorods was carried out via microcontact printing of alkanethiol ink which confirmed that the density of ZnO can also be tuned by microcontact printing technique. Due to the leaky behaviour of SAM, ZnO nanorods grew with varying density on patterned regions. Additionally, the growth of ZnO growth on patterned surfaces is also influenced by migration of SAM molecules during electrochemical deposition.
Chapter 8

Bulk Heterojunction Solar Cells with ZnO Nanorods

8.1 Introduction

ZnO offers the advantages of high electron mobility\textsuperscript{102} and wide band gap.\textsuperscript{47} Therefore, they are widely used as cathode buffer layer to block holes and to transport electrons.\textsuperscript{103,104} ZnO nanostructures are also employed as n-type semiconductor in hybrid solar cells.\textsuperscript{39} However, the phase separation between p-type conjugated polymer and ZnO is bad, resulting in sub-par performance of such solar cells. Nowadays, ZnO nanostructures are embedded in bulk heterojunction mixture of semiconductor. ZnO nanorods serve as pathways for efficient electron collection to cathode.\textsuperscript{40–42} Secondly, they act as scattering elements and enhance light trapping in the semiconductor layer.\textsuperscript{43,44,46,105} In this chapter, the light trapping effect due to ZnO nanorods is studied. ZnO nanorods are electrochemically grown on transparent ITO substrates. Angle-resolved measurements are carried out to investigate the light scattering properties of the ZnO nanorods. The controlled electrochemical growth technique of ZnO nanorod is combined with sol-gel method to get ultrathin ZnO film in between the ZnO nanorods which serves as cathode buffer layer. Since both methods are done at low temperature, this combination is ideal for organic electronic devices on flexible substrates. Bulk-heterojunction organic solar cells are prepared with P3HT:PCBM semiconductor mixture and electrochemically grown ZnO nanorods. ZnO nanorods with appropriate dimensions and density are chosen to enable optimal light scattering and to ensure proper semiconductor filling between the nanorods. Optical simulations and quantum efficiency measurements are carried out to
gain deeper understanding of optical and electrical aspects of solar cells.

8.2 Experimental procedure

Firstly, ITO/glass substrates (with 10 Ω/□ sheet resistance and 25 mm × 25 mm size) were cleaned with acetone, isopropanol and de-ionized water. The substrates are dried with nitrogen. Subsequent cleaning step was performed by placing the substrates inside UV-ozone chamber for 10 minutes. The substrates were immersed into 5 mM solution of 11-mercaptoundecanoic acid (with purity ∼ 95% from Sigma Aldrich) in ethanol for 5 minutes. The substrates were then rinsed with ethanol and dried with nitrogen. For electrochemical deposition of ZnO, aqueous solution of zinc nitrate (Zn(NO$_3$)$_2$) and potassium chloride (KCl) was used as electrolyte, Pt as counter electrode, Ag/AgCl as reference electrode and SAM covered ITO substrate as cathode. The standard parameters of electrochemical deposition were electrolyte concentration of 5 mM (Zn(NO$_3$)$_2$) and 0.1 M KCl, overvoltage of -0.975 V against Ag/AgCl and temperature of 55°C. The deposition was executed in such a manner that half of the ITO surface was covered with ZnO nanorods and the other half left with SAM/ITO. The electrochemically grown ZnO nanorods were spin coated with an ultra thin layer of ZnO layer to serve as cathode buffer layer. For this purpose, ZnO was prepared through the sol-gel route from ZnO precursor solution (0.25 M of Zn-acetate dihydrate and 0.25 M ethanolamine in 2-methoxyethanol). The resulting 15 nm ZnO layer was annealed at 110°C for 15 minutes. To investigate the light scattering properties, angle-resolved transmission measurement was performed on sol-gel ZnO covered ZnO nanorod samples. The measurement was done by illuminating the sample with 406 nm wavelength laser light. A Si photodiode (Thorlabs’ DET 110) was used to measure the light intensity.

Figure 8.1 shows the schematic architecture of the solar cell with inverted configuration type. For the semiconductor layer, 1:1 ratio blend of donor poly(3-hexylthiophene) (P3HT) and acceptor [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) in chlorobenzene was prepared. This was followed by an annealing step performed at 140°C for 15 minutes. For the anode buffer layer, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate or PEDOT:PSS (Clevios PH from Heraeus) was mixed with 1 volume % surfactant (Zonyl FS-300 from Dupont). The solution was spin coated at 1000 rpm, 500 rpm/s for 90s to yield a thickness of 35 nm. The resulting layer was annealed at 120°C for 10 min-
utes. For electrical contact, 85 nm of Ag layer was sputter coated through a shadow mask. This resulted in seven devices (each with area 0.083 cm$^2$) on one sample. Three devices on one side of the sample had ZnO nanorods, three devices on the other side had no nanorod and the middle device lied at the border. Electrical I-V measurements were carried out under illumination of AM 1.5 solar simulator. For solar cell requiring surface modification of sol-gel ZnO, 1mg/ml of 4-methoxybenzoic acid in methanol was spin coated at 4000 rpm, 1000 rpm/s and for 1 min on top of sol-gel ZnO.

8.3 Results and Discussion

8.3.1 Electrochemical growth of ZnO on ITO

Figure 8.2b shows the SEM of electrochemically deposited ZnO on bare ITO using standard parameters. Unlike electrochemically deposited ZnO on Au and Ag, it can be seen that on ITO the distribution of ZnO nanorod crystals is very sparse. The intercrystal spacing ranges from sub-hundred nanometer to few microns. Sparse ZnO distribution was also reported by Schwarz et al.$^{46}$ As shown in Figure 8.2a, the surface of ITO is very rough with ITO grain heights reaching upto 25 nm. There are less defect sites for nucleation of ZnO on ITO. Lee et al. also saw few ZnO nanorods on ITO substrate, and they attributed this observation to low pH in the vicinity of ITO during electrochemical deposition.$^{91}$ In this work, the surface of ITO was modified by self-assembled monolayer (SAM) of 11-mercaptoundecanoic acid (Fig.6.2d). The SEM images of the ZnO nanorods are shown in Figures 8.2c, 8.2d and 8.2e. Since ITO is an oxide compound, the carboxylic group of SAM is anchored on the ITO surface with the thiol group pointing away from the surface.$^{71}$ As shown in Figure 8.2c, ZnO nanorods grow denser on SAM modified ITO in comparison to the ZnO grown on bare ITO. The SAM modifies the surface energy of ITO.
in such a manner that more ZnO nucleate on its surface. The resulting ZnO nanorods are also smaller in size. This can be understood as the number of nanorods increase, the ZnO nuclei deplete the electrolyte and the ZnO crystal diameter decreases.

As the SAM adsorption time increases, the coverage of ZnO increases. For 5 minutes adsorption time, the ZnO coverage is 16.3%, which increases to 20.3% and 23.2% for 10 minutes and 1 hour adsorption times, respectively. The size of nanorods also decreases as the SAM adsorption time increases. This results indicate that it is essential to have good blocking layer of ZnO to promote dense nucleation of ZnO nanorods.

The ZnO nanorod (NR) size and coverage can be tailored by changing the electrochemical growth parameters. For each sample, only one growth parameter was changed at a time. Figures 8.3a, 8.3b and 8.3c show the ZnO nanorods obtained after electrochemical deposition growth times of 5 minutes, 10 minutes and 15 minutes respectively. It can be observed that the size of ZnO nanorods increases significantly for longer growth time duration. Table 8.1 lists the corresponding ZnO nanorod distribution and size values. Additionally, the nanorod count decreases with longer deposition time as the nanorods grow laterally and coalesce. For 5 minutes growth time, the nanorod height is 58 nm which increases to 182 nm for 10 minutes growth time. For 15 minutes growth time, the nanorods are growing tilted on the ITO surface. Although the average length of
Results and Discussion

Figure 8.3: Side view SEM images of ZnO nanorod (NR) on SAM covered ITO electrochemically deposited for growth duration of (a) 5 minutes, (b) 10 minutes and (c) 15 minutes respectively with 5 mM electrolyte concentration, -0.975 V overvoltage and 55°C solution growth temperature. Keeping parameters of (b) as reference, (d) shows the SEM image at solution temperature of 60°C, (e) with increased electrolyte concentration of 8 mM and (f) at -1.075 V overvoltage.

the nanorods is 306 nm, the vertical height of the ZnO nanorod is 240 nm. This is within the expectation as ITO has a very rough surface and they nucleate and grow slanted with respect to the ITO surface (Fig. 8.2a).

