Novel Control Technique For Cadmium Sulfide Chemical Bath Deposition Using Real Time Monitoring Of Cadmium Ion Molarity

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NOVEL CONTROL TECHNIQUE FOR CADMIUM SULFIDE CHEMICAL BATH DEPOSITION USING REAL TIME MONITORING OF CADMIUM ION MOLARITY

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Dean of the Graduate School
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RAFAEL ORDONEZ, B.S.E.E

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NOVEL CONTROL TECHNIQUE FOR CADMIUM SULFIDE CHEMICAL BATH DISPOSITION USING REAL TIME MONITORING OF CADMIUM ION MOLARITY

by

RAFAEL ORDONEZ, B.S.E.E.

THESIS

Presented to the Faculty of the Graduate School of The University of Texas at El Paso in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

Department of Electrical and Computer Engineering THE UNIVERSITY OF TEXAS AT EL PASO MAY 2010
ABSTRACT

Cadmium sulfide Chemical-Bath-Deposition parameters are modified to allow, for the first time, real time monitoring of cadmium ion molarity using a commercially available cadmium ion Ion-Selective-Electrode at 60°C. This modification involves alterations to typical deposition parameters that eliminate the formation of cadmium hydroxide and keep cadmium ion molarity above $10^{-7}$M. The new or atypical parameters developed are pH values below 8.9 and lower mortalities for all chemicals. In order to have complexation of cadmium ion driven mainly by ammonia, parameters that minimized complexation by other chemicals are found. Cadmium acetate concentration below 2mM and ammonium acetate concentration below 10mM minimize complexation. In order to keep cadmium ion molarity within the detection limits during complexation with ammonia, ammonia molarity is kept below 0.05M. For controlling proposes, decomposition of thiourea is studied with the parameter developed for monitoring of cadmium ion molarity. It is found that thiourea complexes cadmium ions, and it precipitates cadmium sulfide homogenously with cadmium ion molarities above $10^{-7}$M and pH value of 8.9. Thiourea decomposition is suppressed for pH values below 7.6, and pH values of 8.2 and 8.4 are found to suppress homogenous precipitation and favor heterogeneous deposition of cadmium sulfide with a deposition rate between 1 to 2 nm per minute. The films are considered of good quality due to a band gap very close to the ideal 2.42eV and a surface roughness of at least three smaller than of typical cadmium sulfide films.
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CHAPTER 1: INTRODUCTION

Cadmium sulfide is a direct band gap semiconductor material used as a thin film layer in solar cells since 1955 [1]. Thin films of cadmium sulfide have also been used since 1964 in other electronics devices such as light sensors [2], gas sensors [3], light emitting diodes [4], and transistors [5]. Since it has been used in so many devices for a very long time, it is obvious that cadmium sulfide should be a well-understood material that no longer needs much research. However, there is actually much research in areas involving this material recently. In fact, there have been about 805 publications since 2008 involving cadmium sulfide thin films research. Besides of still being considered for research by the scientific community, cadmium sulfide thin films are very important for companies that manufacture solar cells of cadmium telluride (CdTe), copper indium diselenide (CuInSe$_2$ or CIS), and copper indium gallium diselenide (CIGS) [6].

Studying production processes of cadmium sulfide thin films contributes to both the scientific community and industry because its results can incorporate understanding of film growth kinetics and reduce production cost. The most common methods for producing cadmium sulfide thin films are Chemical-Bath-Deposition (CBD), Chemical-Vapor-Deposition (CVD), Spray-Pyrolysis (SP), and sputtering. Among these methods, CBD is known for being the cheaper and simpler to execute as well as the most mysterious one because there is a lack of understanding of how nucleation and crystal growth can be controlled [7]. Therefore, studying techniques that allow control of CBD contributes in understanding of cadmium sulfide grow kinetics and making the cheap CBD more appealing for the industrial sector.

