STUDIES OF THE SYNTHESIS AND DEPOSITION OF Cu$_3$BiS$_3$ FOR USE IN PHOTOVOLTAIC DEVICES

by

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ABSTRACT OF THE DISSERTATION

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As the world’s climate continues to change, alternative energy is being adopted more and more. Solar energy is one extremely promising candidate to supplement our ever increasing energy needs. In order for it to be a viable solution, more efficient and less expensive solar panels must be made. While silicon solar panels are the current market leader their high manufacturing energy input and cost warrant looking into alternatives. Many thin film solar materials are being investigated such as CdTe, CIGS and CZTS, but all come with their own drawbacks. With a near ideal band gap, low toxicity and earth abundant elemental make up copper bismuth sulfide, Cu$_3$BiS$_3$, is a promising candidate for use in future photovoltaic devices. The research presented here details multiple methods to synthesize and deposit this material with an effort to keep the methods low cost, energy efficient and environmentally friendly.

Multiple low temperature solvothermal routes to synthesizing copper bismuth sulfide, CBS, have been developed. The resulting powders have been verified as pure
Cu$_3$BiS$_3$ via XRD peak matching. The precursor reactants tested for use were copper and bismuth nitrates, acetates, chlorides and hydroxides. L-cystine, L-cysteine, thiourea and CS$_2$ have all been tested for use as sulfur sources. Seven of these combinations produced pure CBS powders.

Two custom built benchtop reactors have been designed and fabricated with the aim of studying the possibility of a continuous flow reactor as a way to utilize these precipitation chemistries for making thin films of CBS. Heat and liquid flow simulations were performed in COMSOL multiphysics to assist in the reactor design process. The second reactor was designed to promote uniform liquid flow across the fluorine doped, tin oxide coated, FTO, glass. This reactor was also built with a temperature gradient transverse to the liquid flow so that the optimal temperature for the deposition of CBS could be evaluated. This reactor was also used to evaluate the deposition of CdS, an n-type semiconductor often used in thin film solar panels, onto FTO glass.

CBS thin films were also prepared via electrodeposition and thermal treatment. The solution used was a mixture of copper nitrate, sodium sulfite and sodium citrate tribasic dihydrate dissolved in DI H$_2$O and bismuth nitrate dissolved in ethylene glycol. To get the best coating it was found that the electrodeposition should be done at 1.2 V and last 5 minutes. Thermal treatment carried out in a 450°C tube furnace for 90 min in forming gas (95% N$_2$ with 5% H$_2$) along with sulfur vapor was proved best. No further treatment was required to obtain phase pure CBS coatings. This was verified with XRD peak analysis.

Optical absorption, microstructural, and photoconductivity data are reported for CBS materials made using the above techniques.
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Figure 4.18: 4.18A shows an NREL schematic106 of a typical CdTe solar cell that can be used as an analogue to ours. 4.18B shows a schematic of the CBS cell we fabricated. Neither is to 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CHAPTER 1: Introduction

1.1 - Executive Summary:

This work is directed at understanding and improving the production of pure copper bismuth sulfide (Cu$_3$BiS$_3$, “CBS”). This material, composed of earth-abundant elements, is a potential candidate for future low-cost solar panels. Low temperature methods to synthesize a CBS powder, as well as to deposit thin films of the material, have been developed. These low temperature, and thus low energy, procedures to make CBS could eventually lead to reduced processing costs for a solar panel. This would be especially beneficial in light of the expensive purification processes required for manufacturing silicon solar modules, which are currently the most common type.

To obtain CBS powders for testing, a robust, low temperature and simple solvothermal method was developed. This method has been shown to produce phase-pure CBS with a number of different chemical precursor choices, each having different pros and cons. This work has been submitted for publication,¹ and is described in complete detail in Chapter 2. CBS powders produced by two of the most favorable chemical combinations have been subjected to further physical characterization. This work has also been submitted for publication.²

We also worked to produce smooth thin-films of the material with solar device potential. To this end, two different methods were tested. We attempted to convert the precipitation processes to a deposition process via the use of a flow-through reactor. This work is covered in Chapter 3. A two-step electrodeposition and thermal treatment process, described in Chapter 4, was also developed.
The reactor was designed with the aim of diagnosing important thermal thresholds of the solvothermal deposition process. This work is currently under review for publication. While the diagnostic flow-through reactor met our design goals of imposing a temperature gradient and providing uniform flow across the reaction chamber, it ultimately failed to produce a layer of CBS. This was due to the previously discussed precipitation chemistries being incompatible with its design. However, the reactor was able to provide useful insight into the solvothermal deposition of CdS by finding the most favorable temperature for growth.

Our electrodeposition process utilizes mild conditions and low temperatures compared to previously discovered CBS electrodeposition methods. These characteristics are beneficial as they result in a less energy intensive and greener process overall. Of the two methods tested to produce smooth thin-films of CBS, our electrodeposition process has, so far, been more successful. We are preparing this work for publication.

Less energy intensive methods of production, earth-abundant source elements, and the use of less harmful chemicals could all contribute to low production costs for a CBS-based solar module. The present work has developed a number of chemistries and methods that could provide pathways to such modules. Lower production costs for solar modules would allow for lower prices for customers, higher adoption rates of solar energy, more widespread use of green energy and finally lower CO$_2$ emission rates.

1.2 - Global Perspective:

As time advances, problems with our current energy system become painfully evident. Oil and natural gas are pumped out of the ground with ever increasing difficulty.
Every year, developing nations and global powers all require more energy to sustain and improve their citizens’ way of life. Global climate change has become an important topic on the world stage as its effects, such as increased hurricane strength and frequency\(^3\) as well as flooding and droughts,\(^4\) are being seen in earnest. If the system does not change there are forecasts that predict by 2050 our CO\(_2\) emissions will be unsustainably high at 900 to 1000 parts per million by volume.\(^5\)

Thankfully, change is occurring. In the first half of 2015 the USA installed a total of 3888 MW of new energy infrastructure. Renewable sources constituted 70% of this, with 14% of the total being solar. Wind was 50.6% of the total while coal was a mere 0.8%. While the total generating capacity of solar energy installations in the USA is only 1.08% of the total,\(^6\) the trend is going in the right direction.

2013 was the first year that the world installed more renewable power generation than fossil fuel-based generation. This amount installed increased by 17% in 2014 to a total of 103 GW. In the previous two years the amount of installed renewable energy fell due to cheap oil prices. The increase last year is mainly due to the continuing sharp decrease in the cost of solar and wind energy. The amount of green energy generated on earth in 2014 is only 9.1% of the total, but this is up from 8.5% in 2013 and accounts for 1.3 gigatonnes of CO\(_2\) saved.\(^7\)

In 2006 there were approximately 12 million megawatt hours (MWh) of “green” energy bought voluntarily by customers and institutions in the USA, i.e. purchases that were not forced by governmental policy. By 2012 that number had increased to 48 million MWh\(^8\) and in 2013 it was up to 62 million MWh. Of the green energy systems purchased voluntarily in 2013, 75% was wind energy followed by landfill gas/biomass
and hydropower. Solar energy took only 1.0%. This may not be impressive on its own, but it is up from 0.2% in 2011 and 0.6% in 2012. These kinds of increases have led solar production volumes to increased 60-fold in the last decade.

Of the $1.7 \times 10^5$ terawatts (TW) of solar power that is continually striking the earth, only about 600 TW is actually absorbable, as most strikes in the middle of the ocean. This is, however, much larger than the 28 TW of power our civilization is projected to require even by 2050. With a sufficient number of solar modules with a sufficient efficiency rating we may generate all of the power we could ever need. Unfortunately, there are many issues holding back production and adoption of solar energy. Chief among them is economic interest.

Crystalline silicon solar modules are the most popular modules, holding an 87% market share in 2013. Their cost and price has been falling since 2008, the price dropping from 1.30 $/watt in mid 2011 to 1.00 $/watt at the years end alone. While this has been partially driven by Chinese manufacturers taking advantage of lax environmental policies and governmental subsidies it can also be attributed to innovations in the processing and production methods of silicon ingots and solar modules respectively. There was a period where thin film CdTe solar modules were less expensive than silicon modules, but this changed due to the rapid decrease in the price of silicon modules. Still, even with the cost reductions, the prices for solar modules are too high to motivate large scale adoption without subsidies. This is evidenced by the previously mentioned 1.0% of the USA’s voluntary sales in 2013.

Looking ahead, the United States Department of Energy has targeted a 0.50 $/watt module price for utility customers by 2020, a goal that seems achievable. However, the
cheaper solar modules are, the better it is for the customer, the solar industry and eventually the planet itself. With lower prices comes a larger adoption rate of solar panels and that leads to more green energy being produced.

While the price of silicon and other types of solar modules continue to drop, many alternative, low cost, solar cells are also being researched. It is our belief that using already inexpensive processes and precursors would allow for a greater price reduction in solar modules than simply refining expensive ones. If the research presented here continues, copper bismuth sulfide could be used to fabricate thin film solar panels at a cost less than silicon. The rationale for this will be covered in depth in Section 1.5.

1.3 - Background:

1.3.1 - Photovoltaic Device Fundamentals:

The seeds of the solar industry were first sown in 1905 when Albert Einstein discovered the photoelectric effect. His paper described what happens to a metal’s electrons when illuminated with short wavelength visible light. He described the effect as quanta of light, now known as photons, penetrating the surface of the metal and transferring their energy to electrons. This energy causes electrons to be elevated from their ground state, allowing them to escape the bulk metal. When illuminating an appropriate non-metallic semiconductor the energy of the excited electron can be used internally to generate a current and voltage instead of being ejected from the surface.

1.3.2 - Band Gap:

In a metal the photoelectric effect can only be observed when the incident photon has energy above the metal’s work function. The work function is a measure of how
much energy an electron requires to be freed from the crystal’s bonding forces altogether. The electron is allowed to escape the bulk of the solid in the photoelectric effect.

In the photovoltaic effect the electron stays within the bulk material, but is excited into a higher energy state within the structure. This phenomenon requires less energy to occur. In a semiconductor, where the photovoltaic effect might occur, the “band gap” is roughly analogous to the work function of a metal. A semiconductor’s band gap is the energetic gap between the valance electron band and the conduction band. The minimum amount of energy required for an electron to transition from the former to the latter is known as the band gap, \( E_g \). In order for the photon’s energy to be absorbed by an electron, its energy must be greater than or equal to \( E_g \). Light with a lower energy than \( E_g \) will pass through the material without causing a change in the electron’s energy state. When this promotion does occur, the electron will follow an energetically favorable path to return to the ground state. It is here that we can harness the energy stored in the excited-state electron.

**1.3.3 - Holes and Electrons:**

When the electron is excited by illumination of the proper wavelength and is promoted from the valence to the conduction band, a quasi-particle known as a “hole” is left in its place. Solar cell engineers go to great lengths to prevent this electron-hole pair from recombining. The main method used is to create an asymmetrical energy profile within the material itself. This energy profile will make it so the electrons are driven one way while the holes are pushed in the opposite direction. This is done mainly by doping the semiconductor material to create a p-n junction.
1.3.4 - Doping and the P-N Junction:

A p-n junction is created when p-type and n-type semiconductors are physically adjoined. The term p-type refers to a portion of the semiconductor where there are more positive charges, holes, than would ordinarily be present in the semiconductor. An n-type semiconductor has more negative charges, electrons, than normal. These portions of semiconductor are created by adding a small fraction of different elements into the lattice of the pure semiconductor in a process known as doping.

An example of a pure semiconductor, also known as the intrinsic semiconductor, is crystalline silicon. Silicon has four valence electrons. In order to implant positive charges in the lattice one needs to dope with an element with less than four valence electrons. Gallium, aluminum or boron, each with three valence electrons can be used for creating p-type silicon. Arsenic or phosphorous, each having five valance electrons, can be doped in to create n-type silicon.

At the junction where the two types of material meet, a zone known as the “depletion region” develops. As there are a greater number of holes in the p-type and a greater number of electrons in the n-type there is an internal driving force for these charge carriers to diffuse into the opposite region. This is due to electrical forces drawing the negative charges to the positively charged region and vice versa.

After this diffusion has taken place and equilibrium has been achieved, excess electrons fill the area of the p-type semiconductor next to the n-type and the same is true of the holes within the n-type. A “built-in” electric field results from this static charge displacement. This region is the only portion of the solar device that absorbs the light and converts it into usable energy. Because of this set distribution of charge, the excited
electrons will be attracted to the n-type side and the holes to the p-type. The electron hole separation can thus be maintained. A simple schematic of the energy distribution can be seen in Figure 1.1.

Figure 1.1: Schematic drawing of depletion region in a photovoltaic cell. Energy is represented on the Y axis.

1.3.5 - The Shockley-Queisser limit:

As previously mentioned, an incident photon’s energy will only be absorbed by an electron if the photon’s energy is greater than or equal to the semiconductor’s band gap. A small $E_g$ will allow more photons to be absorbed, but each resulting excited state electron will have a relatively small amount of energy. A large $E_g$ will absorb fewer photons but the resulting electrons will have a large amount of energy. This trade off was first analyzed in 1956 in an effort to find an $E_g$ that would have the highest theoretical efficiency and a material with that $E_g$.\textsuperscript{15} The definitive work on this subject was later completed in 1961. In this paper Shockley and Queisser found the link between the theoretical efficiency limit of a solar cell and its absorber material’s $E_g$.\textsuperscript{16} It was shown
that a maximum theoretical efficiency of 33.7% will occur when the $E_g$ is approximately 1.5 eV. The full curve of the Shockley Queisser limit is shown in Figure 1.2.\textsuperscript{17}

![Figure 1.2: The full curve of the Shockley-Queisser limit with selected material’s band gaps noted.\textsuperscript{17}]

It is important to note that the Shockley-Queisser limit is only applicable for single junction solar cells. For multijunction cells the maximum theoretical efficiency increases with the number of junctions. Under the irradiance of a single sun, with ideal conditions, a dual junction solar cell could be 42% efficient and a three junction cell could be 49% efficient. That this is for “the irradiance of a single sun” is an important distinction. One method to increase the efficiency of a solar cell is to use a system of mirrors of lenses to concentrate the incoming light onto a relatively small area. The resulting illumination is measured in the number of suns it would take to match its intensity. A stack with a theoretical infinite number of junctions could convert 68% of unconcentrated sunlight to electricity and 86% of concentrated sunlight under ideal conditions.\textsuperscript{18}
1.4 - Types of Solar Cells and their Latest Efficiencies:

While silicon-based modules dominate the solar industry there are many types of photovoltaics being researched and improved. Even within the silicon solar module category there is a variety. The crystalline solar (c-Si) module is the most advanced. The absorber layer of this module is cut from a large crystalline silicon ingot into 200-300 μm thick wafers.\(^{19}\) The highest efficiencies reported for these solar cells are 27.6% for concentrator cells and 25.0% for non-concentrator.\(^{20}\) While utilizing a concentrator cell results in higher efficiencies, it also results in a higher installation cost.

Amorphous silicon (a-Si) is also used to make thin film solar modules. This material is less expensive to fabricate than the crystalline silicon and has a higher absorption coefficient. This allows for thinner layers of a-Si to be used, 0.2 – 0.4 μm is typical.\(^{19}\) However, these solar cells are not as efficient as c-Si cells. The highest reported laboratory cell is 13.6% efficient.\(^{20}\)

CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) ("CIGS") is another material used in thin film solar modules. The \(x\) in the formula can be tuned so that the material can provide a specific band gap. The best efficiency rating for CIGS cells made in the lab was 20.3% at the very end of 2012,\(^{19}\) but commercial modules were only rated at 10% efficiency.\(^{17}\) In 2015, best-value lab CIGS solar cells have been rated at 21.7% efficient. Concentrator CIGS cells have been rated 23.3% efficient.\(^{20}\)

Cu\(_2\)ZnSnS\(_4\) ("CZTS") solar modules are of the thin film variety as well. As of 2012 the highest reported lab cell was 8.4%. It was fabricated via vacuum evaporation. Fabrication utilizing non-vacuum but high temperature precipitation produced a CZTS cell with an efficiency of 7.37%.\(^{21}\)
Cadmium Telluride (CdTe) solar cells are another relevant thin film technology. In 2013, they reached an efficiency rating of 19.6% in a lab setting\(^\text{22}\) and in 2015 they have increased to a 21.5% rating.\(^\text{20}\)

Dye sensitized solar cells are fabricated using cheap and abundant TiO\(_2\) in the form of nanoparticles. As TiO\(_2\) absorbs mainly in the ultra violet, UV, range they are sensitized with a dye that absorbs visible light. This dye, generally Ru-based, absorbs light which promotes one of its electrons from the molecules highest occupied molecular orbital (HOMO) to its lowest unoccupied molecular orbital (LUMO). The electron is then passed to the TiO\(_2\) and the circuit is completed through a metal back contact. These too have relatively low efficiencies, the highest being between 11.5% and 11.9% efficiency\(^\text{19}\),\(^\text{20}\) where they have remained since 2013.\(^\text{20}\)

Organic Photovoltaics (OPVs) are also an interesting upcoming type of solar cell. While they are environmentally friendly, made mainly from inexpensive carbon based molecules, they have some very bad pitfalls. Their 2015 efficiency is at 11.5%,\(^\text{20}\) only up from 11.1% two years ago.\(^\text{22}\) However, their largest issue is their longevity. Historically OPVs only last for 3-4 years,\(^\text{23}\) however recent studies have found projected lifetimes in excess of a decade.\(^\text{24}\) Still, c-Si solar modules sold in the marketplace are guaranteed to perform for 25 years, and generally last even longer.\(^\text{25}\)

The highest efficiency ratings of the photovoltaic world are by far the multi-junction concentrator solar modules. The best triple-junction concentrator cells have a efficiency rating of 44.4%,\(^\text{20, 22}\) while the four junction concentrators are now at 46.0%.\(^\text{20}\) The cells are generally made from GaAs, AlInP\(_2\), GaInP\(_2\), and AlGaInP and related III-V
alloys. The complexities of these solar cells lead to extremely expensive solar modules, only appropriate for large scale utility installations or NASA space projects.

A visual representation of the many types of solar modules and their highest laboratory efficiency ratings as of 2015 is shown in Figure 3 on the next page. The National Renewable Energy Laboratory, NREL, updates this chart every few months on their website.
Figure 1.3: The 2015 version of the yearly chart assembled by the National Renewable Energy Laboratory, NREL, of the best research cell efficiencies for the most promising solar cell technologies.20
Copper bismuth sulfide, CBS, is related to CIGS and CZTS as they all contain copper. We also anticipate utilizing similar device architectures to the aforementioned solar cells.

1.5 - Benefits of CBS over Competing Absorber Layers:

1.5.1 - Earth Abundance:

Copper, Bismuth and Sulfur are all relatively inexpensive and/or abundant elements compared with Cadmium, Tellurium, Indium, Gallium and Selenium. The latter elements are required for CdTe and CIGS solar panels, two leading thin film photovoltaic, PV, technologies.

<table>
<thead>
<tr>
<th>Element</th>
<th>$/Kg 2013</th>
<th>$/Kg 2014</th>
<th>World Reserves (Metric Tons)</th>
<th>Refinery/Mine Production 2014 (Metric Tons)</th>
<th>Abundance in Earth’s Crust (in $10^{-4}$ wt%)</th>
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<tbody>
<tr>
<td>Cu</td>
<td>7.49</td>
<td>7.09</td>
<td>700,000,000</td>
<td>18,700,000</td>
<td>14.3</td>
</tr>
<tr>
<td>Bi</td>
<td>19.20</td>
<td>25.11</td>
<td>320,000</td>
<td>8,500</td>
<td>0.123</td>
</tr>
<tr>
<td>S</td>
<td>0.076</td>
<td>0.105</td>
<td>&quot;Large&quot;</td>
<td>72,400,000</td>
<td>953</td>
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<tr>
<td>Cd</td>
<td>1.92</td>
<td>1.94</td>
<td>Unknown</td>
<td>22,200</td>
<td>0.102</td>
</tr>
<tr>
<td>Te</td>
<td>112.00</td>
<td>117.00</td>
<td>24,000</td>
<td>95</td>
<td>0.001</td>
</tr>
<tr>
<td>In</td>
<td>615.00</td>
<td>735.00</td>
<td>Unknown</td>
<td>820</td>
<td>0.061</td>
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<tr>
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<td>362.00</td>
<td>Unknown</td>
<td>1,110</td>
<td>14</td>
</tr>
<tr>
<td>Se</td>
<td>16.41</td>
<td>12.24</td>
<td>120,000</td>
<td>&gt;2275</td>
<td>0.083</td>
</tr>
</tbody>
</table>

Table 1.1: Summary of $/Kg from the last two years, total world reserves and abundance in Earth’s crust of various thin film PV related elements. Highlighted elements and numbers are applicable for our material.

Elemental price\textsuperscript{28} is summarized in Table 1.1. The cost volatility of the input materials could have a large effect on the cost of the finished modules as well. From 2004 to 2009 indium alone saw a 400% increase in price, reaching its peak in 2011 and then
coming down slightly. This price increase was mainly due to its widespread use in flat screen displays coupled with its scarcity.\textsuperscript{29,30}

China is a large producer of many of these scarce elements and supply lines are well formed. However, the Chinese government has recently been slowing their export of these elements. This will lower the availability and raise the cost for these elements and thus the solar modules made from them. Because of their greater abundance, the price of the elements needed for the copper bismuth sulfide should remain relatively stable as time goes on.

Not only will the lack of availability of indium and tellurium raise their prices, but such scarcity will eventually restrict the amount of product companies making CIGS and CdTe solar modules will be able to produce. It has been estimated that the amount of these elements will limit the generating capacity of CdTe solar modules to only 4\% of the current global electricity demand. For CIGS, it would be able to supply a mere 1\% of the total global energy demand.\textsuperscript{31}

Total worldwide reserves\textsuperscript{28} as well as abundance of the elements in the Earth’s crust\textsuperscript{32} are also summarized in Table 1.1. The relative abundance of the elements within CBS could allow a large amount of our solar modules to be produced without a significant increase in price.

