I-V Curves for Cylinders Embedded in P3HT

BY

CHING-EN HUANG

B.S., Fu Jen University, 2012

THESIS

Submitted as partial fulfillment of the requirements
for the degree of Master of Science in Electrical and Computer Engineering
in the Graduate College of the University of Illinois at Chicago, 2015

Chicago, Illinois

Defense Committee:

Michael A. Stroschio, Chair and Advisor

Mitra Dutta, ECE

Shripriya Poduri, ECE

ACKNOWLEDGEMENTS

I want to thank a lot of people who helped me to do my thesis and pursue my degree.

First, I want to thank Prof. Michael Stroschio for being my advisor and giving me lots of support and guidance. My research is benefited from his profound knowledge and helpful advices.

I would like to thank Prof. Mitra Dutta, Prof. Michael Stroschio, Dr. Shripriya Poduri for being my committee and spending time to attend my defense.

I also want to thank Dr. Shripriya Poduri for teaching me polymer pn junction and giving me useful papers.

Furthermore, I am very thankful to the meeting member Souvik Mukherjee for helping to solve problem I faced.

Also, I want to thank all the members in Prof. Michael Stroschio's group for discussing the reference I used and giving me good ideas in the meeting.

C.H.

TABLE OF CONTENTS

<u>CHAPTER</u>	<u>PAGE</u>
1. INTRODUCTION.....	1
1.1 Background of CdS.....	2
1.1.1 Characteristics of CdS.....	3
1.1.2 Important parameters of CdS.....	6
1.2 Background of P3HT.....	7
1.2.1 Characteristics of P3HT.....	8
1.2.2 Important parameters of P3HT.....	11
2. PROCESS OF FORMING HETEROJUNCTION.....	12
2.1 Forming procedure of nanoporous template.....	12
2.2 Growth of CdS nanowires.....	14
2.2.1 Characteristics of growth of CdS nanowires.....	15
2.3 Forming a junction of P3HT.....	16
3. CURRENT VOLTAGE CHARACTERS OF CDS/P3HT.....	17
3.1 Band gap lineup.....	17
3.2 Equation of heterogeneous pn junction.....	20
3.3 Measurement of current-voltage curve.....	25
3.4 Comparison of simulation and measurement.....	26
3.5 Interface recombination.....	28
4. CONCLUSION AND FUTURE WORK.....	30
CITED LITERATURE.....	32
APPENDICES.....	37
APPENDIX A.....	38
APPENDIX B.....	40
APPENDIX C.....	41
APPENDIX D.....	43
VITA.....	45

LIST OF TALBES

<u>TABLE</u>	<u>PAGE</u>
I: IMPORTANT PARAMETERS OF CDS.....	6
II: IMPORTANT PARAMETERS OF P3HT.....	11

LIST OF FIGURES

<u>FIGURE</u>	<u>PAGE</u>
1. Band gap structure illustrating a) Direct band gap electron transit b) Indirect band gap phonon assisted electron transit.....	3
2. Wurtzite lattice unit cell of the CdS crystal.....	4
3. CdS electronic band structure.....	5
4. Monomer unit of conductive polymers poly(3-hexylthiophene) (P3HT).....	8
5. Monomers bond together to form polymer.....	9
6. Intra-chain and inter-chain in P3HT, torsional angle (τ) and distance between polymers (D) also affect carrier mobility.....	10
7. Procedure of growing CdS nanowires (a) 5nm thickness titanium layer was deposited on ITO-coated glass substrate. (b) 200nm thickness Aluminum layer was deposited on ITO-coated glass substrate. (c) Nanopores were formed in Aluminum layer after anodization. (d) CdS nanowires were grown after DC electrodeposition.....	14
8. Lineup band structure of CdS and P3HT.....	18
9. The band diagram of CdS/P3HT after they are contacted. The vacuum level of P3HT is lowered by 0.2534eV.....	19
10. I-V curve of simulation.....	24
11. Brief schematic of CdS/P3HT circuit.....	25
12. I-V measurement curve of CdS/P3HT from -2eV to +2eV.....	26
13. Comparison of measurement (blue) and simulation (red) CdS/P3HT I-V curves. The two curves increased at approximate the same voltage, but slope of simulation is much higher than measurement.....	27
14. Band diagram of recombination occurred at the interface.....	29
15. Comparison of measurement (blue) and simulation (red) CdS/P3HT I-V curves after E_A was added in simulation.....	29

LIST OF ABBREVIATIONS

CdS	Cadmium Sulphide
P3HT	Poly (3-hexylthiophene-2, 5-diyl)
I-V	Current-Voltage
LED	light emitting diode
ITO	Indium Tin Oxide
CB	Conduction Band
VB	Valence Band
AAO	Anodized Aluminum Oxide
NaOH	Sodium Hydroxide
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
DMSO	Dimethyl Sulfoxide
VLS	Vapor Liquid Solid

SUMMARY

Nowadays nanoscale devices and semiconductor devices are developed rapidly since there are more requirements in scientific usage and commercial market, more nanostructures such as different kinds of heterojunctions could be used in the future. They may be used in a wide range of electronic devices, for example: solar cells, transistors and polymer diodes ...etc. Recent research of heterojunction semiconductor has improved and revealed different properties such as current-voltage curve and saturation current. Figuring out factors causing these properties for improving the efficiency and usage of these devices is beneficial. The heterojunction formed by cadmium sulphide (CdS) cylinder arrays embedded in the conductive polymer poly (3-hexylthiophene-2, 5-diyl) (P3HT) is investigated for its possible use in photovoltaic applications. Cadmium sulphide (CdS) is a direct band gap II-VI compound for semiconductor usage, it is often used in many optoelectronic devices such as optical switches, sensors, and solar cells. On the other hand, the polymer P3HT is used because of the π bonds results in holes having higher mobility. Therefore, the polymer P3HT has higher conductivity. In this thesis, CdS cylinders were grown by DC electrodeposition and used to form a heterojunction. CdS nanowires are grown in periodic arrays from a nanoporous template which is made by

SUMMARY (continued)

Indium Tin Oxide (ITO) coated glass substrate, then the cast made by P3HT solution is put on it to form pn heterojunction.