In comparison with the standard sample grown at 55°C (Fig. 8.3b), the nanorods grown at 60°C (Fig. 8.3d) show larger ZnO nanorod diameter and height distribution. Electrochemical deposition at higher temperature (60°C) leads to larger nanorod diameter of 160 nm and height of 211 nm, whereas nanorods grown at lower temperature (55°C) exhibit smaller diameter and smaller height. This can be explained by the fact that at higher temperature the reaction kinetics is sped up as more Zn(OH)₂ convert to ZnO. For higher concentration of 8 mM (figure 8.3e), the ZnO nanorods feature larger diameter and stunted height. As the concentration is increased, there is more (Zn²⁺) in the electrolyte solution and the ratio between Zn²⁺ and OH⁻ is increased leading to larger lateral diameter. Increasing the driving overvoltage generates more OH⁻ and the pH at the ITO cathode surface increases. This leads to more ZnO nucleation. The resulting feature is shown in Figure 8.3f with denser distribution of much smaller ZnO nanorods.
Table 8.1: Characteristics of ZnO nanorods based on Figure 8.3 with ZnO coverage \( p_{ZnO} \), average height \( h_{ZnO} \), average diameter \( d_{ZnO} \) and nanorod number density \( N_{ZnO} \). The highlighted bold text corresponds to the electrochemical deposition parameter that is varied in reference to the parameters used in the second entry row.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( p_{ZnO} ) (%)</th>
<th>( h_{ZnO} ) (nm)</th>
<th>( d_{ZnO} ) (nm)</th>
<th>( N_{ZnO} ) (( \mu \text{m}^{-2} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min, 55°C, 5 mM, -0.975 V</td>
<td>15.3 ± 0.02</td>
<td>58 ± 10</td>
<td>91 ± 19.4</td>
<td>20 ± 11</td>
</tr>
<tr>
<td>10 min, 55°C, 5 mM, -0.975 V</td>
<td>16.3 ± 0.01</td>
<td>182 ± 16</td>
<td>136 ± 14</td>
<td>11 ± 5</td>
</tr>
<tr>
<td>15 min, 55°C, 5 mM, -0.975 V</td>
<td>27.1 ± 0.02</td>
<td>240 ± 37</td>
<td>278 ± 31</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>10 min, 60°C, 5 mM, -0.975 V</td>
<td>23.9 ± 0.02</td>
<td>211 ± 21</td>
<td>160 ± 13</td>
<td>12 ± 3</td>
</tr>
<tr>
<td>10 min, 55°C, 8 mM, -0.975 V</td>
<td>20.9 ± 0.01</td>
<td>152 ± 19</td>
<td>181 ± 17</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>10 min, 55°C, 5 mM, -1.075 V</td>
<td>33.6 ± 0.02</td>
<td>107 ± 17</td>
<td>87 ± 17</td>
<td>50 ± 21</td>
</tr>
</tbody>
</table>

Therefore, it can be seen that the controlled growth of ZnO can also be achieved on ITO substrates.

### 8.3.2 Angle-resolved diffusive transmission measurements

To study the dependence of the tailored ZnO nanorods and light scattering properties, angle-resolved transmission measurements were carried out on the ZnO nanorod samples. For comparison, a sol-gel ZnO coated ITO sample without any ZnO nanorod was also prepared. Figure 8.4a shows the scattered solid angle intensity at larger angles and 8.4b displays the specular light intensity at normal incidence. The sample without nanorod transmits most of the incoming light intensity (Fig. 8.4b). Therefore, it exhibits almost no scattering (figure 8.4a). On the other hand, the samples with ZnO nanorods manage to suppress the specular transmitted light intensity. Since ZnO has a high band gap (3.3-3.4 eV)\(^{47}\) in the near UV region, it does not absorb the incoming light at 406 nm (3.05 eV). And this reduction in specular transmission can be attributed to the enhanced light scattering due to ZnO nanorods.

Integration of the scattered solid angle intensity over the scattering angle yields the total amount of scattered light intensity. Table 8.2 lists the fraction of light that is scattered and the fraction of light that is transmitted. Samples with smaller ZnO nanorods (5 min growth time, sample Figure 8.3a) show higher specular transmission and less scattering. For these small nanorods only 8% of the incoming light is scattered. The sample with medium height ZnO nanorods (Figure 8.3b) feature better scattering of 25%. The nanorods grown at -1.075 V (Fig. 8.3f) have slightly better scattering of 27%. Despite the dense coverage of ZnO nanorods on this sample, the heights of nanorods are relatively
Results and Discussion

Figure 8.4: Angle-resolved measurements of ZnO nanorod samples for incoming light of 406 nm wavelength. (a) Scattered solid angle light intensity $I_{sa}$ and (b) specular light intensity $I_{specular}$ normalized to the incoming light intensity $I_0$.

small. Therefore, significant enhancement in scattering is not observed. For samples with larger ZnO nanorod sizes, the scattering peaks are shifted towards smaller angles. This can be explained by the fact that as the nanorod size approaches the wavelength of light (406 nm), most of the scattering happens at small angles. For large and stunted ZnO nanorods (8 mM, Figure 8.3e), 42% of the light is scattered and 41% is transmitted. The sample with the largest ZnO nanorods (Fig. 8.3c) has transmission loss of 34% but a relatively small scattering of 38%. This implies that the remaining photons that are not transmitted nor scattered are lost to reflection. The sample grown at higher temperature (60° C, Fig. 8.3d) shows the highest scattering of 49%. Thus, the parameters of this sample have been used to prepare ZnO nanorod solar cells in the coming sections.

The specular transmittance of ZnO nanorods can be correlated to theoretical expectation (Equation 4.6). In order to do that, the height and the coverage of ZnO nanorods extracted from the SEM images and listed in Table 8.1 are used as the input parameters for the calculation. Figure 8.5 shows the theoretical values of fraction of transmitted light in the specular direction along with the experimental values. It can be seen from this plot that the trend of experimental values agrees with the theoretical values. There is some wide deviation between the experimental and theoretical values, which comes from the deviation of height distribution and coverage determination of ZnO nanorods.
Table 8.2: Characteristics of light scattering due to ZnO nanorods along with the corresponding nanorod coverage $p_{\text{ZnO}}$ and average height $h_{\text{ZnO}}$. $q_{\text{scatter}}$ denotes the fraction of light that is scattered and $q_{\text{specular}}$ is the fraction of transmitted light in the specular direction. Note that all samples have sol-gel ZnO layer. The distance between detector and center of rotation is 9 cm. The active area of the detector is 0.36 cm x 0.36 cm. The refractive index of ZnO is 2.17 at 406 nm wavelength.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$p_{\text{ZnO}}$ (%)</th>
<th>$h_{\text{ZnO}}$ (nm)</th>
<th>$q_{\text{specular}}$</th>
<th>$q_{\text{scatter}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sol-gel ZnO on ITO substrate</td>
<td>0</td>
<td>0</td>
<td>0.88</td>
<td>0.01</td>
</tr>
<tr>
<td>5 min, 55°C, 5 mM, -0.975 V</td>
<td>15.3 ± 0.02</td>
<td>58 ± 10</td>
<td>0.79</td>
<td>0.08</td>
</tr>
<tr>
<td>10 min, 60°C, 5 mM, -0.975 V</td>
<td>16.3 ± 0.01</td>
<td>182 ± 16</td>
<td>0.62</td>
<td>0.25</td>
</tr>
<tr>
<td>15 min, 55°C, 5 mM, -0.975 V</td>
<td>27.1 ± 0.02</td>
<td>240 ± 38</td>
<td>0.34</td>
<td>0.38</td>
</tr>
<tr>
<td>10 min, 60°C, 5 mM, -0.975 V</td>
<td>23.9 ± 0.02</td>
<td>211 ± 21</td>
<td>0.26</td>
<td>0.49</td>
</tr>
<tr>
<td>10 min, 55°C, 8 mM, -0.975 V</td>
<td>20.9 ± 0.01</td>
<td>152 ± 19</td>
<td>0.41</td>
<td>0.42</td>
</tr>
<tr>
<td>10 min, 55°C, 5 mM, -1.075 V</td>
<td>33.6 ± 0.02</td>
<td>107 ± 17</td>
<td>0.55</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Figure 8.5: Normalized specular light intensity with respect to light intensity transmitted through sol-gel ZnO $I_{\text{sol-gel ZnO}}$ plotted as a function of ZnO nanorod height $h_{\text{ZnO}}$. The error bars are shown only for the theoretically determined $I_{\text{sol-gel ZnO}}$ accounting for the standard deviation of height and coverage shown in Table 8.1.
8.3.3 Current-voltage measurements

For the fabrication of solar cells, two types of semiconductor blend P3HT:PCBM thicknesses were considered. The $j-V$ measurement was done under illumination on all solar cell devices with and without nanorods. The current density $j-V$ is averaged over all the relevant devices. The device performance parameters extracted from the $j-V$ curves are displayed in table 8.3. Figure 8.6a shows the $j-V$ curves of solar cells with 320 nm semiconductor layer thickness. It can be seen that the short circuit current density ($j_{sc}$) of solar cell devices without nanorod is slightly higher with a value of 11.2 mA/cm$^2$ compared to the $j_{sc}$ value of 10.8 mA/cm$^2$ for ZnO nanorod devices. At first glance, the $j_{sc}$ values fall within the error range and no significant difference is seen. It is to be noted that the performance of 320 nm thick solar cell was fabricated several times and this trend of no nanorod solar cells exhibiting slightly better performance was reproducible. Looking at the open circuit voltage $V_{oc}$ no significant difference is seen. However, a big difference is strongly noticeable in the fourth quadrant of the $j-V$ curve where the devices without ZnO nanorod yield more power output. These devices have higher power conversion efficiency (PCE) of 3.6% which is similar to literature values.\textsuperscript{107,108} Where as for the solar cells with ZnO nanorods, PCE is slightly lower with 3.2% PCE. The fill factor (FF) is also higher for solar cell devices without nanorods. The shunt resistance ($R_{shunt}$) values estimated from the slope of the $j-V$ curve near 0 V are 528 $\Omega$ cm$^2$ and 809 $\Omega$ cm$^2$ respectively for the devices with and without ZnO nanorods. This gives evidence that the presence of ZnO nanorods in the solar cell stack leads to more leakage current pathways. Interestingly, the devices with ZnO nanorods exhibit better series resistance ($R_{series}$) with a smaller value by 1.5 $\Omega$ cm$^2$.

