

**Optimization of Zinc Oxide Thin Film Deposition as Part of the p-n
Heterojunction for Photovoltaic Applications**

An honors thesis for

The Department of Chemical & Biological Engineering.

By

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Abstract

As global warming and pollution are becoming an ever increasing problem, the need to move to green and renewable sources for energy is becoming more and more important. Solar cells, having a wide range of uses and having already shown potential for mass marketability, are key to moving away from fossil fuels and natural gas as the main sources of energy production. Consequentially, it has also become necessary to reduce both the capital and energy costs of solar cell manufacturing. In this research, only cheap and abundant resources were used along with non-energy intensive processing through electrodeposition in the development of solar cells. Special focus was dedicated to optimizing the deposition of zinc oxide (ZnO) to improve the efficiency of the solar cell. The optimal methodology was the deposition of zinc metal first, followed by the formation of ZnO by annealing the zinc metal film. Cuprous oxide (Cu₂O) was then deposited on top of the ZnO as a means of creating an effective p-n heterojunction. However, due to deposition difficulties, it was not possible to construct an effective p-n junction. Nevertheless, the most effective ZnO deposition process was successfully characterized.

Introduction

Motivation

In a world highly dependent on non-renewable resources such as fossil fuels and natural gas, environmentally friendly and renewable energy sources have become exciting alternatives. An exciting area for the creation of innovative devices rests in the solar cell industry. With solar cells already present in the public sphere (homes, power plants, etc), the next step in solar cell technology is to make them more efficient and cheaper to produce/maintain in order to achieve more universal use.

Although researchers have produced silicon solar cells with efficiencies up to 24% (essentially the thermodynamic maximum)^[1], the costs to buy and maintain such solar cells still makes them unattractive to many consumers. Consequently, the percentage of total energy in the U.S. produced through solar devices, although steadily increasing, is less than 1%, behind energy produced through hydroelectric, biomass, and wind resources^[2].

Background

Solar cells are devices that convert sunlight into useful, electrical energy. A side view image that displays the specific design of the thin film solar cell in this thesis is shown below. Note that the image is not drawn to scale.

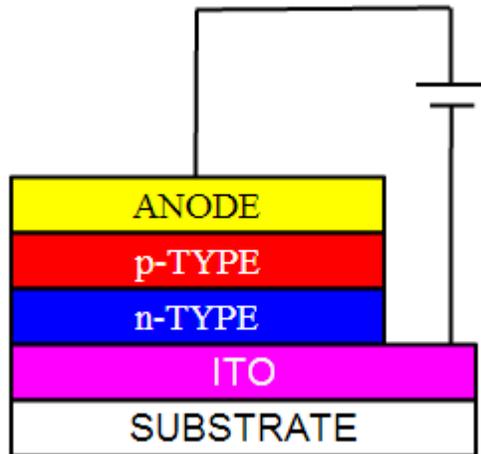


Figure 1. Side view showing the different components of a 2 layer solar cell design.

Referencing Figure 1 as an operational solar cell, sunlight would be allowed to travel from the bottom of the figure to the top. Therefore, sunlight would travel through the substrate (generally glass) and indium tin oxide (ITO) first. Once through the first 2 layers, sunlight would travel into the n-type semiconductor. Then, as the light hits the p-type semiconductor, an electron current is formed where electrons travel to the substrate (cathode) and through the circuit, thus creating a voltage across a load. Through this voltage, electrical work is created for applications such as cars, households, etc.

To explain the generation of the electron current, an energy diagram of the p-type and n-type semiconductors is displayed below in Figure 2. Note that n-type denotes the semiconductor that is rich in electrons while p-type denotes the semiconductor that is deficient in electrons.

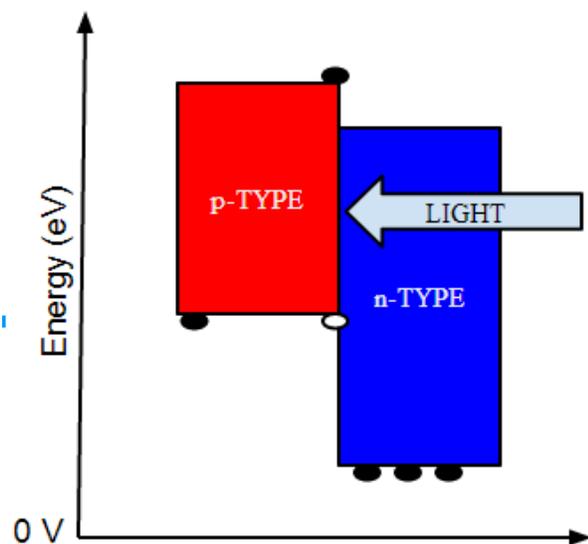


Figure 2. Band diagram for the p-n heterojunction.

Note that in Figure 2, the bottom edge of each box represents the energy in electron volts (eV) of the Highest Occupied Molecular Orbital (HOMO) while the top of the box represents the energy level of the Lowest Unoccupied Molecular Orbital (LUMO) of each semiconductor. The difference in the energies between the HOMO and LUMO is called the semiconductors' band gap. This band gap represents the amount of energy necessary to excite electrons in the ground state (HOMO) into the excited state (LUMO).

In the case of this specific solar cell design, the n-type semiconductor has such a large band gap that sunlight is not able to excite any of this semiconductor's electrons and thus continues to pass through the semiconductor (assuming the semiconductor is not opaque). But, once the sunlight is absorbed at the p-type, n-type semiconductor interface (also known as the p-n junction), it is able to excite a ground state electron in the p-type semiconductor into the excited state because of the significantly smaller band gap. As soon as this electron is excited, it leaves behind a positively charged hole (or a region void of a negative charge) and creates an electron-hole pair.

It is thermodynamically favorable for this recently excited electron to reduce its energy by relaxing into a lower energy state. Although it is energetically more favorable for the electron to recombine with its hole, the electron may also relax down to the LUMO level of the n-type semiconductor, releasing some of its energy. On the other hand, the hole will remain on the HOMO level of the p-type semiconductor because it is energetically more favorable for it to remain in the highest possible energy level. As a result, as sunlight continues to be absorbed by the p-n junction, some electrons are forced to travel through the n-type semiconductor by way of the LUMO to the cathode, and holes are forced through the p-type semiconductor to the anode.

The band gap of a semiconductor is an extremely important material characteristic when deciding on the design of solar cells. Because the interaction between sunlight and the p-n junction is necessary to create a current, sunlight must be allowed to pass through the n-type semiconductor. For this reason, in the solar cell design of this research, a large band gap is desired for the n-type semiconductor as a way of preventing sunlight from being absorbed before it reaches the junction. Another valuable characteristic of the n-type semiconductor is its ability to allow light to travel unimpeded through the n-type semiconductor. As a result, an ideal n-type semiconductor would avoid trapping or reflecting any sunlight that enters into the solar cell.

Choosing the optimum p-type semiconductor involves understanding the influences of its specific band gap. While this semiconductor's band gap should be small enough to allow for the largest percentage of the light spectrum to excite the electrons, the band gap should also be large enough to allow for the creation of a significant voltage across the load. As a result, the optimum band gap for a p-type semiconductor is shown to be in the range of 1.1 to 1.5 eV

(Shockley-Queisser limit).^[3] Choosing a material that is in this range is vital to maximizing the efficiency of a solar cell, yet note that it may be difficult to construct semiconductors that have characteristic band gaps within this range.

Electrodeposition

Electrodeposition is a technique in which the deposition of a material is achieved through electrochemical, reduction-oxidation (redox), reactions. These reactions are achieved in an electrochemical cell that consists of three electrodes as shown in Figure 3. Note that for depositions that require elevated temperatures, the cell is placed in a larger water bath.