---

1 This number of publications was determined with the SciFinder search engine using parameters: Research topic "cadmium sulfide" > refine "film" > refine "2008-2010."
1.1 Background

Monitoring the deposition process using a real time sensor will enable study of reaction kinetics and control possibility. In 1965, the CBD method for cadmium sulfide was introduced because Kitaev et al. [8] after finding the parameters that allow cadmium sulfide to growth in an aqueous solution as a thin film. Since then, many different groups have tried to understand CBD CdS reaction kinetics only using post deposition film characterization and analysis of theoretical equilibrium reactions. Finally, in 1992, Lincon and Ortega-Borges [9] used a Quartz Crystal Microbalance QCM, which is an in-situ sensor to analyze mass exchange at the solution-substrate interface and reaction kinetics. Using a QCM to monitor the deposition made it possible to establish when a dense or porous film is deposited. Lincon and Ortega-Borges concluded that at first a dense film is first formed during the deposition followed by a porous film.

It is possible to find a control technique that detects and suppresses porous film formation in order to achieve only dense films during the deposition. In 2004, Voss et al. [10] used a QCM and theoretical equilibrium reactions of CBD CdS to more accurately explain reaction kinetics. Voss et al concluded that during porous film formation free cadmium ions (Cd$^{2+}$) are consumed in solution. Thus, a Cd$^{2+}$ Ion-Selective-Electrode (ISE) can also be used to monitor formation of the porous films. However, the typical CBD parameters that Kitaev et al. [8] introduced keep Cd$^{2+}$ molarity below ISE detection limits. Fortunately, there have been films of CdS produced with atypical CBD parameters that allow concentrations of Cd$^{2+}$ to be high enough to be measured using an ISE [11][12].

1.1 Contributions

In this work, CBD parameters for proper measurement of Cd$^{2+}$ concentration are developed as well as a control technique that allows the reaction to be stopped before porous films are formed. Typical CBD parameters involve very high pH values and high concentration of ammonia, which are
known to react with most of the Cd\(^{2+}\) ions available in solution. If the pH is decreased and ammonia concentration reduced, Cd\(^{2+}\) molarity is increased and measurable by ISE. Since Kitaev et al. [8] assumed that cadmium sulfide only deposits under high pH, decreasing pH is not often attempted, but it has been proven that this assumption is not true because cadmium sulfide films can be produced by CBD method even in acidic solutions [13][14]. Therefore, parameters are set so that the solution is slightly basic and buffered to allow Cd\(^{2+}\) monitoring using ISE. The control technique implemented is simply the reduction of the pH of the solution to neutral pH when Cd\(^{2+}\) decrement is detected, which stops the reaction that forms homogenous precipitate or porous films. Another contribution is reducing regents by more than 10 times from the amounts used in typical cadmium sulfide CBD. This makes longer deposition times that suppress homogenous precipitation even when it is not dominant [12]. Finally, it is important to emphasize that this work presents, for the first time, real time monitoring of Cd\(^{2+}\) molarity during cadmium sulfide CBD with a commercially available ISE probe.
CHAPTER 2: CHEMISTRY FUNDAMENTALS

This chapter is intended for readers requiring an introduction to basic chemistry concepts. It covers solutions, equilibrium and pH. It can be skipped if the reader is knowledgeable in these chemistry concepts.

2.1 Aqueous Solutions

Water is capable of absorbing many substances and evenly dispersing them to form aqueous solutions. In these solutions, water plays the role of dissolving agent or solvent, and a dissolved substance plays the role of solute. Therefore, aqueous solutions are formed by water as the solvent and soluble substances as solutes.

In general, concentration is defined as the amount of solute per amount of solution. However, mass and volume can be interchangeably used for amounts of either solute or solution, which makes concentration difficult to interpret. This is why molar concentration or molarity is mainly used to define concentration in aqueous solutions. In molarity, mass is used to account for amount of solute in moles, and volume is used to account for amount of solution in liters. Molarity of solution X is defined as follows,

\[ [X] = \frac{\text{moles of solute } X}{\text{liters of solution}} = \frac{n_X (mol)}{V (L)} \quad \text{Eq. 1} \]

where the brackets around X imply “molarity of X” [15][16].