Once the thickness of the active semiconductor layer is increased to 420 nm the performance of the devices with ZnO nanorods improves. This is shown in the $j-V$ curves

Table 8.3: Device performance parameters of OPV with and without ZnO nanorod (NR) with varying P3HT:PCBM thickness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$j_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF(%)</th>
<th>$\eta$(%)</th>
<th>$R_{series}$ ((\Omega) cm$^2$)</th>
<th>$R_{shunt}$ ((\Omega) cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320nm P3HT:PCBM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No ZnO NR</td>
<td>11.2 ± 0.2</td>
<td>602 ± 2</td>
<td>53.1 ± 0.4</td>
<td>3.6 ± 0.1</td>
<td>11.8 ± 0.7</td>
<td>809 ± 53</td>
</tr>
<tr>
<td>With ZnO NR</td>
<td>10.8 ± 0.1</td>
<td>596 ± 1</td>
<td>50.4 ± 0.3</td>
<td>3.2 ± 0.1</td>
<td>10.3 ± 0.4</td>
<td>528 ± 10</td>
</tr>
<tr>
<td>420nm P3HT:PCBM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No ZnO NR</td>
<td>10.6 ± 0.3</td>
<td>582 ± 3</td>
<td>52.3 ± 2.4</td>
<td>3.2 ± 0.1</td>
<td>10.6 ± 0.9</td>
<td>705 ± 235</td>
</tr>
<tr>
<td>With ZnO NR</td>
<td>11.0 ± 0.1</td>
<td>584 ± 1</td>
<td>53.0 ± 1.4</td>
<td>3.4 ± 0.2</td>
<td>9.2 ± 0.2</td>
<td>663 ± 86</td>
</tr>
</tbody>
</table>
Figure 8.6: Measured j-V curves of solar cells with and without ZnO nanorods with (a) 320 nm P3HT:PCBM thickness (b) 420 nm P3HT:PCBM thickness.

In figure 8.6b. From table 8.3 it can be seen that the devices with ZnO nanorods exhibit slightly higher $j_{sc}$ compared to the devices without any nanorod. These $j_{sc}$ values $\sim 11$ mA/cm$^2$ are similar to the solar cells with 320 nm thick P3HT:PCBM. For thicker active layer the separated charge carriers have to travel longer distance to reach the electrodes and the electric field due to the internal built-in potential decreases. The open circuit voltage $V_{oc}$ is lower for 420 nm thick P3HT:PCBM devices. However, the FF values are better than 320 nm thick P3HT:PCBM devices. PCE values of both thickness type solar cells are comparable. A small boost is observed for devices with ZnO nanorods with 3.4% PCE in comparison to the 3.2% PCE of devices without nanorod. In addition, $R_{shunt}$ is higher for ZnO nanorod devices. Like the 320 nm solar cells, the results of the solar cells with 420 nm semiconductor layer thickness were also reproducible. At this point it is clear that incorporating ZnO nanorods influences the solar cells. For thinner solar cells, the nanorods make the solar cell performance worse. For thicker solar cells, improvement due to ZnO nanorods are observed. As stated earlier, this enhancement can be either due to improved light trapping or better charge collection promoted by ZnO nanorods. In order to understand these effects, further analysis has been done in the coming sections.

### 8.3.4 Optical simulations and quantum efficiency measurements

It is imperative to shed light on the optical aspect of the solar cell performance to understand the optical losses and their effect on solar cell performance. Optical simulation of the solar cells on smooth substrate and ZnO nanorod substrates is investigated by
Results and Discussion

Figure 8.7: Schematic cross-section of (a) planar solar cell and (d) solar cell with ZnO nanorod for P3HT:PCBM thickness of 320 nm. Power loss profiles for (a) planar solar cell for an incident wavelength of (b) 406 nm and (c) 550 nm. Power loss profiles for (d) ZnO nanorod solar cell for an incident wavelength of (e) 406 nm and (f) 550 nm. Using Finite Difference Time Domain (FDTD) method.\textsuperscript{109} The FDTD optical simulations consider the calculated interface morphologies and film thickness as input parameters in order to model the solar cell structures. In addition, the complex refractive index of each material of the solar cell layer is considered in the simulation and are taken from literature.\textsuperscript{110–113} A periodic arrangement in a quadratic mesh of circular-based ZnO nanowire array is considered to realize the nanorod solar cells. The dimensions of the nanorod array are estimated from SEM image (8.3d) and are listed in table 8.4. As a reference,

Table 8.4: Parameters used for optical simulation of solar cell with planar configuration without ZnO nanorod and textured configuration with ZnO nanorod.

<table>
<thead>
<tr>
<th>ZnO nanorod height (nm)</th>
<th>ZnO nanorod diameter (nm)</th>
<th>Quadratic mesh spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>265</td>
<td>170</td>
<td>565</td>
</tr>
</tbody>
</table>
Figure 8.8: Schematic cross-section of (a) planar solar cell and (d) solar cell with ZnO nanorod for P3HT:PCBM thickness of 420 nm. Power loss profiles for (a) planar solar cell for an incident wavelength of (b) 406 nm and (c) 550 nm. Power loss profiles for (d) ZnO nanorod solar cell for an incident wavelength of (e) 406 nm and (f) 550 nm.

A planar solar cell with P3HT:PCBM layer thickness of 320 nm and 420 nm are considered as shown in Figures 8.7a and 8.8a, respectively. Furthermore, nanorod solar cells with respective P3HT:PCBM layer thickness are illustrated in Figures 8.7d and 8.8d. In the first step of FDTD simulations, the electric field distributions are calculated for normal incidence light with an electric field amplitude of 1 V/m. Time average power loss profiles are calculated from the electric fields. Afterwards, the quantum efficiency is calculated as the ratio of the power absorbed in the semiconductor layer with respect to the total power incident on the unit cell. It is assumed that all photo-generated charge carriers are collected. Electrical losses are not considered and that means the calculated quantum efficiency represents an upper limit. Therefore, it is assumed that the collection efficiency of the solar cell is \( \sim 100\% \). Finally, the short circuit current density is calculated from the quantum efficiency for 1.5 AM sun’s spectral irradiance. Details on the calculations...
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of these parameters are given elsewhere.\textsuperscript{114}

The power loss profiles for 320 nm and 420 nm thick P3HT:PCBM layer of simulated solar cells for wavelengths of 406 nm and 550 nm are displayed in Figures 8.7 and 8.8 respectively. For both the planar (no ZnO nanorod) and the nanorod solar cells, a strong absorption of light at wavelengths of 406 and 532 nm occurs mainly in the P3HT:PCBM layer. In the case of planar solar cells, light with wavelength of 406 nm is absorbed within several hundreds of nanometers of the P3HT:PCBM layer, close to the P3HT:PCBM/ZnO interface (Figures 8.7b and 8.8b). The same observation is also seen for 550 nm wavelength of incoming light (Figures 8.7c and 8.8c). However, the planar and nanorod solar cells with P3HT:PCBM layer absorbs more light at 550 nm wavelength since this wavelength corresponds to the absorption peak of P3HT:PCBM. Upon introducing the nanorods, absorption of light increases close to the P3HT:PCBM/ZnO interface.

![EQE curves](image)

Figure 8.9: EQE curves of (a) solar cells assuming 100% IQE based on optical simulation and (b) experimentally measured solar cells with and without ZnO nanorods (NR).

The simulated external quantum efficiency (EQE) for the no nanorod and nanorod solar cells for P3HT:PCBM layer thickness values of 320 nm and 420 nm are presented in figure 8.9a. Simulations show that quantum efficiencies for these solar cells are almost unchanged. The quantum efficiency of the solar cells from the previous section were experimentally measured (figure 8.9b) and the shapes of the EQE curves were compared with the simulated results. In both cases, the quantum efficiency has a maximum at 550 nm wavelength due to high absorption by P3HT. The simulated EQE curves show secondary maxima ∼ 400 nm wavelength, which can be due to the contribution of PCBM absorption or due to interference effects. However, this feature is only seen as shoulder in the experimental curves. For the simulated case, around 600 nm wavelength, the solar
cells with 420 nm thick semiconductor layer have a broad shoulder compared to the 320 nm thick solar cells due to the interference effects. Theoretical simulation points out that there is no noticeable difference in EQE for solar cells with and without nanorods.

From the experiments, the measured EQE curves of all devices with nanorods have more EQE gain in the wavelength regions of 600 nm and 450-500 nm. This quantum efficiency enhancement for nanorod solar cell is in agreement with literature findings for nanostructured solar cell.\textsuperscript{43} The shoulders at lower wavelength (450-500 nm) and around 600 nm could be due to absorption enhanced by light scattering from ZnO nanorod or improved charge collection pathway to ITO provided by ZnO nanorods. However, optical simulations reveal that the effects of light scattering are not visible. Therefore, the EQE broadening can be attributed to more efficient charge collection. Overall, the EQE values are higher for the 320 nm thick semiconductor sample devices, which explains why these devices have better $j_{sc}$ compared to the 420 nm thick devices. In the case of 420 nm thick semiconductor sample, the devices with nanorods have broader EQE curve. This enhanced performance was also seen from the $j-V$ curves. (Fig. 8.6b). However, for the 320 nm thick solar cells, the EQE curves are inconclusive and further investigation is required.

For comparison, the corresponding $j_{sc}$ values of the solar cells are displayed in Table 8.5. Based on the optical simulation, similar values of $j_{sc}$ (13.9 mA/cm\textsuperscript{2}) were obtained for planar and nanorod solar cells. Whereas, $j_{sc}$ values obtained from the measured $j-V$ curves are much lower because they include the electrical aspect, which has been not accounted for in the simulations. Nevertheless, it can be concluded that simulations predict no observable light trapping due to ZnO nanorods. This strongly indicates that our experimental findings are dominated by charge carrier transport effects.