The current of the CdS/P3HT junction is measured from -2 to +2 eV, and the equation for a pn heterojunction is used to make the ideal simulation current-voltage (I-V) curve by MATLAB. Then it is seen that there is difference shown upon comparing the measured data and simulations. The most pronounced difference between these two I-V curves is that the current of simulation increases largely when the voltage is higher than 0.8 V, but the current of measurement increases slowly and does not follow an exponential. Recombination near the interface is added in the equation to explain this difference. This yields slopes of two curves that are approximately the same.

Chapter 1 Introduction

Due to the increased demands, more kinds of semiconductors have been invented. Inorganic/inorganic semiconductors are the most popular because of the high mobility of carriers. However, nowadays some organic materials which have high electrical conductivity have been made such as graphene. Inorganic/organic semiconductors contain lots of potential usage needed to be discovered. In this thesis, the CdS/P3HT heterojunction is investigated. CdS (Cadmium sulphide) which is an important II-VI compound for semiconductor was selected since it is widely studied and used in optoelectronic devices because of its direct band gap and suitable semiconducting properties. Cadmium sulphide nanowires contain some advantages such as large surface to volume ratio for forming pn junctions [1]. On the other hand, conductive organic polymers have been discovered and used as conductors of holes in optoelectronic devices, for example: light emitting diodes and solar cells...etc [2]. These conductive polymers are used for optoelectronic applications since they are low-cost and easy to synthesize [3]. CdS/P3HT polymer heterojunction is electrically characterized for its potential use in forming pn diodes.

1.1 Background of CdS

The conductive polymer poly(3-hexylthiophene) (P3HT) has been researched since it contains interesting electrical properties and stability. It is often used in solar cells, switchers, and LED...etc [4]. However, the carrier mobility of organic polymers is usually lower than non-polymer semiconductor material. The low mobility of carriers in polymers causes recombination when they are being transmitted to the electrodes. Adding CdS in the device helps delay recombination after photoexcitation because CdS is a high electron affinity material [5]. Furthermore, cadmium sulphide (CdS) is a suitable II-VI material for semiconductor usage because of its medium band gap and other properties such as high stability and affordable growth [6]. CdS has been widely applied to solar cells because the n-type character it has enables CdS to be made into heterojunctions with p-type semiconductors [7].

1.1.1 Characteristics of CdS

CdS is chosen as an n-type junction due to its high electron affinity, medium band gap, high stability and affordable growth [8]. Due to the deficiency from sulfur, vacancies are created with high electron affinity, and this makes CdS easily to acquire electrons. Therefore, CdS is considered as an n-type semiconductor material. The band gap of CdS is direct, and its value is 2.5eV at 300K [9].

If the minima of the conduction band (CB) and the maxima of the valence band (VB) are at the same value of wave-vector (k), the semiconductor has a direct band gap; as shown in the Figure 1. If the minima of CB and the maxima of VB are not at the same value of wave-vector (k), it is an indirect band gap semiconductor [10].

Figure 1: Band gap structure illustrating a) Direct band gap electron transit b)

Indirect band gap phonon assisted electron transit

There are two kinds of crystal structures existing in CdS: hexagonal wurtzite and cubic crystal structure. In this paper, the crystal structure of the grown CdS nanowires is hexagonal wurtzite structure. Figure 2 is a unit cell lattice of the hexagonal wurtzite CdS [11].

Figure 2: Wurtzite lattice unit cell of the CdS crystal.

Hexagonal wurtzite CdS is a direct band gap semiconductor. Its lowest band gap located at the center (Γ point) of Brillouin zone [12]. Because of the crystal field and spin-orbit coupling in hexagonal CdS, the highest valence band Γ_{15} is split into three different band Γ_9 , Γ_7 , and Γ_7 [13]; as shown in Figure 3.

Figure 3: CdS electronic band structure.

The absorption coefficient of direct band gap semiconductor is higher than the absorption coefficient of the indirect band gap semiconductor. Due to energy and momentum conservation, the electron-photon interaction in the direct band gap semiconductor does not require the absorption or emission of a phonon [14]. An electron can easily transit to an empty state in the conduction band in a direct band gap semiconductor as shown in Figure 1. Therefore, CdS is widely used for optoelectronic applications.

1.1.2 Important parameters of CdS

CdS has high electron affinity (4.79 eV) [15], and effective mass of holes in CdS is

$0.8 \frac{m_p}{m_0}$ (~ 0.8 of effective mass of electron), effective mass of electrons in CdS is 0.21

$\frac{m_n}{m_0}$ (~ 0.21 of effective mass of electron) [16], exciton binding energy E is ~ 0.03 eV.

The band gap is around 2.5 eV [17]. The hole mobility is around $15 \frac{\text{cm}^2}{\text{Vs}}$. Using the

Einstein equation, the diffusion constant of holes in CdS:

$$D_p = \frac{kT}{q} \mu_p = 0.3885 \frac{\text{cm}^2}{\text{s}}$$

The diffusion constant of holes is 0.3885. The lifetime of holes is $10^{-7} \sim 3 * 10^{-7}$ s

(around 20 μm) [18]. Some other parameters of hexagonal CdS are listed in Table I.

Table I: Important parameters of CdS [20].

Band gap (eV)	2.5
Electron affinity (eV)	4.79
Effective mass of electrons ($\frac{m_n}{m_0}$)	0.21
Effective mass of holes ($\frac{m_p}{m_0}$)	0.8
Exciton binding energy (eV)	0.03
Hole mobility ($\frac{\text{cm}^2}{\text{Vs}}$)	15
Electron mobility ($\frac{\text{cm}^2}{\text{Vs}}$)	340
Diffusion constant of holes	0.3885

Life time of holes (μm)	20
Dielectric constant at low frequency along z (ϵ_0)	9.25
Dielectric constant at low frequency perpendicular to z (ϵ_0)	8.7
Dielectric constant at high frequency along z (ϵ_∞)	5.5
Dielectric constant at high frequency perpendicular to z (ϵ_∞)	5.53
Lattice constant along z a_0 (nm)	0.414
Lattice constant perpendicular to z c_0 (nm)	0.67
Thermal conductivity ($\frac{\text{W}}{\text{cmK}}$)	0.2

1.2 Background of P3HT

Polymers poly(3-hexylthiophene) (P3HT) is a hole conducting material. It has been used as solar cells, switches, and light emitting diodes... [21], because electronics made by conductive polymers have less weight and more flexibility compared to small molecules [22]. In this paper, P3HT is used as a p-type semiconductor in the CdS/P3HT heterojunction. There are two hole transport mechanisms, inter-chain and intra-chain conduction, in P3HT as discussed in Section 1.3.