Of the three elements in CBS, bismuth is the least abundant. It has, however, relatively few industrial applications compared to the other elements and thus its supply should remain stable. Moreover, potential methods of obtaining Bi, such as refining it directly from Bi ore, are not typically performed due to lack of demand. We currently rely on bismuth obtained as a byproduct of lead refining.\textsuperscript{28,33}
1.5.2 - Stoichiometric Material:

Our material is a stoichiometric compound, meaning that it will always form as $\text{Cu}_3\text{BiS}_3$. This will be a great benefit for future production as stoichiometry issues are present and detrimental to CIGS and CZTS performance. As previously stated, the formula for CIGS is $\text{CuIn}_{x}\text{Ga}_{(1-x)}\text{Se}_2$ where $x$ can be tuned to obtain a specific band gap. It is very difficult to ensure that the whole cell will consistently have the same stoichiometry with current large scale production methods.\(^{34}\)

The same is true of CZTS, whose formula is $\text{Cu}_2\text{ZnSnS}_4$. Having four elements in this type of compound allows many opportunities for non-desirable phases to be created.\(^ {35}\) If defects due to these factors occur in either material it can dramatically diminish the output of the solar cell. Thus, there is potential for many issues while attempting mass production of either type. Expensive measures would have to be taken to ensure adequate viability metrics.

Of course, CdTe is even simpler than our compound. However, we believe that the cost of the elements as well as the expensive vacuum-based equipment required to make CdTe places our solution-derived compound in a more attractive light.

1.5.3 - A Potentially Less Energy Intensive Production Method:

Another benefit of our chemistry is the low temperature processing. The maximum temperature of our process to form and grow CBS nanoparticles is published as 190°C.\(^ {36}\) Currently in the lab, we have lowered this temperature to 170°C with the same results as presented in this reference.

Silicon solar panels require enormous amounts of thermal energy in their manufacturing process. Tons of sand, $\text{SiO}_2$, must be melted and purified. The then-pure
Si is “pulled” from the molten bath to make the ingots which are cut and layered onto glass. The melting point of silicon is 1,414°C, meaning that the molten bath must be brought at least to that temperature to purify and manufacture ingots. In 2011, these purification and melting costs were shown to contribute approximately one third of the overall cost of the silicon solar module.\(^\text{10}\)

Production of CZTS involves heating to 300-590°C depending on the production method.\(^\text{21}\) Fabricating CIGS solar cells has a maximum temperature of 550°C. CdTe deposition requires heating to 350-450°C in a Cl atmosphere.\(^\text{34}\) These are all quite a bit higher than the temperatures required to synthesize our material in the flask.

Being able to manufacturer our material at a lower temperature will allow us to have a shorter Energy-Pay-Back (EPB) time. This is a metric that measures the length of time it takes for a solar module to generate the amount of energy it took to make the panel. Lowering this EPB at low cost is the only way our society will be able to transition to a zero carbon emission paradigm.

**1.5.4 - Low Toxicity of Elements and Material:**

Our elements are all non-toxic, unlike the cadmium or tellurium in CdTe cells or the arsenic in the gallium arsenide solar panels. Bismuth is uncommonly non-toxic for a heavy metal and is even an active ingredient in Pepto-bismol, a common over-the-counter stomach aide. Sulfur is present in L-cystine which is one of our precursors as well as a commonly ingested amino acid. Copper is present within our bodies to some degree at all times. Copper bismuth sulfide itself is a very stable mineral formed in nature and is non-reactive and non-toxic.
This lack of toxicity would be beneficial should any mishaps occur during manufacturing or when installing the solar panels. If a cadmium telluride solar panel or a gallium arsenide solar panel breaks or is damaged by fire then there might be extra difficulties due to the arduous process of hazardous materials clean up. This increases the overall life-cycle system cost. Even if the clean-up cost is directly borne by an insurance company, the solar module manufacturer’s rates will go up and that cost will be passed to the consumer.

Toxicity is also an issue at the end of life of the solar modules. All CdTe companies are required to have a recycling system in place to collect solar modules that are no longer usable. This adds a costly and time intensive step that has to be included in the upfront cost of the solar modules. Modules made with CBS could avoid such costs.

1.5.5 - Solution Processing:

Solution processing should allow our material the ability to be deposited in roll to roll processing. This is a cheap, reliable and energy efficient method to scale up production of solar modules. This method is currently utilized to great effect in dye sensitized solar cells.37

1.5.6 - Higher Theoretical Efficiency than Silicon:

Silicon is without question the current leader in the solar market. It is also the material that has received the most research backing. Its $E_g$ is 1.1 eV. CBS has a generally agreed upon $E_g$ of $\approx$1.4 eV,33, 38, 39 which translates to a slightly higher theoretical efficiency limit. The theoretical efficiency of a solar material can be derived from the previously explained Shockley-Queisser Limit. The rationale for this argument is shown graphically in Figure 1.4.40
1.6 - Review of Copper Bismuth Sulfide Properties and Synthetic Pathways:

1.6.1 - History:

First described in 1805, CBS is a bismuth sulphosalts of copper. Its chemical formula was analyzed and verified as Cu$_3$BiS$_3$ two years later in 1807. As it was originally mined from Wittichen in Baden Germany, the mineral’s original name of kupferwizmutherz was changed to wittichenite.$^{41}$

1.6.2 - Physical properties:

The crystal structure of CBS is orthorhombic with $a = 7.723$, $b = 10.395$ and $c = 6.716$ Å with a density of 6.19 g/cm$^3$. The mineral is of the space group P2$_1$2$_1$2$_1$ with a Z value of 4. A projection of the room temperature wittichenite structure on (001) is shown in Figure 1.5.$^{41}$
At higher temperatures the crystal structure changes due to the Cu atoms shifting in their lattice positions. The first of these transitions begins at 118°C when wittichenite transforms to an intermediate polymorph with symmetry Pn2₁a. The atoms continue to shift until about 160° where they stabilize until the second high temperature form of CBS is formed at 190°C. In atmosphere, wittichenite does not begin to break down until the temperature reaches about 300°C. This is actually experimentally confirmed in Section 2.3.2.2.

As we will need to dope any material used to make a solar cell it is important that it displays solubility for various elements. It has so far been confirmed that lead, silver and iron are all soluble within CBS. Not only this, but antimony can be substituted for the bismuth in varying quantities. When all of the bismuth has been switched out for antimony, the formula now being Cu₃SbS₃, it is known as skinnerite.
1.6.3 - Electrical Properties:

As previously mentioned, at higher temperatures the positions of CBSs’ Cu atoms begin to shift. This allows CBS to become an ionic conductor of Cu at temperatures above 135°C.\(^{43}\) However, we are not particularly interested in the minerals ionic conductivity. Our success rests solely on CBS’s conductivity with respect to electrons and holes.

CBS is naturally a p-type semiconductor which is thought to be due to Cu deficiencies in the lattice.\(^{42}\) This is beneficial as, unlike silicon, we will only have to dope in elements to make it an n-type material. It displays a Hall mobility for holes of 4 cm\(^2\)/Vs and a free carrier concentration of 2 x 10\(^{16}\) cm\(^{-3}\). Its excess carrier concentration is on the order of 10\(^{17}\) cm\(^{-3}\) when exposed to light.\(^{45}\) The electrical conductivity of CBS has been reported to be 10\(^{-2}\) to 10\(^{-3}\) Ω\(^{-1}\) cm\(^{-1}\)\(^{42}\) or, more recently, as 0.03 Ω\(^{-1}\) cm\(^{-1}\). Thin films of CBS have been shown to have an electrical resistivity of 84 Ω cm, but can be reduced as low as 9.6 Ω cm via annealing in an H\(_2\)S atmosphere.\(^{38}\) The mobility lifetime of photogenerated carrier pairs is estimated to be 3 x 10\(^{-6}\) cm\(^2\)/V. While this is inferior to silicon or CIGS it could be improved by optimization of heat treatment or deposition processes.\(^{46}\) The material’s work function is 4.37 ± 0.04 eV.\(^{45}\)

1.6.4 - Optical Properties:

Copper Bismuth Sulfide, as previously mentioned, has a generally agreed upon E\(_g\) of 1.4 eV.\(^{33, 38, 39}\) This band gap is direct, but an indirect band gap with an E\(_g\) of 0.65 eV has been reported once,\(^{46}\) although it is not likely real. Absorption from an indirect band gap would be easily overshadowed by that from the known direct band gap and so this will be ignored for the purposes of this dissertation. Some have measured the band gap to
be as low as 1.24 eV.\textsuperscript{47} It is likely that these inconsistencies are due to variation in how people analyze their tauc plots. It has also been shown that the $E_g$ of CBS can be tailored anywhere between 1.86 eV and 1.42 eV.\textsuperscript{48}

The optical absorption coefficient of CBS at 650nm (1.9 eV) has been shown to be $10^5\text{cm}^{-1}$.\textsuperscript{46} The absorption has also been measured at 500nm (2.48 eV) resulting in an absorption coefficient of $4 \times 10^4\text{cm}^{-1}$.\textsuperscript{42} These very high values of absorption will allow solar cells made with our material to utilize very thin layers of CBS. This will allow for further monetary savings as well as using less of the world’s bismuth supply.

1.6.5 - Synthetic Pathways to make CBS:

There are many research groups excited by the prospect of low toxicity, earth abundant and high efficiency solar cells and a number of compounds are being studied. Among these, there are several groups looking into how to efficiently make CBS.

The methods to make CBS thin films include the annealing of chemically deposited films of CuS laid onto a Bi$_2$S$_3$ film.\textsuperscript{42} Reactive sputter deposition of CuS and Bi onto a hot substrate and then annealing in H$_2$S has been performed.\textsuperscript{38} Chemically deposited CuS thin films have had Bi evaporated onto them, heated to 300$^\circ$C in a nitrogen atmosphere and formed thin films of CBS.\textsuperscript{46} Heating a sputter deposited copper bismuth metal precursor film in H$_2$S also creates the desired product.\textsuperscript{49} This also works with electroplated Bi and Cu metal precursor films in the presence of elemental sulfur vapor.\textsuperscript{50} Elemental sulfur vapor will also aid to create CBS when co-evaporated with the metallic elements.\textsuperscript{51}

Methods to produce nanoparticles and nanorods of wittichenite have also been studied. Mixing copper chloride, bismuth chloride and thiourea in ethanol and heating to
160°C for 10 hours will produce nanorods. After heating copper (II) acetylacetonate, bismuth chloride and thioacetamide in ethanol to 170°C and leaving for 8 hours a nanopowder will be obtained. A hot injection method to make a nanopowder of CBS can be performed by mixing copper acetylacetonate, bismuth nitrate and oleylamine and heating to 220°C before injecting an oleylamine solution containing dissolved elemental sulfur. A solvothermal method to produce flower type nanorods requires mixing copper chloride, bismuth nitrate and L-Cystine in DMF and heating to 200°C for 16 hours. This last method is most similar to one method the Birnie group utilizes to synthesize our CBS nanoparticles.

1.7 - Scope of Dissertation:

The dissertation is broken into three main chapters dealing with different, but connected, branches of the research. Chapter 2 deals with our efforts to discover more synthetic pathways to produce pure CBS powder with our low temperature solvothermal method. Some of these synthetic pathways have been used in two generations of custom built chemical reactors meant to deposit the material onto a layer of fluorine doped tin oxide coated, FTO, glass. This transparent conducting oxide coated glass is important for solar cell function, as it allows light into the device, as well as allowing for conduction of electricity. These deposition attempts, as well as the design and testing of the reactors themselves will be covered in Chapter 3. In Chapter 4 the deposition of CBS via electrodeposition onto FTO glass and thermal treatment will be discussed. The final chapter, Chapter 5, consists of conclusions and proposals for future work.
CHAPTER 2: Studies of the Synthesis of Cu$_3$BiS$_3$ via Solvothermal and Solid State Methods

2.1 - Introduction:

Copper bismuth sulfide (Cu$_3$BiS$_3$, “CBS”) has drawn attention due to its composition of low cost, non-toxic elements.$^{33,55}$ It also has a band gap of approximately 1.4 eV,$^{33,38,39}$ which is within the ideal range for a photo absorber to have the maximum device efficiency possible.$^{17}$

Known in nature as wittichenite,$^{41}$ the semiconductor has been made in numerous ways. Multiple methods to make thin films$^{38,42,46,49-51}$ as well as nanocrystals,$^{53}$ nanopowders,$^{52}$ nanorods$^{44}$ and nanoflowers$^{54}$ have been reported, including our own group’s previous work on solvothermal synthesis of phase pure CBS nanoparticles.$^{36}$

A recent review argues that a simple “heat-up,” non-injection synthesis is imperative to scaling up production of nanomaterials.$^{56}$ We believe the method presented here to be the simplest and most robust to make CBS nanoparticles so far. We have demonstrated its successful use with six more combinations of reagents that synthesize phase pure copper bismuth sulfide.

Attempts have also been made for solid state synthesis of CBS thin films via sintering of lab made CuS and Bi$_2$S$_3$. While successfully making the mineral, the sintering was not complete enough to deem the results “films.”
2.2 - Studies of in Situ CBS Synthesis:

2.2.1 - Experimental:

2.2.1.1 - Reagents:

All reagents used in the experiments are summarized below. All were purchased and used as received. Attempts were made to purchase the least expensive atom source to demonstrate that small impurity quantities are not important to the outcome.

The Cu(NO$_3$)$_2$ • 3H$_2$O (99-104%), BiCl$_3$ (99.9999%), Bi(CH$_3$COO)$_3$ (99.99%), L-Cystine (≥ 99.6%), Thiourea (99%), and CS$_2$ (≥ 99%) were all purchased from Sigma Aldrich. The Bi(NO$_3$)$_3$ • 5H$_2$O (98%), Bi(OH)$_3$ (≥ 80% Bismuth) and L-Cysteine (99+) were supplied by ACROS Organics. The CuCl$_2$ • 2H$_2$O (99+ %) and Cu(CH$_3$COO)$_2$ • H$_2$O (98-102%) were both manufactured by Alfa Aesar. Both the ethylene glycol (max 0.2% H$_2$O) and the methanol (≥ 99.8%) were made by Fisher Scientific.

2.2.1.2 - Preparation:

6 mmol of the copper salt, 2 mmol of the bismuth salt and 12 mmol of sulfur atoms were mixed into 100 mL of ethylene glycol in most cases. The exceptions are for the nitrates and L-cystine, acetates and thiourea as well as hydroxides and thiourea combinations, where the concentrations of the reagents were doubled. It is important to note that we need double the amount of sulfur atoms than would be required for the stoichiometry of the material. This means that for L-cystine and CS$_2$, molecules with 2 sulfur atoms each, 6 mmol of the reagent was used. For thiourea and L-cysteine, each molecule containing one atom of sulfur, 12 mmols of the molecule contained 12 mmols of sulfur. Some experimentation was done with stoichiometrically balanced amounts of
sulfur but all were unsuccessful in creating Cu$_3$Bi$_3$S$_3$. The chemical structures of the 
chosen sulfur sources are shown in Figure 2.1.

Previous experiments,$^{36}$ found that the CBS precipitation reaction was successful 
when the copper and bismuth salts were prepared as separate solutions and stirred 
overnight with the sulfur source before mixing together and heating. With one exception, 
the present work has shown that good precipitation can be achieved when all reagents are 
added at once and heated immediately according to the descriptions below. The only 
exception is with CS$_2$ which does need to be stirred overnight to disperse it thoroughly in 
the ethylene glycol. Failure to do so results in the liquid CS$_2$ separating out and boiling 
on top of the ethylene glycol solution.

Reagents and the solvent were added to a two necked 250 mL round bottom flask. 
One neck held a thermometer while the other was affixed to a reflux tube with cold water 
running through it. The reaction chamber was under atmosphere during the whole heating
process. The liquid was heated with a Glas-Col 180W Fabric Heating Mantle and Control package over a stir plate. The temperature was raised to 170± 5°C and stabilized there for four hours. The sample was then allowed to cool to room temperature before being centrifuged, rinsed with methanol and dried in a rotary evaporator to obtain a powder.

When doped samples were made, nitrate salts and L-Cystine were used. When 1% Zn CBS (by molar ratio) was synthesized, only 99% of the required copper was added. For amounts less than 0.1%, it was not feasible to take out the called for amount of copper, and so the zinc was simply added to the same amount of copper nitrate.

2.2.1.3 - Instrumentation:

Scanning electron microscope, SEM, images were taken with a Zeiss Sigma Field Emission Scanning Electron Microscope.

X-Ray Diffraction, XRD, patterns were recorded using Cu Kα radiation with a wavelength of 1.54 Å generated with a PANalytical X'Pert PRO using MDI Data Scan as a controller. The scan range was 12.5° to 67.5°, with a step size of 0.0131° scanning at 0.037 °/s. Typically, only 15° to 60° are displayed in the figures below, as all major peaks are found in that range.

Samples were prepared for XRD by coating a microscope slide with a uniform layer of powder thick enough to be opaque when held up to a light source. This powder was applied to the glass by mixing it in methanol to create a slurry and then dripping it onto the slide. The slides were then placed on a bed of adhesive putty housed in a PANalytical 46mm dense sample holder and run in θ/2θ mode.

While this method is quick, easy and requires only a small amount of sample, it can be slightly less geometrically accurate as it allows for the possibility of a slight 2θ
peak shift. This is due to the fact that if the glass slide is not arranged properly it will be at a slight angle or height offset. This will slightly alter the 2θ values of the peaks in a systematic fashion. When necessary, we adjusted for this in the digital files by applying a uniform peak shift to the 2θ data obtained from the scan during fitting. Typical correction factors were approximately ±0.1° applied to all data points. This step was not required for most samples, though. No other data adjustments were carried out. XRD is useful for identification of component phases and great care must be exercised when detailed structure fitting is performed.

2.2.2 - Results and Discussion:

2.2.2.1 - Discussion:

There is extensive literature in which disulfides are reduced or thiols deprotonated in the presence of metal ions to give metal thiolate compounds and these, in turn, also have an extensive literature associated with alkyl/aryl migration to give metal sulfide solids.\textsuperscript{57-60} An example is shown in Reaction 1.

\begin{equation}
\text{M(SR)}_x \rightarrow \text{MS}_{x/2} + \frac{X}{2} (\text{SR}_2)
\end{equation}

The sulfur containing molecules that we attempted to use in this synthetic method were chosen for a variety of reasons. L-cystine was used as previous research has shown that a combination of it and nitrate salts will create phase pure CBS.\textsuperscript{36} L-cysteine is the monomer of L-cystine, so the similarity in bond structure was thought to give it a strong chance of successful CBS synthesis. Thiourea has been used previously with a similar method to make CBS\textsuperscript{44} and so it was also attempted. CS\textsubscript{2} was chosen as it is a commonly used sulfur source.\textsuperscript{61-65}
Experiments with D,L-homocystine, L-homocysteine, methionine and diphenyl disulphide were run with nitrate salts as the Cu and Bi sources. All were unsuccessful in making Cu$_3$BiS$_3$ and thus attempts were not carried out with the full range of metal salt precursors.

Each individual combination of reagents had characteristic color changes throughout the heating process. Included is a summary of the reaction stages of all combinations that produced CBS, save for nitrates and L-cystine, which was covered in a previous paper. Of note is that the previous research indicated that the nitrates and L-cystine solution needed to be heated to 190°C for 4 hours in order to synthesize CBS. We have accomplished the same results by heating to 170°C for 4 hours.

Many of these combinations synthesized pure CBS, while others created the target mineral as well as some notable impurities. Combinations that produced no CBS are not detailed. A summary of all findings, the combinations of salts and sulfur sources, the concentrations attempted and products, can be found in Table 2.1.
2.2.2.2 - Pure CBS Synthesis:

2.2.2.2.1 - Nitrates and L-Cysteine: Upon mixing the L-cysteine with the transparent blue Cu(NO$_3$)$_2$ solution, the white amino acid powder immediately turned black. The transparent colorless Bi(NO$_3$)$_3$ solution turned yellow upon mixing with L-cysteine.

When heated the mixture turned an avocado green, but turned black at 126°C. This was accompanied by brownish yellow outgassing believed to be a mixture of H$_2$O, HNO$_3$, NO$_2$, and H$_2$. At 141°C the solution turned blue and at 145°C there was a second outgassing as the solution turned black a final time.

2.2.2.2.2 - Acetates and L-Cystine: The Cu(CH$_3$COO)$_2$ • H$_2$O and L-cystine solution was a teal blue, opaque with traces of undissolved starting materials. The Bi(CH$_3$COO)$_3$ and

<table>
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<th>Cu and Bi Salt</th>
<th>Sulfur Source</th>
<th>CBS Produced</th>
<th>Additional Phases</th>
<th>Concentration (theoretical CBS)</th>
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</thead>
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</tr>
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</tr>
<tr>
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<td>CS$_2$</td>
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<td>N/A</td>
<td>0.02M</td>
</tr>
<tr>
<td>Chlorides</td>
<td>L-Cystine</td>
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<td>N/A</td>
<td>0.02M</td>
</tr>
<tr>
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<td>L-Cysteine</td>
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<td>N/A</td>
<td>0.02M</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Thiourea</td>
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<tr>
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<td>Yes</td>
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</table>

Table 2.1: Showing all combinations of salts and sulfur sources as well as the concentration the reaction was performed at and products. Highlighted lines are successful combinations resulting in phase pure Cu$_3$Bi$_2$S$_3$. Unsuccessful combinations are not detailed.
L-cystine solution was similar, but white in color. When mixed, the solution was teal blue and opaque.

No color change occurred until 123°C when the mixture began to look darker, and by 128°C the solution was forest green. This color became a very dark green at 137°C and then black by 145°C. No outgassing or further color change occurred before stabilizing at 170°C.