Table 8.5: Comparison of $j_{sc}$ values from simulations and experiments.

<table>
<thead>
<tr>
<th>P3HT:PCBM thickness (nm)</th>
<th>Sample type</th>
<th>Simulated $j_{sc}$ (mA/cm\textsuperscript{2})</th>
<th>Measured $j_{sc}$ (mA/cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>no ZnO NR</td>
<td>13.8</td>
<td>11.2 ± 0.2</td>
</tr>
<tr>
<td>320</td>
<td>with ZnO NR</td>
<td>13.4</td>
<td>10.8 ± 0.1</td>
</tr>
<tr>
<td>420</td>
<td>no ZnO NR</td>
<td>13.9</td>
<td>10.6 ± 0.3</td>
</tr>
<tr>
<td>420</td>
<td>with ZnO NR</td>
<td>13.6</td>
<td>11.0 ± 0.1</td>
</tr>
</tbody>
</table>
### Results and Discussion

#### 8.3.5 Solar cell with SAM-modified sol-gel ZnO layer

It is evident from our experiments that solar cells with ZnO nanorods fare better for thicker 420 nm P3HT:PCBM solar cell. While, it is worse for 320 nm thick P3HT:PCBM solar cell. Two competing aspects can be proposed for this performance. The first one is the presence of dead zone due to disordered P3HT\textsuperscript{115} and unfavorable energetic alignment of PCBM\textsuperscript{116} at the ZnO-P3HT:PCBM interface. The second aspect is the optical absorption. The dead layer at the interface of ZnO nanorod and P3HT:PCBM hampers charge collection process. In that case, the net semiconductor layer which is active for light absorption and charge transport is reduced. For thicker semiconductor layer of 420 nm, the performance is enhanced as the active layer thickness is larger compared to the 320 nm layer. A way to resolve this interface issue would be interfacial modification of ZnO using SAM.\textsuperscript{117,118} Doing so could improve the interfacial dipole to allow proper charge transfer, passivate surface trap states and improve the morphology of the P3HT:PCBM.\textsuperscript{119} Self-assembled monolayer of 4-methoxybenzoic acid (Fig. 6.2c) was employed on the cathode buffer layer of sol-gel ZnO. The resulting $j - V$ curves are depicted in Figure 8.10. It can be observed that modifying the sol-gel ZnO surface with SAM enhances the $j_{sc}$ of ZnO nanorod solar cell compared to the planar solar cell. This means that the interface of ZnO was not ideal for P3HT:PCBM solar cells and it can be overcome by ZnO interface modification. As shown in Table 8.6, the other device parameters have also worsened due to the SAM treatment compared to the $j - V$ parameters extracted from Figure 8.6a. For good comparison, the solar cell fabrication parameters need to be optimized for the introduction of SAM on sol-gel ZnO. Nevertheless, this investigation indicates that interface of ZnO-P3HT:PCBM influences the solar cell performance. The determination of the thickness of the dead zone at the ZnO-P3HT:PCBM interface can be a subject for future studies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$j_{sc}$ (mA/cm\textsuperscript{2})</th>
<th>$V_{oc}$ (mV)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
<th>$R_{series}$ (Ω cm\textsuperscript{2})</th>
<th>$R_{shunt}$ (Ω cm\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ZnO NR</td>
<td>7.6 ± 0.2</td>
<td>588 ± 1</td>
<td>57.6 ± 1.4</td>
<td>2.6 ± 0.1</td>
<td>13.0 ± 0.3</td>
<td>1148 ± 36</td>
</tr>
<tr>
<td>With ZnO NR</td>
<td>8.0 ± 0.1</td>
<td>489 ± 1</td>
<td>47.5 ± 3.9</td>
<td>2.2 ± 0.2</td>
<td>16.5 ± 1.3</td>
<td>730 ± 107</td>
</tr>
</tbody>
</table>
8.4 Outlook

Our findings identify that there is far less light trapping effect due to ZnO nanorods than initially expected. Our P3HT:PCBM layer thicknesses of 320 nm and 420 nm are too thick and most of the incoming light is absorbed already without nanorods. According to literature, at these thicknesses, the expected short circuit current density is already saturated. In order to see light trapping, there should be a phase shift of $\pi$ between light waves travelling through the nanorods and the semiconductor layer. Aside from the light wavelength, the phase shift is affected by the nanorod height, nanorod coverage and the refractive indices of the propagating media (Equation 4.6). In the case of P3HT:PCBM, the refractive index is not significantly different from the refractive index of ZnO. At 400 nm wavelength, the refractive indices of P3HT:PCBM and ZnO are 1.65 and 2.2 respectively. According to theory (4.6), in order to see minimum specular transmission and maximum light scattering, the ZnO nanorod height has to be $\sim 360$ nm at ZnO nanorod coverage of 50%. In that case, even thicker semiconductor layer is needed to make solar cells and most of the incoming light will be absorbed by the semiconductor layer.

Full utilization of nanorods for light trapping purpose can be achieved by decreasing the thickness of semiconductor layer. For organic solar cells, thin semiconductor layer is also beneficial to overcome the limited carrier diffusion length and to improve charge extraction. In order to do that, the heights of ZnO nanorods have to be also decreased and the light scattering properties are compromised. In case of P3HT:PCBM, for a ZnO
Figure 8.11: Schematic illustrations of solar cell with light scattering nanostructures (a) covered with thin layer of semiconductor, (b) combined with filling layer of different refractive index, (c) on transparent top contact and (d) on both top and bottom contacts.

nanorod height of 100 nm and ZnO coverage of 50% more than 70% of incoming 400 nm wavelength of light is transmitted in the specular direction. An ideal solar cell structure with nanorods for optimum light trapping should be with long nanorods and very thin semiconductor layer. Figure 8.11a shows the ideal solar cell structure with nanorods wrapped by a thin layer of semiconductor. Knipp et al. used this configuration to perform optical simulations based on TiO$_2$ nanorods and ZnPc:C60 semiconductor blend. They compared their findings to the normal configuration (Fig. 8.1) where the nanorods are embedded in bulk semiconductor layer. They found that the ideal structure (Fig. 8.11a) gives more efficient light trapping in the solar cell and allows most of the incident light to be absorbed by the ZnPc:C60 layer. However, realization of this structure poses some difficulties. There is the issue of finding a suitable deposition technique to coat thin semiconductor layer around the nanorods. Secondly, if the layer is too thin and not covering the nanorods properly, the possibility of undesirable short circuit arises.

A good solution would be to apply the ZnO nanorods in a semiconductor system with better refractive indices for light trapping. The ZnO nanorods can also be coated with another layer like PEDOT:PSS or a reflective material like Au or Ag. Another alternative is to embed a different refractive material material between the nanorods as shown in figure 8.11b. There is also the possibility to employ nanostructures on top of the top electrode (8.11c). This can be done by spin casting a colloidal solution of ZnO nanoparticles on top of the electrode. In this approach, the contribution to the phase shift essential for light scattering comes from light propagation through air and ZnO. This will resolve the
issue with mismatching refractive indices. The solar cell architecture shown in 8.11d can be employed to utilize the concepts of ZnO on top contact and ZnO on bottom designs.

8.5 Conclusion

Electrochemical growth of ZnO nanorods on bare ITO provided sparse distribution of nanorods. Therefore, the surface of ITO was modified by using self-assembled monolayer to control the ZnO nanorod growth. This technique was coupled with the electrochemical deposition parameters to tailor the ZnO nanorod features and distribution. The electrochemically grown ZnO nanorods was combined with low temperature processed sol-gel ZnO layer to serve as cathode buffer layer for solar cell. Angle-resolved light transmission measurements were carried out to study the light scattering property of the ZnO nanorods. It was found that the light scattering depends on nanorod size and distribution. Solar cells were fabricated based on ZnO nanorods. The resulting solar cells have reasonable power conversion efficiency values comparable to state-of-the-art devices in literature. An increase in performance was seen for solar cells with larger P3HT:PCBM thickness of 420 nm. Quantum efficiency measurements also support our finding that ZnO nanorod solar cells with thicker 420 nm P3HT:PCBM layer exhibited enhanced performance. While FDTD optical simulations revealed no change in the performance between planar and nanorod solar cells. The enhanced performance of the solar cell comes from efficient charge collection due to ZnO nanorods. It can be confirmed that charge collection is the dominant factor contributing to the performance of ZnO nanorod solar cells.

