Optimization of p-Type CZTS Nanocrystal Thin Film Layers For Applications in Low Cost Photovoltaic Devices

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Graduate Program in Chemistry
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science
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OPTIMIZATION OF p-TYPE CZTS NANOCRYSTAL THIN FILM LAYERS FOR APPLICATIONS IN LOW COST PHOTOVOLTAIC DEVICES

Monograph

by

Kyle Scott Brandon Jeffs

Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree of Masters of Science

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Abstract

In this thesis Cu$_2$ZnSnS$_4$ nanocrystal synthesis was optimized by way of photoelectrochemical measurements through tuning the stoichiometry. Formation of a Cu$_2$ZnSnS$_4$ light-absorbing layer was studied using multiple depositions methods. These included dropcasting, electrophoretic deposition, and use of 3-mercaptopropyl trimethoxysilane as a chemical linker. Dropcasting samples were compared according to the solvents used to suspend the nanocrystals. Photoelectrochemical measurements were used to compare dropcasting with electrophoretic deposition and use of 3-mercaptopropyl trimethoxysilane as a chemical linker. Dropcasting was shown to be the least effective method of depositing the light-absorbing layer. Samples prepared by electrophoretic deposition were optimized according to a number of variables, which included deposition time, nanocrystal concentration, solvent and applied potential. A concentration of 2 g/L, in isopropanol with an applied potential of 50 V for 40 seconds gave the largest photocurrent of all films tested (106 µA/cm$^2$). Using 3-mercaptopropyl trimethoxysilane as a chemical linker photocurrent results as high as 74 µA/cm$^2$ was observed from a much thinner layer. Preliminary solar cells were fabricated using electrophoretic deposition, one of the cells fabricated had a fill factor of 0.27.

In this thesis electrophoretic deposition was proven to be the best method of depositing Cu$_2$ZnSnS$_4$ nanocrystals. While a functioning solar cell was fabricated, preliminary cells showed room for much improvement. This shows that upon further optimization, an efficient solar cell can be realized.

Keywords
Solar Cells, CZTS, Photoelectrochemical, Light-Absorbing Layer, Thin Film Solar Cells, Nanocrystals, Electrophoretic deposition, 3-Mercatapropyl Trimethoxysilane
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AM 0, 1.5</td>
<td>Air Mass, number denotes number of atmospheres</td>
</tr>
<tr>
<td>AZO</td>
<td>Aluminum-doped Zinc Oxide</td>
</tr>
<tr>
<td>BA</td>
<td>Benzyl Alcohol</td>
</tr>
<tr>
<td>e-Si</td>
<td>Crystalline silicon</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical Bath Deposition</td>
</tr>
<tr>
<td>CIGS</td>
<td>CuIn$<em>x$Ga$</em>{1-x}$Se$_2$</td>
</tr>
<tr>
<td>CIS</td>
<td>CuIn(Se/S2)</td>
</tr>
<tr>
<td>CZTS</td>
<td>Cu$_2$ZnSnS$_4$</td>
</tr>
<tr>
<td>d</td>
<td>Distance</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>e(^{-})</td>
<td>Electron</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EPD</td>
<td>Electrophoretic Deposition</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped Tin oxide</td>
</tr>
<tr>
<td>h(^{+})</td>
<td>Hole</td>
</tr>
<tr>
<td>H$_0$</td>
<td>Solar Irradiance at Surface of Sun</td>
</tr>
<tr>
<td>i-ZnO</td>
<td>Intrinsic Zinc Oxide</td>
</tr>
<tr>
<td>I$_{SC}$</td>
<td>Short Circuit Current</td>
</tr>
<tr>
<td>ITO</td>
<td>Tin-doped Indium Oxide</td>
</tr>
<tr>
<td>kWh</td>
<td>kilowatt hour</td>
</tr>
<tr>
<td>MPP</td>
<td>2-Mercapto-5-n-propylpyrimidine</td>
</tr>
<tr>
<td>MPS</td>
<td>3-Mercaptopropyl Trimethoxysilane</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NC(s)</td>
<td>Nanocrystal(s)</td>
</tr>
<tr>
<td>OECD</td>
<td>Organization for Economic Co-operation</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>PVC</td>
<td>Photovoltaic Cell</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SC</td>
<td>Semiconductor</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
</tr>
<tr>
<td>TU</td>
<td>Thiourea</td>
</tr>
<tr>
<td>V&lt;sub&gt;OC&lt;/sub&gt;</td>
<td>Open Circuit Potential</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>Θ</td>
<td>Angle</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
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Chapter 1

1 Introduction

1.1 World Energy Consumption

Consumption of energy on our planet is significantly increasing. The world energy usage in 2005 was $1.17 \times 10^{15}$ kWh.\(^1\) A projection shows that from 2008 to 2035 the total world energy consumption will increase by 53%.\(^2\) While energy consumption in OECD (organization for economic co-operation) countries (U.S.A, Canada, Germany...) only increases 0.6% on average per year. The largest increase is seen in non-OECD countries, which include China, India and many more developing countries where energy consumption increases on average 2.3% per year.\(^2\) Due to this rapid increase it is important to continue to find new innovative ways to generate electricity at lower costs with less environmental impact.

The Sun deposits on average $\sim 5$ kWh m\(^{-2}\) day\(^{-1}\) of radiation on the Earth’s surface per day. With this energy we can easily satisfy the Earth’s increasing energy demands. The Earth’s non-renewable resources are rapidly depleting. The depletion of fossil fuels as well as environmental impact of burning them leads to the increasing need for renewable energy.\(^2\) While wind and hydro energies have been used for many years, the solar market has been expanding rapidly as more efficient and cost effective solar devices begin to be developed.

Among solar devices, silicon cells first come to mind. Efficiencies upwards of 13-14% have been achieved for crystalline silicon devices.\(^3\) However, the cost of purifying crystalline silicon is very high and energy intensive. Due to this high cost,
focus has shifted to thin film solar cells, which have greatly reduced cost of production. Currently the most popular thin film device uses CuInGa1-xSe2 (CIGS) as the light-absorbing layer and thus far cell efficiencies of up to 20.4% have been recorded. Although they are cheaper than silicon cells, they still require a significant capital investment and manufacturing cost. Production of CIGS also requires elements that are very expensive, rare, and dangerous to handle. All of these concerns have led to development of cheaper thin film devices that incorporate more abundant metal sources. Cu2ZnSnS4 (CZTS) is considered to be a strong replacement to CIGS as a light-absorbing layer due to the relatively high abundance of its elements, and therefore there is a much lower cost required in cell manufacturing. CZTS thin films are expected to have theoretical efficiencies of 30% and lab efficiencies have reached as high as 11.1%.

1.1.1 Solar Radiation

At the surface of the sun the solar irradiance is termed (H₀); further from the sun the irradiance (W/m²) becomes greatly reduced. Mercury is 57x10⁹ m from the sun and the mean solar irradiance is 9116.4 W/m². When the radiation reaches the Earth (150x10⁹ m away) the mean solar irradiance is 1366.1 W/m². Solar radiation on the Earth’s atmosphere is fairly constant; however the radiation at the Earth’s surface varies widely due to a number of effects, including: atmospheric effects, variations in atmosphere (water vapor, clouds, pollution), latitude and location, as well as the season of the year and time of day. The radiation outside the Earth’s atmosphere is denoted as AM 0. AM stands for air mass, and 0 denotes that the radiation has not traversed though the Earth’s atmosphere. When testing solar cells the standard used is AM 1.5. This implies that the radiation has travelled through 1.5 atmospheres to reach sea level.
Figure 1.1 Solar irradiance spectrum, green corresponds to blackbody emission at 5800 K, red corresponds to intensity at AM 0, and blue corresponds to intensity at AM 1.5\(^9\)
On average solar radiation travels on a $48^\circ$ angle through the atmosphere which is why AM 1.5 is the standard used for solar cell testing.

1.2 Solar Cells

Solar cells directly convert sunlight into electricity through a number of steps. Absorption of light is the catalyst for photogeneration, which is the production of an electron hole pair. This electron hole pair is then separated by an electric field causing them to flow in opposite directions. Electrons might recombine with holes in the ground state after they have travelled through an external circuit.

1.2.1 Three Generations of Solar Cells

Solar cells are classified into three generations, including current and past research in each generation, each one presenting its own advantages and detractors.

1.2.1.1 First Generation Solar Cells

First generation devices use crystalline silicon (c-Si) as the light-absorbing layer. A p-n junction is formed through doping the c-Si with an electron rich (n-type) and an electron poor element (p-type). Most solar cells in production for commercial applications are crystalline silicon devices. They are highly stable and are one of the most efficient single junction cells. The main disadvantage of this technology is that they are rigid and require a lot of energy for production.

1.2.1.2 Second Generation Solar Cells

Second generation solar cells are also known as thin film solar cells. They are fabricated by depositing multiple layers in order to create a p-n junction. Some common materials used as the light-absorbing layer include amorphous silicon, $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$ (CIGS),
CdTe, Cu$_2$ZnSnS$_4$ (CZTS), and CuIn(Se/S)$_2$ (CIS). Second generation devices avoid using expensive silicon wafers. They use much less material, since they are thin films (several microns thick). While they are not as efficient as crystalline silicon devices there is a reduced cost in production making them appealing.\textsuperscript{11} Most second-generation devices require vacuum processing and high temperature annealing, increasing costs of production.\textsuperscript{12,13} CZTS in this thesis was synthesized by an inexpensive one-pot method that does not require annealing or vacuum processing.

1.2.1.3 Third Generation Solar Cells
There are two predominant classes for third generation solar cells: 1) organic or dye sensitized solar cells and 2) multijunction solar cells. While the highest recorded efficiencies are produced from multijunction cells, their cost remains extremely high.\textsuperscript{11} Different light-absorbing layers are used with different band gaps in order to collect as much of the solar spectrum as possible, thus increasing efficiency. The price increase is due to the many steps required and the complexity of fabrication. Organic solar cells or polymer solar cells offer some advantages as they are fairly simple and quick to fabricate, as well as inexpensive. While there are many benefits of organic solar cells the performance and stability is still very limited when compared with first and second generation solar cells.\textsuperscript{14}

1.2.2 Intrinsic p- and n-Type Semiconductors
Solar cells require an n-type and p-type semiconductor for generation of photocurrent from sunlight; semiconductors are made up of crystal lattices. In this thesis copper, zinc, tin, and sulfur form a Kesterite crystal structure (p-type).\textsuperscript{15,16} There are three different types of semiconductors: intrinsic, n-type, and p-type. Intrinsic semiconductors are pure;
they act as semiconductors without doping. In Intrinsic semiconductors the number of excited electrons \( (e^-) \) and the number of holes \( (h^+) \) are equal, which means that the number of electrons in the conduction band is equal to the number of holes in the valence band.

Doping of an intrinsic semiconductor with either an electron-rich or electron-poor element forms an extrinsic semiconductor, which will be p-type (if doped with electron-poor) or n-type (if doped with electron-rich). For n-type semiconductors there is a higher concentration of electrons than holes, therefore electrons are the majority carrier and holes are the minority carrier. This is reversed for p-type, where holes are the majority carrier and electrons are the minority carrier. In the case of CZTS it is a natural p-type semiconductor, as no doping is required for it to be p-type after the nanocrystals were synthesized due to natural defects in the crystal lattice.\(^{17}\)

### 1.2.3 Fermi Energy, Valence and Conduction Band

The bond structure of the semiconductor is of extreme importance because it determines the materials properties under light and dark conditions. Electrons can be locked into the covalent bonds between the atoms. These electrons cannot move or change energy and are not considered free electrons (valence band).\(^{10}\) But if the correct amount of energy (light) is applied to the material these electrons can be excited so that they may move freely throughout the lattice (conduction band). The energy required to excite the electrons from the valence band to the conduction band is known as the band gap of the material.\(^{18}\) The number and energy of these high-energy state (free) electrons is essential to the functionality of electronic devices using semiconductor materials. Once the electron has been excited there is a void (hole) left in the valence band, which can be
viewed as a positive charge moving through the valence band. Intrinsic semiconductors always have an equal number of electrons and holes, which is why the Fermi level lies directly between the conduction and valence band (Figure 1.2).