2.2.2.2.3 - Acetates and L-Cysteine: Upon stirring overnight, the Cu(CH₃COO)₂ • H₂O and L-cysteine solution was an opaque dark blue color with powder still at the bottom of the flask. The Bi(CH₃COO)₃ and L-cysteine solution was an opaque yellow-white color with powder still in the flask as well. When mixed together, the resulting solution was dark blue-grey and opaque.

By 109°C the blue color had disappeared and the mixture had turned a yellow-gray color, which continued to become more pronounced until 122°C. By 132°C the liquid began turning brown and was black by 145°C. Outgassing of a yellowish white gas began at this point and continued until after the solution was stabilized at 170°C.

2.2.2.2.4 - Hydroxides and L-Cystine: Neither Cu(OH)₂ nor Bi(OH)₃ are soluble in ethylene glycol. As such, both solutions had undissolved salts at the bottom. The copper salt and L-cystine solution was teal in color and opaque while the bismuth salt and L-cystine solution was milky white. Mixed, the solution was opaque and teal.
Color change began around 127°C when the solution became greener. By 150°C the solution was forest green and at 153°C the solution began to darken to a brown color. The liquid was totally brown at 157°C. By 168°C it was black.

2.2.2.2.5 - Hydroxides and L-Cysteine: The Cu(OH)$_2$ and L-cysteine solution was a gray teal color with undissolved powder at the bottom of the flask. The Bi(OH)$_3$ and L-cystine solution was a bright yellow color, also cloudy and with sediment at the bottom of the flask. When mixed, the solution looked dull green and opaque.

When the solution reached 80°C it had become more yellow. Further heating to 100°C caused it to shift to a greenish tan color. It darkened to black slowly as the liquid was heated to 140°C. At 154°C a white vapor was observed bubbling from the liquid. Nothing further of note occurred as the temperature was stabilized at 170°C.

2.2.2.2.6 - Hydroxides and Thiourea: Separate solutions of the copper and bismuth salts were not made for this reaction. All of the salts and thiourea were mixed together into one flask. The solution began as teal-blue and opaque. Upon mixing overnight the solution resembled chocolate milk in color and opacity.

When heated, the solution turned black by 82°C and remained that color throughout the heating process. No outgassing was observed.

An attempt to synthesize CBS by heating this solution to 90°C for four hours was unsuccessful.

Further experiments were performed on this combination as its XRD showed the sharpest, tallest peaks. They are detailed in Sections 2.2.2.4.2 through 2.2.2.4.4.
2.2.2.2.7 - Verification of Cu₃BiS₃ Via XRD Peak Matching: XRD patterns for all successful CBS syntheses are shown in Figure 2.2. It can clearly be seen that the XRD peaks match for all seven syntheses, including the six newly discovered ones. The literature XRD peaks are shown at the bottom in black. No extra peaks are seen, thus we can confirm that all six of these new methods create phase pure Cu₃BiS₃.

![Figure 2.2: A graph showing the XRD patterns of all of the successfully made CBS powders. The patterns have been normalized and offset for comparison.](image)

2.2.2.2.8 - Lattice Parameter Determination of Cu₃BiS₃ via XRD Fitting: The two chemistries above with the sharpest XRD peaks were subjected to further analysis of their diffraction data. Hydroxides and thiourea (“H+T”) and nitrates and L-cystine (“N+L”) were selected.
By comparing the patterns shown above in Figure 2.2 to literature data, we were able to assign (hkl) index values to each of the peaks in the two diffraction patterns. Peak positions were determined to a precision generally better than 0.01° 2θ by closely inspecting the raw data files. Peaks with more than one possible (hkl) match were not included in the fitting. Analysis of the H+T data sets in this way resulted in 38 confidently assigned peaks used for the fitting. For N+L, 37 were used.

As the CBS structure is orthorhombic, only the a, b and c lattice parameters were adjusted in the fits. As previously noted in Section 2.2.1.3, a uniform 2θ offset was applied to the entire pattern; thus, four parameters were adjusted. Using a standard least-squares fitting method in reciprocal space, the best fit structures for both patterns was found.

The H+T CBS samples was determined to have unit cell parameters of a = 7.69, b = 10.40, c = 6.71 with an accuracy of ± 0.01 Å. The N+L material was determined to have unit cell parameters of a = 7.66, b = 10.40, c = 6.70 with an accuracy of ± 0.008 Å. These unit cell sizes compare very favorably with the seminal structure determination for CBS by Kocman which gave a=7.723±0.010 Å, b=10.395±0.010 Å, c=6.716±0.005 Å.  

2.2.2.3 - Impure CBS Synthesis:

2.2.2.3.1 - Nitrates and Thiourea: The Bi(NO₃)₃ and thiourea solution was a transparent yellow color while the Cu(NO₃)₂ thiourea solution was opaque and light green. Both colors were very bright. When mixed, the whole solution was an opaque yellow green.

When heated, the solution became more transparent by 40°C with no color change occurring until about 113°C. At this point, an outgassing of yellow brown gas, again believed to be H₂O, HNO₃, NO₂, and H₂, occurred along with a darkening of the
solution to a cloudy opaque yellow. Bubbling continued as the solution turned green, starting at 139°C and completing at 141°C. At 145°C the mixture began turning black. At 153°C a white vapor began to come out of the liquid. Bubbles formed in the solution for a time after a temperature of 170°C was reached.

The XRD of the powder showed a mixture of CBS, CuS, Bi$_2$O$_3$ and graphite. The XRD pattern can be seen in **Figure 2.3**.

![Figure 2.3: XRD spectra for the resulting powder from the nitrates and thiourea synthesis.](image)

### 2.2.2.3.2 - Chlorides and Thiourea

This synthesis is very similar to a previously reported method,\textsuperscript{67} although their method was performed in an autoclave and lasted 8 hours at 170°C. They were also successful in creating pure CBS nanorods.

The CuCl$_2$ • 2H$_2$O and thiourea mixture immediately turned thick, opaque and greenish white. The BiCl$_3$ and thiourea solution was yellow and transparent. These states
remained even after overnight stirring. When mixed, they were opaque and greenish yellow.

As the solution was heated, no color change occurred until 135°C, when a whitish precipitate was seen suspended in the solution. At 138°C the mixture began to turn more yellow and the precipitate began to dissolve. By 151°C the solid had totally dissolved, leaving the mixture transparent yellow. At 159°C the solution began to darken in color until at 161°C it was completely black. No further color change or outgassing was seen before the solution was stabilized at 170°C.

XRD revealed the powder to be CBS as well as CuS. The XRD pattern is shown in Figure 2.4.

**Figure 2.4**: The XRD pattern for the chlorides and thiourea synthesis is shown here.
2.2.2.3.3 - Chlorides and CS₂: The CuCl₂ • 2H₂O and CS₂ solution was a transparent green color, while the BiCl₃ and CS₂ solution was colorless and transparent. The CS₂ was allowed to mix in overnight. When mixed, the final solution was a transparent green.

Upon heating to 82°C, the color became more intense. At 122°C a white vapor was seen to form on the top of the liquid. At 132°C the color was a deeper green, but still transparent. At 166°C the solution began to darken to black. This transformation was complete by 170°C. Upon turning off the stir plate, large black particles were seen easily falling out of suspension. The stir plate was turned back on and the solution stirred at 170°C for the complete 4 hours.

An XRD analysis of the resulting powder indicated the presence of both CuS and CBS. This can be seen in Figure 2.5.

![Figure 2.5: The XRD pattern for the chlorides and CS₂ synthesis is shown here.](image-url)
2.2.3.4 - Acetates and CS<sub>2</sub>: After stirring at room temperature overnight the solution of CS<sub>2</sub>, copper acetate and bismuth acetate was a very dark, opaque, blue that approached black. Black/blue particles were seen undissolved on the bottom of the flask.

When heated to 67°C a white vapor was seen in the round bottom flask. At 104°C, the stir plate was turned off and particles were seen to easily fall down. The stir plate was turned back on and continued on for the rest of the experiment. By 121°C the solution was totally black and vapor continued to be generated until 158°C. No further changes were seen after stabilization at 170°C.

Examination of the resulting powder’s XRD shows the presence of CBS, Bi<sub>2</sub>S<sub>3</sub> as well as CuS. The XRD spectra can be seen in Figure 2.6.

![Figure 2.6: The XRD pattern for the Acetates and CS<sub>2</sub> powder is shown here.](image)
2.2.2.3.5 - Hydroxides and CS$_2$: After stirring overnight, the mixture of Cu(OH)$_2$, Bi(OH)$_3$ and CS$_2$ was an opaque black. No color change was observed as the solution was heated to 170°C. However obvious particles began forming in the solution at 90°C, similarly to the other CS$_2$ experiments. The stir plate was briefly turned off and these particles were seen to quickly fall out of suspension, leaving the ethylene glycol a white, but translucent, color. During the four hours at 170°C a white mist, thought to be unreacted CS$_2$ vapor, was seen above the liquid.

Evidence of CBS as well as Bi$_2$S$_3$, CuS, BiO$_2$ and CuO$_2$ were seen in the XRD pattern of the resulting powder. Some peaks are unaccounted for, but this is clearly not a pure CBS powder, and further scrutiny was not carried out. The XRD results of this experiment are seen in Figure 2.7.

![Figure 2.7: The XRD pattern on top is for the hydroxides and CS$_2$ experiment.](image)
2.2.2.4 - Analysis of Synthesis Mechanics of CBS:

2.2.2.4.1 - Nomenclature for Differentiating Experimental Solutions: Before continuing, the nomenclature of the following tests will be described. As an example, a 50 mL solution containing 0.001 mol of Bi(OH)$_3$, 0.003 mol of Cu(OH)$_2$ and 0.006 mol of thiourea is referred to as a 0.02 M CBS mixture in this document. If this solution fully reacted to form CBS, it would make 0.001 mol of the mineral in 50 mL of liquid. Thus, 0.02 mol/L of CBS. This nomenclature will carry for the remainder of this chapter.

2.2.2.4.2 - Hydroxides and Thiourea Concentration Tests: Copper and bismuth hydroxides are weakly soluble in ethylene glycol. As these efforts to find other reagents to synthesize CBS were researched for use in a flow through reactor, it was important that we have a homogenous liquid. The flow through reactor is discussed later in this document in Chapter 3. It was thought that a small amount of hydroxide salts and thiourea mixed into ethylene glycol might produce a well-dissolved solution that would lead to CBS being formed in the reactor. This was, however, not the case. It was soon found that changing the concentration of the reagents could also change the product of the reaction. This was researched in an effort to find the lowest concentration of reagents that would allow our method to make CBS.

A number of low concentration tests were performed, including 0.002, 0.0035, 0.005, and 0.0075 M mixtures. It was discovered that if more dilute solutions of these reactants were heated to 170°C, even for four hours, the result was a mixture of CuS and Bi$_2$S$_3$ instead of CBS. As these mixtures were all the same in their product composition,
they are not detailed. **Figure 2.8** shows four telling experiments, in the range of 0.01 M to 0.04 M, on how the concentration of the reagents influences the products.

---

**Figure 2.8:** This graph shows the gradual transition of products from CuS and Bi$_2$S$_3$ at low concentrations to CuS, Bi$_2$S$_3$ and CBS at moderate concentrations and pure CBS at higher concentrations.

From visually inspecting the XRD peaks on the previous figure one can see the gradual transition between the mixture of CuS and Bi$_2$S$_3$ to pure CBS. This is especially evident by watching Bi$_2$S$_3$’s large peak at about 25° give way to CBS’s smaller one, the two Bi$_2$S$_3$ peaks surrounding 23° diminish as CBS’s strong 23° peak rises, or the combined CuS and Bi$_2$S$_3$ peak at about 33° flatten to nothing as CBS becomes the dominant, and then single, component of the mixture. From this analysis we can see that the change from a mixture to pure CBS occurs between 0.03 M and 0.04 M.

This minimum concentration leading to CBS, approximately 0.035M, is far above the saturation point of these chemicals in ethylene glycol. As the reaction continues in the flask, what little of the salts that did dissolve in the liquid will react to form CBS and
precipitate out of solution. As the solution is no longer saturated, more of the salts will then dissolve into the liquid and the process will continue until all of the precursors have formed CBS. However, passing undissolved solids suspended in liquid through the reactor, again discussed in Chapter 3, leads to clogging and inhomogeneity of the reagents in the liquid. Because of this, utilizing concentrated hydroxides and thiourea slurries is not a strong option.

The fact that the different concentrations of the reagents in the flask can lead to different products may call for retesting of several of our impure CBS syntheses at higher concentrations. Nitrates and thiourea as well as acetates and CS₂, covered in Sections 2.2.2.3.1 and 2.2.2.3.4 respectively, may be the best candidates for retesting. Their 0.02M concentration reactions produced CBS as well as CuS and Bi₂S₃, the same byproducts that low concentration reactions of the hydroxides and thiourea combination produced. By testing a 0.04M solution, it is possible one could obtain pure CBS with these combinations as well. Unfortunately, these experiments were not able to be completed during this set of experiments.

2.2.2.4.3 - Determining Cause of Concentration Dependence: Preceding an attempt to determine the cause of the concentration dependence, CuS and Bi₂S₃ were prepared in the lab. To make CuS, 6 mmol (0.585 g) of Cu(OH)₂ and 12 mmol of thiourea (0.9134 g) were mixed into 100 mL of ethylene glycol. For Bi₂S₃, 10 mmol (2.60 g) of Bi(OH)₃ were mixed along with 30 mmol of thiourea (2.294 g) into 100 mL of ethylene glycol. This method is similar to a previously used method, although the cited method required more time, a higher temperature and nitric acid to proceed. Both mixtures were heated to
170°C for 4 hours, similarly to how CBS is made in the previously described procedure. The resulting CuS powder was a forest green while the Bi$_2$S$_3$ was gray. X-ray diffraction was performed on these powders to determine their composition. The experimental peaks seem to match the literature ones nearly perfectly. This can be seen in Figure 2.9.

Once the minerals were made, they were mixed together in a 6:1 ratio, according to Reaction 2 where it is assumed that excess sulfur will vaporize and leave the reaction vessel.

\[
\text{(2) } 6 \text{ CuS (s)} + \text{Bi}_2\text{S}_3 (s) \rightarrow 2 \text{ Cu}_3\text{BiS}_3 (s) + 3 \text{ S (v)}
\]

6 mmol of CuS (0.574 g) and 1 mmol of Bi$_2$S$_3$ (0.514 g) were mixed into 50 mL of ethylene glycol to create a 0.04 M solution. This was stirred at 170°C for 4 hours. An XRD of the 6:1 mixture as well as the powder resulting from this experiment is shown in Figure 2.10.
No reaction has taken place whatsoever as the pre and post heat treatment XRD patterns are identical. It was determined that CuS and Bi$_2$S$_3$ will only react to form CBS at 170°C if there is a sufficient chemical driving force. In the case of hydroxides and thiourea, this driving force comes from the OH⁻ polyatomic ion in solution. The concentration of the starting reagents plays into the formation of CBS because the amount of OH⁻ that is dissolved in solution is directly, and unsurprisingly, correlated to how much of the hydroxide salts are stirred into the mixture. While studies on the alternative salts were not performed, it can be assumed that there is lower limit of their concentration in a solution that would lead to CBS as well.

We later began to look into converting CuS and Bi$_2$S$_3$ to CBS after they were deposited on the fluorine doped tin oxide coated, FTO, glass in the reactor. This is discussed in Section 2.3.2.3.
2.2.2.4.4 - The Effect of Concentration on Time Required for Reaction Completion: In order to determine if the concentration of the hydroxide salts and thiourea in solution would affect the time required for the reaction to proceed to completion, two separate reactions were set up. 12 mmol (1.172 g) of Cu(OH)$_2$, 4 mmol (1.040 g) of Bi(OH)$_3$ and 24 mmol (1.828 g) of Thiourea was mixed into 100 mL of ethylene glycol to make a 0.04 M solution. A 0.08 M solution was made by mixing twice the previously stated amount of reagents into the same amount of solvent. These solutions were then heated to 170°C. Aliquots were taken every 30 minutes, starting when the solutions reached the reaction temperature and continuing for four hours. The resulting powders were rinsed with methanol and XRD scans were taken. These XRD results for the 0.04 M and 0.08 M experiment can be seen in Figure 2.11 and Figure 2.12, respectively. Discussions and comparison of the two follow.
Figure 2.11: This graph displays the XRD patterns for the 0.04 M hydroxides and thiourea experiment. Aliquots were taken every half hour for 4 hours.
The relative heights of each peak in relation to the other scans have been preserved, so the lines can be directly compared to one another.

The peaks do not seem to change in width as the reaction continues, indicating that the particles formed in the first moments of the reaction do not grow or shrink during the heating process.

CBS seems to be synthesized rather quickly in both cases presented above. Of particular note is the 0.0 hour scan. There are some indications of CBS’s formation in the 0.04 M graph, with the slopes of the line roughly following the heights of the CBS

Figure 2.12: This graph displays the XRD patterns for the 0.08 M hydroxides and thiourea experiment. Aliquots were taken every half hour for 4 hours.
literature lines. The 0.08 M line for 0.0 hour is more pronounced but not all peaks are seen.

At 0.5 hours, both concentration amounts show strong evidence of CBS being present. In regard to the CBS literature lines, no additional peaks are seen. The 0.08 M sample clearly shows higher, stronger peaks than the 0.04 M sample and this trend continues in virtually all of the remaining aliquot scans for both samples. Care was taken to preserve the peak heights relative to each other so that the graphs can be looked at side by side for a direct comparison. That the 0.08 M sample has a higher peak height is a real experimental result and not an artifact of the graphing process.

This higher peak height in the 0.08 M sample verses the 0.04 M sample could be attributed to a number of different things. It is possible that a larger percentage of the available reagents are formed into CBS per unit time in the more concentrated sample, ie the reaction proceeds faster.

The peak heights of each sample, for the most part, increase relative to the earlier scans as the reaction continues. A similar amount of the product powder was placed on each glass slide, and so two reasons for this could exist. There could be an amorphous phase of the powder that slowly disappears as the reaction continues, leading to the ever increasing peaks heights. The second possibility is that because no great care was paid to portioning out the powder placed onto the slides, this is merely a coincidence. A graph was made of the maximum peak height from each sample and time increment. This graph is shown in Figure 2.13.
While the whole scan was sampled, each maximum value is from the large peak at approximately 32°. This is the largest peak visible in the literature lines as well as the sample scans.

The 0.04 M sample has a much stronger linear characteristic than the 0.08 M with an R^2 of 0.91 versus the 0.08 M’s R^2 of 0.68. The increase of the maximum peak height for 0.04 M is gradual from 0 to 2 hours. It then seems to plateau for a time before resuming its increase at 3 hours and continuing on to 4 hours. The 0.08 M sample shows a sharp increase from 0 to 0.5 hours and then a general, if not chaotic, increase for the rest of the heating process. The inconsistency in the increase indicates an unreliability of these data. If this experiment were to be repeated, greater care would be taken to scan the same amount of powder for each time increment and sample.
The small peak evident in the 0.04 M graph, Figure 2.11, just to the right of 25° is of note. This is not seen on the 0.08 M graph, Figure 2.12, or the original 0.04 M sample in Figure 2.8. It is possible that there was some contamination formed in the sample, possibly an alternative product. This small peak is also seen in the 0.08 M graph in the 1.0 hour scan, but soon disappears. This could indicate that a higher concentration is more resistant to alternative products and contamination, potentially resulting in a more pure product. Thus, while there is no strong indication that the concentration of the reagents has any impact on the kinetics of the reaction, it can be said that a higher concentration is still beneficial. This is due to its resulting in a more pure, consistent product, as well as using less solvent. The latter is always desirable for greener chemical processes.

2.2.2.5 - Solvothermal Synthesis Enabled Zinc Doping of Cu₃BiS₃:

Attempts have also been made to dope the CBS with Zinc. The naturally p-type CBS could become n-type if atoms with a larger number of valance electrons are doped in. In this case, Zn has two valance electrons while Cu has one. As Zn is a similar size to Cu, it was thought that adding a small amount of zinc nitrate to the nitrates and L-cystine precursor solution of CBS could be enough to encourage its incorporation into the CBS lattice structure. As such, 1%, 0.1%, 0.01% and 0.001% Zn doped CBS was synthesized. XRD scans of all resulting powders are shown in Figure 2.14.
All of the XRDs of the Zn doped powders seem to look like single phase CBS plots. This suggests that the Zn has been incorporated into the CBS structure. However, if a separate phase had formed it is unlikely we would see it at these concentrations.

In order to test the electronic properties of the synthesized powders, 0.650 g of each were pressed into discs 13mm in diameter using 2.5 metric tons of pressure. The resulting puck was dark gray and lustrous. A small amount of silver paint, used to ensure good electrical contact, was placed on the edges of the puck directly across from each other. IV plots were generated under the light of the solar simulator, as well as under darkness. Four separate tests were performed for each sample and the results averaged. A picture of the reaction set up, as well as the IV plots for all of the doped samples, can be seen in Figure 2.15. The resistance at every point was calculated and averaged. This value for each sample is shown in Table 2.2. Interpretations follow.
Figure 2.15: 2.15A shows image of experimental set up. 2.15B-F show Zn doped sample IV curves.
The axes range has been standardized in 2.15B-F and so the graphs can be directly compared to one another. In all instances, the lighted IV curve is above the dark curve on the positive voltage side and vice versa for the negative side. This shows that the resistance of the material decreases when it is absorbing photons, as shown explicitly in Table 2.2. This shows that the material is photoconductive, which is a characteristic of semiconductors.

In nearly all instances the doped samples have a higher resistance than the pure, undoped sample. However, the lighted 0.01% Zn sample is slightly less resistive than the CBS, although the dark sample is far more so. The IV curve, shown in 2.15E, almost displays the look of a diode curve. Diodes require a p-n junction and so it seems that we have successfully doped the p-type CBS to be an n-type, at least in parts. The issue is that with the method used one would expect the entire sample to have the same concentration of Zn and be a consistent type. If only pockets of n-type CBS were made there is no way to know their true Zn concentration. Still, these data do point to the 0.01% being the most successful doping concentration of the group.