Two competing factors that influence the performance of ZnO nanorod solar cells can be highlighted, namely - the presence of dead layer at the ZnO-P3HT:PCBM interface hampering charge collection process and the absorption process. The worse performance of 320 nm thick P3HT:PCBM solar cell could arise from the thinner net semiconductor layer available for absorption and charge transport. Solar cells were made with SAM modified sol-gel ZnO layer. The findings prove that the interface of ZnO and P3HT:PCBM is not ideal. In addition, this experiment hints at presence of dead layer and that this issue can be improved by modifying the ZnO interface. The findings prove that it is difficult to see the effects of light scattering for a system with thick P3HT:PCBM layer and ZnO nanorods. To promote efficient light trapping due to ZnO, some alternative solar cell designs were suggested.
Chapter 9

Metal-Insulator-Semiconductor Charge Carrier Extraction by Linearly Increasing Voltage

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9.1 Introduction

One of the main factors affecting the performance of organic solar cells is charge transport. Due to the high degree of disorder in organic semiconductors, charge transport in these semiconductors takes place via hopping mechanism between localized states. This results in charge carrier mobility which is several magnitudes lower than the mobility in inorganic semiconductors. Charge carrier mobility is one of the most important parameters to characterize charge transport and it is crucial to determine independent mobility of hole and electron in organic solar cells. Numerous techniques have been used to determine the mobility such as time-of-flight (TOF), field effect transistor (FET), space charge limited current (SCLC) and charge carrier extraction by linearly increasing voltage (CELIV) and photo-CELIV. However, each of these techniques has some limitations. In TOF method, the charge carriers are generated by light excitation and the semiconductor layer thickness has to be larger than the penetration depth of light. This results in thick semiconductor layers, which is inapplicable to thin film organic solar cells. The FET technique is incompatible with vertical charge transport direction in organic solar cells. The SCLC method has issues with selection of contacts with proper work function to block one type of charge carrier. The family of CELIV techniques can only measure the mobility of the faster charge carrier. In addition, photo-CELIV is unreliable due to the effect of photogenerated charge carriers profile and recombination.

In 2012, Juska et al. introduced an alternative technique called MIS-CELIV (metal-insulator-semiconductor CELIV) to measure the mobility. MIS-CELIV is applied to metal-insulator-semiconductor device, with semiconductor blend layer relevant to organic solar cell. This method offers two advantages. First, it allows selective determination of the mobility of electrons and holes. Secondly, since the technique does not require illumination the erroneous estimation of mobility arising due to recombination effects can be avoided. Armin et al. applied this technique on organic semiconductor blend and they obtained promising results. However, the analytical model that is used to characterize this measurement technique has some limitations. First of all, for the determination of the mobility the electric field is assumed to be zero at the semiconductor-insulator interface, which is not true for all devices. Secondly, the model disregards semiconductor doping, which is unavoidable for semiconductor layers processed in air. Therefore, this technique requires a proper tool to include these aspects. In this work, numerical simulations based on a 1-dimensional drift-diffusion model are used to carry out MIS-CELIV investigations. The effects of doping and presence of traps in semiconductor are
included in the analysis. In addition, an analytical method to determine conductivity of
doped layers is introduced. With this analysis, the conductivity, the hole mobility and
the electron mobility in doped and undoped semiconductor blend are determined.

9.2 Theory

9.2.1 Ideal MIS capacitor

Figure 9.1a shows the structure of metal-insulator-semiconductor (MIS) structure, where
semiconductor and insulator are sandwiched between two electrodes. In this chapter,
we follow the convention that the voltage $V$ applied to the metal is positively biased with
respect to the semiconductor. The energy-band diagram for an ideal MIS capacitor with
p-type semiconductor is shown in figure 9.1b. An ideal MIS capacitor has to meet the
following conditions.

- At zero bias ($V = 0$), the flat-band voltage, which is defined as the energy difference
  between metal work function (minimum energy required by electron to escape
  from an initial energy at Fermi level into vacuum) and the semiconductor work
  function is zero. In other words, the band is flat (flat-band condition) when there
  is no applied voltage.

- Under any biasing condition, the only charges that can exist in the device are in
  the semiconductor and on the insulator, but with opposite sign. This means that
  there are no traps.

- The resistivity of the insulator is infinite such that when a bias is applied there is
  no charge transport through the insulator.

The ideal MIS theory discussed here serves as a basis to understand real MIS struc-
tures and to get an understanding of semiconductor surfaces. Depending on the applied
bias, a typical MIS capacitor operates under three main regimes. Figure 9.2 shows the
energy-band diagrams, charge distribution, electric field distribution and potential dis-
tribution for the case of a p-type semiconductor.

- Accumulation regime: When a bias lower than the flat band voltage is applied to
  the metal, the top of the valence band bends upward and is close to the Fermi
  level. This results in accumulation of majority charge carriers (i.e. holes) near the
Figure 9.1: (a) Basic layout of ideal metal-insulator-semiconductor (MIS) capacitor. (b) Energy-band diagram of ideal MIS under equilibrium ($V = 0$) for p-type semiconductor. $E_f$, $E_i$, $\phi_m$, $\chi_i$, $\chi_s$ denote the Fermi level, intrinsic energy level, metal work function, insulator electron affinity and semiconductor electron affinity, respectively.

insulator-semiconductor interface. For an ideal MIS capacitor with zero flat-band voltage, the accumulation regime happens only under negative bias.

- Depletion regime: For voltages above the flat-band voltage, the band bends downward. The region close to the interface is depleted of majority charge carriers and the fixed negative charge from acceptors are left behind resulting in a space charge region. For an ideal MIS type, depletion occurs only under positive bias.

- Inversion regime: The voltage at which an inversion layer at the insulator-semiconductor emerges is defined as the threshold voltage ($V_{th}$). The inversion regime occurs when a bias higher than the threshold voltage is applied. The bands bend even more downward and the conduction band shifts closer to the Fermi level than the valence band. The number of minority carriers (electrons) at the surface is larger than that of majority carriers (holes), thereby inverting the surface.

For a MIS capacitor, the insulator capacitance per unit area $C_i$ is defined as:

$$C_i = \frac{\epsilon_0 \epsilon_i}{d_i} \quad (9.1)$$

where $d_i$, $\epsilon_i$ and $\epsilon_0$ are insulator thickness, insulator dielectric constant and vacuum permittivity, respectively.
For an ideal MIS structure, one of the requirements is the charge neutrality.

\[ Q_m = -Q_s = Q \]  \hspace{1cm} (9.2)

where \( Q_m \) and \( Q_s \) represent the total charges per unit area on the metal and total charges per unit area in semiconductor.

The applied voltage \( V \) will drop across the insulator and the semiconductor.

\[ V = V_i + \psi_s \]  \hspace{1cm} (9.3)
Metal-Insulator-Semiconductor Charge Carrier Extraction by Linearly Increasing Voltage

Figure 9.3: Capacitance-voltage (C-V) curves of MIS capacitor during low and high frequency measurements.

\[ V_i = F_i d_i = \frac{|Q_s d_i|}{\varepsilon_i} = \frac{|Q_s|}{C_i} \]  

(9.4)

Here \( V_i \), \( \psi_s \) and \( F_i \) are respectively the voltage drop across the insulator, the surface potential inside the semiconductor towards the insulator and the electric field across insulator. According to Gauss’s law, the electric displacement is continuous at the interface. Thus, the total capacitance of the MIS structure is a series combination of insulator capacitance \( C_i \) and the semiconductor capacitance:

\[ \frac{1}{C} = \frac{V}{Q} = \frac{1}{C_i} + \frac{\psi_s}{Q} \]  

(9.5)

In the accumulation regime, accumulation of holes occur. Thus, there is a high differential capacitance of the semiconductor and the total capacitance is equal to the insulator capacitance.

\[ \frac{1}{C} = \frac{1}{C_i} \]  

(9.6)

In the depletion regime, space charge region is present with depletion width and the depletion capacitance \( C_d \) can be expressed as:

\[ C_d = \frac{\varepsilon_0 \varepsilon_s}{W_d} \]  

(9.7)

where \( \varepsilon_s \) is dielectric constant of semiconductor and \( W_d \) is depletion width. The capacitance drops as the bias shifts from flat-band towards inversion. With increasing bias, the depletion region is widened. Therefore, the capacitance is a series connection of the
insulator capacitance and the depletion capacitance.

\[
\frac{1}{C} = \frac{1}{C_i} + \frac{1}{C_d} \tag{9.8}
\]

The depletion width depends on the doping concentration of the semiconductor. A higher doping concentration gives rise to more efficient electric field screening. Therefore, if the doping concentration is high, the depletion width changes slowly for an applied voltage change. The depletion width can be expressed as a function of the terminal voltages:

\[
W_d = \sqrt{\left(\frac{\varepsilon_0 \varepsilon_s}{C_i}\right)^2 + \frac{2\varepsilon_0 \varepsilon_s (V - V_{fb})}{eN_a}} - \frac{\varepsilon_0 \varepsilon_s}{C_i} \tag{9.9}
\]

where \(\varepsilon_s\) is the semiconductor dielectric constant, \(e\) is the elementary charge and \(N_a\) is the doping concentration.

In the inversion regime, minority charge carriers accumulate at the semiconductor-insulator interface. Depending on the measurement frequency, the capacitance of the semiconductor will be dominated by the space charge or the accumulated minority carriers. At low frequencies, the additional charge carriers can follow the applied ac signal. Thus, they are located at the interface. This results in a large capacitance in series with the insulator capacitance. For high frequencies, the charge carriers cannot follow the ac signal since it requires a certain time to generate the minority carriers in the inversion layer. Hence, they are located at the edge of the depletion layer. Similar to the depletion case, the total capacitance is a series combination of the depletion capacitance and the insulator capacitance. Figure 9.3 shows the capacitance-voltage curves of MIS capacitor under low and high frequency measurements.