In n-type semiconductors electrons are the majority carrier, leading to an excess of electrons in comparison to holes. Therefore these extra electrons will lie in the conduction band because the valence band is already full. This will increase the Fermi level (Figure 1.2). The opposite is true for p-type semiconductors; holes are the majority carrier, therefore there will be mobile carriers (holes) in the valence band, which results in a lowered Fermi level (Figure 1.2). The Fermi level will move towards the band of the majority carriers.

1.2.4 Space Charge Region

When the two types of semiconductors are brought together, a p-n junction is formed which is essential for the operation of our chalcogenide solar cell (Figure 1.3). The n-type region has a high electron concentration and the p-type has a high hole concentration so when a p-n junction is formed electrons will diffuse to the p-type and holes will diffuse to the n-type. When the electrons and holes diffuse to the other side of the junction they leave behind exposed charges, which are fixed in the crystal lattice and unable to move. In n-type positive ion cores are left exposed; conversely in p-type negative ion cores are left exposed. These charges fixed in the lattice produce an electric field between the positive and negative ion cores, which is know as the depletion region (Figure 1.3). The name comes from the fact that the electric field quickly sweeps away free charge carriers and therefore the region is depleted of free charge carriers. A built-in
potential $V_{bi}$ is formed at the junction due to the electric field, and the direction of the electric field is towards the p-type.\textsuperscript{19}

Despite the presence of the electric field some carriers will still cross the junction, but most carriers that enter the depletion region will be rejected. Once a majority carrier crosses the junction it becomes a minority carrier and will eventually recombine. The movement of minority carriers is also important in the p-n junction. Minority carriers, which reach the junction, are swept across it by the electric field in the depletion region, this is known as drift current.\textsuperscript{19}

A p- and n-type semiconductors interact this way when in dark (Figure 1.3-1.4A); under illumination the interaction is used to produce electricity (Figure 1.4B). When the light-absorbing layer is struck with a photon that correctly matches its band gap energy, an electron is excited to the conduction band and an electron hole pair is formed. The electrons will then travel in one direction through the conduction band, and the hole will travel in the other direction in the valance band due to the potential gradient set up at the p-n junction. This creates an electrical current, which can be harnessed if the solar cell is connected to an external circuit.\textsuperscript{19}
Figure 1.2 Effect of electrons and holes on Fermi level in semiconductors\textsuperscript{19}
Figure 1.3 Interaction of a p-n junction in dark

Figure 1.4 Interaction of a p-n junction under illumination A) Electric fields formed at the p-n junction, $E_c$ denotes conduction band, $E_v$ denotes valence band, and $E_F$ denotes the Fermi level B) p-n junction under illumination, electron-hole pair is generated and flow of carriers ($h^+$ and $e^-$) in opposite directions produce electricity
1.3 CZTS Thin Film Solar Devices

Sunlight can be converted from a photon to photocurrent using photovoltaic cells (PVC). When a photon hits the material with energy corresponding to, or larger than, the band gap of the material, electrons will be promoted from the valence band to the conduction band. In this thesis $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is used as the light-absorbing layer for solar cells. Currently CIGS is the most common light-absorbing layer being used in second-generation solar devices. There are issues related to the toxicity and price of gallium and selenium in CIGS. CZTS improves on this light-absorbing layer design by using safer and more cost-effective materials.

1.3.1 CZTS Properties

CZTS is a direct band gap semiconductor with a high absorption coefficient ($\sim 10^4 \text{ cm}^{-1}$). It has an optimal band gap that can range from 1.0 to 1.5 eV, which favorably matches the Shockley-Queisser limit of maximum solar cell efficiency. The Shockley-Queisser limit states that the maximum solar cell efficiency of a single junction solar cell can be achieved with a band gap of $\sim 1.09$ eV. The most stable crystal structure of CZTS is Kesterite ($I\bar{4}$). The Kesterite crystal structure is derived from a double blended zinc structure. Doping of CZTS to make it a p-type semiconductor occurs by internal defects on the crystal lattice. For example copper atoms sitting on the places of zinc atoms (Cu on Zn antisite) causes p-conductivity. This is the reason why stoichiometric CZTS is not preferred for solar cell applications. CZTS is essentially derived from the CIGS structure by isoelectronic substitution of two In or Ga atoms by one Zn and one Sn. Because of this similarity to CIGS, CZTS has similar properties and therefore cell structure of CZTS is based on pre-existing CIGS designs (Figure 1.5).
1.3.2 Structure of CZTS Solar Cells

Figure 1.5 shows the layers of a typical CZTS solar cell. In most cases molybdenum is used as a back contact, or another high work function metal. This creates the proper junction between the back contact and CZTS, which promotes the flow of electrons in a designed direction. Fluorine doped tin oxide (FTO) coated glass has also been shown to work as a back contact as the work function is similar to molybdenum.

The next layer is the light-absorbing layer, in this case is p-type CZTS. There are many ways of preparing CZTS, which will be discussed below; however in this thesis CZTS nanocrystals were prepared via a one-pot synthesis method and deposited through multiple methods.

Cadmium Sulfide (CdS) is used as a buffer layer. It is an n-type layer and helps improve lattice matching between the CZTS layer and the n-doped layer on top of the cell. CdS aids in driving out the photogenerated carriers with minimum recombination losses and assists in transporting these carriers to the outer circuit of the cell with minimal resistance. The buffer layer has a large band gap in order to prevent interference with the ability of sunlight to reach the light-absorbing layer (CdS 2.4 eV).
Figure 1.5 Illustrative Schematic of different layers used in CZTS solar cell. Solar cell is illuminated from the top
The top layer is known as the window layer or transparent conducting oxide layer (TCO). In this thesis intrinsic zinc oxide ($i$-ZnO) and aluminum-doped zinc oxide (AZO) were deposited. $i$-ZnO acts as a barrier between the CdS buffer layer and the AZO top layer. Its role is essentially to increase conductivity and allow carriers to flow from CdS to the AZO layer more easily. The AZO layer is the TCO layer and is n-type as well. It is responsible for collecting the carriers that have been produced and transported through the cell and allowing them to leave into an external circuit where electricity can be collected. In standard practice a metal collection grid is deposited on top of the TCO layer to reduce the distance the electrons have to travel and reduce loss by increasing conductivity of the top contact.

### 1.3.3 Current Fabrication Methods For CZTS Thin Films

#### 1.3.3.1 Co-Evaporation

One method of producing CZTS thin films is co-evaporation. In this method simultaneous evaporation of ZnS, Sn, Cu, and S sources was used to produce CZTS. The evaporation was completed at a temperature of 550°C with a sulfur partial pressure of $2-3 \times 10^{-3}$ Pa. In this case a KCN etching step was required to remove unwanted copper sulfide that was formed, as the film was prepared copper rich.

#### 1.3.3.2 Spin Coating and Post-Heating

A precursor solution of copper, zinc, and tin salts was prepared using methanol as the solvent and thiourea as the sulfur source. The precursor solution was then spin coated onto FTO coated glass and heated in air to 150°C. The thin film was then heated to 350°C in an argon atmosphere for one hour to form the CZTS thin film.
1.3.3.3 Electrodeposition

In this study, reline (deep eutectic solvent) was used as an electrolyte in the electrodeposition of CZTS films. CZTS was formed by co-electrodepositing Cu-Zn-Sn precursors with a three electrode system (-1.2 V applied). The precursor thin film was then sulfurized in a mixture of H$_2$S and N$_2$ at 550°C for 1 h to form the CZTS thin film.\textsuperscript{32}

1.3.3.4 Sputtering

There are two main methods used for CZTS sputtering. One method involves co-sputtering using 3 different targets Cu, SnS, and ZnS. The copper target was sputtered under DC power, and RF power was used for the ZnS and SnS targets. After sputtering, the CZTS film was sulfurized in a H$_2$S/N$_2$ environment at 525°C\textsuperscript{16}. The other method used involves using a ceramic quaternary target. A target composed of Cu,Zn,Sn, and S was sputtered onto a substrate via magnetron RF sputtering. A post-process sulfurization temperatures ranging from 460°C to 580°C to increase CZTS crystallinity.\textsuperscript{33,34}

1.3.3.5 Nanocrystals as Thin Film Precursors

While nanocrystals were synthesized by a one-pot synthesis in our lab, most other CZTS nanocrystals are synthesized using long organic chain ligands. In one case, CZTS nanocrystals were synthesized by a hot injection of a solution of elemental sulfur in oleylamine into an oleylamine solution containing copper, zinc, and tin salts. The hot injection was carried out at 225°C. These CZTS nanocrystals were then selenized to create CZTSSe for solar applications.\textsuperscript{35}
1.4 Electrophoretic Deposition (EPD)

Electrophoretic deposition (EPD) was first investigated by Hamaker, Koelmans and Overbeek.\textsuperscript{36,37} EPD combines aspects of electrophoresis (the translation of charged particles suspended in solution due to DC potential applied). As well as dielectrophoresis (The migration of dipolar, polarizable, or charged particles, in solution due to gradient electric fields) to deposit NCs onto conducting electrodes. A potential is applied across two electrodes that are separated in a solution in which the NCs are suspended.\textsuperscript{38}

The NCs will move towards the positive electrode in our case (negative dipole moment) and these particles will assemble into a film on the electrode. Electrophoresis is the main force acting on the particles when they are near the electrodes, when they are far from the electrodes particles are force free and move by electroosmosis in the direction of the potential gradient.\textsuperscript{39}

There are many advantages to EPD, which make it a promising and viable method of forming NC thin films. These advantages include site-selectivity, dense packing of the NCs, size, scalability of the films, and control of the film thickness.\textsuperscript{40} EPD is also easily scalable to an industrial setting. Ceramics have been deposited using EPD techniques for many years, and also is used for depositing a primer coating on automobiles.\textsuperscript{41}

The properties of the film can be easily tuned by adjusting the method of deposition. The conditions required to deposit are easily adjusted to suit the needs of the material in question (i.e. potential) as well the pH of the solution can be altered to change the NC charge and thus direction of flow.\textsuperscript{38}
Figure 1.6 Schematic of EPD setup used in experiments, direction of particle movement depends on the charge of the induced dipole
The solvent chosen for EPD is very important because it controls much of the dynamics of particle movement as well as any electrochemical reactions that may occur at the electrodes. In this thesis non-aqueous solvents are used, such as acetone or isopropyl alcohol. These non-polar solvents aid in suppressing electrochemical reactions that can occur at the electrodes and also suppress dramatic changes in composition and conductivity of the medium due to the generation of charged species near the electrode.\textsuperscript{38}

1.5 Silanization

3-mercaptopropyl trimethoxysilane (MPS) has been proposed as a molecular linker to aid in the formation of a highly crystalline layer of CZTS NCs. Methoxy groups react with various forms of hydroxyl groups, such as the ones found on the surface of metal oxides. These groups can provide linkage with inorganic substrates.