In Section 4.3.3.12 attempts at making a working solar cell with a p-n junction from CBS and 0.01% Zn CBS via electrodeposition will be discussed.

<table>
<thead>
<tr>
<th>CBS Sample % Zn</th>
<th>Avg. Resistance Light (Ω)</th>
<th>Avg. Resistance Dark (Ω)</th>
<th>% Difference Dark to Light</th>
<th>Thickness of Puck (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>244</td>
<td>282</td>
<td>-13.6</td>
<td>15.7</td>
</tr>
<tr>
<td>0.001</td>
<td>541</td>
<td>670</td>
<td>-19.3</td>
<td>15.0</td>
</tr>
<tr>
<td>0.01</td>
<td>240</td>
<td>664</td>
<td>-63.8</td>
<td>15.2</td>
</tr>
<tr>
<td>0.1</td>
<td>699</td>
<td>828</td>
<td>-15.6</td>
<td>14.7</td>
</tr>
<tr>
<td>1.0</td>
<td>579</td>
<td>686</td>
<td>-15.6</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Table 2.2: Summarizing the average resistance of the lighted and unlighted Zn doped CBS samples discs. The thicknesses of the pucks are also included.
2.3 - Studies on Solid State Synthesis of CBS Thin Films via Powder Sintering:

2.3.1 - Experimental:

2.3.1.1 - Reagents:

The CBS used for these experiments was made in our lab via the reaction of hydroxides and thiourea detailed in Section 2.2.2.6. CuS and Bi$_2$S$_3$ were also made in house by the synthesis method detailed in Section 2.2.4.3. All solvents are from the same sources detailed in Section 2.2.1.1. The forming gas (5% H$_2$, 95% N$_2$) and argon used in the tube furnace were supplied and prepared by Airgas.

2.3.1.2 - Preparation:

Samples were mixed with methanol and dropped onto microscope slides. Once the methanol evaporated, a fairly even coat of powder was left. These were then placed into the oven at various experiment specific temperatures, atmospheres and conditions further detailed in this section.

Before being placed into the scanning electron microscope, SEM, the samples were coated with 15 nm of gold to prevent charging during imaging.

2.3.1.3 - Instrumentation:

The XRD and SEM used are the same specified in Section 2.2.1.3. The Energy-dispersive X-ray spectrometer (EDS) used was Oxford X-Max 80 running the software Aztec. The tube furnace used was a CM Inc. Rapid Temp Furnace.
2.3.2 - Results and Discussion:

2.3.2.1 - Morphological Features of Synthesized CuS and Bi$_2$S$_3$:

As discussed in Section 2.2.3.4.2, a 0.0035 M solution of hydroxides and thiourea heated to 170°C for 4 hours lead to a mixture of CuS and Bi$_2$S$_3$. This powder was placed in the SEM to observe the powder’s microstructure. An SEM image of this powder at is seen in Figure 2.16. The scale bar, SB, shows the relative length for 1.0 μm.

![Figure 2.16: An SEM image of the product of the 0.0035 M hydroxides and thiourea reaction.](image)

There are two prominent morphologies present in the image, the roughly 1 μm wide hexagonal flakes and also rods approximately 1 μm long. There is also a nondescript powder that could be either flakes or rods that did not fully form in solution.
In order to determine which morphology was which compound, EDS was performed. The results are displayed in the form of concentration maps, shown in Figure 2.17.

![Figure 2.17](image)

**Figure 2.17:** Displayed, in order from A to D, are an SEM image of the powder, then the prevalence maps via EDS of bismuth copper and sulfur from an area of the powder resulting from a 0.0035 M reaction of hydroxides and thiourea.

From analyzing these images, we found that the hexagonal flakes are CuS and the rods are Bi$_2$S$_3$. In the upper right, about one third of the way from the edge of the image, a large hexagonal flake is seen, roughly perpendicular to the camera view. This is seen mostly in 2.17A, the SEM image. In 2.17C a large concentration of copper is seen in the same spot, along with a similarly highlighted area of sulfur, 2.17D. In fact the upper left corner of the hexagon can be seen fairly clearly in both of those elemental maps, while it
is not well defined in the bismuth image. It is also known that CuS has a hexagonal crystal structure\textsuperscript{69} and has been known to form in solution as hexagonal flakes.\textsuperscript{70}

It can be assumed through process of elimination that the rods are Bi\textsubscript{2}S\textsubscript{3}, but this can also be established through further analysis of the images in the proceeding figure. In the bottom middle of 2.15A a cluster of rods is seen. This area is not brightly lit at all in the copper map, but is shown strongly in both the bismuth and sulfur maps.

It is worth noting that the sulfur map looks to be a combination of the other two elemental maps. This makes sense, as all components in the sample contain sulfur.

As discussed in Section 2.2.2.4.3, samples of CuS and Bi\textsubscript{2}S\textsubscript{3} were also made separately. These powders were also imaged in the SEM. Images of the CuS and Bi\textsubscript{2}S\textsubscript{3} samples are seen in Figure 2.18.
Despite this sample being shown to be pure CuS in 2.18A, the images of CuS display both nanoparticles as well as relatively large sheets of the material. Hexagonal flakes, as previously seen in the 0.0035 M hydroxides and thiourea sample, are not seen. If the nanoparticles are closely inspected, they look to be textured, showing separate planes. It is possible that multiple small hexagonal flakes formed from the same seed crystal at different angles to give the roughly spherical appearance. They are significantly smaller than the previously seen hexagonal flakes, about 500 nm in diameter. Large sheets are also observed in and amongst the nanoparticles. It is possible that these are the result of hexagonal crystals growing unchecked in the more concentrated solution.
The Bi$_2$S$_3$ particles shown in 2.18C and 2.18D are still rods, although small and more even, at approximately 200 nm each, with similar aspect ratios. Also seen are areas where it seems that multiple nanorods have fused together to make more solid pieces.

It is well known that the concentration of the reagents affects the morphology of the products$^{68, 70-75}$ and this case displays that well. While changing the morphology of the particles of both CuS and Bi$_2$S$_3$ are not the main thrust of this research, it is possible that a suite of different morphologies could be generated from these simple synthetic pathways.

Still, our main purpose in synthesizing these materials is to attempt to utilize solid state reactions and sintering to form thin films of CBS. Our attempts at this are covered in Section 2.3.2.3.

2.3.2.2 - Studies on the Thermal Tolerance of CBS in Various Atmospheres:

While the melting temperature of CBS was previously known to be approximately 527°C$^{76}$ it was unknown how CBS would react to elevated temperatures in various atmospheres. The phase diagram of CBS is reproduced in Figure 2.19 from the same work cited above.
The melting temperature is important as we need to approach it in order to sinter the particles of CBS together. We also need the particles to remain CBS as they condense to form the desired dense thin film morphology. In order to determine the conditions that would allow us to sinter CBS into a pure layer, the following experiment was first run in atmosphere.

Particles of CBS were mixed with a small amount of methanol and dropped onto several separate cut microscope slides. These slides were placed into an oven under three different conditions. Slides were left open to the atmosphere of the oven, alone closed within two small petri dishes as well as enclosed in the petri dishes along with a small amount of elemental sulfur powder. When tested, the samples heated in the sulfur atmosphere resulted in a mess of XRD peaks that were clearly not a pure CBS for all

Figure 2.19: A reproduction of the phase diagram for the Cu$_2$S – Bi$_2$S$_3$ system.$^7$ Wittichenite, Cu$_3$BiS$_3$, is seen at approximately 75% Cu$_2$S and has a melting point of 527±5°C.
temperatures and amounts of time attempted. These results are not shown. **Figure 2.20** shows the XRD results when the samples were heated at 300°C for 12 hours open to atmosphere, at 350°C open and closed and 400°C open and closed for four hours each.

**Figure 2.20**: Showing the XRD results of various heat treatments of CBS particles. The “O” denotes “open” and the “C” denotes “closed.”

From these XRD patterns we can see that all samples have undergone some amount of oxidation. This is evidenced by the appearance of BiO$_2$ peaks. It is important to note, however, that the closed samples have less oxidation than their open counterparts. From this information we can determine that, at these temperatures, the reaction that causes pure CBS to oxidize and become a mixture of CBS and BiO$_2$ is a
result of the O$_2$ in the atmosphere “attacking” the material rather than sulfur or other components becoming volatile, and being replaced with oxygen.

With this in mind, CBS particles were heated to higher temperatures in a tube furnace with an argon atmosphere. All samples were run at the noted temperatures for four hours in a closed petri dish with argon running through the tube at 2 liters/min. XRD results for this series of experiments are seen in Figure 2.21. It is worth noting that the set of Pyrex petri dishes that enclosed the 600°C sample broke during the heating process. Due to this issue, no higher temperatures were tested as a container made of a more robust material would have been required.

![Figure 2.21: XRD results from heat treatments of CBS particles placed into an argon atmosphere and heated to the specified temperature.](image)
The 450°C sample remains pure CBS, although for all other samples some reaction seems to have occurred. The 525°C sample has several small unidentified peaks between 25° and 31°, indicating some contamination by another phase. The 550°C and 600°C samples show several small unidentified peaks as well, for instance to the left of the medium peak at 25°. Both also show bismuth metal peaks as well as CBS peaks. It is unknown what happens to the sulfur and copper that allows bismuth to remain behind.

It is possible that higher temperatures could be tolerated by copper bismuth sulfide more readily if it were sealed in an airtight container. Unfortunately, the means to test this were not available at the time of experimentation.

SEM images were taken before and after the heat treatments in air and argon to assess the quality of the sinter. These images are seen in Figure 2.22.
There was clearly no morphological change in the sample during the 12 hours at 300°C. Both the 525°C and 600°C samples show some changes resulting from their 4 hours at temperature. The 550°C sample looked similar to both of these, and is not shown. Both the 525°C and the 600°C samples display threadlike material connecting the larger particles. The larger particles themselves also seem less rough and rounder than in the pre-heat-treat samples. Still, this is obviously not a device quality, dense thin film.

Also of note is that 600°C is far above the proposed melting point of CBS, which is 527°C. A 600°C environment should have melted the CBS to a liquid and coated the glass underneath easily within the 4 hours the sample was at temperature. However, there is no evidence of melting shown in 2.22D. It was, however, well affixed to the glass.
slide. This shows that either the melting temperature of CBS is higher than previously thought, or that the tube furnace used to carry out these experiments is somewhat faulty. It is possible that with higher temperatures or longer baking times that the CBS would sinter. However, this would likely require a better seal around the CBS samples so that no oxidation or evaporation of the material would take place.

2.3.2.3 - Solid State Synthesis of CBS Thin Films from CuS and Bi$_2$S$_3$ Particles:

Also attempted was a solid state synthesis of CBS by thermal treatment of CuS and Bi$_2$S$_3$ nanoparticles. The hope was that this could lead to a smooth film of CBS. CuS and Bi$_2$S$_3$ particles were synthesized in the same manner described in Section 2.2.2.4.3. These were, again, mixed in a 6:1 ratio, exactly as in the same section. In some instances, the resulting powder from a low concentration reaction of hydroxides and thiourea was used. As described in Section 2.2.2.4.2 this results in virtually the same powder. The resulting powder was mixed with a small amount of methanol and dropped onto cut microscope slides. The slides were then placed into the tube furnace for 4 hours at 450, 525, 550 and 600°C under an argon atmosphere. XRD was performed on the slides, and the results are seen in Figure 2.23. It is worth noting that the container of the 600°C sample again broke due to thermal shock.
The CuS and Bi$_2$S$_3$ particles have fused and reacted to form the CBS, as proposed. Previous work done by other groups have reacted CuS and Bi$_2$S$_3$ thin films to form CBS\textsuperscript{42} but this is the first time it has been attempted with particles of the materials. Still, oxide contamination is seen in the XRD patterns for all temperatures above 450°C. This is similar to the heated CBS, shown in Figure 2.21. Peaks for bismuth metal, Bi$_2$O$_3$ and several unidentified compounds are seen as well as CBS.

SEM images were taken of all samples, with results very similar to those previously discussed for the heated CBS samples. These are seen in Figure 2.24.
Based on the EDS data, discussed in Section 2.3.2.1, the flakes are CuS and the rods are Bi$_2$S$_3$. Upon being heated for 4 hours, 2.24B displays the same interconnected thread network as the heated CBS powders displayed in Figure 2.22. These are likely due to the Bi$_2$S$_3$ rods thinning as diffusion occurs in the heated sample. Along the threads are smooth nodules of various sizes. The nodules are thought to be the result of the CuS
flakes crumpling in on themselves, becoming growth sites for diffusing material. This morphology is far removed from the original.

**2.22D** displays similar nodules to **2.22B** growing from a base that looks similar to its “raw” form in **2.22C**. These smooth CBS crystals seem to be much more prone to growing when the starting materials are CuS and Bi₂S₃ than when starting with CBS. Longer dwell times would likely lead to the formation of more and larger nodules. While interesting, these samples still are not smooth thin films, although again 600°C is well above the previously reported melting point of CBS.

On the macroscale, the samples heated to 600°C were resistant to scratching and could not easily be dislodged from the microscope slide. This indicates a good fusion of the material to the glass underneath.

CBS powder as well as mixed CuS and Bi₂S₃ powder were subjected to one more round of testing, this time in an atmosphere of the 95% N₂ 5% H₂ gas mixture known as forming gas. As forming gas is a reducing agent⁷⁷,⁷⁸ these tests were run in order to see if the oxidation present in some of the previously heated samples could be eliminated. If this was successful, the samples could potentially be put into even higher temperatures than before. The temperatures, dwell times and results of these experiments are displayed in **Figure 2.25**.
The chemical integrity of the CBS was entirely compromised. The CBS was reduced to bismuth metal, Cu$_2$S and several other unknown materials at all attempted temperatures and times. SEM images were not taken of these samples as no CBS remained. It is possible that lower percentages of H$_2$ could lead to less reduction.

2.4 - Conclusions:

We have successfully discovered six new solvothermal synthetic pathways to create CBS nanoparticles. The method used is simple, low temperature and robust, as
evidenced by having seven total reagent combinations that successfully produce the desired product. The salts and sulfur sources are mixed into ethylene glycol and heated under atmosphere to 170±5°C for four hours. XRD peak matching has shown that the particles formed are phase pure Cu$_3$BiS$_3$ for all combinations reported. Some of these methods will be tested in a custom made flow through reactor, detailed in Chapter 3.

The mixture of hydroxides and thiourea seems to form CBS the quickest, within one hour, and displays the sharpest XRD peaks. There is a lower limit to the concentration of starting reagents that will lead to CBS. This is verified for hydroxides and thiourea, and assumed for the rest. Above this limit, there does not seem to be proof that higher concentrations will affect the kinetics of the reaction. It could lead to more pure product though. This lower limit seems to be related to the chemical driving force related to the concentration of the anions in solution.

CBS is prone to oxidation at temperatures above 300°C. CBS and the CuS and Bi$_2$S$_3$ mixture are not stable in a 95% N$_2$ 5% H$_2$ atmosphere. CuS and Bi$_2$S$_3$, when mixed in a 6:1 ratio, will react to form CBS when raised to temperatures as low as 450°C. This mixture of particles, and CBS particles, do not readily form dense thin films within four hours of a 600°C heat treatment.

While higher temperatures and longer dwell times in an inert atmosphere could potentially lead to smooth layers of CBS made from nanoparticles, this goes against the point of this research. The main purpose of this study was to find simple low cost, non-energy-intensive methods to synthesize and deposit CBS. Long stays at high temperature are directly in opposition to this. Thus, other methods for the synthesis and deposition of copper bismuth sulfide must be discovered.
CHAPTER 3: Purpose Built Benchtop Reactor Designed for Diagnostic Deposition of Semiconductors

3.1 - Introduction:

Multiple methods to deposit thin films of copper bismuth sulfide (Cu$_3$BiS$_3$, “CBS”) have been discovered, including heating sputtered Cu and Bi metals in H$_2$S gas,$^{49}$ annealing chemically deposited layers of CuS and Bi$_2$S$_3$ or CuS and Bi,$^{42}$ and multiple other ways.$^{38, 50, 51}$ However, all of these methods utilize expensive machinery, high temperatures, exotic atmospheric environments or vacuum. We focused on developing a simple, inexpensive and reliable method for CBS deposition based on the chemical precipitation methods described in Chapter 2.

Continuous flow bench top reactors have been used for the deposition of various materials including CdS,$^{79, 80}$ gold nanoparticles$^{81}$ and ZnO,$^{82}$ as well as being used to continuously synthesize various organic compounds$^{83}$ and molybdenum disulphide.$^{84}$ Continuous flow reactors have proven to be useful with regenerating catalysts.$^{85}$ Studies have also shown that thin films deposited via a continuous flow reactor are smoother, more highly oriented and have better coverage than those deposited with a batch reactor.$^{80}$

The previous chapter dealt mainly with the multiple low temperature solvothermal methods we have developed to make CBS. Efforts to utilize these syntheses in a custom built benchtop reactor meant to deposit the material on fluorine doped tin oxide coated, FTO, glass have been underway for some time, started by a former group member and the author.$^{86}$ A second generation reactor design has been completed that solves many
problems associated with our first reactor. The new design was intended to promote even liquid flow across the FTO glass. This reactor was also built with a temperature gradient transverse to the liquid flow so that the effects of temperature during the deposition of CBS could be studied. The designing and fabrication of this second reactor will be described here. Results from experiments performed with both reactors will also be detailed.

It is important to note that experiments run with the first reactor, covered in Section 3.5.1.2, suggested that particles were precipitating in the solution and falling by gravity onto the upward facing substrate leading to more chaotic coating microstructures. So one of the key factors used in designing Reactor 2 was to place the substrate above the fluid flow channel in an “upside down” configuration.

Before physically building these reactors we tested their performance within the multiphysics simulation program COMSOL. This tool allowed us to iterate easily on our design until our specifications were met.

Aside from experiments meant to yield smooth even coatings of CBS, the second reactor was also tested with a simpler chemistry (yielding CdS) to further investigate the temperature gradient effects during deposition.

Utilizing inexpensive chemical inputs and fabrication processes, this research could pave the way for more cost effective solar technology.

3.2 - Materials and Parts Used in Fabrication of Reactors:

Reactor 1 was very simple and assembled using cut sheets of aluminum, a red silicone rubber gasket from MSC Industrial Supply Co and tubing from Sigma Aldrich.
High temp Red RTV Silicone made by Permatex was utilized to bond the tubing to the gasket. The gasket acted as the walls of the reaction chamber and defined the flow height of the reacting fluid.

Reactor 2 was considerably more complicated. The main body was assembled from a 1” x 3.5” x 12” aluminum block and a ½” x 6” x 6” piece of fluorinated ethylene propylene, FEP, that was cut to ½” x 6” x 5”. All were purchased from McMaster-Carr, which uses imperial notation. FEP was chosen as it had an appropriate melting point and is partially transparent, though this last characteristic was ultimately not utilized.

The silicone rubber gasket was again supplied from MSC Industrial Supply Co and functioned as the walls of the reaction chamber. High temperature red RTV silicone was utilized to prevent leaking in a number of areas.

Reactor 2 was heated by a CIR-5032 120V 650 W cartridge heater supplied by Omega. Also from Omega were 100 Ω G-type resistance temperature detectors, RTDs, with 2-wire leads to measure the temperature in various places.

Arctic Silver’s Ambrosia HT High-Temperature Thermal Compound was graciously supplied for free by the manufacturer. This was used to hold the RTDs in place while still allowing good thermal contact between them and the aluminum block.

A National Instruments myRIO-1900 was used as a controller for Reactor 2, collecting information from the RTDs and sending out signals to control the heater.

A 10 amp 12 volt Panasonic relay along with a NPN 120 volt 50 mA Fairchild semiconductor were purchased from Digi-Key Corporation.

The substrate chosen to deposit on was fluorine doped tin oxide coated, FTO, glass from Sigma Aldrich. Later experiments with Reactor 2 used 3 mm thick glass
described by Sigma Aldrich as ≈ 8 Ω/□, but earlier experiments with Reactor 1 used 2 mm thick glass with ≈ 13 Ω/□. The 8 Ω/□ is significantly rougher than the 13 Ω/□, so this is an important distinction when analyzing SEM images of depositions. If one is purchasing FTO glass from Sigma Aldrich, the units used on their products are “Ω/sq.”

3.3 - Comparison of Reactors 1 and 2 Through COMSOL Simulations and Experimental Verification:

3.3.1 - Liquid Flow:

A uniform flow of a homogenous liquid would be desired and as it would promote more even growth of the deposited layer across the FTO glass. With the salts and sulfur source well dissolved in the solvent, the same amount of reagent would pass over any given area of the substrate allowing the same amount of product to be deposited upon it. Therefore, it is very important that we establish a uniform flow across the maximum area of FTO possible. This was a major goal for Reactor 2.

3.3.1.1 - COMSOL Liquid Flow Simulations:

Digital 3D representations of each reactor were made in Solid Works and imported into the multiphysics simulation package COMSOL. In this program, the ethylene glycol could be distinguished from the solid reactor and made to flow through it at a set velocity. In practice, this velocity would be set by a peristaltic pump running on the lowest setting. It was found that this setting, for the tubes we used, would push liquid through at a rate of 1.83 mL/minute. This rate was converted into the mm/s of liquid being pushed through the inlet tubes for each reactor and entered into COMSOL.
It was assumed that laminar flow would be appropriate for use in the simulation. This was later confirmed, as shown later in this section as well as Section 3.3.1.2. A no-slip condition was also made for all surfaces that the liquid came in contact with.

A color map of the velocity of the liquid as it passed through each reactor was then generated. These maps, as well as photographs of the corresponding reactor chamber, can be seen in Figure 3.1. In all images shown here, the liquid would be coming in on the left and moving to the right.