1.2.1 Characteristics of P3HT

Chains which contain repeating monomers compose Polymers. Monomers are repeating units formed by hydrogen, carbon, and other atoms. The monomer unit of P3HT is shown in Figure 4, and some monomers bond together is shown in Figure 5.

Polymers are usually insulators, otherwise, some polymers are conductive since carriers can transport in overlap bonds. The overlapping carbon p orbitals in the successive units in a conjugated polymer produce two split energy levels. One is π bonding orbital and another is π^* anti-bonding orbital. A series of π bonds form a π energy band which is called the highest occupied molecular orbital (HOMO), and a series of π^* bonds form a π^* energy band which is called the lowest unoccupied molecular orbital (LUMO) in the energy band of the polymer. These two energy bands are similar to the valence band and conduction band of inorganic semiconductors [23][24]. These bands enable carriers to be transported in the polymer.

In our case, holes can hop in P3HT via the π energy band and form the current.

Figure 4: Monomer unit of conductive polymers poly(3-hexylthiophene) (P3HT) [25]

Figure 5: Monomers bond together to form polymer [26].

There are two conduction routes for carriers in polymers, intra-chain conduction and inter-chain conduction. Intra-chain conduction is that carriers transit in the same polymer via π band. Carriers have higher mobility via intra-chain conduction than with via inter-chain conduction. On the other hand, the process where carriers move between different polymer chains via π band is called inter-chain conduction. In most cases, the mobility of carriers is largely reduced via inter-chain conduction compared to intra-chain conduction, so the current is mainly composed by carriers via intra-chain conduction [27]. Because of the inter-chain conduction, the polymers are formed in approximately the shape of nanowires via spin coated in repeating CdS nanowires.

The CdS/P3HT junction is investigated in terms of its electronic properties for

optoelectronic applications.

Figure 6: Intra-chain and inter-chain in P3HT, torsional angle (τ) and distance between polymers also affect carrier mobility [28].

1.2.2 Important parameters of P3HT

The effective mass of electrons and holes in P3HT is $1.7 \frac{m^*}{m_0}$ (1.7 of effective mass of electron) [29]. Hole mobility and electron mobility in P3HT is 3×10^{-4} and $1.5 \times 10^{-4} \frac{cm^2}{Vs}$ [30], respectively. Using the Einstein equation, the diffusion constant of electrons in P3HT:

$$D_n = \frac{kT}{q} \mu_n = 3.885 \times 10^{-6} \frac{cm^2}{s}$$

Table II: Important parameters of P3HT [31][32].

Band gap (eV)	1.9
Effective mass of electrons and holes ($\frac{m^*}{m_0}$)	1.7
Hole mobility ($\frac{cm^2}{Vs}$)	3×10^{-4}
Electron mobility ($\frac{cm^2}{Vs}$)	1.5×10^{-4}
Diffusion constant of electrons	3.885×10^{-6}
Diffusion length of electrons (cm)	10^{-6}

Chapter 2 Process of Forming Heterojunction

In this chapter, the procedure of forming a heterojunction is described. The forming procedure of CdS/P3HT heterojunction was performed by Dr. Shripriya Poduri in nanotechnology lab in University of Illinois at Chicago. The nanoporous templates in which CdS nanowires were grown on, was introduced in Section 2.1. The growth of CdS nanowires is discussed in Section 2.2. The P3HT solution for making a p-type junction is described in Section 2.3.

2.1 Forming procedure of nanoporous template

The ITO-coated glass substrate (size 1"×1", thickness 1mm) is available commercially. This substrate was ultrasonicated in acetone and isopropanol for 60 minutes to clean and remove organic residues on surface, then rinse in the deionized water and dry by an air gun. A 5 nm thickness of titanium was deposited by e-beam evaporation on the substrate as an interlayer [33]. The titanium interlayer is for improving the connectivity and preventing delamination during anodization [34][35]. The next step is using e-beam evaporation to deposit an aluminum layer of 200 nm thickness. For developing the nanopores, the template was anodized in 0.3 M oxalic acid at 40 Volt and current of 0.2 A, then heated the template in a mixture of 5 wt. %

phosphoric acid and 10 wt. % chromic acid at 60 °C to remove the redundant aluminum and oxide layer. After this first anodization, the formed pores were few and non uniform. Therefore, making the second anodization at the same voltage and current condition at 2~8 °C. Diameters of produced nanopores are 10-60 nm. The diameters of the nanopores are varied with condition such as temperature and pH of the acid solution [36].

There was a non uniform layer of oxide at the interface of the Al and Al₂O₃ after these two steps. This oxide barrier would interrupt the growth of the electrodeposited nanowires in the pores and lower the quality. For removing this oxide layer, the substrate was immersed in 5 wt. % phosphoric acid (H₃PO₄) for 3~4 minutes [36][37].

2.2 Growth of CdS nanowires

Dimethyl sulfoxide (DMSO) solution formed by 0.055 M CdCl_2 and 0.19 M elemental sulfur was used as electrolyte for CdS electrodeposition [38][39]. Current density is 15 mA/cm^2 applied for 7~10 s at $120\sim 150^\circ\text{C}$ during the electrodeposition growth. The template was rinsed in hot DMSO then acetone and cleaned in deionized water after electrodeposition. For removing the cast around CdS nanowires, the AAO template was dissolved in 1 M NaOH solution for 8 minutes at room temperature. Then nanowires were annealed for 60 minutes at 500°C for increasing crystallinity. The procedure of growing CdS nanowires is shown in Figure 7.

Figure 7: Procedure of growing CdS nanowires (a) 5nm thickness titanium layer was deposited on ITO-coated glass substrate. (b) 200nm thickness Aluminum layer was

deposited on ITO-coated glass substrate. (c) Nanopores were formed in Aluminum layer after anodization. (d) CdS nanowires were grown after DC electrodeposition.