Typically the reactions of these methoxy silanes involve four steps (Figure 1.7). First hydrolysis of the alkoxy groups occurs. After the first and second groups are hydrolyzed condensation to oligomers will follow. Upon hydrolysis, the silanol groups will be orientated towards and hydrogen bond with the hydroxyl sites on the substrate. Finally a cure cycle of around 110 °C for 15 minutes is used to complete the silanization.\textsuperscript{42} MPS has been used in past and present as a chemical linker. It most often is used to bind with gold nanocrystals. In one example MPS is used as a molecular adhesive in preparation of gold electrodes on glass slides.\textsuperscript{43} Another example involves using MPS for growth of gold nanoparticles on ITO coated glass.\textsuperscript{44}
Figure 1.7 Schematic of chemical reactions that occur during the silanization process
1.6 Characterization Techniques

1.6.1 Scanning Electron Microscopy

SEM is a very useful technique for analysis of film morphology. It is similar to a light microscope, but in this case electrons are used as apposed to light. Since electrons have a much smaller wavelength than light a much higher resolution is produced. In SEM electrons are emitted from a filament and accelerated to an anode. This electron beam is then focused with magnetic or electrostatic lenses. The electron beam is focused onto the sample being analyzed and scanned over the desired surface. During the scanning process secondary or backscattered electrons are produced during scanning and are collected by a detector to produce and image.\(^{45}\)

1.6.2 X-ray Diffraction (XRD)

XRD was used in this thesis to identify the phases of CZTS thin films. The principle is based on diffraction of x-rays by the crystal lattice of the compound being analyzed. Bragg’s law defines how x-rays are diffracted during XRD measurements.

\[
\text{Bragg’s law: } \Theta = \sin^{-1}\left(\frac{\lambda}{2d}\right)
\]

Diffraction will occur at a certain angle \(\Theta\), which depends on \(\lambda\), and the distance of the crystal planes.\(^{45}\)

1.6.3 Sputtering

There are two primary types of sputtering. The first is direct current (DC) sputtering and as the name implies it uses a DC power source to generate the plasma. The second one is
magnetron radio frequency (RF) sputtering in which alternating current is used to generate the plasma.\textsuperscript{46}

1.6.3.1 Direct Current Sputtering
The sputtering chamber is evacuated and a working gas is added, in most cases this working gas is argon. Argon has a low ionization energy and has sufficient mass to promote movement of the target atoms. A glow discharge is initiated when a high voltage is applied. At this point the argon atoms are being ionized and the electrons will move to the anode. The positively charged ions are accelerated towards the target where they knock out atoms. The state at which electrons and atoms exist separately is known as the plasma. DC sputtering only works for conducting materials. With insulating materials the surface will charge up, creating issues during sputtering.\textsuperscript{46}

1.6.3.2 Magnetron Radio Frequency Sputtering
Magnetron RF sputtering is used for insulating or non-conducting samples. A magnetic field is applied in order to keep electrons in the target area. This causes the electrons to suffer more collisions with argon atoms, which increases the plasma density and also helps reduce heating of the substrate.\textsuperscript{46}

1.6.4 Energy Dispersive X-ray Spectroscopy (EDX)
EDX is used to analyze the composition of a material. In principle electrons hit the sample where they excite bound electrons. This process creates vacancies in the atomic shell, which is filled up by electrons from higher shells. The electrons from higher shells release energy in the form of an x-ray in order to match the lower energy required to enter
the lower shell. X-ray photons, which are produced, have element specific energies and can be detected to determine the content of the sample.

1.7 Scope of Thesis

This thesis will focus on the synthesis of CZTS nanocrystals, formation of CZTS thin films and its use as the light-absorbing layer in solar cells.

Chapter 2 will describe experimental procedures and instrumental methods used in this thesis.

Chapter 3 will summarize optimization of CZTS nanocrystal synthesis, which will specifically address how the amount of copper and zinc in the starting ratios will affect the nanocrystals PEC performance.

Chapter 4: will demonstrate the optimization of light-absorbing layer deposition techniques such as dropcasting, EPD, and MPS-linker method.

Chapter 5 will give an overview on multiple steps performed for preparation of a CZTS solar cell and show preliminary testing results of a cell.

Chapter 6 will conclude from the thesis research work and indicate some interesting future work.
Chapter 2

2 Experimental

2.1 Synthesis of CZTS Nanocrystals

CZTS synthesis was based on a method previously developed during the optimization of the nanocrystal recipe. The following is the procedure for the CZTS nanocrystals, which were determined by photoelectrochemical measurements to be the nanocrystals with the highest photoresponse; (10.7 mg) copper(II) acetylacetonate (Cu(acac)$_2$), Sigma-Aldrich 97%; (5.4 mg) tin(II) chloride (SnCl$_2$), Alfa Aesar 99%; (16.6 mg) zinc(II) chloride (ZnCl$_2$); Alfa Aesar 99.99%, (30 mg) 2-Mercapto-5-n-propylpyrimidine (MPP); Alfa Aesar 98%, and (0.6 mL of 200 mM) Thiourea (TU), Sigma-Aldrich 99.0% were the precursors used in the optimized recipe. The initial molar ratios used were 1.44 Cu: 4.28 Zn: 1.00 Sn: 4.21 S. The metal salts were first dissolved in 3 mL of benzyl alcohol (BA) in silicone oil bath at 160°C for two minutes with stirring. After the metal precursors were dissolved sufficiently MPP and TU was added. The reaction vial was then heated at 180°C for 10 min in a silicone oil bath with stirring. The resulting solution was then allowed to cool to room temperature and the NCs were centrifuged (Thermo Scientific Sorvall Legend Micro 21 centrifuge at 12 000 g for 6 min). The supernatant was then discarded and the NCs were dispersed in ~1 mL of acetone using a 1510 Branson Sonicator at 42 KHz. The NCs were then centrifuged again. The supernatant was again discarded and the NCs were left to air dry. The CZTS nanocrystals were analyzed with EDX and the final molar ratios were determined to be 3.17 Cu: 0.51 Zn: 1.00 Sn: 5.28 S.
2.2 Dropcasting

Once the nanocrystals had been dried in air dropcasting was used to plate them onto a substrate for PEC testing. A concentration of 20 g/L was utilized. Many different solvents were used, such as acetone, isopropanol, toluene, dichloromethane etc. Acetone and isopropanol were the best solvents for dropcasting, when comparing PEC measurements from the same nanocrystals dropcasted. The NCs were then sonicated until they were suspended in solution. The substrates were washed with acetone, ethanol and dried under a stream of argon before dropcasting took place. Insulating tape with a hole (0.1 cm$^2$) was placed on the substrate. 5 µL suspension was then used to drop the NC solution onto the hole on the substrate. Once the layer had dried (one minute), the solution was dropcasted one more time in order to produce an appropriate thickness.

2.3 Silane Linker

3-Mercaptopropyl Trimethoxysilane (MPS; Sigma-Aldrich 95%) was used in order to chemically link the CZTS NCs to an oxide substrate (ITO, FTO, MoO$_3$). Substrates were washed with acetone, ethanol and dried under a stream of argon. The substrates were then submerged in a 1% solution of MPS in ethanol for approximately 12 hours at room temperature. After the 12 hour incubation, the substrates were then washed with ethanol three more times and again dried under a stream of argon. Deposition of the CZTS NCs was performed during the standard one pot synthesis method, using the optimized CZTS recipe.$^{26}$ The substrate with the MPS linker attached was placed in the reaction flask with the CZTS precursors after they had been dissolved and the MPP and TU had been added. The flask was then heated to 180°C for 10 min. Upon completion of the deposition the substrate was again rinsed with ethanol and dried under a stream of argon to remove any
unbound NCs. For multiple depositions the same procedure was repeated as many times as required.

### 2.4 Chemical Bath Deposition (CBD)

The chemical bath deposition method used for depositing the cadmium sulfide (CdS) buffer layer was based on Ye et al.\textsuperscript{47} The CdS buffer layer was grown in an aqueous solution containing cadmium salt, ammonium hydroxide, and thiourea. Using 2 mL of 15 mM cadmium(II) sulfate (anhydrous) (CdSO\textsubscript{4}; 99.8%, Fisher Scientific), and 2.15 mL of conc. ammonium hydroxide (NH\textsubscript{4}OH; Caledon) was added to 13.85 mL of Milli-Q water and allowed to stir for 30 min at room temperature. The solution was then heated to 60°C and 2 mL of 75 mM thiourea (99.0%; Fluka) was added. The substrate with a CZTS layer was placed into the bath for different deposition times depending on the thickness of CdS required. The substrate was then removed and rinsed with Milli-Q water and allowed to dry.

### 2.5 Instrumental

#### 2.5.1 Photoelectrochemical Measurements (PEC)

The photoelectrochemical (PEC) measurements were obtained with a CH Instruments electrochemical analyzer model 832A. This method (shown in Figure 1.1) was used to determine the photovoltaic quality of the thin films. It is based on the report from Ye et al.\textsuperscript{47} All of the PEC measurements were done in an aqueous methyl viologen solution (MVCl\textsubscript{2}), Aldrich Chemicals 98%, with concentrations between 0.1-0.05 M. Between 0.1-0.5 M aqueous potassium chloride KCl, Sigma-Aldrich 99.0% was added as a supporting electrolyte. A three-electrode system composed of a saturated calomel
electrode (SCE) as the reference electrode, a platinum wire counter electrode, and a conductive substrate (ITO, FTO, Mo, MoOx) with CZTS nanocrystals deposited on it was used as the working electrode. An electrochemical analyzer (CH Instruments, Austin TX), was used to acquire the current change from the PEC setup. The PEC measurements were done using a linear sweep from the potential ranges of 0 V to -0.4 V at a scan rate of 5 mV/s. The light source used was a 150 W Newport lamp with an AM 1.5D filter. The shutter frequency was 0.333 Hz, which controlled the time the sample was exposed to light and dark.

2.5.2 Electrophoretic Deposition

EPD was completed using the Keithly Series 2400 Source Meter Unit (Figure 1.2). A two-electrode setup was used. The working electrode was either ITO-Glass, or molybdenum metal and the counter electrode was molybdenum metal. The distance between the two electrodes was 1 cm. Several solvents were used for the experiments, such as isopropanol and acetone, but the best solvent was found to be isopropanol. Applied potential varied depending on conditions required. A compliance limit of 100 mA was used for all EPD experiments. Deposition time varied depending on the solvent and deposition conditions. Solution of nanocrystals was sonicated for 30 minutes and kept stirring up until the deposition occurred to ensure the nanocrystals were thoroughly suspended.
Figure 2.1 Photoelectrochemical (PEC) measurement setup 

A) Cartoon drawing of the PEC setup

B) Actual PEC setup
Figure 2.2 EPD setup, on the right is the Keithley 2400 source meter. On the left is the two-electrode setup at which the nanocrystals are deposited.
2.5.3 Annealing

All annealing was done using a Thermoscientific (Lindberg Blue M) furnace and a Alcatel Pascal 2015 SD vacuum pump. An argon atmosphere (~5-10 psi) was used for all annealing. Annealing times ranged from 15-60 minutes and temperatures ranged from 200-500°C depending on required conditions.

2.5.4 Sputtering

Sputtering was completed at the Western Nanofabrication facility using an Edward Auto500 sputterer. The soda lime glass slides used as the substrate when depositing molybdenum were cleaned by the following procedure: glass slides were sonicated in a aqueous 2% Hellmanex (Hellma Analytics) solution for 15 minutes, and were then washed 10 times with Milli-Q water and ethanol. Glass slides were dried under a stream of argon afterwards. The glass slides were then sonicated in ethanol for 15 minutes and dried under an argon stream. The sputtering conditions for each target were as follows: molybdenum was prepared using a DC power source at 150 W for 1.5 hours; the argon flow rate was 15 standard cubic centimeters (sccm); and the deposition resulted in a thickness of roughly 1 µm. When MoOₓ was required for the MPS-linker method the argon flow rate was reduced to 13 sccm and an oxygen flow rate of 2 sccm was added for the final 5 min, which resulted in a thickness of roughly 50 nm. Intrinsic zinc oxide (i-ZnO) was sputtered using an Rf power source (13.56 MHz) at 70 W. Argon flow rate used was 16 sccm and a flow rate of 0.1 sccm was used for oxygen. Deposition time was 30 min, resulting in a thickness of roughly 50 nm. Aluminum doped zinc oxide (AZO) was sputtered using DC power at 75 W. An argon flow rate of 15 sccm was used. AZO deposition time was 1 hour resulting in a thickness of roughly 250 nm.
2.5.5 Raman

Raman spectroscopy was done using a 532 nm wavelength laser with a beam power of 10 mW for excitation. Raman spectra were recorded using a WITec spectrometer with a microscope and a motorized XY stage. The microscope objective was 50x magnification and a numerical aperture of 0.75.