### 9.2.2 MIS-CELIV simulation theory

For the numerical simulation of the MIS-CELIV current curve, the 1-dimensional simulation method developed by Hirwa et al. has been used.\textsuperscript{133} The device has been modelled as a discrete spatial grid with a set of spatial properties such as doping concentration \(N_A\), charge carrier mobility \(\mu\), surface charge \(n_s\) and bulk trap states with trap density \(g(E, x)\). These input parameters are used to get close fit of the MIS-CELIV curve. The model assumes that the effects of minority charge carriers are negligible. When an initial voltage is applied, some charge carriers are generated at the interface and the corresponding
charge carrier density $p(x)$ can be expressed by: \(^{134,135}\)

$$p(x) = \frac{eC_i^2(V - V_{FB})^2}{2kT\varepsilon_s\varepsilon_0(1 + x\sqrt{2L_D})^2} \quad (9.10)$$

where $kT$ is the thermal voltage, $V_{FB}$ is the flat band voltage and the Debye length $L_D$ is given by:

$$L_D = \frac{\sqrt{2kT\varepsilon_s\varepsilon_0}}{eC_i(V - V_{FB})} \quad (9.11)$$

The initial total charge carrier density $p(x)$ is obtained by taking the sum of $p(x)$ and the free charge carriers corresponding to the doping concentration $N_a$ and subtracting the density of trap states. For the traps, a numerical model based on the probability to capture and to release free carriers to and from trap levels has been used. Each trap level $i$ has a density of states $g_i(x)\Delta E$ and energy $E_i(x)$. With the charge carrier capture time constant $\tau_c$, the capture rate of charge carriers $b$ is given by:

$$b(x) = p(x) \sum_i \frac{1}{p_r\tau_c} g_i(x)\Delta E(1 - f_i(x)) \quad (9.12)$$

where $p_r$ is a reference free charge carrier density which has been set to be equal to the doping concentration for convenience. The rate of release of charge carriers from the traps $u(x)$ can be expressed as:

$$u(x) = \sum_i g_i(x)\delta E f_i(x) v_0 e^{-\frac{E_i(x)}{kT}} \quad (9.13)$$

where $v_0$ is the attempt-to-escape frequency of the charge carriers from the traps, $k$ is Boltzmann’s constant, $T$ is absolute temperature and $f_i(x)$ is the fraction of occupied states at trap level $i$ and it has values in the range of 0 and 1. In the subsequent step, the electric potential is calculated from the charge density $\rho(x)$ by using the Poisson equation

$$-\nabla^2 \phi = \frac{\rho(x)}{\varepsilon_0\varepsilon_s} \quad (9.14)$$

and the electric field $F$ is determined from the electric potential $\phi$

$$\vec{F} = -\nabla \phi \quad (9.15)$$

The time-dependent current density $j(t)$ can be obtained from the drift and diffusion of
free charge carriers as shown below:

\[ j(t) = e\mu p(x)F(x) - \mu kT \frac{dp(x)}{dx} \]  

(9.16)

Taking the trapping and detrapping processes into account, the overall change of the system can be formulated by the continuity equation,

\[ \frac{dp}{dt} = -\nabla \left( \frac{j}{e} \right) + b - u \]  

(9.17)

9.3 Experimental procedure

The MIS devices (as depicted in Figure 9.4a) were fabricated on highly n-doped silicon (Si) wafers with a 200 nm thick thermally grown silicon oxide SiO\(_2\). The SiO\(_2\) acts as the insulating dielectric and the highly n-doped Si acts as the counter electrode. The substrates were cleaned in ultrasonic bath with solvents (acetone, isopropanol) and washed with deionized water. This is followed by their exposure to UV-Ozone for 10 min. For the active semiconducting layer, a 1:1 ratio mixture of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) in chlorobenzene solution was doctor bladed on the substrate. The semiconductor layer was annealed at 140°C for 15 minutes. This procedure resulted in a 150 nm to 400 nm thick active layer. The active layer was processed inside a nitrogen glovebox and this resulted in an essentially undoped active layer. Finally, the device was completed by depositing a metal contact onto the semiconductor. In order to selectively access the hole mobility and the electron mobility, two types of devices were prepared. In one case, Ag is used as the injecting electrode and in this case, holes are injected from the Ag contact into the active layer (Device h+). In the second case, Al is used as the injecting electrode and in this case, electrons are injected from the Al contact into the active layer (Device e-). For Device h+, a 150 nm Ag layer was sputtered on top of the semiconductor. For Device e-, a 100 nm Al layer was thermally evaporated on top of the semiconductor. In order to study the effect of doping, Device h+ with a highly p-doped active layer was also prepared. The high doping level was obtained by processing the active layer in ambient air contrary to the previous devices with an active layer processed in the glovebox.

The MIS-CELIV measurement set-up is shown in Figure 9.4b and the shape of the bias function applied to the device is depicted in Figure 9.4c. An initial voltage \(V_0\) is applied
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Figure 9.4: (a) Device structure used for the MIS capacitors with highly doped n++-Si as metal, insulator SiO₂, P3HT:PCBM semiconductor blend and ohmic top contact. (b) Set-up for MIS-CELIV measurements. The current is sensed as voltage drop at the load resistance $R_{\text{Load}}$. (c) Shape of the bias voltage applied on the device.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>$d_s$ (nm)</th>
<th>$d_i$ (nm)</th>
<th>$\varepsilon_s$</th>
<th>$\varepsilon_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device h+</td>
<td>150</td>
<td>200</td>
<td>3.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Device e-</td>
<td>150</td>
<td>200</td>
<td>3.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Device h+ doped</td>
<td>410</td>
<td>200</td>
<td>3.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 9.1: Geometrical parameters of the MIS devices with the semiconductor and the insulator layer thicknesses $d_s$ and $d_i$, and the corresponding dielectric constants $\varepsilon_s$ and $\varepsilon_i$.

to the metal contact inorder to accumulate one type of charge carriers. The applied bias is linearly increased to $V_f$ which creates an electric field that drives charge carriers from the insulator-semiconductor interface across the semiconductor layer and into the top ohmic contact. This movement of charge carriers results in a time-dependent current. The time-dependent current is measured through a 1 kΩ load resistance by a digital oscilloscope. The bias function is applied by a Keithley 3390 function generator. In this experiment, the additional constant voltage and linearly decreasing voltage applied after the usual linearly increasing voltage are not mandatory for MIS-CELIV, they are only used here for double checking reasons during the analysis process. Impedance measurement of the MIS device was carried out using Agilent E4980A LCR meter (20 Hz to 2 MHz measurement range). For lower frequency range (1 mHz to 100 Hz) a lock-in amplifier
SR830 was used.

### 9.4 Analytical model for bulk conductivity

In order to fully understand this new technique, still in its development phase, numerical simulations based on one dimensional drift-diffusion model were used. The extraction transient current was obtained by applying the voltage function (e.g. see Table 9.3). For the simulations, a sample with geometrical parameters representative of our experimental device and a mobility in the range of typical values for P3HT:PCBM blends was assumed (see Table 9.2 and 9.3). \(^{129,130}\)

<table>
<thead>
<tr>
<th>(d_s) (nm)</th>
<th>(d_i) (nm)</th>
<th>(\varepsilon_s)</th>
<th>(\varepsilon_i)</th>
<th>(N_A) (10(^{16}) cm(^{-3}))</th>
<th>(\mu_h) (10(^{-6}) cm(^2)/Vs)</th>
<th>(n_s) (10(^{11}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>200</td>
<td>3.0</td>
<td>3.9</td>
<td>1.5</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 9.2: General parameters used for simulations.

<table>
<thead>
<tr>
<th>(V_o) (V)</th>
<th>(V_f) (V)</th>
<th>(t_p) ((\mu)s)</th>
<th>(t_h) ((\mu)s)</th>
<th>(t_n) ((\mu)s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.025</td>
<td>9.975</td>
<td>500</td>
<td>500</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 9.3: Bias function used for simulations. For the meaning of the parameters, see Figure 9.4c.

From the first set of the simulations, two cases can be differentiated (see Figure 9.5a). Depending on the amount of extracted carriers, the extracted current hits a saturation current and in the second case the extracted current does not hit a saturation current and does show a clear peak. The saturation current corresponds to charging current of the insulator and is given by the geometrical parameters of the insulator through equation 9.22 and amounts to 3.4 A/m\(^2\) in Figure 9.5a. These two cases mainly depend on whether the initial voltage accumulates a sufficient amount of charge carriers at the interface or not. This chapter focusses only on the first case, i.e. case with a high charge accumulation at the interface. However, the obtained results are not affected by the use of either of the two cases. According to literature, the mobility is affected by high electric fields > 10\(^6\)V/m. \(^{136,137}\) In our case the major drop of voltage happens across the insulator and the electric field is very weak inside the semiconductor (see inset Figure 9.5b) to influence the mobility.
The effects of device parameters such as the doping level, the mobility and the surface charge on the current are observed. Figure 9.6 shows different simulations with different parameters. From these simulations, it can be concluded that the mobility and doping concentration have a similar effect on the first rise of the extracted current. Changing the surface charge results in a different behavior. A closer look at the obtained current suggests the presence of two turning points. The first point corresponds to the time where the current reaches the saturation current. The second point corresponds to the time where the current starts to decrease again and this point strongly depends on the surface charge (see Figure 9.6c). After the second turning point, the amount of extracted charge strongly depends on the doping concentration see Figure 9.6b. These simulations show a certain independence in the effect of various parameters. Hence, one would expect to be able to efficiently extract these parameters from MIS-CELIV measurements.