2.2.1 Characteristics of growth of CdS nanowires

It was difficult to etch out aluminum oxide barrier layer completely, so self-assembling and growing CdS nanowires in an AAO template was interrupted by the barrier layer. Therefore, there are defects created in nanowires [40][41]. The procedure of electrodeposition could be described as follows:

- 1) Elemental sulfur and CdCl_2 ionize into S^{2-} and Cd^{2+} ions in DMSO solution.
- 2) Cd^{2+} reacts with S^{2-} , and CdS is formed in the nanopores [42].
- 3) CdS crystallites accumulate into nanotubes on the walls of nanopores, then these nanotubes are filled and become nanowires [43].

2.3 Forming a junction of P3HT

At the beginning, chloroform solution which was w/v ratio of 10 mg/ml was used for the dissolution for P3HT. For dissolving P3HT completely, the solution was heated until the temperature is 100 °C. Then this P3HT solution was put on the CdS nanowires template to form the CdS/P3HT heterojunction. Furthermore, using silver paint to form Ag contact on top helps to measure current-voltage and other properties of Ag/P3HT/CdS/ITO heterojunction.

Chapter 3 Current Voltage Characters of CdS/P3HT

In this chapter, band gap lineup is described in Section 3.1. The equation of simulation is introduced in Section 3.2. Measurement of current-voltage curve is shown in Section 3.3. Comparison of simulation and measurement is shown in Section 3.4.

3.1 Band gap lineup

The conduction band (CB) and valence band (VB) of CdS are -4.3eV and -6.7eV, respectively [44]. The Fermi level of CdS is calculated by the equation:

$$E_c - E_f = kT \ln\left(\frac{N_c}{N_D}\right) = 0.0259 \ln\left(\frac{2.28 \times 10^{18}}{2 \times 10^{18}}\right) = 0.0034 \text{ eV}$$

N_D is the electron concentration which is approximately 2×10^{18} from Reference [45].

N_c is effective density of CB states which is $2.28 \times 10^{18} \text{ cm}^{-3}$ for CdS. As a result, the Fermi level of CdS is 0.0034eV below CB. It shows CdS is a good donor provider.

On the other hand, since P3HT is polymer, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are not locate at a definite level, they alter in a range of band diagram. Therefore, here the numbers used are approximate value. LUMO and HOMO of P3HT are -3eV and -5eV respectively [46]. The Fermi level of P3HT is approximately 0.95eV above HOMO [47], so it is

-4.05eV. These band diagrams are shown in Figure 8.

Figure 8: Lineup band structure of CdS and P3HT

After CdS nanowires contacted with P3HT, the Fermi level of these two materials lined up. The Fermi level of P3HT lowered 0.2534 eV to -4.3034 eV to match the Fermi level of CdS as shown in Figure 9.

Figure 9: The band diagram of CdS/P3HT after they are contacted. The vacuum level of P3HT is lowered by 0.2534 eV.

There is a spike on CB because of heterogeneous, and the vacuum level of P3HT is lowered by 0.2534 eV.

3.2 Equation of heterogeneous pn junction

Equation of heterogeneous pn junction is used to build simulation model. As the general majority carrier equation:

$$N_{n0}(x > x_n) = \frac{2}{\sqrt{\pi}} * N_{cn} * F_{\frac{1}{2}}\left(\frac{E_{F0} - E_{cn}}{kT}\right) \approx N_{cn} e^{\left(\frac{E_{F0} - E_{cn}}{kT}\right)}$$

It is for electrons in the n-type junction. When electrons move to p-type junction, they become minority carriers. Therefore, the equation is modified as:

$$N_{p0}(x < -x_p) = \frac{2}{\sqrt{\pi}} * N_{cp} * F_{\frac{1}{2}}\left(\frac{E_0 - E_{cp}}{kT}\right) \approx N_{cp} e^{\left(\frac{E_{F0} - E_{cp}}{kT}\right)}$$

The index n is modified to p. The same concept can also be applied to holes.

When applied bias is added to the diode, it is non-equilibrium. The Fermi levels of n-side and p-side are different. ($E_{fn} \neq E_{fp}$) Electrons inject from n-side in p-side are as:

$$N_p(x = -x_p) \approx N_{cp} e^{\left(\frac{E_{Fn} - E_{cp}}{kT}\right)}$$

The hole Fermi level on p-side (E_{fp}) is approximately the same with E_{f0} , so the equilibrium equation could be modified as:

$$N_{p0}(x = -x_p) = N_{cp} e^{\left(\frac{E_{F0} - E_{cp}}{kT}\right)} \approx N_{cp} e^{\left(\frac{E_{Fp} - E_{cp}}{kT}\right)}$$

Dividing these two equations could derive this applied voltage expression:

$$\frac{N_p(x = -x_p)}{N_{p0}(x = -x_p)} = e^{\left(\frac{E_{Fn} - E_{Fp}}{kT}\right)} = e^{\frac{qV_A}{kT}}$$

Therefore, multiply N_{p0} on both side and minus N_{p0} on each side:

$$\Delta N_p(x = -x_p) = N_{p0} * (e^{\frac{qV_A}{kT}} - 1)$$

Also,

$$\Delta P_n(x = +x_n) = P_{n0} * (e^{\frac{qV_A}{kT}} - 1)$$

The equation of injected electrons and holes are derived. Then continuity equation is used:

$$\frac{\partial \Delta N_p}{\partial t} = -\frac{\Delta N_p}{\tau_n} + D_n \left(\frac{\partial^2 \Delta N_p}{\partial x^2} \right)$$

The boundary conditions are define below.

P side:

$$\Delta N_p(x = -x_p) = N_{p0} * (e^{\frac{qV_A}{kT}} - 1)$$

N side:

$$\Delta P_n(x = +x_n) = P_{n0} * (e^{\frac{qV_A}{kT}} - 1)$$

Also, the injected carriers are zero at infinity:

$$\Delta N_p(x \rightarrow -\infty) = 0$$

$$\Delta P_n(x \rightarrow +\infty) = 0$$

The equilibrium condition is

$$\frac{\partial \Delta N_p}{\partial t} = 0$$

The equations are derived in the following.