2.5.6 Scanning Electron Microscopy (SEM)

SEM was performed using a Hitachi S-4500 field emission microscope with a Quartz XOne energy dispersive x-ray (EDX) system at Surface Science Western. Cross sectional SEM images of the full cell were done at the Western Nanofabrication facility. They were performed using a Leo (Zeiss) 1530 field emission SEM. Cross sectional SEM samples were prepared by fabrication of the full cell on a silicon wafer substrate.

2.5.7 X-ray Diffraction (XRD)

XRD was done for several samples. CZTS NCs were plated on glass slides via the dropcasting method. XRD analysis was done using an Inel CPS Powder Diffractometer with an Inel XRG 3000 Cu X-ray generator, and an Inel CPS 120 detector.

2.5.8 UV-Visible Spectroscopy

Band-gap data was calculated from UV-Visible absorption spectra using an Agilent Cary 50 spectrometer scanning from 400 to 1100 nm. Data was analyzed according to Xin et al.48
Chapter 3

3 Optimization of Cu$_2$ZnSnS$_4$ Recipe

In an effort to develop solar cells using CZTS nanocrystals as the light-absorbing layer, the nanocrystal recipe was first optimized. CZTS is a more complicated, when compared with previous semiconductors used for solar cells. For example, silicon solar cells use p- and n-doped crystalline silicon and CuInS$_2$ (CIS) has three variables that need to be accounted for during synthesis, CZTS has four elements which makes its synthesis more difficult to control.\textsuperscript{49,50,51,52}

The effect on the photoresponse of the nanocrystals as different ratios of metal precursors were added as well as different metal salts was observed. Testing was also done in relation to the amount of sulfur that was added and the corresponding photoresponse trend. This was carried out by varying the ratios of MPP (capping agent) and Thiourea (sulfur source). Optimization is an essential step as it was important to ensure that the largest possible photocurrent recipe was used for further cell design. The effectiveness of each recipe was tested under illumination using PEC measurements.\textsuperscript{47,53}

As stated previously it is important to understand the relationship between the n- and p-type layers in a solar cell, and how they are used in conjunction to convert sunlight into electricity.

CZTS is a p-type type semiconductor, used in this case as a light absorbing layer.\textsuperscript{54} Methyl viologen (MV$^{2+}$) was used as an electron acceptor to create a pseudo p-n junction where the nanocrystals ability to donate electrons under illumination while applying a negative bias was observed.\textsuperscript{47,55-57}
Figure 3.1 Interaction of methyl viologen and CZTS nanocrystals under illumination
Initial tests for the optimization were completed by observing how the amount of copper added affects the nanocrystals (NCs) photochemical response. Different ratios of copper salts were tested to determine which would be most effective. As observed in the Figure 3.2, excess copper greatly reduced the effectiveness of the NCs. The linear potential sweep in Figure 3.2, was performed from 0.0 V to -0.4 V and as expected the photocurrent change increases as the potential moves toward the negative.

CZTS is a p-type semiconductor, which means that it is slightly positively charged due to the fact that holes are the majority carriers and electrons are the minority carriers. During the PEC measurements a negative bias is applied to CZTS which allows it to donates electrons to the MV$^{2+}$ after it has been photoexcited. As the applied bias becomes more negative, the electrons will transfer from the p-type semiconductor with more ease to aid in restoration of charge balance; this is the reason a larger photocurrent at a more negative bias is observed until the semiconductor material begins to be saturated with electrons. After this saturation point the increasing negative bias will not cause an increase in photocurrent.

From the data in Figure 3.2 it is demonstrated that the addition of more copper decreased the effectiveness of the absorbing layer in converting light into electricity. Table 3.1 shows that the amount of copper added was the only variable changed, where the current density produced from each sample is greatly reduced with the addition of more copper.
Figure 3.2 Effect of NC photoresponse using varying amounts of Cu(acac)$_2$

Table 3.1 Different Cu(acac)$_2$ masses used in samples 1-4 and the resulting current density change

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (mg)</th>
<th>Sn (mg)</th>
<th>Zn (mg)</th>
<th>Thiourea (0.2 M) (mL)</th>
<th>ΔJ (μA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>7.5</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>71.5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>15.2</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>62.6</td>
</tr>
<tr>
<td>Sample 3</td>
<td>22.5</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>7.90</td>
</tr>
<tr>
<td>Sample 4</td>
<td>30.5</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>4.90</td>
</tr>
<tr>
<td>Sample 5</td>
<td>37.8</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>3.40</td>
</tr>
</tbody>
</table>

Table 3.2 Molar ratios of the four samples shown above

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Sn</th>
<th>Zn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 2</td>
<td>2.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 3</td>
<td>3.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 4</td>
<td>4.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 5</td>
<td>5.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
</tbody>
</table>
Once the amount of copper needed for synthesis was determined, which in this case was 15.5 mg in 100 mg of synthesis, the effects of changing copper metal salts was investigated, and how this may or may not have affected the resulting photoresponse of the nanocrystals. When looking at the effect of different copper salts the corresponding molar ratio of the best sample from Figure 3.2 was used. The copper salts tested were as follows CuCl, CuCl$_2$$\cdot$2H$_2$O, CuSO$_4$$\cdot$5H$_2$O, and Cu(OAc)$_2$ and the results can be seen in Figure 3.3. It is important to note that even though sample 1 showed a slightly larger photocurrent change then sample 2, sample 2 was chosen as the starting molar ratio for copper because its PECM showed similar photocurrent change while minimizing any resistive effects observed with sample 1.

As seen in Figure 3.3, Cu(acac)$_2$ showed the best photoresponse when comparing different metal salts using the same method. CuSO$_4$$\cdot$5H$_2$O showed the lowest photoresponse when comparing all the copper salts tested. Consequently Cu(acac)$_2$ is the copper source that was used in the remainder of the studies. After the copper source and the relative amount that was most effective was optimized the effects of varying the amounts of zinc and how the ratio of zinc and copper would affect the NCs photoresponse was tested. Constant starting ratios of copper, tin, and sulfur were used while increasing the ratio of zinc. Results from this experiment are seen in Figure 3.4.
Figure 3.3 Effect of NC photoresponse using different copper salts

Table 3.3 Different copper salt masses used and the resulting current density change

<table>
<thead>
<tr>
<th></th>
<th>Cu (mg)</th>
<th>Sn (mg)</th>
<th>Zn (mg)</th>
<th>Thiourea (0.2 M) (mL)</th>
<th>ΔJ (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(acac)₂</td>
<td>15.2</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>62.5</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>14.4</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>4.22</td>
</tr>
<tr>
<td>CuCl₂·2H₂O</td>
<td>9.9</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>15.9</td>
</tr>
<tr>
<td>CuCl</td>
<td>5.7</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>21.5</td>
</tr>
<tr>
<td>Cu(OAc)₂</td>
<td>11.6</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>32.4</td>
</tr>
</tbody>
</table>

Table 3.4 Molar ratios of the five samples shown above

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Sn</th>
<th>Zn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(acac)₂</td>
<td>2.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>2.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>CuCl₂·2H₂O</td>
<td>2.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>CuCl</td>
<td>2.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Cu(OAc)₂</td>
<td>2.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
</tbody>
</table>
Figure 3.4 Effect of NC photoresponse using varying amounts of ZnCl$_2$

Table 3.5 Different ZnCl$_2$ masses used in samples 6-9 and the resulting current density change

<table>
<thead>
<tr>
<th></th>
<th>Cu (mg)</th>
<th>Sn (mg)</th>
<th>Zn (mg)</th>
<th>Thiourea (0.2 M) (mL)</th>
<th>$\Delta J$ ($\mu$A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 6</td>
<td>7.5</td>
<td>5.4</td>
<td>3.8</td>
<td>0.6</td>
<td>71.5</td>
</tr>
<tr>
<td>Sample 7</td>
<td>7.5</td>
<td>5.4</td>
<td>7.6</td>
<td>0.6</td>
<td>99.8</td>
</tr>
<tr>
<td>Sample 8</td>
<td>7.5</td>
<td>5.4</td>
<td>11.4</td>
<td>0.6</td>
<td>69.4</td>
</tr>
<tr>
<td>Sample 9</td>
<td>7.5</td>
<td>5.4</td>
<td>15.2</td>
<td>0.6</td>
<td>55.2</td>
</tr>
</tbody>
</table>

Table 3.6 Molar ratios of the four samples shown above

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Sn</th>
<th>Zn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 6</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 7</td>
<td>1.00</td>
<td>1.00</td>
<td>2.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 8</td>
<td>1.00</td>
<td>1.00</td>
<td>3.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 9</td>
<td>1.00</td>
<td>1.00</td>
<td>4.00</td>
<td>4.21</td>
</tr>
</tbody>
</table>
From Figure 3.4 it was observed that while more zinc added did decrease the photocurrent there was an optimal level when the ratios of zinc, copper, and tin were 2:1:1. From these results a starting ratio of 2 moles of zinc were optimal. The previous two studies were then combined and the effects of changing copper and zinc ratios and how this would potentially effect the photocurrent production of the NCs was observed. The starting molar ratio of zinc was set constant each time and the amount of copper was increased in the starting ratio. Seen in Figure 3.5 the molar ratio of 2 for zinc was chosen and the copper ratio was increased.

From Figure 3.5 sample 7 showed the largest change in photocurrent while sample 17 showed no photoresponse, which correlates well with the negative effects of high copper ratios. This study was further tested with increasing zinc ratios, which can be seen in Figures 3.6 and 3.7.

The largest photocurrent observed was for sample 11 which had a zinc to copper ratio of 3:2. The change in photocurrent density for sample 11 was 107 μA/cm². The PEC results also demonstrated minimal resistance during the measurement, which is positive moving forward towards full device fabrication. As some resistance is expected in each semiconductor layer, minimizing the resistance of a layer will decrease the overall series resistance of the full cell.
Figure 3.5 Effect of NC photoresponse using varying amounts of Cu(acac)$_2$ with a starting molar ratio of 2 for zinc

Table 3.7 Different Cu(acac)$_2$ masses used in samples 7, 10, 16, and 17 including the resulting current density change

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (mg)</th>
<th>Sn (mg)</th>
<th>Zn (mg)</th>
<th>Thiourea (0.2 M) (mL)</th>
<th>ΔJ (μA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 7</td>
<td>7.5</td>
<td>5.4</td>
<td>7.6</td>
<td>0.6</td>
<td>99.8</td>
</tr>
<tr>
<td>Sample 10</td>
<td>15.2</td>
<td>5.4</td>
<td>7.6</td>
<td>0.6</td>
<td>66.3</td>
</tr>
<tr>
<td>Sample 16</td>
<td>22.5</td>
<td>5.4</td>
<td>7.6</td>
<td>0.6</td>
<td>6.39</td>
</tr>
<tr>
<td>Sample 17</td>
<td>30.5</td>
<td>5.4</td>
<td>7.6</td>
<td>0.6</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 3.8 Molar ratios of the four samples shown above

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Sn</th>
<th>Zn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 7</td>
<td>1.00</td>
<td>1.00</td>
<td>2.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 10</td>
<td>2.00</td>
<td>1.00</td>
<td>2.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 16</td>
<td>3.00</td>
<td>1.00</td>
<td>2.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 17</td>
<td>4.00</td>
<td>1.00</td>
<td>2.00</td>
<td>4.21</td>
</tr>
</tbody>
</table>
Figure 3.6 Effect of NC photoresponse using varying amounts of Cu(acac)$_2$ with a starting molar ratio of 3 for zinc

Table 3.9 Different Cu(acac)$_2$ masses used in samples 8, 11, 13, and 18 including the resulting current density change