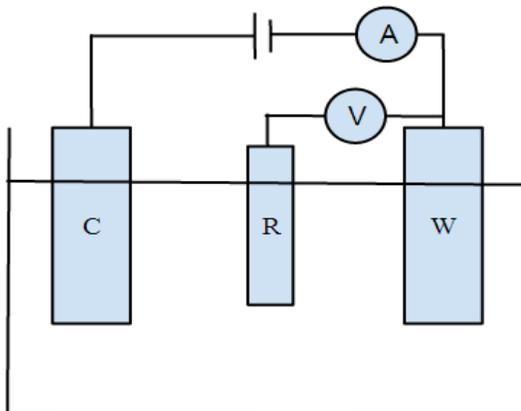


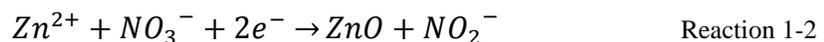
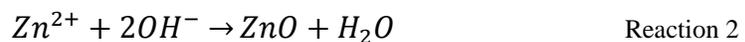
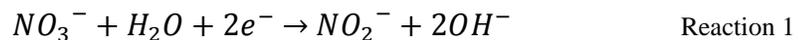
Figure 3. An electrochemical cell with three electrodes: a counter electrode (C), a reference electrode (R), and a working electrode (W). The ammeter (A) and voltmeter (V) are also present. Note that the horizontal line running across the cell represents the electrolyte solution level.

In this cell, the working electrode is where the deposition actually occurs. As a result, the working electrode is chosen to be a glass substrate covered with ITO. ITO is used because of its characteristically large electrical conductivity, its optical transparency, and its ability to facilitate the deposition of thin films. The reference electrode does not pass current and remains at equilibrium throughout the deposition process^[4]. The purpose of this electrode is to provide a reference voltage with respect to the working electrode as a means of creating the appropriate voltage difference (potential) across the cell. Finally, the counter electrode is used to complete

the external circuit of the electrochemical cell. Preferable counter electrodes are those that are stable and do not degrade during the deposition process.

Once electrodeposition has begun, a redox reaction will occur near the surface of the working electrode. Note the actual mechanism of the reaction and the resulting film compositions are specific to the ions in the solution. Nonetheless, if the voltage potential is positive, oxidation will occur near the surface of the working electrode. As a result, electron/s (depending on reaction stoichiometry) will be released and the electron/s will run through the external circuit. These electrons will then return to the electrolytic solution through the counter electrode. Note that reduction (balancing out the oxidation) will occur near the surface of the counter electrode with the electrolytes. As a result, maintaining the integrity of the counter electrode is essential for effective deposition at any length of time. If reduction is required at the working electrode then it is necessary to create a negative voltage potential across the cell. Note that this would promote oxidation near the surface of the counter electrode and the electrons will travel in the opposite direction with respect to the scenario with positive potential^[4].

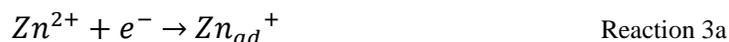
Three depositions are examined and conducted in this research endeavor. The first is the deposition of zinc oxide from a zinc nitrate precursor^[5].



Initially, nitrate ions in the water solution approach the working electrode on which they are reduced to nitrite ions (reaction 1). Next, the hydroxide ions formed in the reduction reaction

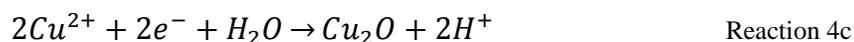
react with zinc ions to form zinc oxide (reaction 2). The net reaction for this process is shown as reaction 1-2.

The second is the deposition of the zinc nitrate precursor into zinc metal ^[6].



In this deposition, the zinc ions are reduced at the working electrode, initially forming an intermediate zinc cation that is adsorbed to the surface (reaction 3a). This intermediate is quickly reduced to zinc metal (reaction 3b). The net reaction can be represented by the reduction of zinc ions directly to zinc metal (reaction 3c).

The third is the deposition of copper sulfate and sodium acetate precursors into cuprous oxide ^[7].



Reaction 4a represents the reduction of copper (2+) ions to copper (1+) ions. The copper (1+) ions then react with the water in solution to form cupric oxide and protons (reaction 4b). The net reaction is represented by reaction 4c.

Novelty

It is important to note that there exists a large amount of literature for both the depositions of zinc oxide thin films and cuprous oxide films. Additionally, cuprous oxide has been successfully deposited on top of zinc oxide to form a heterojunction, although less literature exists for electrodeposition for both depositions. However, the formation of a zinc oxide thin film from the deposition and annealing of zinc metal is a novel design. This design, although more energy intensive than direct deposition of zinc oxide, provides a zinc oxide film with more desirable properties that are expected to improve the efficiency of the designed solar cell.

Goal

The goal of this research endeavor was the construction of a solar cell from abundant and green resources. Low process and energy costs were also desired in the production of these cells. Such design characteristics were implemented to take a step toward the possibility of mass producing solar cells. Another characteristic, although beyond the scope of this research, would have been the maximization of the solar cell efficiency. With larger efficiencies, lower production costs, and a smaller impact on the environment, there would be a greater incentive for the public to buy solar cells. In the end, such solar cell devices could be implemented as an alternative for automobile fuel and an alternative for household power.

Consequently, the reagents used in this research were nitrates, acetates, copper and zinc ions, and deionized water; all reagents were abundant, non-hazardous, and inexpensive. Electrodeposition and a current vs. voltage (I-V) test were also relatively inexpensive processes with respect to equipment and energy costs.

Overall, this project focused on:

- Optimizing the zinc oxide deposition
- Constructing a p-n junction between zinc oxide and cuprous oxide
- Testing efficiency characteristics of the solar cell device

Experimental Methods

Cleaning Procedure

Sonication was an exceptionally important technique in the cleaning of not only the glass substrates used in each experiment, but also in the creation of the precursor solution. First, in each experiment a sonication bath was created (100% DI water solution) in order to clean the glass substrate by removing any particles that had adhered to its surface. Second, the sonication bath worked to break intermolecular bonds in the precursor solution, thereby speeding the dissolution process of the specific precursors in DI water.

The overall cleaning of the glass substrate was a four step process. Note that for each step, the substrate was placed in a specific solution beaker that was then placed into the sonication bath. First, the substrate was sonicated in 0.2% Micro 90 soap solution for 10 minutes. Next, the substrate was immediately transferred from the soap solution into DI water solution that was also sonicated for 10 minutes. Then, the substrate was again immediately transferred to acetone solution and sonicated for another 10 minutes. Finally, after sonicating in acetone solution, the substrate was placed into a boiling IPA solution for a duration of 10 minutes on a hot plate with a set point of 195 °C. Note that for the IPA soak, the 10 minute duration only applies once the IPA solution has visibly begun to bubble. Once cleaning was complete, the substrate was dried with nitrogen gas to prevent streaking and then stored in a plastic container.

After completion of the substrate cleaning process, the precursor solution was sonicated for 10 minutes to ensure that the reagents (also referred to as precursors) had completely dissolved in the solution.

Zinc Oxide Precursor Preparation

The precursor solution necessary for preparation of zinc oxide (ZnO) consisted of a specific concentration of zinc nitrate hexahydrate as a solute in the DI water solvent. Note that several different concentrations of the zinc nitrate complex were utilized in either a solution volume of 230 mL or 210 mL. Tables 1 and 2 show the different masses of zinc nitrate that were dissolved in DI water to produce the respective zinc nitrate complex concentrations in solution.

Solute Concentration	Solute Mass
0.08 Molar	5.47 grams
0.04 Molar	2.74 grams
0.03 Molar	2.05 grams
0.01 Molar	0.68 grams

Table 1. Preparation for 230 mL solution.