**Figure 3.1:** 3.1A and 3.1C are photographs of the exposed reaction chambers for Reactor 1 and 2, in that order. 3.1B and 3.1D show the COMSOL simulated velocity maps of the liquid flow through these chambers. 3.1E shows the side on view, perpendicular to 3.1D, of the liquids path up to and through the reaction chamber. Dark blue is slow moving and dark red is fast moving liquid.
3.1B displays the non-uniformity of the liquid flow through Reactor 1. The portion in the center is fairly uniform, but roughly 2/3 of the FTO is exposed to heterogeneous flow velocities. This would allow for significant inconsistency in the thickness of the layer grown. The irregularities in the flow are due to having only one inlet and outlet into the reaction chamber, leaving the liquid in the corners relatively stagnant.

Comparing 3.1B to 3.1D shows a vast improvement in the uniformity of the flow. In Figure 3.1D we are only concerned about uniformity in the center portion of the image. The sections to either side are the compressive pathways that the flowing liquid takes to become uniform in velocity across the reaction chamber. While COMSOL does predict the liquid changing velocity as it moves across the chamber, this is an artifact of how the program calculates these values. As we are only using this program as a tool to determine if this design is sound, this type of inaccuracy is tolerable.

3.1E shows these pathways in combination with the inlet channels designed to even the flow. This image is taken from a side-on perspective, perpendicular to 3.1D. Here we can see the liquid being pushed down through the four inlets. This was achieved with one feeder tube being split into two, and two again with y-splitters. It collects in a reservoir that empties through nine 1 mm holes cut into a piece of Al and leads to another reservoir. The liquid leaves this chamber by way of a small slat above it, so the liquid must push against gravity to enter the reaction chamber. This chamber is free from obstruction and the liquid flows uniformly under the glass, directly against the FTO layer. The liquid leaves in a mirrored version of how it entered, with the four outlet tubes emptying into a waste receptacle.
Locations were selected in the middle of the moving liquid of both reaction chambers so that the velocities of the liquid at those positions could be graphed. The locations used, as well as the graphical display of the velocity for Reactor 1 is shown in Figure 3.2.
Again, we see the flow is inconsistent, with the liquid near the inlet and outlet going far faster than that in the center of the reaction chamber.
The same graphs and figures were made for Reactor 2 and are displayed in Figure 3.3.

**3.3A**: Graphical lines across liquid flow

**3.3B**: Graphical lines along liquid flow

**3.3C**: Graph of the liquid velocity taken from lines across liquid flow.

**3.3D**: Graph of the liquid velocity taken from lines along liquid flow.

*Figure 3.3*: Positions of the lines used to generate liquid velocity graphs and the graphs themselves for the liquid velocity in Reactor 2. **3.3C** and **D** display velocity in $10^5$ m/s vs. position across the reaction chamber in meters.
In 3.3A and 3.3B, notches designed to house the RTDs made it somewhat difficult to see the lines that the graphical data were taken from. The red lines are where the data in 3.3C and 3.3D were gathered from. Still, the velocity is clearly much more even in 3.3C and 3.3D than Reactor 1’s data. The liquid does, as expected, not move much at all when close to the walls of the chamber because of the no-slip flow boundary condition.

From looking at the graphs we can see that a velocity of about 0.27 mm/s is seen virtually all the way across the reaction chamber of Reactor 2. With this information we can confirm, using **Equation 1**, that laminar flow is appropriate for use for these simulations as the Reynolds number, 2.7, is far below the threshold for turbulent flow (typically having Re’s in the 1000s).

**Equation 1:**

\[
Re = \frac{\rho v L}{\mu} = 2.7
\]

\(\rho =\) Density of fluid (Ethylene Glycol) = \(1110 \text{ kg/m}^3\)

\(v =\) Velocity of fluid = \(2.7 \times 10^{-4} \text{ m/s}\)

\(L =\) Characteristic linear dimension = \(2 \times \text{channel height} = 2 \times 0.00635 \text{ m} = 0.0127 \text{ m}\)

\(\mu =\) Dynamic viscosity of fluid (Ethylene Glycol) = \(1.4 \times 10^{-3} \text{ Pa.s}\)

### 3.3.1.2 - Experimental Verification of COMSOL’s Flow Simulations:

To verify the flow simulations performed in COMSOL, an experiment was conducted. First, the reaction chamber of Reactor 1 was filled with ethylene glycol. More ethylene glycol, dyed dark with food coloring, was pumped in to observe the liquid flow through the reaction chamber. Pictures were taken of this experiment at various times, and are shown in Figure 3.4.
Towards the inlet, the flow looks very similar to that predicted in Figure 3.1B. Again, this flow is clearly not uniform across the reactor width.

The same experiment was performed with Reactor 2. When being used, the reaction chamber would ordinarily not be visible, so a special part was made to allow us to look in through a piece of glass. The same part was used in Figure 3.1C. The results of the dye test for Reactor 2 are seen in Figure 3.5.

Figure 3.4: Images of dye flowing through Reactor 1. 3.4A to 3.4C are sequential.

Figure 3.5: Images of dye flowing through Reactor 2. 3.5A to 3.5C are sequential.
Upon quick observation, this looks far improved from Reactor 1. Three of these experiments were performed. By analyzing the times that the images were taken and how far across the reaction chamber the four dye fronts had traveled it was found that the average flow velocity in the reaction chamber is 0.18 mm/s. This had a standard deviation across the flow of 0.011 mm/s, or 6.3%, a large improvement over the previous reactor. The notches in the coloration fronts visible in 3.5B and 3.5C are believed to be due to the way that four feeder tubes pump fluid into the reservoir before being fed through the 9 small channels that even out the flow through the reaction chamber. Some paths required a longer path/time for the dyed liquid to reach those small channels and thus the color front didn’t start as a flat front. The shapes of the fronts stay consistent from 3.5A to 3.5B, however, indicating that the velocity of the liquid is uniform across the chamber. This was also confirmed to move evenly through by our measurements of the front’s motion.

With this new flow information Equation 1 was again used to determine that the Reynolds number of this system is 1.8, even further below the threshold for turbulent flow.

3.3.2 - Heating:

Heating for Reactor 1 was predicated on a color change occurring in the solution when the reaction occurred. The reactor was placed upon a standard laboratory hot plate that would be slowly turned up until the characteristic color change was observed through the window cut in the top. Besides this, there was no way to assess the temperature inside of the chamber. Because of this, no COMSOL simulations or verification experiments were run on Reactor 1 and this section will now focus solely on Reactor 2.
3.3.2.1 - Methods to Adjust, Monitor and Maintain a Linear Temperature Gradient within Reactor 2:

A linear temperature gradient transverse to the liquid flow was desired to enable diagnostics of temperature effects on coating deposition and quality, and so the decision was made to provide a heating source with a temperature gradient. This was created by heating one end of an aluminum block and cooling the other. A cylindrical cartridge heater was placed into a hole drilled in one end of a 1” thick aluminum block. The aluminum block would be cooled on the other end via air flow generated by the chemical hood it was enclosed in, or tap water being pumped through holes drilled into it. The large thermal mass and high thermal conductivity of the aluminum block would allow a linear temperature gradient, and would be affixed directly to the back of the FTO glass, heating it and the liquid under it. The aluminum is much more conductive than any of the system/reactor/chemistry components, so the gradient would be maintained.

3.3.2.1.1 - RTD Circuitry and Calibration: RTDs are used to monitor the temperature of the reactor, and also play a large role in controlling the heating of the reactor. The RTDs and heater are connected to a National Instruments myRIO-1900 via the circuit schematic shown in Figure 3.6.
The myRIO utilized a feedback control loop, detailed in the next section, to maintain the temperature of the heater at a set point by switching a relay with a NPN transistor connected to the high-power output of the myRIO. The transistor was switched with the analog output control pin on the myRIO. Once activated, the relay connects AC power from a standard wall outlet to the heater.

Once this circuit was established, a LabView program was written to calibrate the RTDs. The RTDs and a laboratory thermometer were bundled together and submerged in ice water, boiling water and boiling ethylene glycol. The resistance of the given RTD was measured at each temperature independently and a custom calibration equation was generated for each one. To test the limits of the calibration, the RTDs and the same thermometer were placed into silicone oil and heated. The resistance was taken at various temperatures up to 247°C. As expected, both of these plots proved linear. $R^2$ values of 0.9999 were found, as can be seen in Figure 3.7. Note that the dependent/independent

![Figure 3.6: Schematic of the electronics that link the myRIO-1900 to the RTDs and heater.](Image)
axes were reversed to allow the slope and intercept values to be used directly for measuring the temperature during reactor operation.

3.3.2.1.2 - LabView Programming to Control and Monitor Temperature of Reactor 2:

All of the aspects of the reactor relating to temperature are monitored and controlled with a LabView program. LabView is a visual programming language so it can be followed relatively easily, compared to other forms of programming. An image of the entire program is shown in Figure 3.8 on the next page with a description of how it functions following.
Figure 3.8: The program to control the reactor, displayed within LabView.
In all cases, the Voltage Input comes from the myRIO-1900. Measurements are taken from the RTDs every 2 ms, which are fed into a running average with the 1500 previous measurements. These averages are then plugged into a calculation which converts the voltage to resistance. This resistance is then converted into temperature via the individually determined conversion equations for each separate RTD. The temperatures measured by the monitor RTDs are simply displayed.

One RTD, embedded approximately 2 mm from the heater, is specified as the control RTD, cRTD. The cRTD’s temperature feeds into a simple logic gate that states if the measured temperature is below a specified value the heater will turn on. If it is above, the heater turns off. This is done by switching on or off the analog output from the myRIO. This value, 198°C in the case of the above image, can be adjusted as the program runs. This value will be called the control temperature, or $T_c$.

Any temperature oscillation due to the heater turning on and off would be significantly dampened first by the high thermal mass of the 1” thick, 12” long aluminum bar and then the glass that the thermal energy must travel through to heat the liquid.

3.3.2.2 - COMSOL Heat Simulations and Verification of Results:

The temperature range of the gradient is controlled within COMSOL by changing the temperature of heating and cooling tubes. COMSOL maintains their set temperatures and then calculates the temperature of every other point within the reactor’s geometry. Every material used in the construction of the reactor is input into COMSOL so that it can accurately simulate how thermal energy will move through them. Below, in Figure 3.9, is a 3D heat model of Reactor 2, shown from several vantage points.
In these images, white is hottest at about 202°C and the dark red is coldest at 20°C. This simulation has a temperature gradient of 25°C, from 185°C-160°C. In order to achieve this ΔT in the simulation the heater tube, on the left of 3.9A, was set to 202°C and the cooling tubes, on the right, were set to 127°C. Initially, it was thought that the real reactor would require cooling to achieve this temperature gradient. It was found that running the reactor in an actively ventilated chemical hood forced enough air through the cooling holes to maintain this 25° temperature gradient. A larger gradient could be imposed by passing water through them, as will be discussed in Section 3.5.

This temperature gradient is only measured along the length of the reaction chamber, from the left most notch in the bar on top to the right most. Again, these notches are used in the physical reactor to hold the RTDs. In the physical reactor, there is
a small hole drilled 2 mm from the heating tube where the cRTD sits. This was not reflected in COMSOL so that a temperature line could be placed in this spot to help in predicting what $T_c$ should be set to. In this case, $T_c$ was predicted to be 200°C. Temperature lines were also placed evenly across the aluminum-glass interface, where the RTDs would be measuring temperatures.

The next step was verifying the COMSOL data. The reactor was set up and allowed to reach temperature. The temperatures from the real reactor were noted, along with their variance, and placed on top of the COMSOL simulated temperature data taken from lines on the Al-glass interface. The temperature oscillation is shown as error bars. This data is seen, along with a graph confirming the linearity of the results, in Figure 3.10.
In 3.10A the sharp spikes are the result of the notches for the RTDs cut into the 3D model of the reactor and are not thought to be real data. Still, the experimental data matches up fairly well with the simulated. Again, for this gradient the $T_c$ was predicted to be 200°C. Experimentally this was found to be 201.5°C.
The discrepancy between experimental and computational is likely caused by COMSOL not taking into account the air movement around the reactor and the cooling that that provides, among other anomalies computational data are prone to.

**3.10B** shows the linearity of the gradient, found using Excel. A $R^2$ value of 0.98 was found, indicating good linearity.

Temperature lines were also placed inside of the liquid, very close to the liquid-FTO interface to make sure that it would reach reaction temperature. The graph for these data is shown in **Figure 3.11**

![Figure 3.11: Simulated temperature of the liquid as it flows through the reaction chamber of Reactor 2.](image)

As the experimental data from **3.10A** matches the simulated data well, we can be confident in this simulated data as well. In this graph a higher “distance” values for the lines means they are closer to the inlets. The blue dashed line assigned a value of 0.0484 is the line directly running across the inlet slot of the reaction chamber. The reaction chamber is 0.0484 m from inlet to outlet (48.4mm), hence COMSOL’s nomenclature. From this we learn that the liquid will get hotter as it flows under the heated FTO glass.
This is not surprising, but it is something that will have to be considered when looking at deposits on the glass.

The experiments run using Reactor 2 all required different temperature ranges, so a separate simulation was run for each. These will be detailed in Section 3.5.

3.3.3 - Reactor Set Up:

3.3.3.1 - Reactor 1:

Figure 3.12 shows the set up for Reactor 1, with the white letters denoting points of interest. A shows the unreacted solution that is being pumped into the reactor via tubing. This flow is controlled and maintained by B, the peristaltic pump. The tubing goes through C, an oil bath whose temperature is monitored by a lab thermometer D. The pre-heating of the solution was ultimately found to be superfluous for this reactor. The now heated solution is passed through an insulated section of tubing and into the reaction chamber E. The reactor sits on top of the hot plate which is the source of heat for the reactor. The knob is turned up until the color of the solution inside changes. This can be
observed through the window on top of the reactor. The depleted solution is then passed into the waste receptacle, F.

3.3.3.2 - Reactor 2:

![Figure 3.13: Picture of the Reactor 2 set up, annotated with letters.]

The set up for Reactor 2 is shown in Figure 3.13 with white letters designating points of interest. A is the reaction solution that is being pumped through the tubing into the reactor with the use of a peristaltic pump, B. Before the solution reaches the reactor itself, C, the flow is split into four inlets by 3 y-splitters. In this configuration, the reactor has water being pumped through one of the cooling holes so a larger temperature gradient can be generated. The liquid is then pumped through the reactor and the spent solution is pumped into the waste container, D.

The heater and the RTDs are hooked into the switch box, E. This houses the circuitry shown in Figure 3.6 and is plugged into the wall to supply electricity to the cartridge heater in the reactor through the leftmost red and black jacks. Connected to the
control box is the National Instruments myRIO-1900, \textbf{F}. This relays instructions to the control box, as well as wirelessly sending information to the laptop, \textbf{G}. This enables the temperature of the aluminum bar to be monitored and adjusted as the experiment proceeds.

3.4 - \textbf{Experimental}:

3.4.1 - \textbf{Substrate Preparation}:

The roughly 100 mm x 100 mm x 3 mm FTO glass from Sigma Aldrich was cut into 100 mm x 75 mm x 3 mm by scoring deeply with a glass cutter on both sides, laying a 100 mm wide tile chisel carefully on the scored line, and tapping firmly with a hammer. This typically led to a clean break. The side of the glass coated with FTO was then clearly marked with the cutter on all four corners, which would not be in contact with the reaction solution. The hot and cold sides were also marked for Reactor 2.
The FTO glass was then placed into a 0.1N KOH solution and left overnight to remove any organics on the surface. When taken out of the solution the glass was rinsed with DI H₂O and methanol and then dried. The reactor was then assembled around it.

3.4.2 - Reactor 1:

Ethylene glycol was first pumped into the reactor, making sure to get all of the air out of the tubing and reaction chamber. If pre-heating was to occur, the tubing was placed into the silicone oil bath, which was brought to 115°C. Again, this step was later determined to be unnecessary as the hot plate was sufficient to heat our solution to temperature. The desired solution, one of those detailed in Section 2.2.2, was mixed continuously as the experiment proceeded. This solution was then pumped into the reaction chamber on the lowest setting of the peristaltic pump; about 1.83 mL/minute.

Once the chamber was full of the reaction liquid, the pumping was stopped and the hot plate slowly turned up. Most of the solutions detailed in Section 2.2.2 have a visible color change that occurs at the reaction temperature, and some release a gas. The liquid was left in the reaction chamber until the solution had completely changed color and gas had stopped being generated. Fresh reactant was then pumped in until it completely filled the chamber. The process was repeated until the solution was all passed through, at which point plain ethylene glycol was pumped in. The reactor was then taken apart, the glass rinsed with DI water and methanol and prepared for analysis, typically XRD or SEM.

Early experiments with Reactor 1 had the liquid continually flowing through the reactor, but most were performed with this “stop and start” method. The method used in the specific experiment will be specified in the following section talking about the results.
3.4.3 - Reactor 2:

The FTO glass was placed FTO side down on the cut silicone mat that made the walls of the reaction chamber, making sure to line the side marked “H” with the hot side and “C” with the cold. One mL of silicone oil was spread over the plain glass side of the FTO glass to aid in heat transfer. The aluminum bar was placed on top and screwed into place, making sure that there were no gaps between it and the glass beneath.

Once assembled, the reactor was held upside down to allow ethylene glycol to completely fill the four inlet tubes. Care was taken to ensure they were completely filled with the liquid, with no air bubbles. As this reactor did not have a window to look in, it was difficult to ensure that all of the air was forced out of the reaction chamber. A system of slow manual movements and tilts was found to be fairly effective for this purpose. When assembled, the reactor sat upon four long screws. As another method to help ensure total contact between the liquid and FTO glass, the back two screws, near the outlets, were placed on a raised platform to allow any air bubbles still present in the reaction chamber to be pushed up and out of the chamber with the flow of the liquid and force of gravity.

Once the liquid was present in the outlet tubes, the flow of ethylene glycol was stopped and the heat was turned on. If a large temperature gradient was desired, then water was pumped through the cooling hole at the same time. The Tc was increased by 25°C every three minutes or so until the desired temperature gradient was in place.

The reaction solution was stirred during the entirety of the experiment. The speed at which the liquid was pumped through the reactor changed with various experiments, and will be specified at the beginning of the section talking about the specific experiment.
When the reaction liquid was low, a small amount of plain ethylene glycol was added while stirring. This step was repeated three times to ensure all of the unreacted solution made it through the reactor. 80 mL of plain ethylene glycol was then pumped though, then air. When bubbles were seen coming out of the outlet holes, the heat was turned off and the reactor was allowed to cool to room temperature.

Once disassembled, the glass was rinsed with DI H$_2$O, methanol and acetone and then allowed to dry. It was then prepared for XRD or SEM.

3.5 - Results and Discussion:

3.5.1 - Attempts at Deposition of CBS with Reactors:

3.5.1.1 - Overview of CBS Syntheses with Reactor Deposition in Mind:

When we set out to discover new combinations of reagents that would lead to CBS we had an ideal outcome in mind. We wanted the product to be pure CBS and we did not want it to produce a gas during the reaction. If a gas was released, it would pool against the FTO glass roof of Reactor 2. The pooling of the gas would prevent deposition in those areas as no liquid would be in contact with them. The major impetus for this temperature gradient is to essentially do multiple deposition experiments at once along the length of the reaction chamber. It would be a hindrance to have a portion of those experiments stopped at random due to gas filling the chamber. It was also important that the solution be fully dissolved so that every given volume of solution had the correct proportions of reagent within.
Table 3.1 shows that this ideal solution did not exist within the reagent combinations that have been attempted. Still, best case combinations were attempted for use in Reactor 1 and 2. Telling experiments will be described.

<table>
<thead>
<tr>
<th>Cu and Bi Salt</th>
<th>Sulfur Source</th>
<th>CBS Produced</th>
<th>Additional Phases</th>
<th>Gas Produced</th>
<th>Fully Dissolved at RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrates</td>
<td>L-Cystine</td>
<td>Yes</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Nitrates</td>
<td>L-Cysteine</td>
<td>Yes</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Nitrates</td>
<td>Thiourea</td>
<td>Yes</td>
<td>C, Bi₂S₃, CuS</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Thiourea</td>
<td>Yes</td>
<td>CuS</td>
<td>No</td>
<td>Suspended</td>
</tr>
<tr>
<td>Chlorides</td>
<td>CS₂</td>
<td>Yes</td>
<td>CuS</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Acetates</td>
<td>L-Cystine</td>
<td>Yes</td>
<td>N/A</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Acetates</td>
<td>L-Cysteine</td>
<td>Yes</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Acetates</td>
<td>CS₂</td>
<td>Yes</td>
<td>Bi₂S₃, CuS</td>
<td>Yes</td>
<td>Mostly</td>
</tr>
<tr>
<td>Hydroxides</td>
<td>L-Cystine</td>
<td>Yes</td>
<td>N/A</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Hydroxides</td>
<td>L-Cysteine</td>
<td>Yes</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
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<td>Thiourea</td>
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<td>N/A</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Hydroxides</td>
<td>CS₂</td>
<td>Yes</td>
<td>Multiple</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 3.1: A reprinting of Table 2.1 with factors important to reactor use included and combinations that produced no CBS removed. Highlighted lines are combinations resulting in pure CBS.

3.5.1.2 - Nitrates and L-Cystine:

Discovered by a former group member, nitrates and L-cystine was the first combination of chemicals found to make CBS with our method. During the same period of time, this combination was the first solution to be put through Reactor 1. SEM scans of various Reactor 1 runs with this combination of reagents are seen in Figure 3.15. Discussions follow.

It is important to note that the 13 Ω/□ FTO glass used here was very smooth and is seen as completely featureless in the following micrographs. For size reference, the scale bar, SB, sizes are displayed above the images.
3.15A: SB = 20 μm  
3.15B: SB = 1 μm

3.15C: SB = 1 μm  
3.15D: SB = 200 nm

3.15E: SB = 20 μm  
3.15F: SB = 2 μm

Figure 3.15: SEM images of three separate depositions carried out in Reactor 1 with nitrates and L-cystine. 3.15A and 3.15B are from the same experiment, 3.15C and 3.15D another and 3.15E and 3.15F yet another.