Although molarity has the units moles per liter (mol/L), M or molar unit is the preferred unit for aqueous solution concentration. For example, a solution with concentration of 10 moles per liter can also be said to have a concentration of 10 M or 10 molar. Even the metric system prefixes milli- and micro- can be used together with M or molar unit, such as mM or millimolar and µM or micromolar.
Lowering solution concentration is used for preparing solutions from concentrated solutions, such as concentrated acids and bases. From Eq. 1, it is understood that concentration can be reduced by reducing moles of solute or increasing solution volume. Reducing moles of solute is achieved by reacting or evaporating the solute, and since this is complicated, it is rarely used. In contrast, increasing solution volume or dilution is a very simple and widely used method to reduce concentration from a concentrated solution. By keeping the amount of moles the same, a mathematical expression for dilution is found to be:

\[ n_x = [X]_{\text{concentrated}} \times V_{\text{concentrated}} = [X]_{\text{diluted}} \times V_{\text{diluted}} \quad \text{Eq. 2} \]

Manufacturers of concentrated solutions do not usually provide molarity with their products. Instead, they provide assay, density of solution, and formula weight of solute, which can be used to find molarity. Assay is another form of concentration that uses mass to account for both amounts of solute and solution, so assay is the ratio of solute mass per solution mass, and it is provided as a unitless quantity in percentage. Density and formula weight are used together with assay in the following equation to estimate molarity of a concentrated solution:

\[ [X]_{\text{concentrated}}(M) = 10 \times \frac{\text{Assay} \times D}{\text{F.W.}} \quad \text{Eq. 3} \]

where: Assay is the mass ratio of solute in percentage (%); D is the density of the concentrated solution in kilograms per liter (Kg/L); F.W. is the formula weight of the solute in grams per mol (g / mol). In Table 1, molarity for concentrated hydrochloric acid (HCl), sulfuric acid (H₂SO₄), and ammonia (NH₃) solution is calculated with Eq. 3 [15].

<table>
<thead>
<tr>
<th>Solute</th>
<th>Assay (%)</th>
<th>D (Kg/L)</th>
<th>F.W.(g/mol)</th>
<th>Molarity (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>36</td>
<td>1.18</td>
<td>36.46</td>
<td>11.65</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>98</td>
<td>1.84</td>
<td>98.07</td>
<td>18.39</td>
</tr>
<tr>
<td>NH₃</td>
<td>28</td>
<td>0.88</td>
<td>17.03</td>
<td>14.47</td>
</tr>
</tbody>
</table>

Table 1: Molarity from Eq.1 for Concentrated HCl, H₂SO₄, and NH₃
2.2 Chemical Equilibrium

Chemical reactions are processes of change in which substances are converted. Frequently, they are assumed to go to completion because all reactants change to products [15]. For example, Figure 1 shows a reaction going to completion. At the beginning of a reaction \((t = 0)\), only reactants \(A\) and \(B\) are present, and after some time \((t = t_o)\), these \(A\) and \(B\) react and disappear completely turning into \(C\) and \(D\) products.

\[
\begin{array}{c}
\text{Reactants} \\
A + B \\
\end{array} \quad \Rightarrow \\
\begin{array}{c}
\text{Products} \\
C + D \\
\end{array}
\]

\[\begin{array}{llll}
@ t = 0, & [A] > 0, & [B] > 0, & [C] = 0, & [D] = 0 \\
@ t \geq t_o, & [A] = 0, & [B] = 0, & [C] > 0, & [D] > 0 \\
\end{array}\]