Solute Concentration	Solute Mass
0.08 Molar	4.97 grams
0.03 Molar	1.86 grams
0.01 Molar	0.62 grams
0.005 Molar	0.31 grams

Table 2. Preparation for 210 mL solution.

Cuprous Oxide Precursor Preparation

The preparation of the cuprous oxide (Cu_2O) precursor is very similar to that of zinc oxide.

However the precursor solution volume was 50 mL. For production of the p-type semiconductor, copper sulfate pentahydrate was mixed with sodium lactate at a concentration ratio of 1:10.

Table 3 summarizes the necessary parameters of the precursor solution.

Solute	Solute Concentration	Solute Mass
Copper Sulfate	0.02 Molar	0.250 grams
Sodium Acetate	0.2 Molar	0.820 grams

Table 3. Preparation for p-type cuprous oxide.

Zinc Oxide Thin Film Formation

Electrodeposition

After the production of the precursor solutions was complete, the solutions (Table 1 and 2) were used in an electrodeposition cell to deposit zinc oxide onto the glass substrate. The cell consisted of three electrodes: the working electrode (glass substrate), the counter electrode (steel), and the reference electrode (Ag/AgCl). The three electrodes were placed inside of the precursor solution.

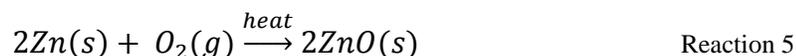
Note that two deposition methods were evaluated by changing deposition parameters (temperature, potential, and time) as shown in Table 4.

Solid Formed	Potential	Temperature	Time
Zinc Oxide	-1.0 V	80 °C	30 minutes
Zinc Metal	-2.0 V	25 °C	5 minutes

Table 4. Deposition parameters for deposition of zinc oxide vs. zinc metal. Note that the second method was the method used for the formation of the heterojunction.

Conversion of Zinc Metal to Zinc Oxide

Since the second method only produced zinc metal, it was necessary to convert the zinc metal into zinc oxide. Such a conversion was achieved through an exothermic reaction of the zinc metal with air at elevated temperatures as shown by reaction 5. The zinc metal was heated on a hot plate in a chemical hood exposed to air as the temperature on the hot plate was manually increased at 40°C per minute. Once the hot plate had reached its maximum temperature (540 °C) the sample was left on the hot plate until the zinc metal had appeared to have fully converted into zinc oxide. Since zinc metal is a dark gray color and thin zinc oxide is clear, full conversion was observed when it became possible to see the top of the hotplate through the film and substrate and no dark gray film was observed.



Cuprous Oxide Film Deposition

Initially, cuprous oxide was deposited onto bare ITO as a means of obtaining the parameters for the desired deposition results. Once the parameters were obtained, the cuprous oxide was deposited onto the zinc oxide thin film as a means of creating the p-n heterojunction. The major difference between the two methods was the magnitude of the potential across the cell. While the deposition of cuprous oxide on bare ITO had a potential of -0.05V with respect to the Ag/AgCl electrode, the potential for the heterojunction deposition was -0.1V as a means of inducing a larger driving force onto the much less conductive surface. The three electrodes for the deposition of cuprous oxide on zinc oxide remained consistent with the zinc oxide deposition except the working electrode was no longer bare ITO, but rather the zinc oxide film. Also note that the solution acidity was maintained at pHs between 5.8 – 5.9. Note that this pH was expected to not have an effect on the stability of the ZnO film.

Observing Conductivity

Measuring Resistance of ZnO

In order to measure the conductivity and resistivity of the films created, it was necessary to construct a circuit similar to the one illustrated by Figure 4. An external voltage source, Kiethley 2602A System Sourcemeter, was used to create a voltage sweep across the circuit and a computer was used to measure the corresponding current across the circuit. Note that the negative side (liquid metal, Gallium-Indium eutectic, EGaIN) was contacted with the film (light blue area) while the positive side (clip) was contacted with the bare ITO (white area). The voltage sweep was run from +1V to -1V and a current versus voltage graph was depicted by the computer.

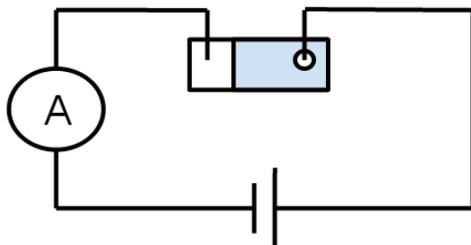


Figure 4. Schematic of the circuit used to measure current versus voltage.

Measuring Film Thickness

The ideal method of measuring the average thickness of a film was through Atomic Force Microscopy. The AFM provided data that allowed for the calculation of the average thickness of a film; it also provided a surface roughness estimate and displayed an image of the surface roughness based on changes in thickness across the surface of the film.

A second method of measuring average film thickness was by using Scanning Electron Microscopy. Using the Scanning Electron Microscope (SEM) to image a cross sectional area of

the film, the thickness of the film was determined by measuring by the distance between the top of the film and the top of the ITO. Using the SEM would require a very large number of images to be analyzed in order to get an estimate of the thickness across the entire film. Note that due to technical difficulties with the Atomic Force Microscope (AFM) in the Science and Technology Center at Tufts, all imaging data and film thicknesses for the following research was determined by using the SEM.

Results and Discussion

Note that the method involving the deposition of the zinc nitrate precursors directly to zinc oxide was not utilized for the construction of the heterojunction. The method of first depositing zinc metal and then converting the zinc metal to zinc oxide created thinner, more complete, and more homogeneous films (all three characteristics were expected to improve the efficiency of the heterojunction). So, although this second method was more energy intensive due to the use of a hot plate at its maximum temperature, it was a necessary sacrifice to potentially increase device efficiency. Therefore, the discussion of the direct deposition method was included in the appendix at the end of this research paper.

Zinc Metal Thin Film

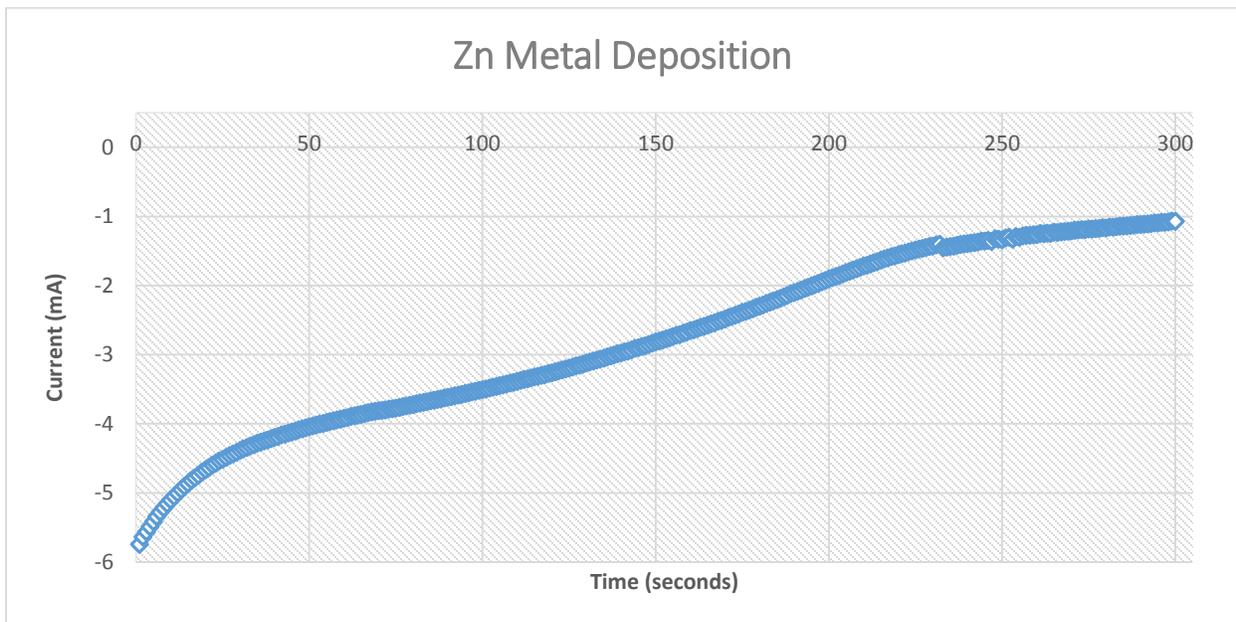


Figure 5. The current versus time graph for the deposition of zinc metal onto an ITO-coated glass slide.