3.15A and 3.15B are taken from an experiment where 50 mL of the standard concentration of solution, described in Section 2.2.1.2, was passed through the reactor at a constant rate. In 3.15A the irregularity of the coating is clearly shown. There are large
plate-like deposits as well as smaller nodules. There also seem to be large portions that are plain FTO. **3.15B** is a zoomed in SEM image of the red square present in **3.15A**. Here, true evidence of CBS growing directly from the glass can be seen. The material has clearly fused with the FTO in certain locations. From this image it seems as though the large platelets grew from these small nodules.

Taken from an experiment where 50 mL of the standard concentration of solution were pumped into the chamber and allowed to sit until completely reacted, **3.15C** and **3.15D** show a better coating of CBS. **3.15C** highlights the various particle sizes present in the coating. There is some agglomeration of nanoparticles which form large irregularly shaped clumps. **3.15D** shows that a layer of CBS can grow up from the glass in an even coating. However, this is seemingly covered by nanoparticles that fall out of solution. The coating under the nanoparticles seems to be tightly packed and grown in a columnar fashion. This is optimal. Though, there is still the issue of the nanoparticles falling from above and unevenness of the coating.

The next set of images, **3.15E** and **3.15F**, are taken from an experiment similar to that from **3.15C** and **3.15D**, but here 150 mL of the solution was passed through the reactor. The layer seems much thicker than that seen in **3.15C** and **3.15D**, as would be expected. **3.15E** shows a view of the middle of the glass, and displays a large amount of nanoparticle agglomeration over top of a layer of CBS growth. **3.15F** shows a closer view of a sample of coating, again from the middle of the FTO glass. Here, columnar growth of the CBS from the FTO is seen, as evidenced by the large, tightly packed particles. They are larger than the particles shown in **3.15D**. While this even layer exists, there is still evidence of nanoparticles settling out of solution on top of the layer.
While this reactor is obviously not ideal for deposition for the reasons discussed previously in this chapter, these runs did offer important information that fed into decisions we would make for the design of Reactor 2. We can see from the images in Figure 3.15 that CBS will grow directly from the FTO glass under the right conditions. The theme seen here of columnar growth with particles on top that had fallen from solution inspired the change in Reactor 2 of putting the FTO face down so that particles formed in solution would fall away from the glass.

A run of nitrates and L-cystine was attempted in Reactor 2, as we knew it worked in Reactor 1. The temperature gradient was 160°C-185°C and the liquid was pumped through at a constant 1.83 mL/min. The deposition resulting from the Reactor 1 and Reactor 2 runs with nitrates and L-cystine were scanned with the XRD. These scans are shown in Figure 3.16.

![Figure 3.16: XRD scans of depositions made with Reactor 1 and Reactor 2 using a nitrates and L-cystine solution.](image)
While Reactor 1’s deposition is not ideal, it has made CBS on the FTO glass, albeit with some impurities. In Reactor 2 this was not the case. The methods used to even the flow, such as the small holes and the vertical trip to the reaction chamber, have filtered out the undissolved particles from the suspension of nitrates and L-cystine. When the reactor was opened, a white soggy powder, the undissolved L-cystine, was seen inside the first two reservoirs.

If the reactants are not present in the proper concentrations, then CBS cannot be formed in the reaction chamber, as is clearly shown by the XRD scan of Reactor 2 in Figure 3.16.

3.5.1.3 - Acetates and CS2:

This combination was attempted as the standard solution mostly dissolved in solution, with only a few grains of powder still showing on the bottom of the vessel. This is described in Section 2.2.2.3.4. Although a gas is produced with this combination, it was described as a white vapor that sits above the reacting liquid and so it was hoped that the relative pressure of the reaction chamber could keep it within the liquid. The major reason it was attempted was that its impurities are CuS and Bi₂S₃ which, as described in Section 2.3.2.3, we know to convert to CBS upon heating. Should an even deposition of product be made a thermal treatment could convert it all to CBS and a pure layer could be obtained. For this deposition the temperature gradient was again 160°C-185°C and the liquid was pumped through at constant 1.83 mL/min. After an attempt at the deposition, pictures of the FTO glass and the reactor were taken. These images are shown in Figure 3.17.
Looking at 3.17A, deposition has not taken place with any noticeable pattern related to the temperature of the liquid. No XRD scan was performed.

3.17B shows that a reaction did, however, occur. In Section 2.2.2.3.4, it is stated that in the middle of the heating process “the stir plate was turned off and particles were seen to easily fall down,” indicating that large particles formed quickly. In the reactor it seems that particles formed too quickly in the solution to stick and grow against the FTO.

Figure 3.17: 3.17A is an image of the FTO glass post deposition with acetates and L-cystine. 3.17B shows the precipitate left in the reaction chamber, clogging the reactor.
glass. This left a sludge clogging the reaction chamber. Tellingly, the sludge is concentrated in the “hot” end of the reactor.

Attempting chlorides and CS$_2$ was briefly considered as this combination fully dissolved. However, in Section 2.2.2.3.3 the same observation was made about particles easily falling out of solution during the heating process and so the idea was dismissed.

3.5.1.4 - Chlorides and Thiourea:

The chlorides and thiourea solution, while not completely dissolved, made a suspension that stayed stable for days. As reactor runs only take a few hours, and the suspension could be stirred until it was introduced into the lines, this was sufficient. The reaction also produced no gas. The combination does not make a pure CBS in the flask, however. Some amount of CuS was shown to be present. It was thought that if the reactor run was successful in creating CBS the extra CuS might be eliminated by adding more bismuth chloride than was standard.

A full concentration solution was made and passed through the reactor at a constant 1.83 mL/min with a temperature gradient of 160-185°C. When the FTO glass was taken out of the reactor, a thick black coating was seen all along the exit side of the FTO glass. This mostly fell off when rinsed. This temperature gradient was deemed too small to learn anything, and the concentration of the solution too high.

For the next experiment, water was passed through a coolant hole to push the temperature differential up to 130-200°C. A 10x dilution was made of the standard suspension and this was passed through at 1.83 mL/min for 15 minutes, stopped for 15 minutes and then repeated until all of the suspension was passed though. Deposition results and COMSOL temperature simulations are shown in Figure 3.18.
Figure 3.18: Graphs of COMSOL simulated temperature (°C) vs. position (m) of the liquid against the FTO glass for the 130-200°C run with chlorides and thiourea. Figure continued on next page.
Figure 3.18: 3.18C shows COMSOL generated heat map of liquid directly against FTO glass. Reaction chamber is within black line. White is hottest and dark red is coldest. 3.18D shows an image of the deposition with a grid corresponding to the lines in 3.18A and 3.18B.
The flow is moving from the bottom of 3.18C and 3.18D to the top of the image.

Deposition of the material begins when the liquid is 130°C at the start of the hot side. On the cold end, the 0.0498 line shows that the solution must reach about 142°C for light deposition to occur. The thick black deposition occurs when the liquid is at approximately 197°C on the 0 line along the flow. According to COMSOL, this temperature is reached in the liquid when it is approximately halfway through the reaction chamber. The black deposition, however, does not appear until the last portion of the chamber. Black deposition is seen on the 0.0142 line as well when the liquid has supposedly only reached 185°C. In the moving liquid, the COMSOL simulations can clearly only be relied upon to give approximate temperature data.

If the temperature gradient were shifted up 15 degrees on either side we would expect the deposition to occur further to the left. This experiment was attempted with the same concentration and flow condition as the experiment discussed above. The temperature gradient was adjusted to be 145-215°C. The same graphs and images were generated and collected. They are displayed in Figure 3.19.
Figure 3.19: Graphs of COMSOL simulated temperature (°C) vs. position (m) of the liquid against the FTO glass for the 145-215°C run with chlorides and thiourea. Figure continued on next page.
Figure 3.19: 3.19C shows COMSOL generated heat map of liquid directly against FTO glass. Reaction chamber is within black line. White is hottest and dark red is coldest. 3.19D shows an image of the deposition with a grid corresponding to the lines in 3.19A and 3.19B.
The flow is moving from the bottom of 3.19C and 3.19D to the top of the image.

As expected, the deposition extends further across the glass, nearly across the entirety of the surface. Some is even seen at the cold start corner. This corner is about 135°C, which is where faint deposition began in the last experiment. The black deposition is seen along the 0.0284 line along the flow when the solution is shown to be 185°C.

COMSOL begins to show its limits when looking at the areas where black deposition occurred. Nearly the entirety of the 0 line going along the flow is shown to be 210°C, which is greater than the boiling point, $T_b$, of ethylene glycol (197.3°C). There is evidence of bubbling along the edges of the hot corner, but it is unlikely that boiling would have gone unnoticed in this reactor. Assuming that all material dissolved, a pressure of 1.52 atm would be required to increase the $T_b$ to 210°C, and so the pressure inside the reactor would need to be greater than this for the solution to remain liquid. The reactor is prone to leaking, so it is unlikely that this pressure was attained. It is more likely that COMSOL’s simulations are in error.

Still, we can see trends in the data. By analyzing the images we can see that the faint green deposition occurs when the liquid has reached approximately 135°C. The black deposition, likely a thicker coating of the green material, occurs when the liquid has reached 185°C and above. The hotter the ethylene glycol the better the deposition seems to stick, leading to a thicker coating in the hot zones.

There was some concern that the drastic temperature gradient would lead to a difference in viscosity of the ethylene glycol across the chamber and in turn a significant variance in velocity and material growth. Figure 3.20, generated from the 145-215°C
simulation, shows although there is an effect, it is slight. The difference in deposition across the chamber is from the variance in temperature, and not velocity of the liquid.

Figure 3.20: Velocity graph from the 145-215°C simulation, showing the slight effect that the change in viscosity plays in the velocity profile.

The hot end corner of glass coated with the black material was cut from both reactor runs and XRD was performed on them. The results are shown in Figure 3.21.

Figure 3.21: XRDs of hot end corner of both chlorides and thiourea reactor runs.
No copper bismuth sulfide was deposited. The black material is a combination of CuS and Bi$_2$O$_3$. It is likely that the green deposition is CuS as this is its color, as described in Section 2.2.2.4.3.

It is unlikely that the chamber became hot enough to degrade the CBS, as we have seen in Section 2.3.2.2 that the material is relatively stable in air at temperatures up to 300°C. After 12 hours at 300°C it became slightly oxidized, but that is far longer than the time required for the reactor run, and far higher in temperature.

It is possible that the vapor released in the flask reaction is an important step in the synthesis of CBS from chloride salts and thiourea. Because it is sealed within the reaction chamber this gas may not be released which could have influenced the products formed. Or it may be that the CBS precipitation chemistry requires longer incubation times than provided in the flow-through reactors.

3.5.2 - CdS Deposition with Reactor 2:

The reagents and solution made to deposit the CdS are discussed in Chapter 4 in Section 4.2.1.3 and 4.2.2.3.1 respectively. The solution formula itself was previously used by another group who was also using a custom built reactor to deposit CdS onto FTO glass.$^{79}$ As they successfully deposited their target material on the FTO this was a good opportunity to use our diagnostic reactor to study temperature effects on deposition.

The solution used for this experiment was water based rather than ethylene glycol based. The temperature gradient was set to 70-100°C and the solution was passed through at 30 mL/min, as was called for in the previously mentioned work.$^{79}$ COMSOL was adjusted to these parameters. The same graphs were then generated as in Section 3.5.1.4 and displayed, along with an image of the deposition, in Figure 3.22.
Figure 3.22: Graphs of COMSOL simulated temperature (°C) vs. position (m) of the liquid against the FTO glass for the 70-100°C run to deposit CdS. Figure continued on next page.
Figure 3.22: 3.22C shows COMSOL generated heat map of liquid directly against FTO glass. Reaction chamber is within black line. White is hottest and dark red is coldest. 3.22D shows an image of the deposition with a grid corresponding to the lines in 3.22A and 3.22B.
The yellow color observed at the end of the FTO is indicative of CdS. Here, the deposition has only occurred between the 0.0081 and 0 lines that run across the reactor flow. It has still occurred across the entire reaction chamber length. According to the COMSOL generated temperature maps, the region from 0 to 0.0081 is roughly 10°C “thick.” The deposition does seem to be more colored near the very end of the reactor, line 0, as opposed to the lightness seen near line 0.0081.

The deposition is also about 30°C “long” from the cold side to the hot side of the reactor. Again looking at the generated lines, this region begins on the left side at about 65°C and ends at 95°C.

However, if the deposition began at 65°C we should see it along the vast majority of the FTO surface. It is possible that the glass is dampening the temperature gradient more than COMSOL has predicted.

The fact that the deposition has occurred all along the end of the reactor points to the solution taking time to get up to temperature.

Another experiment was run with the same solution. This time, the temperature gradient was pushed to 80-110°C and the liquid slowed to 15 mL/min. It was predicted this would allow for greater coverage of the FTO glass. Images and simulations are displayed in Figure 3.23.
Figure 3.23: Graphs of COMSOL simulated temperature (°C) vs. position (m) of the liquid against the FTO glass for the 80-110°C run to deposit CdS. Figure continued on next page.
Figure 3.23: 3.23C shows COMSOL generated heat map of liquid directly against FTO glass. Reaction chamber is within black line. White is hottest and dark red is coldest. 3.23D shows an image of the deposition with a grid corresponding to the lines in 3.23A and 3.23B.
As predicted, more of the FTO surface is coated in CdS. The deposition has occurred preferentially on the sides of the reaction chamber. As the liquid moves slower near the walls, this makes sense. Along the 0.064 line, we see that deposition has begun at approximately 65°C, as was the case in the last experiment. At the start of the hot end, along the 0 line, we find that the temperature of the liquid begins at about 70°C and increases from there. There is deposition all along this line.

Of course, again, if the deposition occurs above 65°C then even more of the glass should be coated. The COMSOL calculations also state that the solution’s temperature is 107°C in some places. Accounting for the ions in solution, the pressure would need to be held above 1.10 atm inside the reactor for the solution to remain liquid at this temperature. This is, however, more likely for this run as the liquid was pumped through the reactor with a significant pressure, allowing the fast flow velocity.

On the macroscopic level, it does seem that the thicker deposition results from higher temperatures. In order to assess the quality of the deposition, small pieces from the four corners of the FTO glass were cut, coated with 15 nm of gold and SEM images were taken of them. Images of these follow in Figure 3.24 along with SEM images of the bare FTO glass for comparison. The temperature included explains which end the sample came from, hot or cold. The “start” or “end” describes if the glass section was from where the solution was first introduced or where it exited.
Figure 3.24: SEM images of FTO glass, as well as CdS-80°C-Start and CdS-80°C-End. Figure continued on next page.
Shown in 3.24A and 3.24B, the FTO glass is textured with smooth triangular prism shaped grains evenly covering the surface. This surface will serve as the template for any deposition occurring on top. It is distinct enough that material on top can be easily picked out.

3.24C displays a magnified image of the bottom left corner of 3.23D. Despite there being no yellow color displayed on the macro scale, 3.24C does show some amount of material growing on top of the FTO. It is an uneven coating, mostly appearing as large chunks. 3.24D, is a much further zoomed in picture of the same area. Here we observe small nodules, about 10nm in size, growing from the otherwise smooth sides of the FTO grains. At this point, according to the COMSOL simulations, the liquid is only 65°C or
less, and has been in contact with the hot FTO for only a very short amount of time, yet the beginnings of growth is seen.

Looking to 3.24E, which is cut from the end of the 80°C region, we can see a more widely spread deposition than seen in 3.24C. There are areas that seem to be relatively flat. In these regions the texture of the FTO has been filled in with CdS. There are also sections that are raised and separate from the rest of the coating. Some have stacked on top of each other. 3.24F is a closer image of a piece of the coating where the FTO can almost be seen underneath. It has been completely covered by a bumpy coating of CdS. At this point, the liquid has reached approximately 77°C and has made a far better coating than the 65°C deposition.

3.24G, from the start of the 110°C side, shows very little difference from the FTO glass. There is one distinguishable piece of extra material in the middle of the image. Looking closer at the same area, 3.24H displays the later stage of the small nodules present on 3.24D. It seems that they have grown together to make a new surface, with many of the grooves present on the FTO being filled in and the sharp edges being softened. The sample does display some small nodules on certain grains as well. The solution that was in contact with this sample was about 80°C.

Moving on to 3.24I the image displayed here shows a texture not unlike that of the FTO. There are small pieces sticking off of it, but they are not widespread. The coating is relatively consistent throughout the image. When looking at the further zoomed in image in 3.24J we see that the CdS has completely, and densely, coated the FTO. Again, the coating looks bumpy. The CdS has completely encased the FTO, without filling the spaces in between, unlike in image 3.24F. This seems to be the best deposition,
as its tightly packed nature would make it easier to control the thickness of the coating. On the macro scale, this region was also iridescent, implying the good even coating seen in the micrographs. Here, the simulations point to the solution being heated to 107°C, which would again require a pressure of 1.10 atm to occur. The best coating again seems to be from the hottest region.

3.6 - Conclusions:

Reactor 2 is a vast improvement over Reactor 1 for a multitude of reasons. We can control and monitor the temperature applied to the solution inside, it has an even flow across the reaction chamber and it can aid in determining the best temperature for deposition with its temperature gradient. On a mechanical note, while Reactor 2 does sometimes leak, Reactor 1 leaked more and was more prone to breaking the FTO glass placed inside of it.

Unfortunately, Reactor 2 has so far been unable to deposit CBS onto FTO coated glass. This is, however, more to do with the chemistries that produce CBS being incompatible with its design rather than the reactor itself. Should a new chemistry be found that forms a pure CBS, whose reactants completely dissolve in the solvent at room temperature and does not produce a gas, then the reactor would be of use for this material.

With it, we were still able to experiment with the CdS deposition process and learned that the best deposition occurs at temperatures of 107°C, under a small amount of pressure. At this temperature, there is little variation in the quality of the coating and nanosized tightly packed nodules that display iridescence grow across the whole surface.
Having been demonstrated with CdS as an example, Reactor 2 would still be of use for other materials able to be deposited via a solvothermal process occurring onto glass substrates.
CHAPTER 4: Electrodeposition and Optimization of Cu$_3$BiS$_3$

Thin Films for use in Photovoltaic Devices

4.1 - Introduction:

Electrodeposition is a technique that has been used for hundreds,\(^87\) possibly thousands,\(^88, 89\) of years to deposit thin coatings of a desired material onto a substrate. It can be used to deposit single elements such as gold,\(^90\) sulfur\(^91\) and even silicon\(^92\) as well as binary materials like Bi$_2$Te$_3$\(^93\) or Bi$_2$O$_3$\(^94\). This technique has even been used to deposit the tertiary compounds CuInSe$_2$,\(^95\) CuFeS$_2$\(^96\) and CuInS$_2$\(^97-99\) and the quaternary compounds CuSCN\(^100\) and Cu$_2$ZnSnS$_4$\(^101\). It can be used to deposit large scale, smooth layers of materials,\(^102\) which is extremely important when fabricating solar panels. The fact that many solar materials\(^92, 95-99, 101\) have already been deposited using this technique was an encouragement to attempt its use for depositing copper bismuth sulfide, CBS.

While CBS has been deposited via electrodeposition and sulfurization before, ours improves upon previous methods in several ways. One procedure recommends the use of commercially available solutions and requires shipping out to a separate team to do the deposition.\(^50\) Another procedure states that 30 minutes at 500°C in a nitrogen atmosphere is required for the heat treatment, but the XRD patterns generated by samples made with our method look significantly more pure.\(^47\) Both of the previously mentioned methods require a harsh 2M NaOH solution.\(^47, 50\) Our comparatively mild solution leads to less expensive waste disposal and is better for the environment.
Creating a large area of evenly thin, smooth layers of CBS could lead to cost effective, energy efficient solar panels. Using and improving upon inexpensive processes such as electrodeposition to deposit these thin films will further reduce cost.

We have utilized our two step CBS electrodeposition method to fabricate a heterojunction photovoltaic, PV, device with CdS as the n-type and CBS as the p-type. An attempt was also made to make devices with a 0.01% Zn doped CBS as the n-type.

4.2 - Experimental:

4.2.1 - Reagents and Substrate:

4.2.1.1 - Substrate:

The fluorine doped tin oxide coated, FTO, glass was purchased from Sigma-Aldrich. The surface resistivity, as reported by Sigma-Aldrich, is \( \approx 8 \Omega/\square \). Their notation describes it as “\( \approx 8 \Omega/sq. \)”.

4.2.1.2 - Reagents for CBS Electrodeposition:

\( \text{Cu(NO}_3\text{)}_2 \cdot 3 \text{H}_2\text{O} \ (99-104\%), \text{sulfur powder} \ (99.98\%), \text{Na}_2\text{SO}_3 \ (\geq 98\%) \) and sodium citrate tribasic dihydrate \( (\geq 99.0\%) \) were purchased from Sigma-Aldrich. \( \text{Bi(NO}_3\text{)}_3 \cdot 2 \text{H}_2\text{O} \ (98\%) \) was prepared by ACROS Organics. The \( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \ (99+\%) \) was manufactured by Alfa Aesar. The \( \text{Zn(NO}_3\text{)}_2 \cdot 6 \text{H}_2\text{O} \) (educational grade), methanol (Certified ACS) and ethylene glycol (max 0.2% \( \text{H}_2\text{O} \)) was made by Fisher Scientific.

The forming gas \( (5\% \text{ H}_2, 95\% \text{ N}_2) \) and argon used in the tube furnace were supplied and prepared by Airgas.
4.2.1.3 - Reagents for CdS Deposition:

CdCl$_2$ • 5/2 H$_2$O (99+ %) and the 28-30% NH$_4$OH solution were manufactured by Acros Organics. Reagent grade NH$_4$Cl was purchased from and manufactured by Fisher Science. Thiourea ($\geq$ 99.0%) was made by and bought from Sigma-Aldrich.