P side:

$$\Delta N_p(x < -x_p) = N_{p0} * (e^{\frac{qV_A}{kT}} - 1) e^{\frac{x+x_p}{L_n}}$$

$$L_n = \sqrt{D_n * \tau_n}$$

N side:

$$\Delta P_n(x > +x_n) = P_{n0} * (e^{\frac{qV_A}{kT}} - 1)e^{-\frac{x-x_n}{L_p}}$$

$$L_p = \sqrt{D_p * \gamma_p}$$

Then the carrier density made by electrons and holes are derived:

$$J_n(x < -x_p) = q * \frac{D_n}{L_n} * N_{p0} * (e^{\frac{qV_A}{kT}} - 1)e^{\frac{x+x_p}{L_n}}$$

$$J_p(x > +x_n) = q * \frac{D_p}{L_p} * P_{n0} * (e^{\frac{qV_A}{kT}} - 1)e^{-\frac{x-x_n}{L_p}}$$

Adding these two together at the boundary of depletion region we find:

$$J = J_n(x = -x_p) + J_p(x = +x_n)$$

$$J = q * \left[\left(\frac{D_n}{L_n} \right) * N_{p0} + \left(\frac{D_p}{L_p} \right) * P_{n0} \right] * \left(e^{\frac{qV_A}{kT}} - 1 \right)$$

Then multiplying by the area, the current equation is derived:

$$I = A * q * \left[\left(\frac{D_n}{L_n} \right) * N_{p0} + \left(\frac{D_p}{L_p} \right) * P_{n0} \right] * \left(e^{\frac{qV_A}{kT}} - 1 \right)$$

N_{p0} and P_{n0} are the numbers of minority carriers without applied bias.

$$N_{p0} = N_{cp} * e^{\left(\frac{E_{F0} - E_{cp}}{kT} \right)}$$

$$P_{n0} = N_{vn} * e^{\left(\frac{E_{vn} - E_{F0}}{kT} \right)}$$

and,

$$N_{cp} = 2 * \left[\frac{m_n * kT}{2 * \pi * \hbar^2} \right]^{\frac{3}{2}} = 2.51 * 10^{19} * \left(\frac{m_n}{m_0} \right)^{\frac{3}{2}}$$

$$N_{vn} = 2 * \left[\frac{m_p * kT}{2 * \pi * \hbar^2} \right]^{\frac{3}{2}} = 2.51 * 10^{19} * \left(\frac{m_p}{m_0} \right)^{\frac{3}{2}}$$

m_n which is effective mass of electrons in P3HT is $1.7 m_0$.

m_p which is the effective mass of holes in CdS is $0.8 m_0$.

$(E_{F0}-E_{cp})$ which is the Fermi level minus CB of P3HT is -1.05 eV.

$(E_{vn}-E_{F0})$ which is VB minus the Fermi level of CdS is -2.2966 eV.

After calculation,

$$N_{p0} = 1.27 \times 10^2 \text{ cm}^{-3}$$

$$P_{n0} = 4.695 \times 10^{-20} \text{ cm}^{-3}$$

$$\mu_n \text{ (mobility of electrons in P3HT) is } 1.5 \times 10^{-4} \frac{\text{cm}^2}{\text{Vs}}.$$

$$\mu_p \text{ (mobility of holes in CdS) is } 15 \frac{\text{cm}^2}{\text{Vs}}.$$

Using the Einstein equation,

The diffusion constant of electrons in P3HT is then,

$$D_n = \frac{kT}{q} \mu_n = 3.885 \times 10^{-6} \frac{\text{cm}^2}{\text{s}}$$

The diffusion constant of holes in CdS is,

$$D_p = \frac{kT}{q} \mu_p = 0.3885 \frac{\text{cm}^2}{\text{s}}$$

The lifetime of holes (γ_p) is approximately 2×10^{-7} s.

Using γ_p and D_p to calculate diffusion length of holes in CdS,

$$L_p = \sqrt{D_p * \gamma_p} = 2.787 \times 10^{-4} \text{ cm}$$

The diffusion length of electrons in P3HT (L_n) is 10^{-6} cm.

The area of junction (A) is 0.25 cm^2 .

Putting these constants in the current equation,

$$\begin{aligned}
 I &= 1.6 * 10^{-19} * 0.25 * \left[\frac{3.885 * 10^{-6} * 1.37 * 10^2}{10^{-6}} + \frac{0.3885 * 5.55 * 10^{-20}}{2.787 * 10^{-4}} \right] \\
 &\quad * \left(e^{\frac{V_A}{0.0259}} - 1 \right) \\
 &= 1.6 * 10^{-19} * 0.25 * [5.32245 * 10^2 + 7.73377 * 10^{-17}] \\
 &\quad * \left(e^{\frac{V_A}{0.0259}} - 1 \right) = 1.981 * 10^{-17} * \left(e^{\frac{V_A}{0.0259}} - 1 \right)
 \end{aligned}$$

The result of simulation by this equation is shown in Figure 10.

Figure 10: I-V curve of simulation

3.3 Measurement of current-voltage curve

The current-voltage (I-V) curve of CdS/P3HT sample was measured by Dr. Shripriya Poduri using HP4156B semiconductor analyzer and a probe at room temperature. The brief schematic of CdS/P3HT measurement circuit is shown in Figure 11. The sample was measured from -2 eV to +2 eV. The measured I-V curve is shown in Figure 12, and the Ag/P3HT/CdS/ ITO circuit is shown in Figure 11.

Figure 11: Brief schematic of CdS/P3HT circuit

Figure 12: I-V measurement curve of CdS/P3HT from -2eV to +2eV

3.4 Comparison of simulation and measurement

Comparison of simulation and measurement result are plotted in Figure 13. It shows that the current increased at approximate the same voltage, but slopes of two curves are much different. The current of simulation increased as an ideal exponential equation, but the current of measurement increased much slowly, and the slope of measurement curve changed many times.