Figure 5 shows a steady decrease in the magnitude of the current in the cell as the deposition progressed, which is consistent with theory. Initially, the cell current was very large because the

zinc ions (refer to reaction 3) had a very large driving force to react on the conductive ITO surface. As the ITO surface began to be completely covered with zinc metal, the driving force of the reaction decreased due to a decrease in the concentration gradient of zinc ions at the surface of the working electrode. Once the film was completely covered by zinc metal, the current appeared to approach a steady state value as the zinc ions would only be deposited onto zinc metal at the electrode surface.

One significant experimental observation with this deposition was that the zinc metal deposition had a larger driving force close to the edges of the ITO. It was visible that deposition began at the edges of the ITO film and that at the end of the deposition, the edges of zinc metal film were thicker as expressed by a darker color with respect to the rest of the film inside of the edges. Such a phenomenon led to complications in the design and testing of the heterojunction due to the decrease of conductivity in the thicker edge areas as described by the combination of Equations 1 and 2. This phenomenon is further discussed in the *p-n heterojunction* section of the discussion.

Zinc Metal Thin Film Formation

After electrodeposition, the zinc metal film was annealed to form a zinc oxide thin film by heating to 540 °C at a rate of 40°C per minute. It was important to heat the zinc metal film at a steady and relatively slow rate as a means of avoiding film cracking, which could have led to holes in the zinc oxide film. Avoiding such holes was very important because due to ITO's relatively large conductivity, any other deposition would be driven to the surface of the ITO (created by the cracks) as opposed to the zinc oxide film itself. Such a result was undesirable when a junction with zinc oxide and not ITO was preferred.

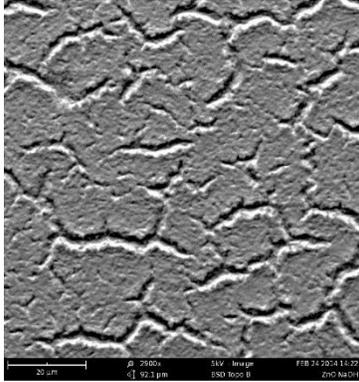


Figure 6. An SEM image of a zinc oxide film after annealing. Note the cracks on the film.

Heating at a rate of 40°C per minute did not completely prevent cracking from occurring, but it did appear to prevent the cracks from creating a hole in the zinc oxide to the ITO. As shown in the SEM image in Figure 6, the cracks on the zinc oxide film are gray in color. Note that the SEM images produced shades that were darker when an area was more conductive and produced lighter shades when an area was less conductive.

When the surface of the zinc oxide was scratched off to expose the glass/ITO, the scratch area was very dark (almost black) because that region was very conductive. Since the cracks in Figure 6 were not as dark as that observed with the crack, it was believed that the cracks only penetrated the surface of the film.

The crack's partial surface penetration has the potential to improve the solar cell efficiency. Once cuprous oxide was deposited on top of the zinc oxide layer, some cuprous oxide would have been deposited into the surface cracks. Such a phenomenon would have led to the formation of a significantly larger p-n heterojunction area, which, theoretically, would have led to a more efficient device design. Yet, although increasing the area of the junction could have increased the number of electron-hole pairs that existed, increasing the area could also have led to more area available for recombination. So, more of the excited electrons could have found a hole to rest in and would have never created a current in the external circuit. In the scope of this research, there was no evidence of the effect of these cracks on solar cell efficiency.

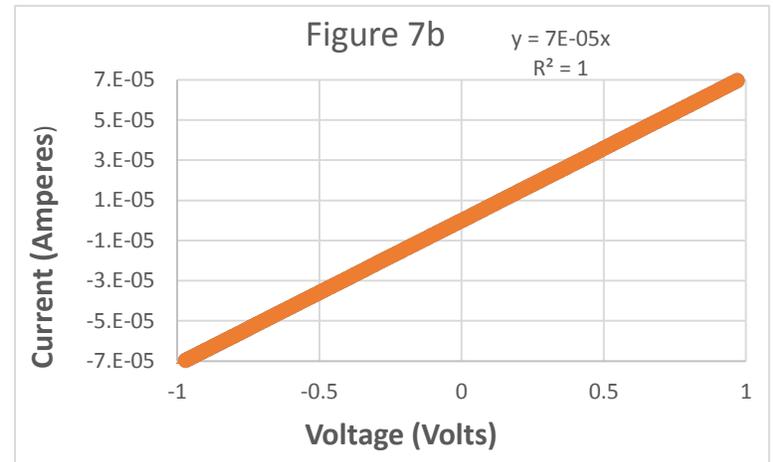
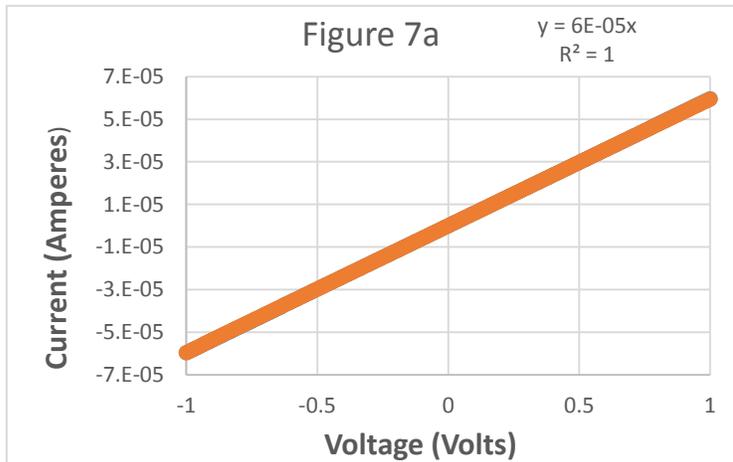


Figure 7. Curves that represented the relationship between current and voltage of a ZnO thin film at room temperature. Figure 7a showed the curve at one spot on the film while Figure 7b showed the curve on a different spot of the film. Note the curves were relatively identical.