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (mg)</th>
<th>Sn (mg)</th>
<th>Zn (mg)</th>
<th>Thiourea (0.2 M) (mL)</th>
<th>ΔJ (μA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 8</td>
<td>7.5</td>
<td>5.4</td>
<td>11.4</td>
<td>0.6</td>
<td>69.4</td>
</tr>
<tr>
<td>Sample 11</td>
<td>15.2</td>
<td>5.4</td>
<td>11.4</td>
<td>0.6</td>
<td>107</td>
</tr>
<tr>
<td>Sample 13</td>
<td>22.5</td>
<td>5.4</td>
<td>11.4</td>
<td>0.6</td>
<td>5.40</td>
</tr>
<tr>
<td>Sample 18</td>
<td>30.5</td>
<td>5.4</td>
<td>11.4</td>
<td>0.6</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 3.10 Molar ratios of the four samples shown above

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Sn</th>
<th>Zn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 8</td>
<td>1.00</td>
<td>1.00</td>
<td>3.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 11</td>
<td>2.00</td>
<td>1.00</td>
<td>3.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 13</td>
<td>3.00</td>
<td>1.00</td>
<td>3.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 18</td>
<td>4.00</td>
<td>1.00</td>
<td>3.00</td>
<td>4.21</td>
</tr>
</tbody>
</table>
Figure 3.7 Effect of NC photoresponse using varying amounts of Cu(acac)$_2$ with a starting molar ratio of 4 for zinc

Table 3.11 Different Cu(acac)$_2$ masses used in samples 9, 12, 14, and 15 including the resulting current density change

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (mg)</th>
<th>Sn (mg)</th>
<th>Zn (mg)</th>
<th>Thiourea (0.2 M) (mL)</th>
<th>$\Delta J$ ((\mu) A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 9</td>
<td>7.5</td>
<td>5.4</td>
<td>15.2</td>
<td>0.6</td>
<td>52.5</td>
</tr>
<tr>
<td>Sample 12</td>
<td>15.2</td>
<td>5.4</td>
<td>15.2</td>
<td>0.6</td>
<td>48.2</td>
</tr>
<tr>
<td>Sample 14</td>
<td>22.5</td>
<td>5.4</td>
<td>15.2</td>
<td>0.6</td>
<td>7.24</td>
</tr>
<tr>
<td>Sample 15</td>
<td>30.5</td>
<td>5.4</td>
<td>15.2</td>
<td>0.6</td>
<td>6.39</td>
</tr>
</tbody>
</table>

Table 3.12 Molar ratios of the four samples shown above

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Sn</th>
<th>Zn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 9</td>
<td>1.00</td>
<td>1.00</td>
<td>4.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 12</td>
<td>2.00</td>
<td>1.00</td>
<td>4.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 14</td>
<td>3.00</td>
<td>1.00</td>
<td>4.00</td>
<td>4.21</td>
</tr>
<tr>
<td>Sample 15</td>
<td>4.00</td>
<td>1.00</td>
<td>4.00</td>
<td>4.21</td>
</tr>
</tbody>
</table>
Surface morphology was examined through use of scanning electron microscopy (SEM). Confirmation of the NC structure was also done via X-ray diffraction (XRD) as well as determining the final molar ratios after NC synthesis using energy dispersive X-ray spectroscopy (EDX). Two of the most effective samples and two of the least effective samples were chosen to be analyzed for comparison sake. The samples chosen were samples 7 and 11 (most effective) and samples 13 and 17 (least effective). Sample 17 was chosen because essentially no photocurrent was observed and sample 13 was chosen because it showed a very small amount of photocurrent. Determination of the differences between very little and none, in respect to photocurrent generated during PEC measurements was done for comparison. Figures 3.8 through 3.11 show SEM images of the four samples used for comparison.

From these images it is evident that the PEC data correlates nicely with the SEM images. Sample 11 shows the most uniform film and a tightly packed film at the highest magnification. In contrast samples 17 and 13 show a highly irregular film, with large difference in crystal sizes. As well many of the nanocrystals were very large in size. Ordinarily, a nanocrystal size of ~50 nm is standard for this CZTS nanocrystals synthesis method but in the case of these two samples the nanocrystals were several microns. These factors all play a role in the effectiveness of the nanocrystals ability to convert light to electricity.
Figure 3.8 SEM images of Sample 7 A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)

Figure 3.9 SEM images of Sample 11 A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)
Figure 3.10 SEM images of Sample 13 A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)

Figure 3.11 SEM images of Sample 17 A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)
During comparison of different NC recipes it was important to consider the crystal structure and any similarities or differences. When synthesizing CZTS the optimal crystal structure desired is Kesterite (Space Group: \( \text{I}\text{4} \)). Stannite (Space Group: \( \text{I}\text{4}\text{2m} \)) is also another common crystal structure, which is less favorable.\(^{15,59}\) There are also many impurities and binary compounds that may form during the synthesis that will also negatively effect the nanocrystals effectiveness.\(^{23}\) The results of XRD can be seen in Figures 3.12 and 3.13. The XRD patterns for all four samples are not sharp peaks, which can be attributed to the differences in NC sizes in the thin film as well as overlap of reflections from the crystal lattice. While it is very difficult to obtain exactly which crystal structures are present, much information can be taken from the peak shape and height. From the XRD patterns it can be seen that samples 7 and 11 are more crystalline and uniform because the XRD peaks are sharper and more intense. When analyzing XRD patterns it is also important to take note of the peak shape. In samples 7 and 11 the peaks are more Gaussian shaped in comparison with samples 13 and 17, which also correlates to increased crystallinity in samples 7 and 11. There are also relatively little to none unwanted peaks in the pattern which could correlate to impurities and/or binary compounds. Observing the XRD pattern for samples 13 and 17, it was noted that the peaks are broader which indicates that the sample is less uniform. These results also correlate well with the SEM images, as these samples are very irregular in crystal size and orientation. There may also be a few small peaks that show some impurities such as ZnS.\(^{60}\)
Figure 3.12 XRD data from the two most effective samples (11 and 7)

Figure 3.13 XRD data from the two least effective samples (17 and 13)
Table 3.13 Final molar ratios of copper, zinc, tin, and sulfur in samples 7, 11, 13, and 17 from EDX analysis

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:</td>
<td>3.07</td>
<td>0.33</td>
<td>1.00</td>
<td>3.56</td>
</tr>
<tr>
<td>11:</td>
<td>4.60</td>
<td>0.37</td>
<td>1.00</td>
<td>4.08</td>
</tr>
<tr>
<td>13:</td>
<td>5.17</td>
<td>0.24</td>
<td>1.00</td>
<td>4.06</td>
</tr>
<tr>
<td>17:</td>
<td>6.90</td>
<td>0.25</td>
<td>1.00</td>
<td>4.66</td>
</tr>
</tbody>
</table>

Table 3.14 Starting molar ratios of copper, zinc, tin, and sulfur in samples 7, 11, 13, and 17

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:</td>
<td>1.00</td>
<td>2.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>11:</td>
<td>2.00</td>
<td>3.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>13:</td>
<td>3.00</td>
<td>3.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
<tr>
<td>17:</td>
<td>4.00</td>
<td>2.00</td>
<td>1.00</td>
<td>4.21</td>
</tr>
</tbody>
</table>
The one main problem with the XRD instrumentation is that there are some impurities that overlap where the CZTS Kesterite peaks are expected so it is very hard to be certain that you have exclusively CZTS Kesterite nanocrystals with very little or zero impurities. EDX was also carried out on samples 7, 11, 13, and 17 in order to gain a better understanding of the final molar ratios. When comparing the starting and final molar ratios it is clear that more copper added increases the amount of copper in the final NCs; with that amount of copper present there are likely some impurities present. There is also a very small amount of zinc in the final NCs and sulfur is relatively unchanged. It should be noted that sample 11 was the most effective sample tested with a photocurrent change of 107 µA/cm² and this sample also corresponds to the largest amount of zinc in the final NCs. Samples 13 and 17 had the least amount of zinc and the most amount of copper and produced the least effective PEC results, which confirms earlier statements regarding the amount of copper that should be in the starting ratios to make the NCs photoresponse effective.

Other members of the lab also did these optimizations for tin, and varying amounts of MPP, and thiourea. After months of optimization, it was determined that the CZTS recipe discussed in the experimental section (Chapter 2) was the best CZTS synthesis route and that is the method that was used for the EPD and Silane deposition methods, as well as full cell design to be discussed in chapters 4 and 5.

While the optimized recipe gave a good starting point for development of thin film CZTS solar cells there was still much work to be done, specifically involving deposition of the light-absorbing layer. There are some issues with formation of a uniform highly crystalline thin film. At higher magnifications in SEM images the
nanocrystals are oriented well, but there are areas of defects and cracks that will affect the photogeneration of electricity when the full device is complete. In chapter 4 alternate techniques for deposition of the thin film was used in order to produce a more uniform and therefore more efficient light-absorbing layer.
Chapter 4

4 Optimization of CZTS Light Absorbing Layers

In order to fabricate an effective solar device one must ensure that the light absorbing layer is deposited as uniform and crack-free as possible.\textsuperscript{62} Three methods of depositing the CZTS nanocrystals were tested and compared.

The first method used was dropcasting the nanocrystals (NCs) onto one of three substrates tin-doped indium oxide (ITO), fluorine-doped tin oxide (FTO), and molybdenum coated soda lime glass (Mo-SLG).\textsuperscript{26} This method involved suspending the nanocrystals in a solvent and then allowing the suspension to dry upon deposition on the substrate. Firstly the effect that different solvents will have on the morphology of the thin film was investigated.

The second method tested was electrophoretic deposition (EPD). In EPD a potential is applied across two electrodes (working electrode and counter electrode) separated in solution. An electromotive force drives the suspended NCs towards one of the electrodes. The direction of particle flow depends on the charge associated with the nanocrystals.\textsuperscript{38} In theory this method should allow for tightly packed highly crystalline NC films due to the aggregation and arrangement that occurs on the surface of the electrode.\textsuperscript{41}

The final deposition tested was silanization, using (3-mercaptopropyl)trimethoxysilane (MPS) as a chemical linker, to bond the CZTS NCs to the substrate. The silane terminus of MPS forms silicon-oxygen bonds with a metal
oxide in the substrate.\textsuperscript{42} Once the MPS was bound to the substrate CZTS was deposited onto the linker using the sulfur terminus to encourage NC growth to the linker.\textsuperscript{43} Thin film optimization was important in ensuring that the resulting solar device was as efficient as possible; a method of deposition was needed that would minimize any cracks and voids in the light-absorbing layer. This allows for high conversion of photons to electricity while reducing recombination, dark current, and other factors that would negatively influence the effectiveness of a device. Dropcasting was examined first as it is the simplest method of the three discussed and was used for optimization of the NC.

### 4.1 Dropcasting

Dropcasting is one of the most rudimentary methods of depositing the NCs onto a substrate. Dropcasting was very useful when optimizing the NCs because it consists of suspending the NCs in a solvent, as the name implies dropping small volumes of the sample onto the surface of the substrate and allowing it to dry. While it is easily operated there are some concerns that have arisen related to its consistency and reproducibility.