As mentioned previously, the CB (LUMO) and VB (HOMO) of P3HT locate in a range of band diagram due to polymer property. The band structure of P3HT is not continuous. Furthermore, a part of carriers have lower mobility when they propagate via inter-chain conduction. The inter-chain distance between two polymers also

influences mobility of carriers. Also, there are defects produced during junction-forming process such as in grown CdS nanowires, sequence of P3HT polymers, and at junction contact. The defects at semiconductor-polymer contact play an important role in decreasing the current since they could be traps for carriers in recombination process.

These properties result in deviation between simulation and measurement. The measured current is lower than ideal one, and the slope changes repeatedly.

Figure 13: Comparison of measurement (blue) and simulation (red) CdS/P3HT I-V curves. The two curves increased at approximate the same voltage, but slope of simulation is much higher than measurement.

3.5 Interface recombination

There are defects at the interface. The defects cause some carriers recombine at the interface. As the reference said, the recombination could be presented by motivation energy (E_A) in the equation [48]. Motivation energy (E_A) relates to band structure at the interface. In the solar cell, E_A is constant when the voltage is unchanged as open circuit voltage. However, the voltage is changed in this pn junction. The Fermi level and band structure also vary, so E_A is not an invariable value. Therefore, E_A is added in the current equation. After several attempts, simulation is closest to measurement when E_A is set to be $0.3*V_A^{1.88}$. The I-V curves are shown in Figure 15. The equation of current becomes:

$$I = I_0 * \left(e^{\left(\frac{qV_A}{kT} - \frac{E_A}{kT} \right)} - 1 \right)$$

$$I = I_0 * \left(e^{\left(\frac{qV_A}{kT} - \frac{0.3*q*V_A^{1.88}}{kT} \right)} - 1 \right)$$

$$I_0 = A * q * \left[\left(\frac{D_n}{L_n} \right) * N_{p0} + \left(\frac{D_p}{L_p} \right) * P_{n0} \right] = 1.981 * 10^{-17}$$

Figure 14: Band diagram of recombination occurred at the interface

Figure 15: Comparison of measurement (blue) and simulation (red) CdS/P3HT I-V curves after E_A was added in simulation.

Chapter 4 Conclusion and Future Work

The CdS/P3HT sample is derived from nanoelectronic lab in University of Illinois at Chicago. The forming process is described in Chapter 2. In Chapter 3, the simulation equation is given based on the heterojunction equation with the characteristics of CdS and P3HT, and the measurement data is compared with simulation. The current increased with voltage at approximately the same value, but the slopes are much different. The current of measurement increased slower than simulation. It is probably because of the defects and the properties of polymers. After adding the recombination equation, the shapes of curves are similar. Although there are still some differences existing, it is unavoidable because the HOMO and LUMO of P3HT are not as continuous as CB and VB of non polymer material and the carriers have different mobility via intra-chain and inter-chain conduction.

Until now, CdS/P3HT shows the potential of being used for photovoltaic devices. In the future, making the measurement curve become more similar with simulation helps to derive better data for forming photoelectronic devices. The I-V equation may need to be modified to suit polymer material case. The constant values of motivation energy (E_A) have not been proven yet. Which spots of band gap the defects exist at should be verified. Furthermore, figuring out the causes of the defects and trying to

minimize them are necessary. Therefore, comparing the simulation with samples formed from different methods (Ex: VLS) may help to figure out the causes.

CITED LITERATURE

1. Shripriya Poduri: CdS Nanowires and CdSe/ZnS Quantum Dots Properties and Applications, *thesis*, 2014
2. Heeger, A.J.: Nobel Lecture: Semiconducting and metallic polymers: The fourth generation of polymeric materials. *Rev. Mod. Phys.*, 73: 681-700, 2001.
3. Y. Pang, X. Li, H. Ding, G. Shi and L. Jin, *Electrochim. Acta*, 52 (2007) 6172.
4. M. J. L. Santos, J. Ferreira, E. Radovanovic, R. Romano, O. L. Alves and E. M. Girotto, *Thin Solid Films*, 517 (2009) 5523.
5. H. Karami and A. Kaboli, *Int. J. Electrochem. Sci*, 5 (2010) 706.
6. Ing, Yah Chzeh, et al. "Electrochemical Preparation of Bilayer pn Junction of n-CdS/p-P3HT." *Int. J. Electrochem. Sci* 6 (2011): 2898-2904.
7. Rössler, ed., Landolt-Börnstein Group III: Condensed Matter, B: II-VI and I-VII Compounds; Semimagnetic Compounds (Springer-Verlag Berlin Heidelberg New York):
8. H. Karami and A. Kaboli, *Int. J. Electrochem. Sci*, 5 (2010) 706.
9. Wang, Jifeng, and Minoru Isshiki. "Wide-bandgap II–VI semiconductors: growth and properties." *Springer Handbook of Electronic and Photonic Materials*. Springer US, 2007. 325-342.
10. http://en.wikipedia.org/wiki/Direct_and_indirect_band_gaps
11. http://en.wikipedia.org/wiki/Wurtzite_crystal_structure#mediaviewer/File:Wurtzite-unit-cell-3D-balls.png
12. Rössler, ed., Landolt-Börnstein Group III: Condensed Matter, B: II-VI and I-VII Compounds; Semimagnetic Compounds (Springer-Verlag Berlin Heidelberg New York).

CITED LITERATURE (Continued)

13. Hoang, B.T: Investigation of Single Semiconductor Nanowire Heterostructures Using Polarized Imaging Spectroscopy. PhD Thesis, University of Cincinnati, Cincinnati, 2008.
14. Shripriya Poduri: CdS Nanowires and CdSe/ZnS Quantum Dots Properties and Applications, *thesis*, 2014
15. Wang, Jifeng, and Minoru Isshiki. "Wide-bandgap II–VI semiconductors: growth and properties." *Springer Handbook of Electronic and Photonic Materials*. Springer US, 2007. 325-342.
16. Brus, Louis E. "Electron–electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state." *The Journal of chemical physics* 80.9 (1984): 4403-4409.
17. Wang, Jifeng, and Minoru Isshiki. "Wide-bandgap II–VI semiconductors: growth and properties." *Springer Handbook of Electronic and Photonic Materials*. Springer US, 2007. 325-342.
18. Mort, J., and W. E. Spear. "Hole Drift Mobility and Lifetime in CdS Crystals." *Physical Review Letters* 8.8 (1962): 314.
19. Mort, J., and W. E. Spear. "Hole Drift Mobility and Lifetime in CdS Crystals." *Physical Review Letters* 8.8 (1962): 314.
20. Wang, Jifeng, and Minoru Isshiki. "Wide-bandgap II–VI semiconductors: growth and properties." *Springer Handbook of Electronic and Photonic Materials*. Springer US, 2007. 325-342.
21. Y. Pang, X. Li, H. Ding, G. Shi and L. Jin, *Electrochim. Acta*, 52 (2007) 6172
22. http://en.wikipedia.org/wiki/Polymer_solar_cell
23. Coropceanu, V., Cornil, J., da Silva, D.A., Olivier, Y., Silbey, R., and Bredas, J.L.: Charge transport in organic semiconductors. *Chem. Rev.*, 107: 926-952, 2007.