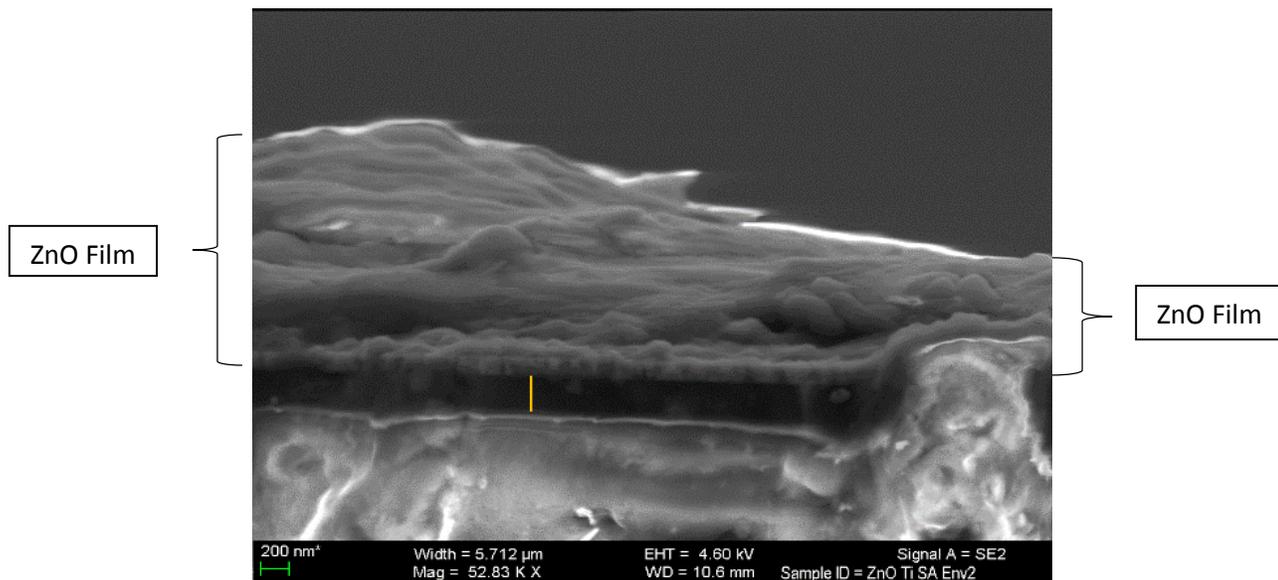


Figure 8. This SEM image depicts a cross-section of the zinc oxide film. Note that the thickness ranges from approximately 600 to 1000 nanometers. Note that the region depicted by the yellow line is the ITO layer and the ZnO film is the top section as depicted by the picture labels on the right and left. The substrate is the region below the ITO, which was not fully depicted in the image.

The curves in Figure 7 showed a perfectly linear relationship between the voltage sweep induced on the film and the circuit current measured by the ammeter ($R^2=1$). This linear relationship was consistent with the fact that the liquid metal and ZnO film shared an ohmic contact. Note that the

slopes of the two curves were in units of conductance (Ω^{-1}). As a result, the inverse of the slopes was taken to acquire the two resistances. With each resistance value, the resistivity and conductivity of each position on the film was calculated as shown in Table 5. Note that the contact area represented the surface area of the liquid metal that made contact with the ZnO film and the thickness (th) of the ZnO film was approximated to being $1\mu\text{m}$ as depicted in Figure 8. The maximum thickness was used as a means of analyzing the ‘worst case’ scenario of the film because using a larger thickness provided for a smaller value of conductivity for the zinc oxide film. Additionally, the equations for resistivity and conductivity are displayed below:

$$\text{Resistivity } (\rho) = \frac{R \cdot A}{th} \quad \text{Equation 1}$$

$$\text{Conductivity } (\sigma) = \frac{1}{\rho} \quad \text{Equation 2}$$

A (cm²)	th (cm)		
0.02545	0.0001		
Position	R (Ω)	ρ ($\Omega \cdot \text{cm}$)	σ ($\text{S} \cdot \text{cm}^{-1}$)
1	1.67E+04	4.24E+06	2.36E-07
2	1.43E+04	3.64E+06	2.75E-07

Table 5. A summary of all key characteristics of the ZnO film. Note that the contact area remained constant throughout the testing process and the thickness was approximated through SEM images.

Considering the typical conductivity range for semiconductors is between 10^{-8} to 10^2 Siemens per centimeter ($\text{S} \cdot \text{cm}^{-1}$)^[8], the conductivity of the ZnO film was on the insulating end of semiconductors ($\sim 10^{-7} \text{S} \cdot \text{cm}^{-1}$). Yet, such results were relatively consistent with other literature approximations of ZnO conductivity at room temperature ($7.261 \cdot 10^{-7} \text{S} \cdot \text{cm}^{-1}$)^[9]. Although such

a low characteristic conductivity may have appeared to impede the efficiency of the solar cell, it was believed that increasing the film's temperature would drastically improve its electric conductivity. Bae and Choi were able to acquire a ZnO film with a conductivity on the order of 10^{-4} ($S \cdot cm^{-1}$) when the film was at temperatures near $500^{\circ}C$ ($773K$)^[10].

Note that such a low characteristic conductivity would not only have played a role in the efficiency of the solar cell junction, but in the actual deposition process of the junction. With lower film conductivity due to zinc oxide formation, there was a smaller driving force in the deposition of cuprous oxide on top of the zinc oxide film. As a result, as discussed later in the report, the deposition current for the cuprous oxide deposition was significantly lower than that of the zinc metal deposition.

p-n Junction

In designing the heterojunction, it was necessary to develop the optimum deposition parameters for the process. As a result, before performing the deposition to create the heterojunction, a linear voltage sweep deposition was developed as a means of understanding the necessary characteristics of the deposition with varying cell potential, which was one important deposition parameter. As seen in Figure 8, the sweep was performed from a potential of 0.35 Volts to -0.8 Volts (with respect to the Ag/AgCl electrode). As discussed in the *Introduction*, a negative potential created the appropriate driving force for the cuprous oxide deposition. Also, as the magnitude of the negative potential increased, so did the current across the cell. Thus, it showed that the greater the magnitude of the negative potential induced on the cell, the greater the potential across the cell, and the faster the overall deposition of the cuprous oxide. However, one important phenomenon to take note of was that fact that increasing the magnitude of the

potential not only increased the deposition rate, but also influenced the nature of the deposition's film product. As shown in Figure 8, there was a slight plateau in current between approximately -0.2 Volts of potential and -0.3 Volts of potential. This plateau represented the beginning of the deposition of copper metal onto the ITO-coated glass slide. Then after the potential dropped below -0.3 Volts, the current began to steadily increase in magnitude again. Such an observation was extremely important in showing that when creating the heterojunction, it was necessary to avoid the deposition of copper metal since that material would not be desired in the formation of the solar cell. As a result, during the deposition of cuprous oxide, it was necessary to keep the magnitude of the negative potential below 0.2 Volts as a means of ensuring that no copper metal was formed during the process. Therefore, the potential chosen for deposition was -0.1 Volts with respect to the Ag/AgCl electrode, which, although producing a smaller current (and slower deposition), allowed for the deposition of the desired p-type semiconductor: cuprous oxide.

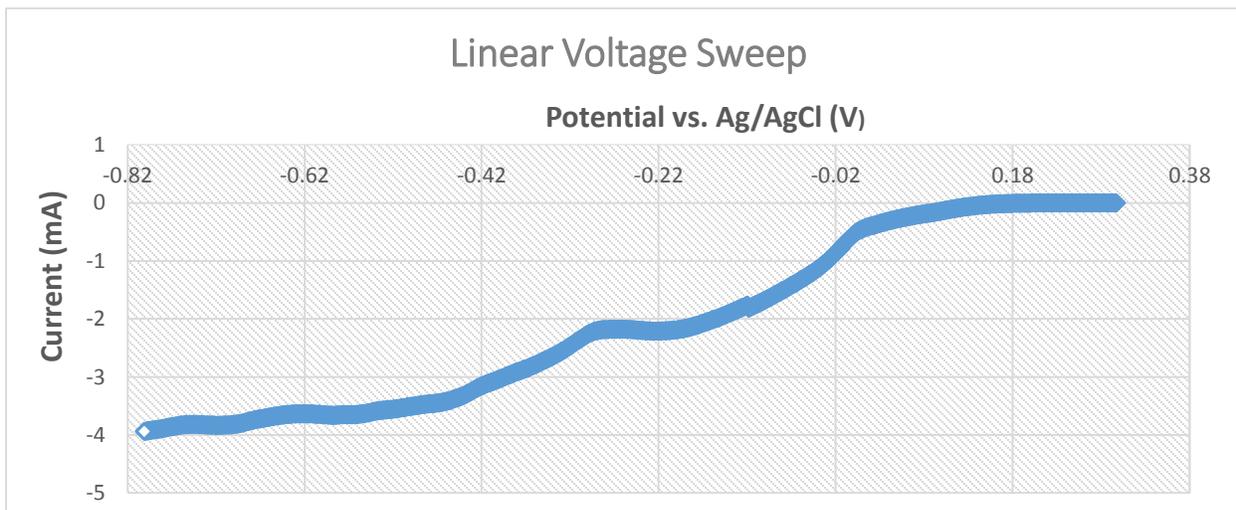


Figure 8. A plot of current versus potential during the electrodeposition of cuprous oxide onto an ITO-coated glass slide.