The main concern that has been stated previously is in regard to cracks and voids that occur throughout the thin film. This was not a problem during PEC measurements, as the other contact was liquid and could easily fill these spaces and therefore reduce the impact of these defects. The problem became more concerning when attempting to fabricate a full cell. Layers deposited on top do not have a good contact, which causes resistance. This resistance, which in some instances, can be so large that the conversion of light to electricity will be minimized to essentially zero since there needs to be flow of electrons for the full cell to be functional.\textsuperscript{19} Acetone was used as the primary solvent for the dropcasting procedure.
Figure 4.1 Dropcasted films using acetone (20 g/L) A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)

Figure 4.2 Dropcasted films using isopropanol (20 g/L) A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)
Figure 4.3 Dropcasted films using ethanol (20 g/L) A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)

Figure 4.4 Dropcasted films using dichloromethane (20 g/L) A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)
Figure 4.5 Dropcasted films using toluene (20 g/L) A) Magnification (x50.0) B) Magnification (x500) C) Magnification (x5.00K) D) Magnification (x30.0K)
The first task was to observe the effect that the solvent used for dropcasting had on the film quality and if a solvent could be selected to limit the amount of defects in the thin film. SEM images of the CZTS sample dropcasted onto soda lime glass (SLG) using different solvents are shown in Figures 4.1-4.5. The SEM images paint a clear picture of some of the main concerns that are encountered while using the dropcasting technique. While dropcasting is fairly quick and easy the real problem lies in the lack of control. Figures 4.1-4.4 demonstrate the negative aspects clearly, as it is evident that the surfaces of the films are not smooth and crystalline.

At high magnification there are many cracks and voids present, which as stated previously will serve as a great detriment to the energy production capability of a full cell. While it is apparent from these images that toluene appears to be a great candidate there are several negative factors including its toxicity and the fact that it is extremely difficult to disperse the CZTS nanocrystals well in this sample. PEC measurements were also taken using toluene as the dropcasting solvent and the results show substantially less photocurrent when compared to acetone or isopropanol, the other predominate solvents used for dropcasting.

The other issue with dropcasting is that the film does not always adhere well to the substrate. This is a major issue as the next step in production of a full cell is deposition of a cadmium sulfide buffer layer through an aqueous chemical bath deposition. If the CZTS NC thin film is not firmly attached to the substrate it will flake off during the CBD, which in turn would result in CdS being deposited onto the substrate, essentially rendering the device useless or extremely ineffective upon completion. It is because of these many detractors that alternate methods of deposition were sought after.
Regardless of the ease and quickness of dropcasting it was necessary to look elsewhere in order to maximize the effectiveness and ensure there is reproducibility when attempting to fabricate a full cell.

4.2 Electrophoretic Deposition (EPD)

EPD is very tunable and versatile because different substrates, concentrations, deposition times, and solvents can be used to optimize the procedure. A potential is applied across two electrodes separated in solution. The NCs are suspended in the solution and are driven towards one of the electrodes depending on their charge. Once they reach the electrode they deposit on the surface forming a tightly packed thin film layer. The effect of different concentrations, deposition times, solvents and annealing temperatures were investigated in an effort to obtain a uniform CZTS thin film. In Figure 4.6 multiple examples of PEC measurements of CZTS thin films deposited via EPD can be seen. Through these investigations it was found that a concentration of 2 g/L gave the best deposit in terms of PEC measurements.

When higher concentrations were used the deposit became too thick, which caused some of the NCs to flake off of the substrate, which greatly reduces the PEC efficiency. There are several mechanisms for the movement of charged particles under the influence of an electric field, but in this case it is a result of an induced dipole moment on the NCs. Two mechanisms of particle aggregation require an induced dipole moment on particles; the particles will move by dielectrophoresis when the electric field gradient is non-zero and the velocity of the particles is proportional to the gradient of the electric field intensity. The direction of particle movement is often not the same as the direction of the electric field, as this is dependent on the charge type of the dipole
moment on the NCs. An induced dipole will interact with the electric field gradient and with each other, either in attraction or repulsion. Due to the induced dipole if the concentrations are too high, there will be repulsion between the NCs and they will not form a uniform, tightly packed layer. At 2g/L a good balance between unwanted NC-NC interactions and sufficient NC concentration was reached. While some positive results were observed using EPD there are still issues that decrease the effectiveness of the method. After investigating deposition times it was discovered that a five-minute deposition time was too long. With a five-minute deposition the thin film was very thick, greater than 10 µm, and this led to the CZTS layer easily detaching from the substrate.

A post-processing densification step was required in order to solidify the deposit when longer times were used. This required annealing the samples in the range of 200-500°C for 15-60 minutes. The negative aspect of this densification step is that it greatly increases the energy input required to form the thin film. Figure 4.7 gives a representation of how post processing annealing temperatures affect the film effectiveness. Annealing at 300°C for 45 minutes yielded the best results and substantially increased the photocurrent when compared to pre-annealing. EPD was also compared with the dropcasting method of the same NCs to determine if there was a photochemical advantage to using EPD as a deposition method. EPD does show potential for depositing crystalline thin films with higher photocurrent conversion in comparison with the dropcasting technique. But there are still a few issues with the process. The EPD sample had a photocurrent of 28.4 µA/cm² compared to dropcasting which was 27.6 µA/cm².
Figure 4.6 PEC measurements of EPD samples at different concentrations. CZTS sample that was outlined in optimization procedure was used. Solvent was isopropanol.

Table 4.1 Experimental conditions for EPD samples measured

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. (g/L)</th>
<th>Potential (V)</th>
<th>Time (min)</th>
<th>ΔJ (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>2.12</td>
<td>50</td>
<td>5</td>
<td>8.57</td>
</tr>
<tr>
<td>Sample 2</td>
<td>5.20</td>
<td>50</td>
<td>5</td>
<td>1.83</td>
</tr>
<tr>
<td>Sample 3</td>
<td>11.97</td>
<td>50</td>
<td>5</td>
<td>1.78</td>
</tr>
</tbody>
</table>
SEM images of CZTS deposited by EPD (Figure 4.8) show that there are still cracks and voids in the thin film and there are still issues with the crystallinity of the thin film. Possible solutions to this problem include annealing in a selenium or sulphur atmosphere, would hinder the ability to produce low cost thin film devices, which would counteract what previous studies have been working towards.\textsuperscript{17,67} As well there are many issues with selenization and sulfurization, some of which include loss of zinc at the high temperatures required (~500°C), and migration of sulfur to the molybdenum CZTS contact where formation of sulfur by-products occurs.\textsuperscript{21,68}

There are other possible solutions that can be investigated in an effort to produce a more uniform CZTS thin film. Changes in solvent and how it will affect the CZTS thin film deposited by EPD was investigated. It is thought that cracks may form when the solvent (isopropanol) is drying.\textsuperscript{62} One attempt to counteract this was using acetone, ethanol, or a mixture of solvents. A change in the procedure was investigated in an attempt to allow for more uniform thin films. The new method involved intervals of two minutes of deposition, followed by allowing the deposit to dry, and then depositing again for two minutes in an attempt to fill any voids left during the drying process. Upon further investigation isopropanol proved to be the most consistent and gave the largest photocurrent of all solvents tested. The alternate deposition procedure did not prove to be very effective, instead shorter deposition times allowed for a better CZTS thin film to form.
Figure 4.7 PEC measurements of EPD samples at different annealing temperatures with comparison to dropcasting. Solvent used was isopropanol

Table 4.2 Experimental conditions for samples measured

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>Potential (V)</th>
<th>Time (min)</th>
<th>ΔJ (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300°C</td>
<td>2.0</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>350°C</td>
<td>2.0</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Dropcasting</td>
<td>20.0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 4.8 SEM images of optimized CZTS NCs, deposited onto Molybdenum coated Stainless steel substrate by EPD. (2 g/L conc. 50 V for 5 min) A) Magnification (x1.00K) B) Magnification (x3.00K) C) Magnification (x15.0K) D) Magnification (x60.0K)
It was discovered that a five-minute deposition time was far too long. When making a full cell the CZTS layer should be less than 2 µm thick. Figure 4.8 shows the results of shorter EPD deposition times with isopropanol as the solvent and with a concentration of 2 g/L. The largest photocurrent observed was for 20 s and 40 s deposition times at 102 µA/cm² and 106 µA/cm², respectively. Through shortening the deposition times drastically there is a large enhancement, likely due to increased crystallinity and decreased distance travelled by the electrons. It is clear when comparing Figure 4.6 and Figure 4.9 that there is much lest resistance in the samples when they are deposited for a much shorter time, which is very promising for full cell fabrication.

Film quality is of upmost importance to take note of through use of both SEM images as well photocurrent production (PEC measurements). While PEC measurements are a great tool in comparing the ability of different samples to photogenerate current, SEM images are important in explaining why one sample is more or less effective based on the change in the film morphology.

The main negative aspect of the shorter deposition times is the increased recombination prevalent in Figure 4.9. While this is an issue that may be rectified with further studies the enhancement gained overweighs the recombination as there will be some recombination occurring in the full cell and the amount of photocurrent generated will determine how much of a role the recombination will play in the cell efficiency. SEM images in Figure 4.10 show the CZTS thin film deposited by EPD deposited for 40 seconds at 50 V in a 2 g/L solution of isopropanol.
Figure 4.9 PEC measurements of different EPD deposition times. Nanocrystals suspended in isopropanol solvent at 2g/L with an applied potential of 50 V

Note: Experiments in Figure 4.9 were mainly completed by Dr. Lorenzo Perini

Table 4.3 Current Density change for samples

<table>
<thead>
<tr>
<th>Conc. (g/L)</th>
<th>Potential (V)</th>
<th>ΔJ (μA/cm²)</th>
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<tbody>
<tr>
<td>20 s</td>
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<tr>
<td>40 s</td>
<td>2.0</td>
<td>50</td>
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<tr>
<td>60 s</td>
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<td>50</td>
</tr>
<tr>
<td>80 s</td>
<td>2.0</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure 4.10 SEM images of CZTS on FTO coated glass, deposited by EPD in isopropanol for 40 s at 50 V at 2 g/L. A) Magnification (x200) B) Magnification (x500) C) Magnification (x1.00K) D) Magnification (x10.0K) Cross Sectional Image with Thickness of (3.437 µm)
While there are still some cracks visible they are very small and do not penetrate to the substrate, which was confirmed through several cross sectional images. The surface is very smooth and uniform and the cross sectional images show that the layer is \( \sim 3 \, \mu m \). The characteristics of a 40 s deposition parameters are very promising and should be well suited for full cell fabrication. There is no issue with adhesion to the substrate with the thinner deposition, at 40 s, which means that no annealing step is required for any of the PEC measurements or SEM images with shorter deposition times. Eliminating the annealing step is a great advantage, as it requires a large energy input, which detracts from the low cost and easy production of a thin film that is strived for with this CZTS NC recipe.

### 4.3 MPS Linker

In an attempt to produce more uniform thin films the use of a chemical linker (3-mercatapropyl)trimethoxysilane (MPS) was investigated. Its function was to chemically bind the nanocrystals to the substrate.\(^ {42,43} \) This would theoretically would help reduce the issue of adhesion to the substrate. It should also lead to the formation of a more ordered and crystalline thin film due to the method through which the nanocrystals are be linked to the substrate. It is proposed that the silicon will form Si-O bonds with the substrate during incubation with the substrate. After the linker had been attached to the substrate the thiol terminus was used to attach the nanocrystals to the substrate. During nanocrystals synthesis 3-mectapo-5-n-propylpirimidine (MPP) was used as a capping ligand. The MPS linker plays a similar role as the MPS also acts as a capping ligand, but in this the case the other end of the molecule is attached to the substrate, binding the nanocrystals to the substrate. This is expected to enhance the contact of the CZTS NCs to
the substrate increasing crystallinity and minimizing defects, which in turn is expected to increase photocurrent production.

Figure 4.11 shows PEC measurements for the silane linker and dropcasting of the same NC recipe. The CZTS NCs were deposited onto ITO coated glass using MPS as a chemical linker. This method gives a very thin layer of nanocrystals because CZTS can only bond to the MPS at the sulfur terminus. The other end of the MPS molecule forms an oxygen-silicon-oxygen bond with the substrate during the silanization process discussed earlier. While it is possible that some NC growth may be observed on top of the initially bonded NCs, the deposit is essentially transparent and can be observed as a yellow/brown discoloration on the substrate. Due to the extremely thin layer of NCs it is encouraging to see that similar and in some cases larger photocurrent can be generated when compared to the traditional dropcasting method. Dropcasted samples usually have a thickness of a couple of microns where the MPS linked samples have a thickness of approximately 70 nm for 2 depositions. Cross sectional SEM images confirm the film thickness, which can be seen in Figure 5.2. The enhancement of this layer is most likely due to the increased crystallinity and the decreased amount of cracks and voids that occur during the dropcasting procedure. SEM images of the MPS linked CZTS sample can be seen in Figures 4.12 and 4.13.