CITED LITERATURE (Continued)

24. Heeger, A.J., Kivelson, S., Schrieffer, J.R., and Su, W.P.: Solitons in Conducting Polymers. *Rev. Mod Phys.*, 60: 781-850, 1988.
25. <http://www.sigmaaldrich.com/catalog/product/aldrich/698997?lang=en®ion=US>
26. <http://www.rheothing.com/2011/11/fringed-micelles-and-photoconductivity.html>
27. Lan, Yi-Kang, Cheng Han Yang, and Hsiao-Ching Yang. "Theoretical investigations of electronic structure and charge transport properties in polythiophene-based organic field-effect transistors." *Polymer International* 59.1 (2010): 16-21.
28. Lan, Yi-Kang, Cheng Han Yang, and Hsiao-Ching Yang. "Theoretical investigations of electronic structure and charge transport properties in polythiophene-based organic field-effect transistors." *Polymer International* 59.1 (2010): 16-21.
29. Ai, Xin, et al. "Photoinduced charge carrier generation in a poly (3-hexylthiophene) and methanofullerene bulk heterojunction investigated by time-resolved terahertz spectroscopy." *The Journal of Physical Chemistry B* 110.50 (2006): 25462-25471.
30. Choulis, S. A., et al. "High ambipolar and balanced carrier mobility in regioregular poly (3-hexylthiophene)." *Applied physics letters* 85.17 (2004): 3890-3892.
31. Zhong, Min, et al. "Improving the performance of CdS/P3HT hybrid inverted solar cells by interfacial modification." *Solar Energy Materials and Solar Cells* 96 (2012): 160-165.
32. Ayzner, Alexander L., et al. "Reappraising the need for bulk heterojunctions in polymer– fullerene photovoltaics: the role of carrier transport in all-solution-processed P3HT/PCBM bilayer solar cells." *The Journal of Physical Chemistry C* 113.46 (2009): 20050-20060.

CITED LITERATURE (Continued)

33. Yin, A., Tzolov, M., Cardimona, D.A., and Xu, J.: Template-growth of highly ordered carbon nanotube arrays on silicon. *Ieee T. Nanotechnol.*, 5: 564-567, 2006.
34. Liu, P.A., Singh, V.P., Jarro, C.A., and Rajaputra, S.: Cadmium sulfide nanowires for the window semiconductor layer in thin film CdS-CdTe solar cells. *Nanotechnology*, 22, 2011.
35. Foong, T.R.B., Sellinger, A., and Hu, X.: Origin of the Bottlenecks in Preparing Anodized Aluminum Oxide (AAO) Templates on ITO Glass. *ACS Nano*, 2: 2250-2256, 2008.
36. Routkevitch, D., Bigioni, T., Moskovits, M., and Xu, J.M.: Electrochemical fabrication of CdS nanowire arrays in porous anodic aluminum oxide templates. *J. Phys. Chem.*, 100: 14037-14047, 1996.
37. Liu, P.A., Singh, V.P., and Rajaputra, S.: Barrier layer non-uniformity effects in anodized aluminum oxide nanopores on ITO substrates. *Nanotechnology*, 21, 2012.
38. Xu, D.S., Xu, Y.J., Chen, D.P., Guo, G.L., Gui, L.L., and Tang, Y.Q.: Preparation and characterization of CdS nanowire arrays by dc electrodeposit in porous anodic aluminum oxide templates. *Chem. Phys. Lett.*, 325: 340-344, 2000.
39. Yang, Y., Chen, H.L., Mei, Y.F., Chen, J.B., Wu, X.L., and Bao, X.M.: Anodic alumina template on Au/Si substrate and preparation of CdS nanowires. *Solid State Commun.*, 123: 279-282, 2002.
40. Klein, J.D., Herrick, R.D., Palmer, D., Sailor, M.J., Brumlik, C.J., and Martin, C.R.: Electrochemical Fabrication of Cadmium Chalcogenide Microdiode Arrays. *Chem. Mater.*, 5: 902-904, 1993.
41. Chakarvarti, S.K., Vetter, J.: Microfabrication of metal-semiconductor heterostructures and tubules using nuclear track filters. *J. Micromech. Microeng.*, 3: 1993.

CITED LITERATURE (Continued)

42. Mondal, S.P., Das, K., Dhar, A., and Ray, S.K.: Characteristics of CdS nanowires grown in a porous alumina template using a two-cell method. *Nanotechnology*, 18: 2007.
43. Li, Y.D., Li, X.L., He, R.R., Zhu, J., and Deng, Z.X.: Artificial lamellar mesostructures to WS(2) nanotubes. *J. Am. Chem. Soc.*, 124: 1411-1416, 2002.
44. Sun, Ke, et al. "Applications of colloidal quantum dots." *Microelectronics Journal* 40.3 (2009): 644-649.
45. Li, Dehui, Jun Zhang, and Qihua Xiong. "Surface depletion induced quantum confinement in CdS nanobelts." *ACS nano* 6.6 (2012): 5283-5290.
46. Zhong, Min, et al. "Improving the performance of CdS/P3HT hybrid inverted solar cells by interfacial modification." *Solar Energy Materials and Solar Cells* 96 (2012): 160-165.
47. Park, Yeong Don, et al. "Energy-level alignment at interfaces between gold and poly (3-hexylthiophene) films with two different molecular structures." *Electrochemical and solid-state letters* 9.11 (2006): G317-G319.
48. Wilhelm, Helena, Hans-Werner Schock, and Roland Scheer. "Interface recombination in heterojunction solar cells: Influence of buffer layer thickness." *Journal of Applied Physics* 109.8 (2011): 084514.