Once the correct deposition parameters were determined, the deposition of cuprous oxide on top of zinc oxide ran for 3 hours (10,800 seconds) in order to achieve a film of cuprous oxide that completely covered the surface of the zinc oxide film. Figure 10 shows a graphical representation of the deposition process. At the beginning of the process, the current across the cell was at a maximum value of approximately $-500 \mu\text{A}$. The magnitude of the current then began gradually dropping as the zinc oxide film was completely covered by cuprous oxide. The deposition then reached a steady state current of approximately $-50 \mu\text{A}$. Such a small current provided a negligible degree of deposition and thus once the current across the cell began to approach that small current value, the deposition process was terminated.

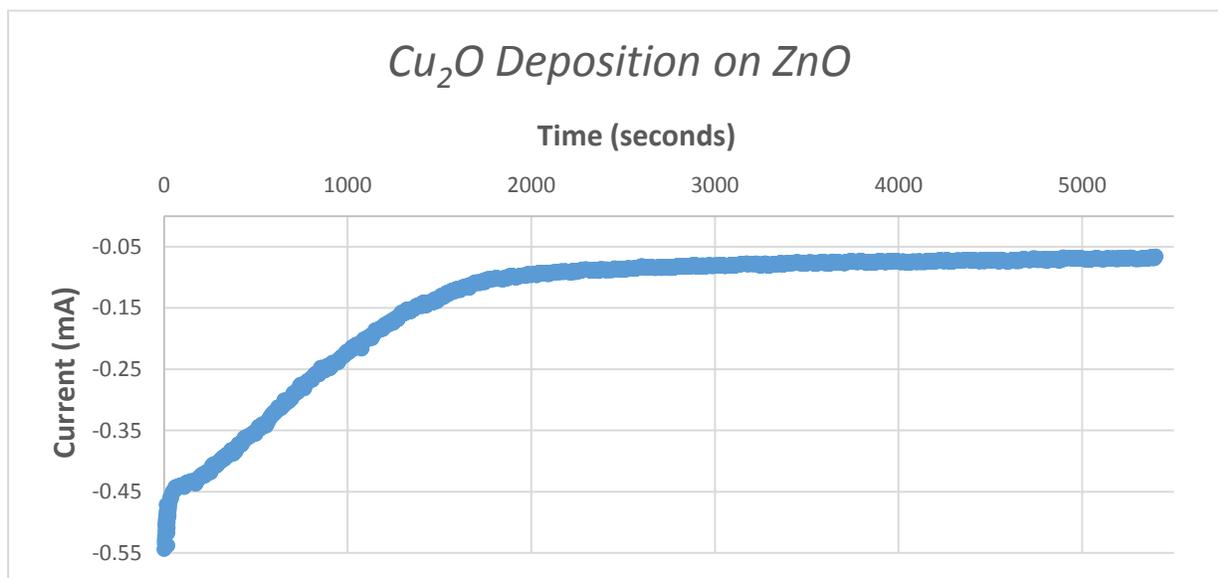


Figure 9. The current versus time graph for the deposition of cuprous oxide on top of a thin film of zinc oxide. Note that this figure showed only the first half of the 3 hour period of deposition. The second half data was not included because it was almost identical to that of the tail end of the first half data.

One key component of this deposition that varied greatly from that of the deposition of the zinc oxide film was not only the current observed, but also the amount of time necessary to achieve a complete coverage of the film by the deposited material. Such differences were in great part a result of the differences between conductivities of the two different surfaces of the working electrodes in each scenario. In the zinc metal deposition, the working electrode surface was

composed of ITO, which, being relatively conductive ($\sim 10^4$ S/cm)^[11], created a strong driving force for the deposition of the zinc metal. On the other hand, during the deposition of cuprous oxide, the surface of the working electrode was composed of zinc oxide, which had a significantly smaller conductivity ($\sim 10^{-7}$ S/cm). Thus the driving force for the deposition of cuprous oxide onto the zinc oxide film was significantly smaller and, consequently, the deposition took a significantly larger amount of time to execute. Note that because the cuprous oxide deposition was performed at elevated temperatures, the conductivity of the zinc oxide film may have been slightly larger, which would still correspond to a much slower deposition than that of the zinc metal deposition process.

Efficiency Testing

After development of the p-n junction, the solar cell device and p-n junction could be represented by the diagrams in Figures 10 and 11 respectively.

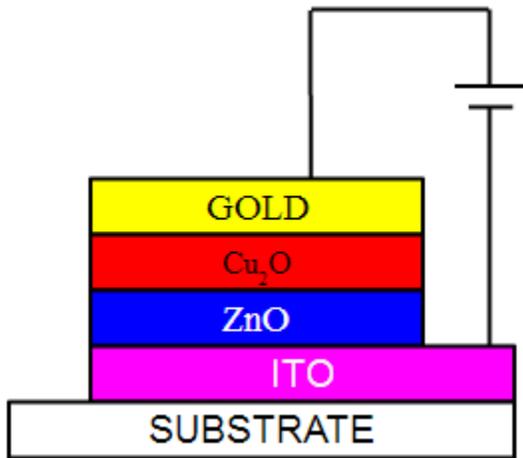


Figure 10. A side view depiction of the solar cell that was designed. Note that the pieces in the figure are note to scale.

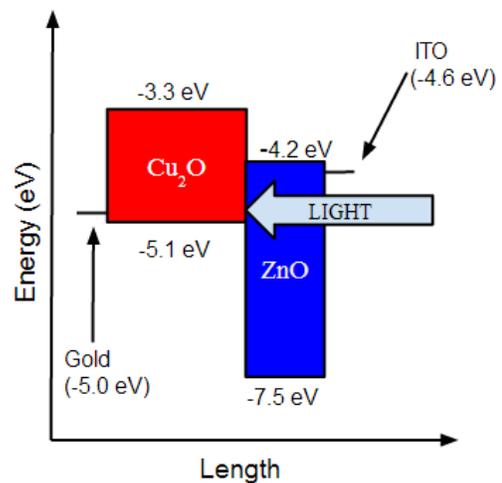


Figure 11. A band diagram representation of the energy levels (LUMO and HOMO) of the p-n junction of the solar cell that was designed.

Gold was used as the anodic material because it had a favorable work function with respect to the cuprous oxide; the band energy of the gold (-5.0 eV) was close to that of the HOMO level of the cuprous oxide (-5.1 eV). A similar comparison worked between the ZnO LUMO level (-4.2 eV) and ITO (-4.6 eV).