The surface structure of the MPS linked CZTS is very promising since unlike dropcasting or EPD there are no cracks or voids present. This is most likely due to the chemical bonds formed between the silane linker and the NCs during the CZTS synthesis process.
Figure 4.11 Comparison of MPS linked CZTS deposited on tin doped indium oxide (ITO) coated glass and dropcasted CZTS by PEC measurements

Table 4.4 Current Density change for samples

<table>
<thead>
<tr>
<th></th>
<th>$\Delta J$ (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPS-CZTS</td>
<td>33.1</td>
</tr>
<tr>
<td>Dropcast-CZTS</td>
<td>27.6</td>
</tr>
</tbody>
</table>
Figure 4.12 SEM images of MPS linker on ITO coated glass. Before CZTS was deposited. A) Magnification (x300) B) Magnification (x1.00K) C) Magnification (x15.0K) D) Magnification (x30.0K)

Figure 4.13 SEM images of optimized CZTS NCs, deposited onto a ITO glass substrate using the MPS linker method A) Magnification (x300) B) Magnification (x1.00K) C) Magnification (x30.0K) D) Magnification (x30.0K)
Since the NCs are chemically bonded to the substrate in the MPS method, electrons seem to travel through the semiconductor to the back contact with greater ease than previously observed. This is observed by the increase in the current density produced during the PEC measurements.\textsuperscript{47} By using the silane method the current density produced was increased from 27.6 \( \mu A/cm^2 \) to 33.1 \( \mu A/cm^2 \). While this may not seem like a large increase it is important to note that the linker method produces a much thinner layer (~70 nm). Another positive that can be taken from this PEC measurement is the minimal dark current as well as negligible resistance in the sample (Figure 4.11). When preparing a suitable material for the absorbing layer of a photovoltaic cell it is important to keep the dark current and resistance to a minimum.\textsuperscript{18,20,69}

As seen in Figure 4.14, there is a substantial amount of dark current in this sample, which greatly affects the PEC transient. Dark current is a result of random generation of electrons and holes in the charge depletion region, and is more prominent at a higher bias because the potential gradient allows the species to move through the cell with greater ease.\textsuperscript{18} The charge generation is related to crystal defects in the light-absorbing layer, and thus it is fair to assume that a sample with less dark current will have less defects and a more crystalline ordering of the CZTS nanocrystals. Many of the MPS CZTS samples showed substantial dark current at more negative bias. However, upon refining the procedure many of the more recent samples prepared have shown reduced dark current and increased photocurrent.

In an effort to increase the photocurrent generated multiple depositions were tested. The MPS CZTS substrate was placed in the reaction flask multiple times in an effort to increase the layer thickness and thus increase the resulting photocurrent. Figure
Figure 4.14 PEC measurements of CZTS nanocrystals deposited on ITO coated glass via MPS linker. There is an increased slope at negative potentials due to dark current.
4.15 shows the results of multiple CZTS depositions. The current density increased after the first three depositions to a maximum of 58.5 $\mu$A/cm$^2$. After the fourth deposition the current density decreased slightly to 42.1 $\mu$A/cm$^2$ and the dark current was much more prevalent. This decrease is most likely due to the repeated heating of the substrate to 180°C during the deposition process. Prolonged heating may have damaged the ITO layer and/or the NCs that were previously deposited leading to crystal defects and a decreased effectiveness in terms of photogeneration. During full cell fabrication multiple depositions were used as it has been shown to enhance the photocurrent generation of the MPS-linked CZTS.

Deposition of the MPS-linked CZTS onto molybdenum was tested, as its band gap matches well with CZTS for full device fabrication. Molybdenum coated glass was sputtered in the Nanofab lab at UWO with the settings outlined in the instrumental section. It was necessary to apply a flow rate of 2 standard cubic centimeters (sccm) of oxygen gas for the last five minutes of the sputtering process in order to produce a MoO$_x$ layer on the surface.

As stated previously the MPS linker requires a metal oxide in order to form the silicon-oxygen bonds during the silanization process. The work function of the molybdenum metal is very important for it to be an effective back contact, it was confirmed that MoO$_x$ would not negatively affect the function of the back contact. The work functions of molybdenum and the molybdenum oxides are as follows: 4.4 ± 0.2 eV (Mo), 5.9 ± 0.2 eV (MoO$_2$), and 6.82 ± 0.05 eV (MoO$_3$).
Figure 4.15 PEC measurements of CZTS nanocrystals deposited on ITO coated glass via MPS linker. The number in the legend denotes the number of depositions.

Table 4.5 Current Density change for different depositions

<table>
<thead>
<tr>
<th>Number of Depositions</th>
<th>ΔJ (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.6</td>
</tr>
<tr>
<td>2</td>
<td>35.3</td>
</tr>
<tr>
<td>3</td>
<td>58.5</td>
</tr>
<tr>
<td>4</td>
<td>42.1</td>
</tr>
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</table>
While the work function of the molybdenum oxides are substantially higher, the work function of the MoO$_x$ created in the Nanofab lab should be very similar to molybdenum because in order to form a full oxide heat is required during the sputtering process. No heat was applied externally while sputtering, which leads to the conclusion that the work function of the MoO$_x$ is slightly higher than 4.4 eV.

The MoO$_x$ substrate was then used for deposition of the MPS-linked CZTS, through the same method that has been optimized on ITO coated glass. The PEC results demonstrate that this method does work effectively on MoO$_x$ substrate as well (Figure 4.16). A change in current density ($\Delta J$) of 74.0 $\mu$A/cm$^2$ is larger than the previous best sample prepared on ITO coated glass, which was 58.5 $\mu$A/cm$^2$. CZTS was deposited on the MoO$_x$ MPS-linked sample twice because it was shown that multiple depositions increase the photocurrent produced. Upon optimizing the deposition procedure it was necessary to test the effectiveness of the CdS buffer layer. Previously, photocurrent enhancement was shown for dropcasted CZTS when depositing CdS for eight minutes through chemical bath deposition (CBD). CBD was tested on the MPS-linked CZTS to determine if the same results could be observed on a much thinner CZTS layer. Figure 4.17 shows the results from the CdS deposition. The deposition was done for six minutes, as longer deposition times were not very effective with the very thin CZTS layer. There was still photoenhancement with an eight-minute deposition but recombination was dominant and there was a reversal of the change in photocurrent with light on and light off. This implies that the CdS layer deposited was too thick and was dominating the photochemistry of the absorbing layers.
Figure 4.16 MPS-linked CZTS with MoO$_x$ as the substrate. $\Delta J$ for this sample is 74.0 $\mu$A/cm$^2$. 
After modifying the deposition time to six minutes the CZTS was not negatively affected by the CdS deposition and there was still photocurrent enhancement observed.

Before the depositions the photocurrent generated was 23.7 μA/cm² and 24.7 μA/cm² for the pre CdS samples six and eight respectively. It is important to note that both pre CdS samples were prepared in the same reaction vial when depositing CZTS to minimize experimental error. After the CdS deposition the photocurrent generated was 66.1 μA/cm² and 82.9 μA/cm² for post CdS samples six and eight, respectively. Note that the photocurrent measure for post CdS eight minutes was at the beginning of the scan. At this point when the light was shone on the sample the photocurrent generated was negative whereas in all other samples light on corresponds with a positive response in photocurrent. Overall it is clear that there is a photocurrent enhancement with six minutes of deposition time, which is promising when attempting to make a full cell via the MPS-linked method. Although the enhancement received was not as large as initially expected more work should be done to optimize this deposition further. Confirmation of a CZTS deposition was not yet known and some of the commonly used elucidation techniques would not be effective, as the layer was too thin. XRD was not viable due to this issue along with EDX; Raman and UV band gap measurements were used to confirm that the deposit was in fact Kesterite CZTS with the correct band gap needed for photovoltaic cell fabrication. Figure 4.18 shows the results from one of the Raman measurements taken. There are three common peaks that correlate with Kesterite CZTS. The first peak is at 286 cm⁻¹, the second is at 338 cm⁻¹, and the third is at 358 cm⁻¹. In Figure 4.18 there are three peaks at 291 cm⁻¹, 340 cm⁻¹, and 358 cm⁻¹, which correspond well with literature values.
Figure 4.17 Comparison of MPS-linked CZTS on ITO coated glass before and after CdS deposition for six and eight minute deposition time.

Table 4.6 Current Density change for samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta J$ ($\mu A/cm^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre 6 min</td>
<td>23.7</td>
</tr>
<tr>
<td>Pre 8 min</td>
<td>24.7</td>
</tr>
<tr>
<td>Post 6 min</td>
<td>66.1</td>
</tr>
<tr>
<td>Post 8 min</td>
<td>82.9</td>
</tr>
</tbody>
</table>
This was the first step in confirming the Kesterite structure. UV-Vis band gap measurements were also taken because the peaks in the Raman spectra were very broad. This is again a result of the very thin layer being measured; there was also found to be some fluorescence from the MoO$_x$ by way of diffraction photoluminescence studies. These factors combined would contribute to the low convolution and broadness of the Raman peaks.$^{45}$ UV-Visible band gap spectroscopy measurements were then done, in this case on ITO coated glass, through use of a Tauc plot. The Tauc plot was calculated based on the following equation.

\[
(\alpha h\nu)^2 = \frac{A^2 E^2}{\log (e)}
\]

A variable (r) in $(\alpha h\nu)^r$, changes with respect to the type of band gap transition. R will be equal to $\frac{1}{2}$ if an indirect band gap semiconductor is being tested. In this case, CZTS is a direct band gap semiconductor, which means that (r) will be equal to 2.$^{48}$ The capabilities for reflective UV-visible measurements with an integrated sphere were not readily available, and the sample is semi-transparent so it was deemed unnecessary.$^{48}$ Figure 4.19 shows the results of the UV-visible band gap absorbance measurement.

The average of the multiple measurements taken was 1.39 eV, which corresponds well with literature values for CZTS which are $\sim$ 1.5 eV.$^{12,35,51,67}$ Confirmation of the band gap value along with the Raman spectroscopy confirms that in fact CZTS was deposited onto a metal oxide substrate via the MPS-linker method. MPS as a linker was
proved to be viable for CZTS deposition as well as CdS deposition for a potential method of preparing the CZTS thin film for full device fabrication. EPD was also shown to be an effective and reliable deposition technique, while dropcasting proved inconsistent and unreliable over multiple tests. In the coming sections using MPS-linked CZTS and CZTS deposited via EPD for applications in photovoltaic cells will be discussed.
Figure 4.18 Raman spectra of MPS-linked CZTS on MoO$_x$ coated glass. Three peaks shown correspond with Kesterite CZTS$^{71}$
Figure 4.19 UV-Visible Spectroscopy band gap measurements of two MPS-linked CZTS sample deposited on ITO coated glass.

Table 4.7 Measured Band Gap of Several MPS-linked CZTS Samples. Average Band Gap was 1.39 eV.