Though numerical analysis is clearly a powerful tool in order to understand our system, development of simple analytical tools is of high interest as it simplifies the analysis. Hence, it is of high interest to look at some of limiting assumptions usually used in MIS-CELIV measurements for analytical analysis. First, the expected behaviour for a sample assumed to be totally undoped \((N_a = 0)\) is observed. From Figure 9.5c, it can be seen that the shape of the initial rise of the current strongly depends on whether the active layer is undoped or doped. The extraction transient current trace for undoped samples is characterized by a linear increase with a negative curvature, whereas the extraction transient current trace of doped samples is singled out by the initial sharp rise with a positive curvature. From this, it can be concluded that assuming zero doping while analyzing samples with substantial doping will lead to erroneous results. In most of the MIS-CELIV analysis so far, it is assumed for the electric field at the interface semiconductor-insulator \(E(x = 0) = 0\). From the simulations, using a typical MIS capacitor (see Table 9.2), the time evolution of the electric field in Figure 9.5b shows that the electrical field is non zero at the interface semiconductor-insulator. These latter two findings call for the development of new analytical approaches in order to estimate the mobility from the MIS-CELIV measurements. In this work, a new analytical method that can be used in order to determine the conductivity of the bulk semiconductor is introduced. The obtained conductivity accounts for the effect of the mobility and the doping concentration.

This analytical model is based on the fact that the initial sharp increase of the extraction current is caused by the RC behavior of the MIS diode. The RC behavior is due to
Figure 9.5: Transient current simulations. (a) Illustration of the effect of the starting voltage on the obtained current. The simulation parameters of the sample are given in Table 9.2. (b) Time evolution of the electric field of the first current trace (black solid line) in Figure 9.5a. The inset corresponds to the zoom in at around $E = 0$. (c) Illustration of the effect of doping on the initial rise of the current. The simulation parameters of the sample are given in Table 9.2 with $N_a = 1.5 \times 10^{16}$ cm$^{-3}$ for the doped case and $N_a = 0$ for the undoped case. The applied bias voltage is given in Table 9.3.

the doping of the bulk of the active layer that leads to a finite conductivity in addition to the accumulated carriers at the interface. Assuming doping dominated conduction in the semiconductor layer, the current density that is flowing through the MIS diode can be formulated as:

$$ j = C_i \frac{d(V - V_s)}{dt} = \frac{V_s}{R_s} + C_s \frac{dV_s}{dt} $$

(9.18)

where $V_s$ is the voltage drop over the semiconductor layer, $V$ is the outside applied voltage, $C_i$ is the insulator capacitance, $C_s$ is the semiconductor capacitance, $R_s$ is the semi-
Figure 9.6: Effects on the extraction transient current in MIS-CELIV measurements: (a) Mobility (b) Doping concentration (c) Surface charge (→ Flat band voltage). The non varied simulation parameters are found in Table 9.2 and Table 9.3.

A rearrangement of the two sides of equation 9.18 leads to

\[
\frac{dV_s}{dt} + \frac{V_s}{\tau} = \frac{C_i}{C_s + C_i} \frac{dV}{dt}
\]  

(9.19)

with the time constant \( \tau = R_s(C_s + C_i) \). Taking ramp speed \( a \) and assuming a linear ramp with \( V(t) = at \) for \( t > 0 \), this differential equation can be easily solved. An expression of the extraction transient current is determined to be:

\[
j = aC_i \frac{1 + \frac{C_i}{C_s} - e^{-\frac{t}{\tau}}}{1 + \frac{C_i}{C_s}} = j_o + j_o \frac{C_i}{C_s} (1 - e^{-\frac{t}{\tau}})
\]  

(9.20)
The exponential dependence on the time constant can be used to determine the conductivity of the semiconductor. The conductivity can be accurately determined from the time constant expression as the insulator capacitance and the semiconductor capacitance are readily determined from the displacement current and the saturation current. It is expected that at \( t = 0 \), the obtained current corresponds to the displacement current resulting from the geometric capacitance of the whole device composed of the insulator capacitance in series with the semiconductor capacitance

\[ j_0 = a \left( \frac{1}{C_i} + \frac{1}{C_s} \right)^{-1} \]  

(9.21)

At \( t \to \infty \), a saturation current is reached as shown that corresponds to the displacement capacitance of the insulator as the electric field in the semiconductor is essentially screened by free charge carriers accumulated at the interface semiconductor-insulator.

\[ j_{\text{sat}} = a C_i \]  

(9.22)

For a smaller voltage offset, the current peaks at a certain time. Once all the charge carriers are extracted, the current goes back to the displacement current level \( j_0 \), which is present due to the geometrical capacitance of the MIS diode. For higher voltage offsets, the current peak is expected to rise and at a certain offset level, the current saturates.

### 9.5 Results and Discussion

Impedance measurements were first used to prove the presence of electron injection and hole injection and to find the proper voltage range for the MIS-CELIV measurements. C-V measurements were carried out on doped and undoped samples are illustrated in figures 9.7a, 9.7b and 9.7c. For the doped Device h+, at high negative voltages, accumulation is seen and the insulator capacitor is reached. This signifies that this sample is highly p-doped. For positive voltages, the capacitance decreases and depletion regime is seen. In the forward direction, an inversion point is seen, which can be the threshold voltage beyond which inversion starts and electrons are injected into the semiconductor. However, full inversion is not observed as a hump appears in between 10-20 V region. Processing P3HT:PCBM in air is known to create high level of oxygen traps in the semiconductor bulk.\(^{138}\) In addition, there are \( \text{OH}^- \) at the \( \text{SiO}_2 \) interface which like to trap
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Figure 9.7: C-V measurements of samples (a) doped Device h+, (b) undoped Device h+ and (c) undoped Device e-.

Electrons. Thus, beyond this hump, the injected electrons get trapped and the capacitance decreases. In the backward direction, the capacitance values are higher resulting in a hysteresis. Since more voltage has to be applied in order to compensate the charges in the semiconductor and at the interface, the flat band voltage is higher in the backward scan. In strong accumulation regime, no hysteresis is observed since the holes accumulate and recombine with the fixed electrons at trap sites. Theoretically, the doping could be determined from the depletion width capacitance. Due to the influence of trap states resulting in the hysteresis, the doping concentration cannot be extracted in a straightforward way.

For the undoped case, i.e. Device h+, the usual switch from accumulation at negative voltage to positive voltage is seen. However, even at high voltages, the insulator capacitor is not reached. Since the sample is undoped, the conductivity is low. The injected charge
Results and Discussion

carriers cannot easily follow the ac signal at these frequencies and cannot reach the semiconductor-insulator interface. Evidence of inversion is not clearly seen, i.e. electrons are not properly injected into the semiconductor. Very few electrons are trapped at the interface resulting in small hysteresis. For the undoped Device e-, the capacitance is lower in negative voltages and higher in positive voltages. This is an indication that electrons accumulate at positive voltages. Since the sample is undoped, the insulator capacitance is not reached. The capacitance is higher in the forward scan and lower in the backward scan. The crossing point of the forward and backward curves at 20 V can be attributed to the onset of electron trapping, resulting in lower capacitance in backward scan.

For the undoped samples, very low frequencies are needed in order to accumulate carriers at the interface and to be able to see the insulator capacitance (Fig.9.8a and Fig.9.8b). For very low frequencies (< 10 Hz), the frequency dependence of the impedance shows that charge carriers are able to follow the ac signal and reach the insulator interface (Figure 9.8a and Figure 9.8b). The effect of choosing injecting contacts with two different workfunctions can be differentiated. For the sample with Ag contact, accumulation of charges at the interface is observed upon applying negative voltages (Figure 9.8a). Whereas, the sample with Al contact shows higher capacitance at positive voltage (Figure 9.8b). This is solid proof that holes are injected and accumulate at the interface in Device h+ and that electrons are injected and accumulate at the interface in Device e-.

For analysis the analytical model was applied to the doped sample (Figure 9.9a). The MIS capacitor with a hole injecting contact and with a doped active layer showed the expected impedance response with an accumulation of holes at the interface for negative voltages and formation of a depletion zone for positive voltages. For the MIS-CELIV measurements, the voltage ramp was chosen to drive the MIS devices from accumulation regime to depletion regime during MIS CELIV measurement. The initial rise of the extraction transient current showed the typical positive curvature of a doped sample and was fitted with the simple analytical equation 9.20 showing a very good agreement (see Figure 9.9a). From this agreement, the semiconductor conductivity was determined to be $4.2 \times 10^{-6}$ Sm$^{-1}$. These results were confirmed by numerical simulations. Table 9.4 enlists the input parameters for the simulation. In Figure 9.9b, the experimental current trace is perfectly matched by the numerical simulations over the full ramp time. From the numerical simulation, a hole mobility of $1.9 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ is obtained, which agrees
Figure 9.8: Impedance measurements for different bias voltages showing successful injection and accumulation of holes (black line) in Device h+ with Ag contacts (a) and of electrons (blue line) in Device e- with Al contacts (b). Two instruments were used to cover the wide frequency range.

with air-processed mobility values in literature. Based on the high p-type doping level of $1.5 \times 10^{16}$ cm$^{-3}$, the conductivity was determined to be $4.57 \times 10^{-6}$ Sm$^{-1}$. The numerically obtained parameters are in good agreement with the initially obtained conductivity value by the analytic model. This confirms the validity of the analysis tool to obtain the conductivity of the active layer. Experimental data of a highly doped sample can be simulated without even including the effect of trap states. For highly doped sample the effect of traps is negligible since the high doping concentration dominates over the effect of the trap states within time scale of milliseconds in accumulation conditions.