4.2.2 - Preparation:

4.2.2.1 - Substrate Preparation:

FTO glass was cut into approximately 25mm x 25mm squares and scrubbed with methanol and KimWipes. The pieces were stored in 0.1N KOH, to remove organics on the surface, until they were deposited on. Typically, they were left for at least one night.

4.2.2.2 - Electrodeposition of CBS:

4.2.2.2.1 - CBS Deposition Solution: 0.5 mmol of Bi(NO$_3$)$_3$ • 2 H$_2$O (0.243 g) was dissolved into 20 mL of ethylene glycol to form a transparent, colorless solution. 1.5 mmol of Cu(NO$_3$)$_2$ • 3 H$_2$O (0.362 g), 25 mmol of Na$_2$SO$_3$ (3.151 g) and 10 mmol (2.941 g) of sodium citrate tribasic dihydrate (Cit-Na) were dissolved into 30 mL of DI H$_2$O leading to a transparent blue solution.

4.2.2.2.2 - Solution for 0.01% Zn CBS Deposition: 0.004 grams (1.34 x 10$^{-5}$ mol) of Zn(NO$_3$)$_2$ • 6 H$_2$O were dissolved into 100 mL of ethylene glycol. 1.11 mL of the transparent, colorless solution containing 1.5*10$^{-7}$ mol of Zn$^{2+}$ was added to 18.89 mL of ethylene glycol that had been stirring with the previously noted amounts of Na$_2$SO$_3$ and sodium citrate tribasic dihydrate. Only 1.485 mmol of Cu(NO$_3$)$_2$ • 3 H$_2$O (0.358 g) were used in this formulation.
4.2.2.3 - Electrodeposition and Heat Treatment Process: The following procedure was carried out at room temperature. With one solution stirring, the other was poured in slowly leading to a transparent blue solution. The mixing order was not found to be important. The two separate solutions are very stable, but it is important to carry out the electrodeposition quickly upon mixing. If left for several hours, some amount of solid would precipitate out, even if the solution was left stirring. An attempt was made to mix all reagents and solvents together at once. This resulted in a blue, opaque mixture that was not used. Previous research indicates that the pH is an important factor but for this deposition it was not found to be important, and was not accounted for or adjusted.

The clean FTO glass was attached via alligator clip to the negative electrode of the power supply, while the positive electrode was affixed in the same way to a roughly 25 mm x 25 mm piece of platinum foil. Both were submerged approximately 75% of the way to make sure that the alligator clip was not touching the stirring liquid. The voltage was set to 1.2 V or 2.5 V, depending on the experiment, and the deposition was allowed to proceed for 3, 5, 10 or 20 minutes. One electrodeposition was performed for one hour, as recommended by a paper about the synthesis of CuInS₂ that this research was based on. After this, the voltage was shut off.

The coating left on the FTO glass was notably different depending on the voltage applied. 1.2 V left a copper colored coating while the 2.5 V left a black coating. Both were rinsed with DI H₂O and methanol. It was ultimately found that 1.2 V lead to better results over all.

The FTO glass slides were then placed into a small glass dish along with approximately 0.4g of sulfur powder. A top was placed on the dish and it was set in the
middle of a tube furnace. The ramp speed, up and down, was set to 150°C/hour with a maximum temperature of 450°C. This temperature was applied for 90 minutes. The tube furnace was fed a mixture of 95% N₂ and 5% H₂, also known as forming gas, at a rate of 2.0 L/min for the entire duration. Argon was attempted, but found to lead to inferior results. No further treatment was required to obtain CBS films, which were gray in color.

4.2.2.2.4 - CBS and 0.01%Zn CBS P-N Junction Preparation: When attempting to form a p-n junction, the Zn doped CBS mixture was applied first as the junction needs to be at the site of the light source. Four experimental devices were made with this junction. The deposition was performed at 1.2 V. The Zn doped CBS mixture was deposited for 5, 10, 30 and 60 seconds. The pure CBS mixture was then allowed to deposit on the coatings for 4 minutes 55 seconds, 4 minutes 50 seconds and so on respectively to allow the same film thickness and total deposition time for all samples. All remaining steps were the same as detailed above.

4.2.2.3 - Preparation for Deposition of CdS Films on FTO Glass:

4.2.2.3.1 - CdS Deposition Solution: While the method of deposition is original to this work the solutions used were formulated by a separate group in previously completed work. The solutions used were formulated by a separate group in previously completed work. 79

0.043 g of CdCl₂ • 5/2 H₂O (0.188 mmol), 0.101 g of NH₄Cl (1.89 mmol) and 2.754 mL of 28-30% NH₄OH solution were brought to 47 mL with DI H₂O and dissolved. It is important to note that 28-30% NH₄OH is approximately a 7 M solution. Together, this is a 0.004 M CdCl₂ • 5/2 H₂O, 0.04 M NH₄Cl and 0.41 M NH₄OH solution.
In a separate flask 0.143 g (1.88 mmol) of thiourea was mixed into 47 mL of DI H₂O to give a 0.04 M solution.

**4.2.2.3.2 - Procedure for CdS Deposition:** A glass petri dish, known to hold 95 mL of liquid at capacity, was placed on a hot plate with a large stir bar inside. Cleaned FTO glass was cut into four strips approximately 100 mm x 25 mm and placed on top of the petri dish, FTO side facing down, resting on the dish’s edges. With the stir bar spinning, the two solutions described above were poured into the petri dish at the same time. A thermometer was placed into the liquid, making sure that it did not touch the bottom of the dish. An image of this set up is seen in **Figure 4.1.**

![Figure 4.1: Image of the experimental setup to deposit CdS on FTO glass.](image)

It is important to have the FTO cut into strips, as it is easy to extricate any bubbles that might form during the deposition process. With the resulting liquid now fully in contact with the FTO glass, the heat on the hotplate was turned on to low heat.

At 52°C the liquid began to turn yellow and continued to become more intense until 68°C when deposition became evident on the glass. At 75°C CdS was readily
forming in solution. To prevent large chunks from agglomerating on the surface of the FTO, the heat was turned off and the strips removed. The now yellow strips were rinsed with DI H$_2$O and methanol.

4.2.2.3.3 - CBS and CdS P-N Junction Preparation: The CdS coated strips of FTO glass were cut into roughly 25 mm x 25 mm squares. Deposition of CBS was then performed upon them with the same method described above.

4.2.3 - Instrumentation:

X-Ray Diffraction patterns were recorded using Cu K$_\alpha$ radiation with a wavelength of 1.54 Å generated with a PANalytical X’Pert PRO using MDI Data Scan as a controller. The scan range was 12.5° to 67.5° with a step size of 0.0131° scanning at 0.037 °/s.

SEM images were again taken with a Zeiss Sigma Field Emission Scanning Electron Microscope.

The power supply used to deliver the current to the electrodeposition system was a BK Precision Model 1660 Triple Output DC Power Supply.

The tube furnace used to bake the samples was a CM Inc. Rapid Temp Furnace.

A Newport Lamp, model 91160-1000, with a Newport 300 watt xenon bulb was used as a solar source during the solar efficiency experiments.

The, ultraviolet-visible spectroscopy, UV-Vis, tests were carried out with a Thermo Scientific Evolution 300 using the software VISIONpro. Scans were made from 300nm to 1100nm with a 2nm step size.
4.3 - Results and Discussion:

4.3.1 - Nomenclature for Sample Referencing:

Many factors were altered and tested in the attempts to find the best method for obtaining a smooth, properly thick and phase pure CBS coating. The voltage used for the electrodeposition, the time spent electrodepositing, as well as the gas were all changed a number of times. The temperature and time in the tube furnace were kept constant at 450°C and 90 minutes but still factor into the naming scheme in order to indicate if the samples were pre or post bake.

If, for instance, a sample was deposited upon at 1.2 V for 5 minutes and put into the oven for 90 minutes at 450°C under argon, that sample would be called 1.2V-5m-450C-Ar. If electrodeposition occurred at 2.5 V for 20 minutes, and the atmosphere in the oven was forming gas it would be called 2.5V-20m-450C-Form. Before baking, this same sample would be called 2.5V-20m-Raw.

This nomenclature will be used as needed throughout this chapter to distinguish samples from one another.

4.3.2 - On Choosing the Salts:

Previous papers detailing electrodeposition of copper sulfides, CuInS$_2$, suggest the use of chloride salts dissolved in water. However, bismuth chloride reacts with water to form BiOCl, which is insoluble in water. Most bismuth salts are insoluble in water and so the two solution method described above was developed.

Before testing with nitrates began, chloride salts in the same concentrations as previously discussed were attempted. Despite the bismuth chloride not dissolving at all, CBS was still formed using it and copper chloride in the same procedure described
above. Still, we believe having a well dissolved solution is preferable to a slurry as it is easier to control. We will only be detailing samples made with nitrate salts, unless expressly stated.

4.3.3 - Analysis of Samples for Determination of Best Treatment Conditions for Deposition of Target Material:

4.3.3.1 - Accounting for FTO Glass Background in XRD Results:

As we were depositing thin films of CBS on FTO glass, there was concern that the XRD would show a pattern for both it and for the material we synthesized. To account for this, we scanned a plain piece of FTO glass and compared it with literature peaks. Our scan and the literature lines can be seen in Figure 4.2.

![Figure 4.2: The XRD pattern for plain FTO glass is shown here.](image)

The scan matches well with literature values, except that the peak at about 38° on the experimental scan is much higher than shown with the literature peaks. As the SnO$_2$ is grown on glass, this is likely due to an expression of a preferred growth orientation. As
the difference between our scan of FTO and the literature XRD is noticeable and consistent throughout our experiments, our experimental scan of FTO will be used throughout this document for comparison.

4.3.3.2 - Characterization of the as Deposited Film:

An XRD scan of the 1.2 V and 2.5 V electrodeposition was performed before they were heat treated. The XRD patterns of FTO glass and both 1.2V-5m-Raw and 2.5V-5m-Raw are shown in Figure 4.3. A photograph of the as-deposited films can also be seen. Discussions follow.

Figure 4.3: 4.3A shows the XRD patterns for the “raw” 1.2 V and 2.5 V 5 minute depositions, before it is put into the tube furnace. 4.3B and 4.3C show images of a 1.2V-5m-Raw sample displaying a copper like color and of a 2.5V-5m-Raw sample displaying a black color, respectively.
The 1.2 V, while it had a copper color, displayed peaks for only SnO$_2$ and Bi. This is puzzling as it is estimated that Bi has only 0.25 - 0.5% solid solubility in Cu$^{103}$ and Cu has only 0 - 0.010% solubility in Bi.$^{104}$ There is a metastable phase, Cu$_3$Bi$_2$, that could develop$^{103,104}$ but the stoichiometry doesn’t justify it as if it formed there would be copper left over, and not bismuth. No indication of this metastable phase was found in the XRD data. Other studies have said the layer to be Cu$_3$Bi,$^{47,50}$ but our XRD peak matching did not confirm this. Because of the reasonable match to crystalline Bi perhaps it is possible that the Cu-Bi mixture was deposited as a metastable solid solution with a structure matching pure bismuth’s.

For the 2.5 V sample, while there was an obvious black deposition layer on the glass, the XRD scan only showed FTO. As these films do convert to CBS this indicates that the mixture of copper and bismuth (and possibly sulfur) present on the glass is amorphous before it is treated in the oven. The sample with 0.01% Zn looked identical to the pure CBS sample.

Both samples displayed patterns of thick and thin coating, as one could see through portions of the deposition when the square was held up to a light source. These are thought to be due to turbulence across the FTO surface resulting from the stirring liquid’s path around the edges and corners of the 3 mm thick glass. This would lead to varying liquid velocities and, as discussed in Section 3.3.1, different deposition rates.

**4.3.3.3 - Impact of Electrodeposition Voltage on Product Formation:**

After treatment in the tube furnace, the slides were scanned with the XRD once more. This revealed that the copper, bismuth and sulfur had formed Cu$_3$BiS$_3$ for both samples. The XRD peaks for the FTO glass are still seen through the CBS, so our FTO
XRD as well as the literature CBS patterns are shown under the sample results. Again, these results are for 5 minutes of electrodeposition. The patterns can be seen in Figure 4.4. Again, the 0.01% Zn sample looked identical to these XRDs, as seen in Section 2.2.2.5 with solvothermal synthesis of doped CBS, and is not shown here.

![Figure 4.4: The XRD scans shown indicate that phase pure CBS has been made on FTO glass using both 1.2 V and 2.5 V.](image)

We now know that while there is a noticeable difference in the pre-treated film, the voltage of the electrodeposition does not ultimately alter the product synthesized, at least on a phase assembly level.

**4.3.3.4 - Attempting a One Hour Electrodeposition:**

The paper that this research is based off of calls for 1 hour of electrodeposition on the substrate. This was attempted for completeness. This sample was run for 1 hour at 1.2 V. This test was done early in the research, and prepared using copper chloride and bismuth nitrate in the same molar proportions described in Section 4.2.2.2.1.
This sample was baked at 450°C for 90 minutes in an argon atmosphere and then an XRD scan was taken. An XRD scan of this sample can be seen in Figure 4.5. Also included in this figure is the scan of a 5 minute deposition using the same voltage and salt combination. This is to show that this formulation has the potential to make pure CBS, but did not in the case of the hour long deposition.

![Hour Long Electrodeposition Test](image)

**Figure 4.5:** An XRD scan of a 1.2V-1hr-450C-Ar and a 1.2V-5m-450C-Ar sample both made using a combination of copper chloride and bismuth nitrate.

Pure CBS has been made on the 1.2V-5m-450C-Ar sample, made with copper chloride and bismuth nitrate. The 1.2V-1hr-450C-Ar sample made with the same salt combination shows some evidence of CBS growth, but also other unidentified compounds.

Before this sample, a 2.5V-1hr-450C-Ar sample was also prepared. Towards the end of the electrodeposition process, it was noted that a black powder was flowing off of the layer as the liquid stirred around it. This shows that the outermost layer of the
electrodeposition was not as well adhered as the innermost. This was likely the case for the \textbf{1.2V-1hr-450C-Ar} sample as well.

As the different ions in solutions have different charges, they would also have different degrees of attraction to the growing layer of copper, bismuth and sulfur. In the beginning of the deposition, the ions seem to deposit according to their concentration in the solution, which is expected and desired. Later on, with the thicker layer, they stick in proportion relating to the driving force pushing them to adhere to the surface. This force would, again, relate to their charge. This would mean that with a thicker layer, as produced by a longer deposition time, ions could attach in the “wrong” proportions. When the sample was heated, some CBS could be formed, as shown in the figure above, but also other compounds due to the “wrong” proportions of elements being available in the layer. With more focused effort, it is possible that one could determine the correct chemical makeup for a solution that would make the desired CBS phase with a 1 hour deposition, but this was not pursued.

\textbf{4.3.3.5 - Assessing Necessity of Sodium Citrate Tribasic Dihydrate:}

This work is inspired by previous research on the electrodeposition of CuInS\textsubscript{2},\textsuperscript{99} so changes to the experimental procedure had to be made in order for us to synthesize Cu\textsubscript{3}BiS\textsubscript{3}. Aside from requiring different elements, we have found we need to use nitrate salts while the previous research used chloride salts. Electrodeposition for 1 hour does not lead to CBS where as it did lead to CuInS\textsubscript{2}. The pH of our solution was not found to have an influence on the synthesis of our material, where as it was carefully controlled in the previous research. These differences lead to wondering if sodium citrate tribasic dihydrate (Cit-Na) was truly required for our procedure to work.
In the previous research it was hypothesized to function as a complexing, or chelating, agent. As we were using different salts and solvents it was possible that our method would work without it. An electrodeposition solution was made in the same method as described in Section 4.2.2.1, but without the Cit-Na. While the separate solutions were both similar looking to before, the bismuth solution clear and colorless and the copper solution a transparent blue, the combined solution immediately turned an opaque yellowish white.

As described in Section 4.3.2 a well dissolved electrodeposition solution is not necessarily required to form CBS and so the solution was tested. A 1.2V-5m-450C-Ar and a 2.5V-5m-450C-Ar sample were prepared with the solution and the resulting films were scanned with the XRD. The results are shown in Figure 4.6.

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**Figure 4.6:** XRD of samples prepared without sodium citrate tribasic dihydrate. Clearly, no CBS was formed in either sample.
It can clearly be seen that no CBS was made on the FTO glass. For all remaining samples, Cit-Na is included in the solution in the proportions previously described.

4.3.3.6 - Vulnerability of Raw Electrodeposited Film to Atmosphere:

It was found that it is important to move to the “baking” step quickly, as excessive time spent in atmosphere will cause the black coating to oxidize and turn yellow, rendering it less efficient at making CBS during the next step. A raw sample was left in a covered petri dish for 10 days, baked, and then scanned. The XRD results can be seen in Figure 4.7.

![Figure 4.7: An XRD, post bake, after a raw sample had been left out in a closed petri dish for 10 days.](image)

While CBS was made, there is significant contamination present as well. Some of this is from Bi$_2$O$_3$. This oxidation occurred before the heat treatment due to the electrodeposited layer reacting with ambient oxygen. It is possible that forming gas, as discussed in the next section, could help to reverse this oxidation. Still, from this
experiment forward, samples were placed into the tube furnace as quickly as possible after the electrodeposition.

4.3.3.7 - Determining the Best Atmosphere for Heat Treatment:

The first attempts at making an electrodeposited layer of CBS were heated in an argon atmosphere. When these samples were scanned with XRD CBS as well as Bi$_2$O$_{3.96}$ was found via XRD peak matching. While this partial oxidation is possibly due to leakage issues in our tube furnace, a change of gas helped ensure a pure product. A mixture of 95% N$_2$ and 5% H$_2$, known as forming gas, was chosen to replace argon. As a reducing agent$^{77,78}$, forming gas prevented the formation of oxides, leading to pure CBS thin films. The gas was allowed to flow through the tube furnace at 2 Liters/minute. Lesser amounts lead to some minor oxidation. XRD scans from a 2.5V-5m-450C-Ar and a 2.5V-5m-450C-Form are shown in Figure 4.8.
Due to these results, the remainder of the samples discussed in this chapter were made with forming gas.
4.3.3.8 - Analysis of Influence of Voltage Magnitude on Morphology of Deposition via SEM:

4.3.3.8.1 - Surface Morphology of FTO Coated Glass: In order to visually distinguish between the layer we have grown and the FTO glass substrate, SEM images of FTO glass were taken at various magnifications for comparison. The FTO glass samples were prepared as if they were to be deposited upon. These images are shown in Figure 4.9. The scale bar, SB, sizes are displayed for reference.

The FTO is angular, with sharp angles and flat sides almost looking to be little cubes or triangular prisms embedded in the surface.
**4.3.8.2 - Imaging Raw Samples Electrodeposited at Varying Voltages:** Representative pieces of the 1.2 V and 2.5 V samples, both before and after heat treatment, were collected and imaged using the scanning electron microscope, SEM. A 15 nm coating of Au was used to prevent charging during SEM imaging. Figure 4.10 displays SEM images of both 1.2V-5m-Raw and 2.5V-5m-Raw samples.

**Figure 4.10:** Image 4.10A and 4.10B are of the 1.2 V sample, before baking. Image 4.10C and 4.10D are of the “raw” 2.5 V sample.

It can clearly be seen from these images that the 1.2 V sample has a much smoother, more even coating of material than the 2.5 V sample. The lower voltage could result in a smaller driving force for the ions in solution, leading to a slower and “more
careful” assembly of the layer. This would allow for a smoother coating and a thinner coating per unit of deposition time.

4.3.3.8.3 - Imaging Heat Treated Electrodeposited Samples at Varying Voltages:

Separate 1.2 V and 2.5 V samples were baked in the tube furnace and imaged as well. SEM images are shown of both in Figure 4.11.

![SEM images of 1.2 V and 2.5 V samples](image)

**Figure 4.11**: Image 4.11A and 4.11B are of the 1.2V-5m-450C-Form sample after heat treatment. Image 4.11C and 4.11D are of the “cooked” 2.5V-5m-450C-Form sample.

The images are easily contrasted. The 1.2 V sample is clearly the smoothest and most even of the two. This is evidenced by both the “far” and “close” views of the samples. While there are still slight rough patches and small holes in the 1.2 V layer, it is still the far better deposition. It is worth noting that at the macroscale, the 1.2 V layer
looked gray and lustrous implying a smooth layer. The 2.5 V sample was gray but matte, suggesting more differentiated and chaotic deposition. The 1.2 V layer was also more consistently smooth across the whole surface.

The smoother and more even the layer, the better the electrical contact would be expected to be between it and the electrode. With two smooth layers of material, one p-type and one n-type, laid on top of each other the p-n junction would be aligned perpendicular to the incoming light. This would allow the maximum amount of light to be absorbed. With all this in mind, it was decided that the 1.2 V method was the best suited for photovoltaic, PV, devices.

4.3.3.9 - Analysis of the Effects of Varying Deposition Time for 1.2 V Electrodeposition Via XRD and SEM:

As we have seen in Section 4.3.3.4, excessive deposition time can lead to an impure CBS layer forming. However, varying the deposition time will change the thickness of our CBS layer, which is a useful tool. Also of concern is the physical quality of the film being deposited. For these reasons, various deposition times were tested using 1.2 V electrodeposition.

1.2 V electrodeposition was run for 3, 5, 10 and 20 minutes. These samples were cut in half before being put into the oven. The raw halves were only imaged using SEM while the baked halves were scanned with the XRD and then imaged with SEM. The XRD results for all four samples can be seen in Figure 4.12.
This figure shows that all four preparations have synthesized CBS on the FTO glass. While the 1.2V-3m-450C-Form is the most difficult to parse out, the tallest peaks of the CBS literature lines show through. No other lines are seen on any sample, aside from the FTO.