Two tests were available to test the performance of the device: one to test for the existence of a heterojunction and one to determine the efficiency of the solar cell. In the first test, as with the I-V test for zinc oxide, a voltage sweep was induced onto the solar cell. One of two potential results was expected to occur: a linear relationship or a diode-like relationship between the current (measured) and voltage (induced) would be observed. A linear relationship would have proved that the device was not performing like a p-n junction solar cell. This type of result would have been explained by two phenomena as a result of incomplete semiconductor deposition. The first phenomenon would have been the incomplete deposition of the zinc oxide film. With a more preferable route directly to the ITO (due to holes in the zinc oxide), cuprous oxide would have made contact with the ITO film during deposition. Travelling through only the cuprous oxide and ITO would have become the electrons' preferable route, thus making the zinc oxide film 'invisible'. As a result, the device would have acted like a single junction solar cell. The second phenomenon would have been the incomplete deposition of cuprous oxide onto the zinc oxide film. As with the first phenomenon, the electrons would have preferred to only travel through the zinc oxide and ITO films, this generating a linear curve representative of a single junction solar cell. In the end, either of these phenomena would have led to a linear I-V curve, which would have represented a failed attempt at a successful p-n heterojunction. On the other

hand, a diode-like relationship would have shown a successful p-n heterojunction as the diode relationship was characteristic of solar cells.

The second test of performance involved setting up the device under a solar simulator as a means of measuring and testing its efficiency characteristics. In order to successfully perform this test, the design of the solar cell, specifically the placement of the gold (from Figure 10) was altered as depicted by Figure 12.

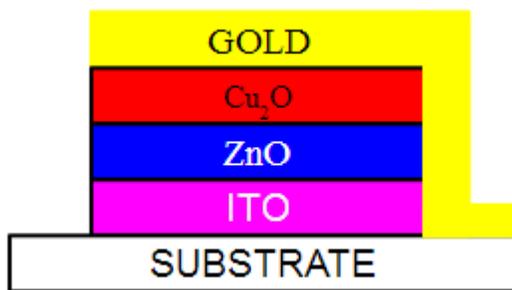


Figure 12. Theoretical representation of alternative gold deposition from the front/back view of the solar cell. Here the gold is not only deposited on top of the cuprous oxide film, but also on top of the substrate.

The purpose of such a design was to ensure the integrity of the semiconductors was maintained. In order to perform the test, the solar cell was flipped upside down because the light was shone from above and it was necessary to have the light travel through the substrate and into the heterojunction. Thus, using the Gallium-Indium eutectic was not feasible since it would have fallen off the surface due to gravity. Therefore, clips were used to not only hold the solar cell in place, but to also work to complete the circuit as depicted in Figure 10. Holding the top layer of gold with a clip was not feasible because it would have damaged the heterojunction. As a result, the gold deposition was bridged to the substrate so that the clip could secure the solar cell by clamping down on the gold/substrate component in Figure 12. Any current generated was able to flow through the entire bridged gold as a means of reaching the heterojunction.

The major drawback with creating the gold bridge mentioned above was a result of the difficulty involved in covering the edges of the zinc oxide film with cuprous oxide. As a result, on the edges of the zinc oxide film, there existed a direct contact between the gold anode and the zinc oxide. Therefore, electrons generated only travelled through the zinc oxide film and not the p-n junction. So, when the first test was performed, a linear relationship between current and voltage was observed.

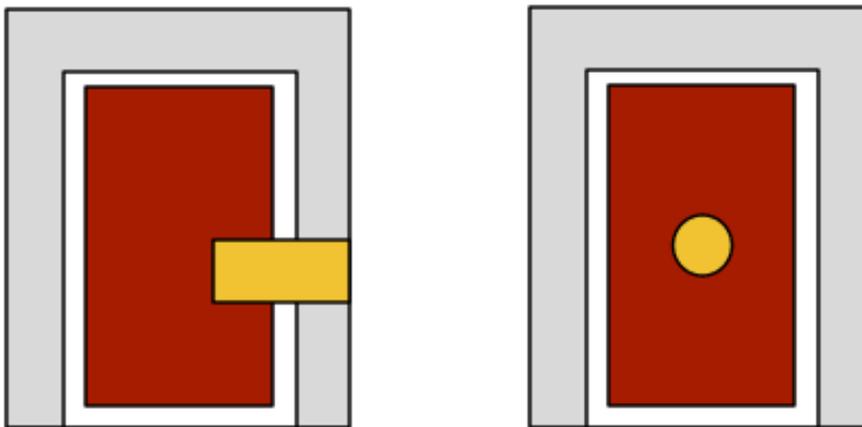
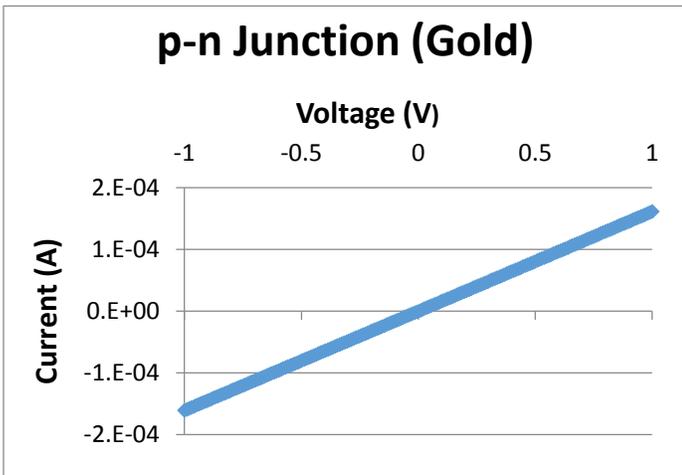


Figure 13. Left hand picture (13a). Design 1: Top view of the solar cell design with gold across the junction and glass films. Grey represented glass, white represented the zinc oxide film, orange-red represented the cuprous oxide, and the gold represented gold. **Right hand picture (13b).** Gold was deposited only on top of the junction.

Figure 13a represents the problem discussed above. The cathode clip made contact with the right hand side of the gold film that was deposited only on top of the glass slide. As discussed previously, such a contact was made as to avoid harming the two semiconductors. Ideally, when a current was generated, electrons would travel through the gold and then through the part of the junction that made contact with the gold. However, Figure 13a shows the experimental design of the solar cell. In this design, the gold did not only make contact with the junction, but also made contact with the zinc oxide. As a result, the current versus voltage relationship that was observed

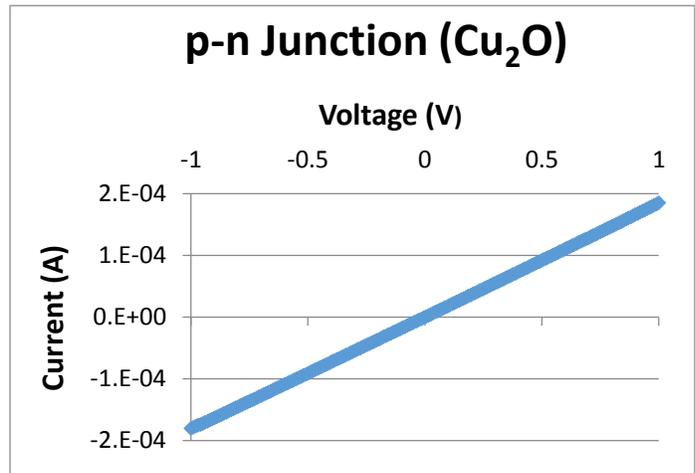
mirrored that of a single zinc oxide solar cell junction. Note that the variation of current values in Figures 14 and 7 were determined to have been a result of experimental variation (they were different by only a factor of 2).

To avoid such complications gold was deposited onto the center of the cuprous oxide film as depicted in Figure 13b. Such a method made it possible for the current to travel only through the p-n heterojunction. Note that the EGaIn was placed on top of the gold in order to complete the circuit. Thus, p-n junction behavior was expected to be observed.



Right hand picture (14b) I-V curve of a circuit with anodic connected created through the liquid metal and cuprous oxide surface.