Figure 1: Chemical Reaction Going to Completion

Most commonly, reactions do not go to completion, but instead reach only an equilibrium steady state that has both products and reactants [15]. For example, Figure 2 shows a reaction going into chemical equilibrium. At the beginning of a reaction \((t = 0)\), only \(A\) and \(B\) are present with concentrations \(x_i\) and \(y_i\). After some time \((t = t_o)\), these \(A\) and \(B\) reactants stop reacting and do not disappear completely. Thus, a small concentration of reactants is left untouched and coexisting with \(C\) and \(D\) products.

\[
\begin{array}{c}
\text{Reactants} \\
a A + b B \\
\end{array} \quad \Leftrightarrow \\
\begin{array}{c}
\text{Products} \\
c C + d D \\
\end{array}
\]

\[\begin{array}{llll}
@ t = 0, & [A] = x_i, & [B] = y_i, & [C] = 0, & [D] = 0 \\
@ t \geq t_o, & [A] = x_f < x_i, & [B] = y_f < y_i, & [C] > 0, & [D] > 0 \\
\end{array}\]

Figure 2: Chemical Reaction Going to Chemical Equilibrium

All substances in the reaction of Figure 2 are non-zero and constant after reaching equilibrium, so it is possible to find an equilibrium constant, \(K\), for it. According to Brown [15], Jones [17], and Kotz [16], this constant is defined as follows:
where: \(a\), \(b\), \(c\), and \(d\) are stoichiometric coefficients used in balancing the reaction of figure 2; \([A]\), \([B]\), \([C]\), and \([D]\) are the equilibrium concentrations after time \(t_0\).

2.3 pH

H\(_3\)O\(^+\) and OH\(^-\) ions are always dissolved in water because water molecules react with each other in an equilibrium reaction called autoprotolysis \([18]\). In pure water, autoprotolysis produces an equal amount H\(_3\)O\(^+\) and OH\(^-\) ions, which is why pure water is said to be neutral, but a dissolved solute can increase the amount of H\(_3\)O\(^+\) or OH\(^-\) forming an acid or a base. Since H\(_3\)O\(^+\) and OH\(^-\) molarities can be increased by many orders of magnitude, negative logarithms give a convenient scale for molarity \([17]\). Therefore, concentrations of H\(_3\)O\(^+\) or OH\(^-\) are usually expressed in terms of negative logarithms as follows:

\[
pH = -\log ([H_3O^+]) \tag{Eq. 5}
\]
\[
pOH = -\log ([OH^-]) \tag{Eq. 6}
\]

Although both H\(_3\)O\(^+\) and OH\(^-\) ions are always present in water, pH is the standard used to express both concentrations. This is possible because both ions are linked by the autoprotolysis equilibrium constant, so the concentration in terms of pH for both ions is given as:

\[
[H_3O^+] = 10^{-(pH)} \tag{Eq. 7}
\]
\[
[OH^-] = K_w * 10^{(pH)} = 10^{-(pK_w - pH)} \tag{Eq. 8}
\]

\(^2\) Water autoprotolysis is commonly oversimplified assuming that it produces H\(^+\) and OH\(^-\) ions, but H\(^+\) or protons cannot exist in water because they are solvated into H\(_3\)O\(^+\) cations \([18]\).
where: $K_w = [H_3O^+] [OH^-]$, and it is water’s autoprotolysis equilibrium constant in (mol/L)$^2$ or M$^2$; $pK_w$ is the negative logarithm of $K_w$ [15].

Solutions are considered acidic if their pH value is below the neutral pH of water or basic if it is above it. The neutral pH of water is simply $pK_w$ over two, but since $pK_w$ is temperature dependent, the neutral pH of water can vary from 7.00 at 25°C to 6.13 at 100°C. In Table 2, $pK_w$ values from 0°C to 100°C are presented along with water’s neutral pH [19].