Looking at this scan also reveals that the thickness of the CBS layer increases as the deposition time increases. This is expected, but still helpful to see. This can be reasoned from looking at the heights of the FTO peaks relative to the CBS peaks. As we buy our FTO from Sigma-Aldrich, we can assume that the conductive oxide is a similar
thickness on all samples. With the 3 minute sample, the FTO peaks clearly tower over the CBS peaks, while the opposite is true on the 20 minute sample. The 5 minute and 10 minute samples are between these extremes, as expected.

Now that the chemical makeup of the layer has been established to be CBS, we imaged the layers in the SEM. The 3, 10 and 20 minute raw samples are shown in Figure 4.13. The 5 minute sample is not shown as it was previously displayed in Figure 4.10.
The three images on the left all look very similar, mostly flat planes speckled with small widely dispersed protrusions. These protrusions appear less frequently in the portion of 1.2V-3m-Raw shown in 4.13A, than in the 10 and 20 minute samples, shown
in 4.13C and 4.13E respectively. All three look virtually identical to the 1.2V-5m-Raw 500X image shown in 4.10A and display good uniformity at this magnification.

Looking at image 4.13B, 1.2V-3m-Raw, an area of inconsistency can be seen in the upper right. This indicates that a three minute deposition is not optimal for deposition. If there are gaps in the CBS layer then the solar cell that would eventually be made from it could easily short out. The longer the deposition time, the better the chance there is to form a consistent layer of CBS.

The more zoomed in images on the right show that all of the 1.2 V samples display a collection of small, round nodules collected on the surface of the FTO glass. For 1.2V-5m-Raw, 1.2V-10m-Raw and 1.2V-20m-Raw these cover the entire surface of the FTO glass and seem to be uniform in their size and coating.

**Figure 4.14** shows the same samples preparations, 3, 10 and 20 minute depositions at 1.2 V, however these images were taken after the samples had been heat treated in the tube furnace.
1.2V-3m-450C-Form looks very similar to 1.2V-5m-450C-Form, but the latter seems more textured than the former. This is likely a result of the 3 minute layer being thinner than the 5 minute layer. The 3 minute layer certainly seems flatter and smoother.
than the 5 minute layer, although holes are still present. This would seem to make it more at risk of short circuits. On the macro scale, the 3m sample was also easily seen through in many places with the naked eye, pointing to a layer too thin to absorb all incoming light adequately.

The 10 and 20 minute samples look similar to each other, yet very different from the 5 minute sample. In 4.14C and 4.14E images of 1.2V-10m-450C-Form and 1.2V-20m-450C-Form strange texturing can be seen. The more magnified images, 4.14D and 4.14F, reveal portions of the CBS pointing up and away from the surface. In the 10 minute sample, these “spikes” are less dense than in the 20 minute samples. These points do not appear to be continuous, having holes throughout. It would appear that they are the result of dendritic growth, although we know that is not the case as the raw samples look smooth in comparison.

A possible reason for this morphology is the difference in unit cell volume as the layer changes from amorphous copper, bismuth and sulfur into CBS during the baking process. The CBS could need to expand or contract, forming the shapes seen here. The CBS crystals that form in the oven seem to grow preferentially in certain directions quickly and others slowly, which makes this strange pointed morphology. The wide variety of growth morphologies of CBS are seen in Section 2.3.2.2 and 2.3.2.3 as well. They imply a large variance of growth velocities and/or surface tension during the heat treatment.

It can be concluded that 5 minutes of deposition at 1.2 V leads to the best copper bismuth sulfide layer as it is moderately thick, mostly even and smooth.
4.3.3.10 - CdS Deposition Analysis via SEM and Tauc Plots:

After the treatment discussed in Section 4.2.2.3.2, the once clear FTO glass took on a yellow color where the reactant solution had touched. This glass was cut and then imaged with the SEM. A photograph of the CdS coated glass and SEM images of plain FTO and CdS coated FTO are seen in Figure 4.15. The image of the FTO is also featured in Figure 4.9, but is placed here as well for ease of comparison.

Comparing 4.15B and 4.15C, there is a clear difference in the surface texture. While the plain FTO glass displays angular grains with smooth edges, the CdS coated
FTO displays a rather flat smooth surface. While some FTO may be seen through the CdS, this does seem to be a mostly even coating of the material.

CdS is the same yellow color observed on the glass in 4.15A and this chemistry has been verified to lead to CdS in previous research, so we can be fairly sure that this is what we obtained as well. To confirm, a UV-Vis measurement was made on the CdS on FTO, using a scan of FTO glass as a background. These data were analyzed and made into a Tauc plot, which is a method of determining the band gap of a material. This plot can be seen in Figure 4.16. The red line has a slope and position averaged from the 20 data points between 2.48 eV, extending to 3.47 eV. “α” here is absorbance.

CdS has a direct bandgap of 2.42 eV and the value obtained from this plot is 2.45 eV. This offers further corroboration that we have obtained our target material.
4.3.3.11 - XRD analysis of CBS on CdS coated FTO glass:

In an attempt to make the p-n junction required for a solar cell to generate electricity, we electrodeposited CBS upon FTO glass coated with CdS. This would, in theory, give an FTO|CdS|CBS structure. However, as the electrodeposited layer of copper, bismuth and sulfur has to be heat treated to become CBS, there was concern that the CdS and the CBS might react in the furnace to give undesirable products. Thus, XRD was taken of the 1.2V-5m-450C-Form as well as the 1.2V-20m-450C-Form that were made on top of this CdS coating. The reason that both of these were made and tested is covered in the next section. These scans can be seen in Figure 4.17.
From 4.17A we see that we have obtained CBS as expected, and that FTO peaks are still seen through the two layers. However, it is difficult to see the CdS peaks in this
plot as they are very close to the CBS peaks in the same region. 4.17B provides a zoomed in look at the telling region of \(24^\circ\) to \(29^\circ\). Here, two CdS peaks are seen to correspond to small peaks on the sample scans. We can now be sure that CdS remains as a distinct layer even after the CBS heat treatment, though some interfacial reaction between the two cannot be ruled out.

### 4.3.3.12 - Characterizing Lab Made CBS CdS Solar Cell:

An attempt was made to test the efficiency of a solar cell made via the method described in the previous section. Two types of these devices were made, one with 5 minutes of CBS deposition and the other with 20 minutes. Four cells of each type were made. A schematic made by the National Renewable Energy Laboratory, NREL, of a comparable solar cell\(^{106}\) and that of our CBS cell are shown in **Figure 4.18**.

![Figure 4.18](image)

**Figure 4.18:** **4.18A** shows an NREL schematic\(^{106}\) of a typical CdTe solar cell that can be used as an analogue to ours. **4.18B** shows a schematic of the CBS cell we fabricated. Neither is to scale.

The \(\text{SnO}_2\text{Cd}_2\text{SnO}_4\) in the NREL schematic is our FTO, which coats the glass. The CdS remains the same for our cell, but the CdTe is replaced by \(\text{Cu}_3\text{BiS}_3\). In place of
C-Paste or a metal backing, another piece of clean FTO glass was pressed onto the bare CBS and affixed with binder clips. Care was taken so that the FTO glass of the back contact did not come into direct contact with the FTO that the CdS was deposited upon. The layers were also staggered so that a conductive surface was available for an alligator clip to be fastened to it.

The current passing through the device was measured as the voltage was changed both under the light of the solar simulator and under darkness. The results for representative samples of each type are seen in Figure 4.19.

![Figure 4.19: The IV curves of the 5m and 20m solar cells.](image)
The machine saturates at 10 mA, explaining the horizontal lines seen at the extreme ends of the lines of both samples. These are artifacts of the instrument and are not real data.

Unfortunately no samples of either type made the IV plots one would expect from a solar cell. They both instead displayed the IV plots one sees in an ohmic resistance, indicating an electrical short. The 5 minute sample was made first. When it failed, the 20 minute sample was made in an effort to fix the assumed short circuit by way of ensuring a thicker coating of CBS. However, this test failed as well.

The samples do display a type of photoactivity, as their resistances change when they are illuminated, although they change oppositely from what is expected of a semiconductor. The IV plots indicate that the resistance actually increases when the sample was exposed to light. It is unknown why this has occurred, but it could be due to some failure of structure rather than a true display of these materials’ properties.

It is hoped that with further refining of the deposition and device fabrication that a working solar cell could be made with these materials.

4.3.3.13 - Characterizing Lab Made CBS 0.01% Zn CBS Solar Cell:

Fabricating and optimizing a solar cell made with CBS as the p-type and 0.01% Zn doped CBS as the n-type was also attempted. Several cells, similar in structure to the schematic displayed in Figure 4.18B with 0.01% Zn CBS in place of CdS, were made. As discussed in Section 4.2.2.4, the 0.01% Zn CBS was deposited directly against the glass for 5, 10, 30 and 60 seconds. The pure CBS solution was then deposited for a corresponding amount of time so that the entire deposition process lasted for
5 minutes. The IV plots for these devices were measured, when exposed to light and in darkness, and are displayed in Figure 4.20.

![Figure 4.20: 4.20A to D display the IV curves for the 5, 10, 30 and 60s 0.01% Zn CBS solar cells under light as well as darkness.](image)

Again, the machine’s sensitivity saturates at 10 mA, explaining the horizontal lines seen at the ends of 4.20A and 4.20B. These are not real data.

All cells display ohmic resistance, indicating an electronic short. Several oddities, relating to the photoactivity of the material, are also on display. The 5, 30 and 60 second cells do not display any photoactivity. This is at odds with the findings of Section 2.2.2.5 and 4.3.3.11. Only the 10 second sample displays the property, and it displays in the opposite manner than expected, similarly to the CdS CBS cells discussed in the previous section, the illuminated test shows a higher resistance than the dark experiment. Any
analysis of trend is disrupted by the 5 second sample’s lack of photoactive display as well.

Again, this failure could be physical in nature and does not necessarily rule out the possibility of this material combination forming a working solar cell.

4.4 - Conclusions:

Copper bismuth sulfide has been deposited on FTO coated glass via electrodeposition and heat treatment. It was found that electrodeposition at 1.2 V for 5 minutes provides the best coating overall. This sample must be heated very shortly after deposition along with sulfur vapor in a 450°C tube furnace with a 95% H₂ 5% N₂ atmosphere for 90 minutes to be converted to phase pure CBS.

The electrodeposition liquid was found to work best with nitrate salts. The copper nitrate dissolves into water, but the bismuth nitrate needs to be dissolved into ethylene glycol before mixing with the aqueous copper solution. The solution formulated here is less harsh and more environmentally friendly than previously found methods. On an industrial scale, this could prove less expensive than comparable electrodeposition methods.

CdS is easily deposited onto FTO by heating a precursor solution directly against the glass. This material does not react substantially with the forming CBS in the previously mentioned 450°C furnace.

Future work may allow for improvement of the morphology of the deposited films and electrical properties, which could lead to working solar cells made from CBS.
CHAPTER 5: Conclusions and Future Work

5.1 – Conclusions:

Renewable energy is finally becoming more prevalent in our world, not only in policy but in practice as well. Green energy infrastructure is now being installed at a rate that outpaces fossil fuels and shows no signs of slowing. Still, solar energy lags behind in adoption due mainly to its high price to the consumer and cost to the manufacturer. While silicon solar panels are presently the cheapest and most common, their expensive and time consuming manufacturing processes are holding solar technology back from rapid growth. The research summarized in this dissertation represents an effort to develop a new semiconductor composition that has the potential of lowering the manufacturing costs of solar energy and, in turn, broaden its adoption.

A low temperature, simple, solvothermal method has been extended to six new combinations of precursor chemicals, all resulting in phase-pure Cu$_3$BiS$_3$. Hydroxide salts and thiourea did not outgas during the reaction, made the purest material and also reacted to completion the fastest. There is a lower limit to the concentration of the solution that will make CBS. This is because a low concentration of starting materials does not have enough of the chemically active basic anion in solution to initiate precipitation of CBS. The concentration of the reagent solution does not strongly influence the time it takes for the reaction to continue to completion; however a more concentrated solution does use less solvent. This is always favorable for a green chemical process. Table 5.1 includes relevant information on all combinations of reagents tested
that produced CBS as well as additional comments about their characteristics and the viability of future experiments with them.

<table>
<thead>
<tr>
<th>Cu and Bi Salt</th>
<th>Sulfur Source</th>
<th>Additional Phases</th>
<th>Gas Produced</th>
<th>Fully Dissolved at RT</th>
<th>Additional Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrates</td>
<td>L-Cystine</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
<td>Made CBS in Reactor 1, but not 2 due to undissolved L-cystine</td>
</tr>
<tr>
<td>Nitrates</td>
<td>L-Cysteine</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
<td>Worth attempting at higher concentration.</td>
</tr>
<tr>
<td>Nitrates</td>
<td>Thiourea</td>
<td>C, Bi$_2$S$_3$, CuS</td>
<td>Yes</td>
<td>No</td>
<td>Worth attempting with higher Bi concentration. Did not produce CBS in Reactor 2, might require more reaction time than was available</td>
</tr>
<tr>
<td>Chlorides</td>
<td>Thiourea</td>
<td>CuS</td>
<td>No</td>
<td>Suspended</td>
<td>Worth attempting with higher Bi concentration. Large particles formed quickly in solution and precipitated easily</td>
</tr>
<tr>
<td>Chlorides</td>
<td>CS$_2$</td>
<td>CuS</td>
<td>Yes</td>
<td>Yes</td>
<td>Worth attempting at higher concentration. Large particles formed quickly in solution and precipitated easily. Did not deposit in Reactor 2</td>
</tr>
<tr>
<td>Acetates</td>
<td>L-Cystine</td>
<td>N/A</td>
<td>No</td>
<td>No</td>
<td>Worth attempting at higher concentration. Large particles formed quickly in solution and precipitated easily. Did not deposit in Reactor 2</td>
</tr>
<tr>
<td>Acetates</td>
<td>L-Cysteine</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Acetates</td>
<td>CS$_2$</td>
<td>Bi$_2$S$_3$, CuS</td>
<td>Yes</td>
<td>Mostly</td>
<td></td>
</tr>
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<td>Hydroxides</td>
<td>L-Cystine</td>
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<td>No</td>
<td>No</td>
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</tr>
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<td>Hydroxides</td>
<td>L-Cysteine</td>
<td>N/A</td>
<td>Yes</td>
<td>No</td>
<td>XRD patterns point to this combination producing best product.</td>
</tr>
<tr>
<td>Hydroxides</td>
<td>Thiourea</td>
<td>N/A</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Hydroxides</td>
<td>CS$_2$</td>
<td>Multiple</td>
<td>Yes</td>
<td>No</td>
<td>Large particles formed quickly in solution and precipitated easily</td>
</tr>
</tbody>
</table>

Table 5.1: Summary of chemical combinations resulting in CBS, additional comments about their reaction characteristics and recommendations of further experimentation.

An advantage of the solvothermal process is the ability to dope the material by simply adding a salt with the desired dopant to the reagent solution. Zinc doping was performed in an effort to turn the normally p-type CBS to n-type. The electronic
properties of the CBS samples were altered due to this addition, though the varying Zn levels tested did not cause proportionate changes in the conductivity. This remains a puzzle.

CuS and Bi$_2$S$_3$ nanoparticles will react to form CBS when mixed together in a 6:1 ratio and heated, although the time and temperatures required to attain a thin film from this process would be too long and too high to make it feasible.

In an attempt to adapt these chemistries to deposit thin films of CBS onto fluorine doped tin oxide coated (FTO) glass, a diagnostic flow through reactor was designed. This would allow the solvothermal reaction to occur directly against the glass, allowing the forming Cu$_3$BiS$_3$ particles to adhere and grow upon it. Computer simulations performed with the program COMSOL Multiphysics were employed to predict the properties of the reactor before it was built. The flow and heat simulations were tested experimentally and proved quite accurate. This reactor was designed with a temperature gradient transverse to the flow of the liquid, essentially allowing us to perform many deposition experiments at once. With the reactor we hoped to determine the optimal conditions for the deposition of CBS using the previously discussed combinations of chemicals that lead to the pure material through the solvothermal process. Unfortunately, while some deposition was observed, the chemical solutions did not form CBS on the surface. The reactor was unable to accomplish the desired task. Ultimately, undissolved chemicals in the as-mixed solutions proved problematic, as they were filtered out by small channels designed to produce a uniform liquid flow. With the most of the particulates filtered out of the flow, those chemicals still left in the reaction chamber were not in the correct proportions to form CBS. And, while the presence of the FTO glass was a good substrate to initiate
growth, it was found that strongly anisotropic growth of the CBS phase occurred. This prevented us from making device-quality thin films by direct chemical precipitation.

Our diagnostic reactor was further tested on a simpler chemical precipitation system. It was utilized to determine the best reaction conditions of CdS. It was proven that heating the reaction liquid very near to boiling deposits the most even coating for the solvothermal deposition process we tested.

The desire to deposit thin films of CBS led us to examine other ways of making this material. Electrodeposition has been previously utilized to make this material, but previously discovered methods are complicated, result in an impure material or require the use of harsh chemicals. The method presented here is more environmentally friendly. Experiments designed to optimize the coating were performed and in the end we were left with a fairly smooth, even coating. Unfortunately, during electrical testing the device stacks behaved as simple resistors with relatively low resistance and no response to light. Clearly, we need to learn more about the electronic carriers and doping possibilities of the material to produce quality heterojunction PV devices in the future.

This research represents several steps in the right direction, but there is still a long way to go towards making a working CBS solar cell. Still, should this research help others to achieve that goal, copper bismuth sulfide could become an important part of the plan to bring about a greener future.
5.2 – Future Work:

5.2.1 - Solvothermal Synthesis and Deposition of CBS via Continuous Flow Reactor:

Table 5.1 in the previous section details some potential new experiments with previously attempted chemical combinations. Some did not result in pure CBS under the attempted reaction conditions, but may if the conditions were changed. The nitrates and thiourea and acetates and CS$_2$ combinations may be worth attempting at a higher concentration as their products are identical to those produced by low concentration reactions of hydroxides and thiourea. Chlorides and thiourea as well as chlorides and CS$_2$ might produce pure CBS if reacted with a higher Bi concentration as they produced CBS and CuS.

More combinations of chemicals should be tested with our solvothermal method to determine if they will make pure CBS. Combinations that dissolve completely in ethylene glycol, do not produce a gas and produce the pure crystalline phase should be developed so that chemical bath deposition of device-quality thin film CBS can be performed. Once this combination is found it should be tested within the diagnostic reactor immediately. When the best conditions for deposition are found a new heating mechanism could be added so that the optimum temperature could be applied across the whole area of the substrate. This could allow for dense coatings of uniform thickness to be produced. With this, a comparatively large scale deposition could be carried out with the bench-top reactor. If this reactor is successful in creating device quality thin films of CBS, it would be easy to imagine a larger model producing large commercial solar panel sized sheets of CBS coated FTO glass.
It is also possible to design a new generation of reactor that would not be sensitive to a small amount of undissolved particles, yet still even the flow of the liquid through some other means. This would open the possibility of using one of the previously discovered chemical combinations detailed in this dissertation.

While we attempted to dope the CBS with zinc in an effort to stay away from toxic elements and chemicals, other elements could certainly be attempted. Zinc was expected to provide the n-type doping required for making the desired device structures. It would be beneficial to attempt to make n-type CBS by doping untested elements into CBS via the solvothermal synthesis. Many elements are available in salt form, and we would need one that would dissolve completely and not release a gas byproduct as it reacts.

Other substrates could be placed into the reactor as well to see how that influences the best conditions for deposition of the target material. Thin seeding layers of CBS might also be beneficial for initiating growth from the precipitation chemistries.

A newer version of COMSOL with careful editing of and iterations on the existing simulations could result in more accurate results and a better idea of the temperatures that the solution within the reactor must reach to allow deposition.

The reactor could easily be used to find optimal conditions for other materials that can be produced via solvothermal syntheses. The reactor is a potentially valuable tool that could be used in the future for many syntheses.

Further investigation into the properties of CBS should also be undertaken. The wide variety in band gap values reported in the literature, for instance, could be narrowed
considerably with carefully made measurements on pure material produced using the new chemistries found in our studies.

**5.2.2 – Electrodeposition of CBS:**

While the layers we have obtained have been of a relatively high quality, they are clearly not consistent enough throughout to prevent electrical short circuits in a solar device. This issue can be investigated in two ways. A study to find the lowest viable voltage for deposition, which will require more studies on the optimal deposition time, could be performed in order to find one that allows for a smoother more consistent coating of the as-deposited material. Lower annealing temperatures or shorter times in the oven should also be investigated as they could lead to a better, more even coating of CBS. They would also provide a less energy intensive fabrication process.

A study done at this voltage to see how deposition time relates exactly to layer thickness could be performed using a profilometer. This would enable specific tuning of the film thicknesses which could factor into optimization of the proposed solar cells.

When the electrodeposition is occurring, the FTO glass is in a liquid that is being stirred. The stirring is itself important as it keeps the concentration of ions consistent within the solution. The container is cylindrical and the FTO square. Attempts were made to force the glass as close to the walls as possible, but still there could be turbulence in the liquid directly around the FTO, and differences in velocity of the liquid across it. Occasionally, these differences were observed to result in macroscopic patterns on the deposit. An even flow across the glass could go a long way towards enhancing and optimizing the CBS coating.
With this in mind, a third generation reactor could be designed, using all of the pieces of Reactor 2 designed to even the flow, but utilizing electrodeposition. This would require another custom program to be made and new electronics as well. It is suggested that the study on finding the best voltage for deposition be performed before this is made. This would allow electronics that will only output that voltage to be devised, instead of more complex ones to allow for variation.

This could prove to be a method for in lab large scale deposition of CBS thin films onto a conductive surface, be it FTO, aluminum or molybdenum.

A study into alternative n-type materials for use in a CBS solar cell should also be undertaken, as CdS has thus far not been shown to produce the desired result.
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