Figure 14. Left hand picture (14a). I-V curve of a circuit with anodic connection created through the liquid metal and gold onto the cuprous oxide surface. **Right hand picture (14b)** I-V curve of a circuit with anodic connected created through the liquid metal and cuprous oxide surface.



However, as depicted by Figure 14a, the expected p-n junction did not perform like a p-n junction, but like a single junction solar cell as represented by the linear slope. However, because the current observed in the voltage sweep was small, it was concluded that no direct contact to the ITO film was made because the ITO's conductivity was much larger than the currents observed. This meant that one of the two semiconductors was not completely deposited,

thereby preventing any direct path to the ITO film. So, a second I-V test was conducted as depicted in Figure 14b. In this test, instead of contacting EGaIn with the gold anode, EGaIn was contacted directly to the cuprous oxide surface. If cuprous oxide was a complete film with no holes, the I-V curve would have exhibited a Schottky^[12] relationship because the EGaIn and cuprous oxide would not have had ohmic contact (due to non-favorable band energies). However, because a linear curve was observed, ohmic contact between zinc oxide and the liquid metal was observed. Thus, it was believed that the cuprous oxide film was the incompletely deposited semiconductor. As discussed before, such a result was a direct result of the low conductivity of zinc oxide, which made it difficult to deposit a complete film of cuprous oxide on top of the zinc oxide.

Conclusion

The deposition of zinc oxide was successful because a complete, transparent film was constructed through electrodeposition with a conductivity that was consistent with theory. However, a heterojunction was not successfully constructed due to the inability to deposit a complete cuprous oxide layer on top of a complete layer of zinc oxide. Consequently, cell efficiency testing was not conducted since a true solar cell was not constructed (due to the lack of the p-n junction). Yet, this thesis did reach some success as a novel design was created for the formation of thin, homogeneous, and complete ZnO films.

A possible future step in this research topic is the optimization of the cuprous oxide deposition onto zinc oxide. Two parameters could be changed to effect optimization. As noted in the *Procedure*, the solution pH for cuprous oxide deposition was acidic at 5.86 while it is also

possible to deposit cuprous oxide at a basic pH level of 12.2. Such an increase in pH could potentially speed up the deposition process. However, zinc nitrate would have to be added to the solution as a means of avoiding degrading the zinc oxide film (due to its potential instability at high pH's). The second parameter that could be optimized is the cell potential. Since it appeared as though copper metal began to form at -0.2V of potential, instead of using a potential of -0.1V, the magnitude of the potential could be increased to discover the maximum magnitude of the potential that would not induce the formation of copper metal. Additionally, a method of equalizing the deposition driving force across the entire ITO film when depositing zinc oxide would ensure uniform deposition of both zinc and cuprous oxide.

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Appendix A

Introduction to Cupric Oxide

At the beginning stages of this research, cupric oxide (CuO) was regarded as the ideal p-type semiconductor to be deposited to use in a photovoltaic device. Its band gap, at 1.2 eV was exceptionally favorable as depicted in Figure A.1.

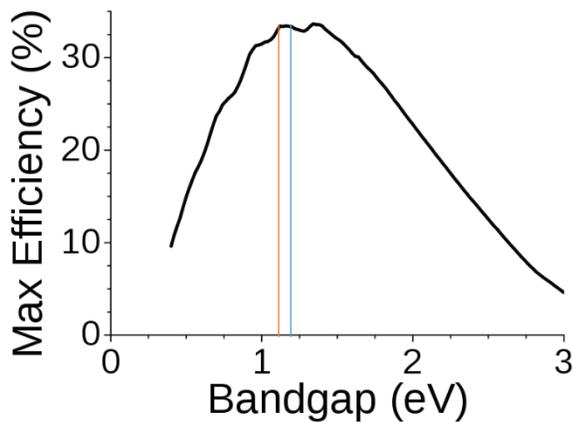


Figure A.1. A Shockley-Queisser limit curve representing solar cell efficiencies with respect to semiconductor band gaps. The red line represented a silicon semiconductor (1.1 eV) and the blue line represented a CuO semiconductor (1.2 eV).

The Shockley-Queisser limit not only showed cupric oxide to have the potential to produce a device with the largest theoretical maximum efficiency, but it also had essentially the same efficiency value as that of silicon. This was important because currently, the majority of solar cells used are those with a junction composed of a silicon semiconductor, thus, if CuO could have been produced with low economic and environmental costs, it had the potential to replace silicon.

Cupric Oxide Deposition

The reason that CuO was not used in this research as the p-type semiconductor was because electrodeposition of CuO was not only inefficient, but also non-replicable. The deposition parameters employed were shown in Table A.1.

Copper Acetate Concentration	0.01 mol/L
Sodium Acetate Concentration	0.1 mol/L
Solution pH	5.95 – 6.05
Solution Temperature	60 – 65 °C
Cell Potential	1.1 V

Table A.1. Electrodeposition parameters for the deposition of CuO. Note that pH, temperature, and potential were all very sensitive parameters that were strictly maintained at the values shown in the table.

These parameters initially helped deposit what appeared to be an incomplete thin cupric oxide film. Although having an incomplete film was not acceptable if cupric oxide was expected to be used as a p-type semiconductor, this was an acceptable start to the optimization of cupric oxide deposition. However, because there is widely accepted and proven mechanism for the deposition of cupric oxide, it was difficult to optimize its deposition any further. As a result, it was necessary to test whether the deposition was limited by reaction kinetics or mass transfer; a deposition was performed in which a step potential was applied to the cell. The step consisted of an ON condition (potential = 1.1V) and an OFF condition (potential = 0.5V). This OFF condition allowed the copper ions to approach the working electrode while the ON condition pushed the redox reaction to completion. In the end, the step potential method proved to be unsuccessful as very little deposition actually occurred on the working electrode. Finally, an attempt to re-perform the initial CuO deposition as shown in Table A.1 was unsuccessful as almost no deposition occurred. Thus, not only was optimization of the deposition not successful, but replication of previous depositions was also unsuccessful. Since deposition on conductive ITO was unsuccessful, deposition onto a ZnO film was not attempted due to the significantly lower conductivity of the ZnO film.

Although the deposition of CuO remains an innovative and interesting area of study for solar cell heterojunctions, the successful deposition of CuO was beyond the scope of this research. Much more time and resources would be needed in order to fully study the deposition techniques and the deposition process.

Appendix B

Zinc Oxide Deposition

As mentioned in the *Introduction* and *Experimental Methods* sections, there were two methods of depositing cuprous oxide onto ITO. The first method was extensively studied and discussed as a two-step process, which involved depositing zinc metal and then annealing the zinc metal to form a zinc oxide film. The second method involved directly depositing cuprous oxide through electrodeposition. Both methods held the same recipe as described by Tables 1 and 2. On the other hand, the deposition parameters altered the deposition mechanism as described by Table 4 and Reactions 1 and 2.

The disadvantages of depositing zinc oxide directly involved not only deposition parameters, but also deposition results. Parameter disadvantages involved the need for a much longer deposition, 30 minutes as opposed to 5 minutes, and elevated temperatures (80 °C). Both of these methods, not only increased the cost of deposition, but also the total process time (note that heating the solution to 80° C using a water bath took a significant amount of time).

The resulting disadvantages involved homogeneity, completeness, and amount of reagents used. This method consistently produced visibly less homogeneous films, which was not desired for the n-type semiconductor. Seemingly random areas were thicker than others on the films, which made it difficult to predict the average film thickness without using AFM. Additionally, it was more difficult to deposit complete zinc oxide films, so a larger concentration of reagents was used for the cell solution. As a result, compared to the two-step process, this method required significantly larger reagent concentrations to achieve completion.