<table>
<thead>
<tr>
<th>Temperature</th>
<th>pKw</th>
<th>Neutral pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td>14.95</td>
<td>7.48</td>
</tr>
<tr>
<td>25°C</td>
<td>13.99</td>
<td>7.00</td>
</tr>
<tr>
<td>50°C</td>
<td>13.26</td>
<td>6.63</td>
</tr>
<tr>
<td>75°C</td>
<td>12.70</td>
<td>6.35</td>
</tr>
<tr>
<td>100°C</td>
<td>12.25</td>
<td>6.13</td>
</tr>
</tbody>
</table>

Using least-square approximation on all the values from Table 2[20], the following quadratic equations are obtained with low absolute relative errors of less than 0.2% for all values of $pK_w$ and neutral pH:

\[
pKw (T) = (1.36 \times 10^{-4}/°C^2) \times T^2 - (0.0404/°C) \times T + 14.94
\]

\[
\text{neutral pH} (T) = (6.8 \times 10^{-5}/°C^2) \times T^2 - (0.0202/°C) \times T + 7.47
\]

**Figure 3: Neutral pH vs. Temperature from Eq. 10**
CHAPTER 3: THE CHEMISTRY BEHIND CADMIUM SULFIDE CHEMICAL BATH DEPOSITION

3.1 Cadmium Ion

3.1.1 Precursors

Soluble salts of cadmium are critical in CBD of cadmium sulfide. They are separated into Cd\(^{2+}\) ions and anions by water molecules forming aqueous solutions. Ideally, once a soluble salt is dissolved, its components do not recrystallize. Thus, Cd\(^{2+}\) ions are free to react with other substances while in solution and form the insoluble cadmium sulfide. The most used soluble salts of cadmium for CBD are cadmium acetate, cadmium chloride, cadmium nitrate, and cadmium sulfate.

3.1.2 Cadmium Complexation

Once dissolved in water, cadmium ion can coordinate with other ions or molecules forming complex ions. In a complex ion, cadmium is at the center coordinating other molecules or ligands around it. In CBD, cadmium coordinates with thiourea and ammonia reducing free cadmium ion concentration. Figure 4 shows the complex molecules that cadmium forms with ammonia and thiourea-carboxylate[21].

![Figure 4: Complexation of Cadmium with Ammonia and Thiourea-Carboxylate](image-url)
Even some cadmium ion precursor salts form complexes that are soluble, and the concentration of cadmium is reduced by these complexes. Table 3 shows common cadmium ion precursors and their complexes. For example, a 1M solution of cadmium chloride produce less than 1M of cadmium ions and less than 1M of chloride ions because the rest form soluble complexes such as \([\text{CdCl}_6]^{4-}\) and \([\text{CdCl}_4]^{2-}\) [18].

<table>
<thead>
<tr>
<th>Common Cadmium Salts</th>
<th>Dry Salt Formulas</th>
<th>Ions Formed by Dissolved Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium Acetate</td>
<td>(\text{Cd(CH}_3\text{CO}_2\text{)}_2)</td>
<td>(\text{Cd}^{2+}, \text{CH}_3\text{CO}_2^-, \text{complexed: Cd(CH}_3\text{CO}_2\text{)}_3^-)</td>
</tr>
<tr>
<td>Cadmium Chloride</td>
<td>(\text{CdCl}_2)</td>
<td>(\text{Cd}^{2+}, \text{Cl}^-, \text{complexed: [CdCl}_6\text{]}^{4-}\text{ and [CdCl}_4\text{]}^{2-})</td>
</tr>
<tr>
<td>Cadmium Nitrate</td>
<td>(\text{Cd(NO}_3\text{)}_2)</td>
<td>(\text{Cd}^{2+} \text{ and NO}_3^- \text{ (No Complexing)})</td>
</tr>
<tr>
<td>Cadmium Sulfate</td>
<td>(\text{CdSO}_4)</td>
<td>(\text{Cd}^{2+} \text{ and SO}_4^{2-} \text{ (No Complexing)})</td>
</tr>
</tbody>
</table>

### 3.2 Thiourea Decomposition into Sulfide Ions

Thiourea is a sulfide ion precursor in cadmium sulfide CBD that keeps reaction rate slow by producing sulfide ions slowly. This slow production of sulfide ions is the key for the formation of cadmium sulfide films. For example, 1 mM of a soluble sulfide salt like sodium sulfide produces 1mM of sulfide ions almost instantly forcing a fast formation of cadmium sulfide, which produces only cadmium sulfide powder. Instead, 0.1M of thiourea produces sulfide ions slowing giving the reaction time to react with the substrate surface and form cadmium sulfide films.