APPENDICES

APPENDIX A

Program to calculate simulation of CdS/P3HT I-V curve in MATLAB.

```
clear
```

```
k=8.617e-5;
```

```
q=1.6e-19;
```

```
T=300;
```

```
Dp=0.3885;
```

```
Dn=3.885e-6;
```

```
taup=2e-7;
```

```
Lp=sqrt(Dp*taup);
```

```
Ln=1e-6;
```

```
A=25*10^-2;
```

```
Nvn=2.510*(1e19)*(0.8^(3/2));
```

```
Ncp=2.510*(1e19)*(1.7^(3/2));
```

```
Pn0=Nvn*exp(-2.3966/(k*T));
```

```
Np0=Ncp*exp(-1.05/(k*T));
```

```
VA=linspace(-2,2);
```

```
I0=q*A*((Dn/Ln)*Np0+(Dp/Lp)*Pn0);
```

```
I1=I0*(exp((VA)/(k*T))-1);
```

APPENDIX A (Continued)

```
close
```

```
plot(VA,I1,'r-');grid;
```

```
ymin=-5e-3; ymax=22e-3;
```

```
axis([-3,3,ymin,ymax]);
```

```
xlabel('VA(volts)'); ylabel('I(amps)');
```

APPENDIX B

Program to draw measurement of CdS/P3HT I-V curve in MATLAB.

```

plot([-2,-1.5,-1,-0.5,0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1,1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,2],[-0.099999e-3,-0.099997e-3,-0.099996e-3,-0.075228e-3,0,0.013306e-3,0.026125e-3,0.037893e-3,0.052255e-3,0.064388e-3,0.074277e-3,0.061444e-3,0.06604e-3,0.0966e-3,1.902e-3,2.581e-3,2.923e-3,3.492e-3,3.805e-3,5.135e-3,8.126e-3,12.556e-3,15.889e-3,17.769e-3,20.61e-3],'-');

grid;

ymin=-5e-3; ymax=22e-3;

axis([-3,3,ymin,ymax]);

xlabel('VA(volts)'); ylabel('I(amps)');
```


APPENDIX C

Program to compare measurement and simulation of CdS/P3HT I-V curve in MATLAB.

```
clear
```

```
k=8.617e-5;
```

```
q=1.6e-19;
```

```
T=300;
```

```
Dp=0.3885;
```

```
Dn=3.885e-6;
```

```
taup=2e-7;
```

```
Lp=sqrt(Dp*taup);
```

```
Ln=1e-6;
```

```
A=25*10^-2;
```

```
Nvn=2.510*(1e19)*(0.8^(3/2));
```

```
Ncp=2.510*(1e19)*(1.7^(3/2));
```

```
Pn0=Nvn*exp(-2.3966/(k*T));
```

```
Np0=Ncp*exp(-1.05/(k*T));
```

```
VA=linspace(-2,2);
```

```
I0=q*A*((Dn/Ln)*Np0+(Dp/Lp)*Pn0);
```

APPENDIX C (Continued)

```

I1=I0*(exp((VA)/(k*T))-1);

close

plot(VA,I1,'r-');grid;

hold on;

plot([-2,-1.5,-1,-0.5,0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1,1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,2],[-0.0999999e-3,-0.099997e-3,-0.099996e-3,-0.075228e-3,0,0.013306e-3,0.026125e-3,0.037893e-3,0.052255e-3,0.064388e-3,0.074277e-3,0.061444e-3,0.06604e-3,0.0966e-3,1.902e-3,2.581e-3,2.923e-3,3.492e-3,3.805e-3,5.135e-3,8.126e-3,12.556e-3,15.889e-3,17.769e-3,20.61e-3],'-');

ymin=-5e-3; ymax=22e-3;

axis([-3,3,ymin,ymax]);

xlabel('VA(volts)'); ylabel('I(amps)');

```

APPENDIX D

Program to compare measurement and simulation with recombination of CdS/P3HT

I-V curve in MATLAB.

```
clear
```

```
k=8.617e-5;
```

```
q=1.6e-19;
```

```
T=300;
```

```
Dp=0.3885;
```

```
Dn=3.885e-6;
```

```
taup=2e-7;
```

```
Lp=sqrt(Dp*taup);
```

```
Ln=1e-6;
```

```
A=25*10^-2;
```

```
Nvn=2.510*(1e19)*(0.8^(3/2));
```

```
Ncp=2.510*(1e19)*(1.7^(3/2));
```

```
Pn0=Nvn*exp(-2.3966/(k*T));
```

```
Np0=Ncp*exp(-1.05/(k*T));
```

```
% VA=linspace(-2,2);
```

APPENDIX D (Continued)

```

for VA=0:0.002:2

    I01=q*A*((Dn/Ln)*Np0+(Dp/Lp)*Pn0);

    I1=I01*(exp((VA)/(k*T))-0.3*(VA)^(1.88)/(k*T))-1);

    plot(VA,I1,'r-');grid;

    hold on

end

hold on;

plot([-2,-1.5,-1,-0.5,0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1,1.1,1.2,1.3,1.4,1.5,1.6,1.7,1.8,1.9,2],[-0.099999e-3,-0.099997e-3,-0.099996e-3,-0.075228e-3,0,0.013306e-3,0.026125e-3,0.037893e-3,0.052255e-3,0.064388e-3,0.074277e-3,0.061444e-3,0.06604e-3,0.966e-3,1.902e-3,2.581e-3,2.923e-3,3.492e-3,3.805e-3,5.135e-3,8.126e-3,12.556e-3,15.889e-3,17.769e-3,20.61e-3],'-');

ymin=-5e-3; ymax=22e-3;

axis([-3,3,ymin,ymax]);

xlabel('VA(volts)'); ylabel('I(amps)');

```

VITA

NAME Ching-En Huang

EDUCATION MS, Electrical and Computer Engineering,
University of Illinois at Chicago, 2015
BS, Physics, Fu Jen Catholic University, 2012