<table>
<thead>
<tr>
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<th>Band Gap (eV)</th>
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<tbody>
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<td>1</td>
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</tr>
<tr>
<td>2</td>
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</tr>
<tr>
<td>3</td>
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<td>4</td>
<td>1.28</td>
</tr>
<tr>
<td>5</td>
<td>1.56</td>
</tr>
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</table>
Chapter 5

5 Full Devices

In terms of thin film devices, the most common light-absorbing layers used are Cu(In,Ga)Se$_2$ (CIGS), CdTe, CIS, and CZTS. Currently CIGS is the most frequently used for commercial applications of the thin film devices because of its reported efficiency up to 20.3%.\textsuperscript{73} CZTS is rapidly becoming a suitable and superior replacement as it uses earth abundant metals (Cu, Sn, and Zn), which greatly reduce the cost of production. CZTS also doesn’t use any toxic or hazardous components that are found in some of the other current light absorbing layers such as CIGS or CdTe. Even though current CZTS efficiencies (11.1%) are not as high as CIGS, the most important aspect is the dollar per watt\textsuperscript{5} value that is a measure of counter balancing the energy required to fabricate the device with the total energy output that will be produced from the cell.\textsuperscript{74}

Full Devices were fabricated using CZTS samples deposited via EPD and the MPS-linker method. A schematic of full cell can be seen in Figure 1.5. Two different back contacts were used during device fabrication. Molybdenum was sputtered on soda lime glass in the Nanofab lab to a thickness of $\sim 1 \, \mu\text{m}$, and for the MPS-linked full cell MoO$_x$ was deposited for a very short time to ensure some metal oxides were available for the MPS linker to bond to the substrate during silanization. Fluorine doped tin oxide (FTO) coated glass was also used as a back contact. The work function of molybdenum metal is $4.4 \pm 0.2 \, \text{eV}$ while $4.4 \pm 0.1 \, \text{eV}$ for FTO.\textsuperscript{70,75} Tin doped indium oxide (ITO) coated glass has a work function of $4.2 \pm 0.2 \, \text{eV}$ which correlates well with FTO and
Mo.\textsuperscript{76} ITO is frequently used as a transparent conducting oxide on top of the cell, but historically it has not been used as a back contact for CIGS or CZTS cells.\textsuperscript{5,16,32,67}

The CZTS layer was deposited by the optimized EPD and MPS-linker method for full cell testing. The cadmium sulfide (CdS) buffer layer was then deposited via chemical bath deposition to the optimized thickness discussed previously. Intrinsic zinc oxide (\textit{i}-ZnO) and aluminum-doped zinc oxide (AZO) were deposited to complete the fabrication process once the bottom three layers were made (Mo,FTO\textbackslash CZTS\textbackslash CdS). \textit{i}-ZnO was deposited first as it is a n-type semiconductor material and aids in transfer of electrons from the CdS buffer layer to the AZO layer.\textsuperscript{77} The \textit{i}-ZnO layer was sputtered with a radio frequency (Rf) power of 70 W. Argon flow rate was \textasciitilde 15 standard cubic centimeters (sccm) and the oxygen flow rate was 0.1 sccm. \textit{i}-ZnO was sputtered for 30 minutes to a thickness of \textasciitilde 50 nm. The final layer sputtered was AZO (2\% doped with aluminum).

AZO is the window layer, it is a conducting metal oxide that is transparent and is used to prevent degradation of the \textit{i}-ZnO layer while still allowing light to pass through. AZO also has a role in electron transfer to the top contacts of the cell.\textsuperscript{78} The AZO layer was sputtered with a DC power of 75 W with an argon flow rate of 15 sccm. Sputtering time was one hour and the deposited layer was \textasciitilde 250 nm thick. In most cases a gold top contact was deposited via e-beam evaporation to provide good conduction for the full cell test. Cross sectional SEM images in Figure 5.1 and 5.2 show the full cell after all layers have been deposited. In Figure 5.1 CZTS was deposited via EPD. The CZTS layer in this sample is \textasciitilde234 nm. The thickness of the CZTS layer in Figure 5.2 is \textasciitilde 75 nm which was deposited via the MPS-linker method.
Figure 5.1 Cross sectional SEM images of full cell. Cell was fabricated on silicon wafer for ease of imaging. Layers are as follow Mo/CZTS/CdS/ZnO/AZO. CZTS was deposited via EPD in isopropanol for 40 seconds at 50 V in a 2 g/L solution. A) Image magnification (25.00 K) shows the entire cell B) Image magnification (25.00 K) shows the molybdenum layer thickness (1.181 µm) C) Image magnification (25.00 K) shows the CZTS layer thickness (234 nm) D) Image magnification (25.00 K) shows the ZnO/AZO layer thickness (267 nm).
Figure 5.2 Cross sectional SEM images of full cell. Cell was fabricated on silicon wafer for ease of imaging. Layers are as follow Mo/CZTS/CdS/ZnO/AZO. CZTS was deposited via MPS-linker. A) Image magnification (25.00 K) shows the entire cell B) Image magnification (25.00 K) shows the molybdenum layer thickness (1.177 µm) C) Image magnification (50.00 K) shows the entire cell D) Image magnification (50.00 K) shows the CZTS and ZnO/AZO layer thickness (75 nm) and (328 nm).
In the cross sectional images it is important to note that the AZO and ZnO layers are indistinguishable; they are essentially the same material. The only difference is that AZO is doped with 2% aluminum. A combined thickness of ~ 300 nm with some variation was observed. This variation is most likely a result of orientation of the sample during sputtering, which was not directly above the target and rotating. The CdS buffer layer cannot be distinguished on the SEM images as well, while in some cases there appears to be a slight change in the crystal orientation, CdS is chosen because its crystal structure matches well with CZTS. Cross sectional images shown in Figure 5.1 and 5.2 validate claims made in the experimental method.

### 5.1 Testing of Solar Cell Efficiency

Currently one working cell has been fabricated. The I-V curve measured can been seen in figure 5.3. The CZTS was deposited via electrodeposition in this case. The CZTS layer was deposited by Dr. Xujin Wang, CdS deposition and sputtering was carried out under the standard procedures. Solar cell efficiency was calculated according to the following equation.

\[ \eta = \frac{V_{oc}I_{sc}FF}{P_{in}} \]

The Calculated cell parameters were: 0.183 V (V_{oc}), 4.41E-6 A (I_{sc}), and 0.27 (FF). While this solar cell was functional the efficiency was extremely low (3.11E-8 %). It is encouraging to have observed a somewhat functioning device, although it shorted when attempting to run a second I-V curve. While the open circuit potential is not that bad the short circuit current is extremely low.
Figure 5.3 I-V curve of CZTS full cell. CZTS was deposited through electrodeposition of copper, zinc, and tin, followed by sulfurization to form CZTS. CdS, \textit{i}-ZnO, and AZO were deposited under normal conditions discussed in this thesis.
This means that when the applied bias is zero the current produced from the cell under illumination is 4.41E-6 A. The main reason for this cell producing such a low efficiency can be described in terms of shunt resistance. In this case the current is not always flowing through the specific layers deposited in order to form the full cell. This correlates previously with work done in order to minimize cracks and voids in the light-absorbing layer. During the I-V test the shunt resistance was very low, allowing the current to pass through the circuit without passing through all of the deposited layers. This factor greatly limits the current production capability of the full cell. In order to improve on current working efficiencies, a better contact should be formed between each layer deposited to make up the full cell, as well as minimizing cracks and voids that could allow for current to pass freely through the cell.

Presently no stable full cells have been fabricated using EPD and MPS-linker as the CZTS deposition method. There are many possible reasons for this lack of success. The back contact may be an issue; molybdenum-coated glass was purchased from a manufacturer recently, as an alternative to sputtering in an attempt to minimize engineering procedure. In some cases the CdS deposition may not be as uniform and equal in thickness depending on the certain variables, namely the pH of the solution, stirring speed, as well as the temperature the solution is at while deposition is occurring. Impurities could form (mostly carbon deposits, and some oxidation) on the surface of the individual layers in between deposition of separate layers. Better results could be obtained if the deposition of CZTS and CdS were completed in a glove box and transferred to the Western Nanofabrication facility in an oxygen free environment. Lastly
more work should be done to ensure that AZO and $i$-ZnO are sputtered at optimal conditions.

The images (Figure 5.1 and 5.2) emphasis the need to optimize the CdS, $i$-ZnO, and AZO deposition methods further as the top layer is irregular and non-uniform. Currently AZO depositions have not been conducting, which is of great concern for the window layer, as it aids in electron transport throughout the cell. Optimization of these top three layers will greatly enhance the effectiveness of the full cell.
Chapter 6

6 Conclusions and Future Work

With increasing energy demand and diminishing natural resources it is important to develop new energy production capabilities designed on readily available and inexpensive materials. \(\text{Cu}_2\text{SnZnS}_4\) (CZTS) was shown to be a promising candidate that adheres nicely to these prerequisites. In this thesis CZTS was synthesized through a low cost one-pot synthesis method, greatly reducing energy input when compared to other current preparation methods, which require vacuum processing and annealing at high temperatures in sulfur and/or selenium atmospheres.

Optimization of the nanocrystal preparation was completed. Results showed that increasing the amount of copper in the precursor solution decreased the photoresponse of the nanocrystals. Conversely increasing the amount of zinc used in the starting ratio increased the photoresponse to a certain point. Five different copper salts were tested and compared to determine which was the most effective for use during synthesis. Copper(II) acetylacetonate \((\text{Cu(acac)}_2)\) was proved to be the best choice when comparing photocurrent production. The best starting ratio observed was 2.00 Cu: 3.00 Zn: 1.00 Sn: 4.21 S, which is very close to the optimized recipe. The optimized recipe had starting molar ratios of 1.44 Cu: 4.28 Zn: 1.00 Sn: 4.21 S. Various analytical methods such as XRD, Raman… were performed to confirm that a Kesterite crystal structure is present in the optimized recipe.

Thin light-absorbing layer optimization was performed using dropcasting, electrophoretic deposition, and MPS-linker as deposition methods. Dropcasting with
several solvents (acetone, isopropanol, etc…) was tested for comparison. Toluene showed the most promising results as the films produced were smooth and crack free but was ineffective during PEC measurements. Electrophoretic deposition (EPD) was studied as a possible alternative to dropcasting. Experiments showed that isopropanol was the most consistent and effective solvent for EPD. The largest photoresponse generated during thin film optimization was 106.0 µA/cm², which corresponds to the optimized EPD procedure. SEM images showed minimal crack and voids in samples deposited via EPD. 3-Mercaptopropyl Trimethoxysilane (MPS) was used as a chemical linker to bond the CZTS nanocrystals to the substrate. The photocurrent generated from the MPS-linked CZTS thin film reached 74.0 µA/cm² through use of multiple depositions. Three depositions produced the maximum photocurrent generated while minimized negative affects of the procedure. SEM images revealed that there were no cracks or voids present. MPS-linked CZTS was shown to produce a photoenhancement when cadmium sulfide deposition was performed, increasing the photocurrent from 23.7 µA/cm² to 66.1 µA/cm². Raman spectroscopy studies confirmed that CZTS was deposited using the MPS-linker method. UV-Visible band gap measurements were used to confirm the average band gap of the CZTS, which was 1.39 eV.

Photovoltaic devices were fabricated using EPD and MPS-linker method for thin film deposition. SEM images show the thickness of each layer that was deposited. \( i-ZnO \) and AZO was ~ 300 nm as they are indistinguishable in the images. The molybdenum back contact was ~ 1 µm. The CZTS layer was ~ 234 nm for CZTS deposited by EPD and ~ 75 nm when deposited by MPS-linker. A full cell was produced
and had an efficiency of 3.11E-8 %. While it is encouraging to see positive results, a layer-by-layer approach should be taken to enhance the cells efficiency.

Currently a working cell has been fabricated but more testing should be completed to increase the efficiency of the full cell. Some variables that could be studied include, sputtering of metal and semiconductor films, further optimization of CdS buffer layer, and CZTS deposition. By use of a layer-by-layer strategy optimization of the full cell could be completed. The CZTS layer has been optimized in this thesis but much work can still be done optimizing all layers of the solar cell.
References


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Professor: Paul Ragogna

Grade Earned: 79%

Conferences and Workshops

1) “Cu₂ZnSnS₄ Nanocrystal Monolayer on ITO-Glass” Kyle Jeffs, Dr. Zhifeng Ding. 2013 CAMBR Day, Western University, London, ON. November 1, 2013 (poster)