For the undoped samples, from Figure 9.5c, it is evident that the lack of the sharp rise of current seen in doped samples will limit the use of the previously used analytical tool for undoped samples. Figure 9.10a depicts the MIS-CELIV curve of the undoped sample for hole extraction. As expected, in contrast to the highly doped sample, the numerical simulation of the undoped sample exhibited a low doping concentration of $2.0 \times 10^{14}$ cm$^{-3}$. The obtained hole mobility $\mu_h$ is $1.5 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ and is slightly lower compared to the doped case. In the case of the MIS device for electron extraction (see Figure 9.10b), the doping concentration is even lower and can be assumed non existent. A fact supported by the presence of the negative curvature of the initial transient current, characteristic of undoped samples. The lower doping level in Al samples is due to fact that the sample has undergone more dedoping during the vacuum process for thermal evaporation of Al. From the numerical simulation, the electron mobility $\mu_n$ in the
Results and Discussion

Figure 9.9: Analytical model applied on MIS-CELIV measurements of the doped sample. (b) The same experimental data as in (a) are now closely fitted by numerical simulations. The simulation parameters in table 9.4, line 1. The bias voltage parameters are $V_o = -19$ V, $V_f = 0$ V, $t_p = 1$ ms.

P3HT:PCBM blend is found to be $7.0 \times 10^{-6}$ cm$^2$V$^{-1}$s$^{-1}$. The obtained electron mobility is 2 times lower than the hole mobility in the P3HT:PCBM blend. Though opposite conclusions have been previously suggested, this conclusion is not totally unexpected. In fact, previous studies have shown that during the annealing process PCBM forms clusters dispersed in the P3HT matrice and this hinders electron transport.$^{125,140,141}$

Contrary to the highly doped case, the numerical simulations for undoped samples still show partly a clear mismatch with the experimental data. For the undoped sample with less charge carrier concentration, the effect of traps has to be taken into account. During extraction, more charge carriers are released from the traps leading to higher current transient across the sample at longer times. Hence, the obtained transient current is distributed over longer times. This effect is seen upon starting to include traps in the simulations. The traps are represented by a single trap level located at an energy level $E_t = 0.357$ eV, with a traps density $N_t = 5 \times 10^{15}$ cm$^{-3}$ and characterized by an attempt-to-escape frequency $\nu_0 = 1 \times 10^{11}$ s$^{-1}$ and a capture time constant $\tau_c = 1000$ ns. The traps are assumed neutral when occupied by a trapped carrier and act like a dopant without a trapped carrier. By adding a single trap level, the shape of the current transient can be changed into the required direction, see e.g. around $t = 0.6$ ms in Figure 9.10a or $t = 0.4$ ms in Figure 9.10b. Although, the effect of traps on the MIS-CELIV measurements was shown and some relevant parameters were extracted, complete inclusion of...
Figure 9.10: (a) The experimental data of Device h+ are closely fitted with numerical simulations with a trapping effect and without a trapping effect. The simulation parameters are listed in table 9.4, line 2 and 3. The bias voltage parameters are \( V_o = -10 \text{ V}, \) \( V_f = 10 \text{ V}, \) \( t_p = 1 \text{ ms} \). (c) The experimental data of Device e- are closely fitted with numerical simulations with a trapping effect and without a trapping effect. The simulation parameters are listed in table 9.4, line 3 and 4. The bias voltage parameters are \( V_o = 19 \text{ V}, \) \( V_f = 6 \text{ V}, \) \( t_p = 0.65 \text{ ms} \).

a distribution of trap states for a full analysis has not been done in this work.

9.6 Conclusion

In this chapter, analytical and numerical tools for MIS-CELIV measurements analysis were presented. These tools were used to determine the semiconductor conductivity and the electron and hole mobility in a device structure that is relevant to organic solar cells. A look at different limiting cases was used to verify the validity of the analyti-

Table 9.4: Parameters for numerical simulations of MIS CELIV measurements in Figure 9.9b, 9.10a and 9.10b.

<table>
<thead>
<tr>
<th>MIS device type</th>
<th>( \mu ) (cm(^2)/Vs)</th>
<th>( N_a ) (cm(^{-3}))</th>
<th>( n_s ) (cm(^{-2}))</th>
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<td>Doped, hole</td>
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<td>( 5.0 \times 10^{-6} )</td>
<td>-</td>
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<td>Undoped, electron, with traps</td>
<td>( 7.0 \times 10^{-6} )</td>
<td>-</td>
<td>( 0.9 \times 10^{11} )</td>
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</tbody>
</table>
Conclusion

cal equations. Impedance measurements were performed to choose appropriate voltage ranges for MIS-CELIV and to prove the type of injected charge carriers that was then analysed. The obtained mobilities are in accordance with previously obtained mobilities for air-processed P3HT:PCBM blends. Using the numerical simulation, the effect of different parameters such as doping concentration and the trap states on the MIS-CELIV measurements were established, and the hole and electron mobility in undoped active layers were determined.
Conclusion and Outlook

For applications in organic solar cells, it is critical to control the morphology, the distribution and the size of ZnO nanostructures. This work has successfully demonstrated that all these aspects can be tailored via electrochemical deposition of ZnO. Not only can the dimensions of ZnO be tuned by varying the parameters of electrochemical deposition, the nucleation density of ZnO can also be controlled. This latter key aspect has been achieved by employing self-assembled monolayer on the metal surface. With solid evidence from impedance analysis, a model has been proposed for the role of SAM in the growth of ZnO nanorods. The findings reveal that SAM acts as a blocking layer to prevent dense nucleation of ZnO. Theoretical fittings of the impedance measurements have been done to extract the thickness of SAM. The obtained thickness values corroborate with literature findings for alkanethiols on Au. Attempts at patterned growth of ZnO by using microcontact printing were done. The findings reveal that complete suppression of ZnO growth at desired regions is difficult to achieve. However, it is possible to obtain patterned growth of ZnO with varying density. These investigations indicated an interesting phenomenon which was not seen for unpatterned SAM modified samples. Possible evidence of SAM migration was seen and it was reflected on the density coverage of ZnO nanorods. These observations point out that the kinetics of ZnO and patterned SAM/metal surface is not simple. A comprehensive understanding of this phenomenon is required, which can serve as a topic for future investigations.

Electrochemical growth of ZnO has been performed on ITO substrates, which are widely used as window electrodes in organic solar cells. The surface of ITO offers few sites that are energetically favourable for nucleation of ZnO. Denser nucleation of ZnO nanorods has been achieved by modifying the ITO surface with SAM. The light scattering properties of ZnO nanorods have been successfully demonstrated. The obtained results are in good correlation with theoretical expectations. Additionally, another layer of ZnO obtained via sol-gel route has been applied as cathode buffer layer. ZnO nanorods have been effectively incorporated into P3HT:PCBM solar cells. The solar cells show good performance with values comparable to state-of-the-art solar cell performance. This work shows that ZnO nanorods do indeed enhance the performance of organic solar cells.
It has been observed that ZnO nanorods broaden the quantum efficiency curves. This outcome can be attributed to enhanced light trapping or to improved charge carrier collection by ZnO nanorods. Optical simulations reveal that there is far less light scattering than initially expected. These studies have identified that ZnO nanorods improve solar cell performance by acting as pathways for efficient electron transport to the cathode.

The investigations also indicate that the interface between ZnO and P3HT:PCBM is not ideal. The effect was seen for solar cells with thinner layer of 320 nm P3HT:PCBM, where the enhancement due to ZnO nanorods was not observed. This issue was remedied by applying self-assembled monolayer on the cathode buffer layer of sol-gel ZnO. Further analysis of the interface issue and the optimization of the processing parameters of solar cells with SAM treatment on ZnO could be the subjects of future work. These investigations highlight that an optimized interface between ZnO and P3HT:PCBM is essential for organic solar cells. The thesis has shown that tailored ZnO nanorods achieved via self-assembled monolayer can enhance performance of organic solar cells. To employ them for light trapping effects, some alternative ideas have been proposed. ZnO nanorods can be applied to other semiconductor systems with matching refractive indices to allow optimum light scattering. They can be coated with some other material to enable better incoupling of light towards the semiconductor layer. Another novel idea is to embed ZnO nanorods on top of different layers of the organic solar cell. The insights from these investigations are not only beneficial to solar cells, but they can be extended to other devices where controlled application of ZnO nanorods is desired.

Lastly, MIS-CELIV technique has been used to measure independent mobility of holes and electrons in organic semiconductor blend of P3HT:PCBM. A numerical simulation method based on 1-D drift-diffusion equation has been used to fit the MIS-CELIV measurements. The simulations include doping and traps which have not been accounted for in traditional MIS-CELIV analysis. Additionally, an analytical model has been introduced which allows determination of the conductivity of the doped semiconductor layer from the MIS-CELIV measurement. The doping concentration and the mobility of holes and electrons have been extracted from the simulation fit. The obtained values of charge carrier mobility agree with literature values for air-processed P3HT:PCBM mixture. This simulation method paves a way towards proper analysis of MIS-CELIV measurements as it includes doping and traps. The simulation needs a more appropriate model for the traps. Doing so would allow deeper understanding of the charge transport mechanism in organic semiconductor blend systems.
Appendix A

A.1 Optical constants

The following figures show the optical constants that have been used for the optical simulations on organic solar cells (Chapter 7.4).

Figure A.1: Refractive index ($n$) values of ITO,\textsuperscript{111} ZnO,\textsuperscript{110} P3HT:PCBM,\textsuperscript{112} PEDOT:PSS\textsuperscript{111} and Ag\textsuperscript{110} as a function of wavelength ($\lambda$).
Figure A.2: Extinction coefficient ($k$) values of ITO, ZnO, P3HT:PCBM, PE-DOT:PSS and Ag as a function of wavelength ($\lambda$). The inset figure shows the zoom-in of the plots.

Figure A.3: Product of $n$ and $k$ values of ITO, ZnO, P3HT:PCBM, PEDOT:PSS and Ag as a function of wavelength ($\lambda$).
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## List of Samples

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