The reaction that produces sulfide ions is known as thiourea decomposition or thiourea hydrolysis, and it is an equilibrium reaction. Thus, only some of the thiourea present during the deposition produces sulfide ions, and in order to have enough sulfide ions during the deposition,
thiourea should be higher than the cadmium ion concentration. The overall decomposition of thiourea is commonly presented as follows [12]:

\[
\text{Thiourea} + 2 \text{OH}^- \rightarrow \text{S}^{2-} + \text{CN}^- + \text{H}_2\text{O}
\]

![Figure 5: Thiourea Decomposition](image)

In cadmium sulfide CBD, thiourea is used because it turns into sulfide ions slowly, but the reaction times can be too slow for practical applications and basic pH values should be used. In Figure 6, Shaw and Walker [22] show reaction rate constants of thiourea vs. pH, and it is noted that it increases at basic pH values. Chu et al. [12] also reports high reaction rate constants at high pH values during cadmium sulfide CBD. It is clear that thiourea works as an acid because it neutralizes hydroxide ions producing sulfide, but the reaction is extremely slow at acidic or neutral pH values, where hydroxide concentrations are below or equal to $10^{-7}$ molar.

![Figure 6: Thiourea Reaction Rate vs. pH @ 100°C [22]](image)
3.3 Ammonia Chemistry

Ammonia is a soluble gas that interacts with water producing ammonia ions and increasing hydroxide concentration or pH, which is why it is considered a base. In cadmium sulfide CBD, it is used as a complexing agent in order to reduce cadmium ion concentration and as a base in order to activate thiourea. Thus, ammonia acts increasing the production of sulfur ion and decrease cadmium ion concentration. The ammonia equilibrium reaction is given as:

\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

\[
K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} \text{ at } 298 \text{ K}
\]

Figure 7: Equilibrium Reaction of Ammonia and Water

3.4 Surface Functionalization: Oxides, Water, and pH

Surface chemistry is of particular interest for cadmium sulfide CBD because the deposition of cadmium sulfide is intended to be on the surface of a substrate or a film. The materials commonly used to interface with cadmium sulfide are quartz substrates, glass substrates, indium tin oxide (ITO) films, and tin oxide films. It is known, but rarely emphasized, that the surface of these materials should be modified or prepared in order to be more compatible with CBD and to produce cadmium sulfide films with uniform thickness.

Cleaning and preparing surfaces for cadmium sulfide CBD are two different processes. A cleaning process is meant to remove particles and other substances attached on the surfaces, but a preparation process is meant to make the surface chemically right for the deposition. Thus, a very common mistake is to assume that a clean surface is enough to have a cadmium sulfide film with uniform thickness. For example, piranha cleaning uses sulfuric acid and hydrogen peroxide, and it leaves a very clean and hydrophilic surface on oxides, but it also makes the surface charge of the oxide
positive due to the extremely low pH value of the cleaning process. Thus, piranha cleaning leaves a surface that complicates cadmium sulfide deposition.

In fact, metal oxides surfaces have Lewis acid sites that coordinate water molecules changing the surface. For most oxides, this coordination forms hydroxyl groups on the surface of the oxide. It is estimated that the hydroxyl group surface density is between 4 to 10 molecules per 10 nm. Then, it is possible to change the charge of these hydroxyl groups using pH. In figure 8, the acid-based reactions of surface hydroxyl groups are presented. For neutral pH values, the surface of the oxide is also neutral with the OH termination, but if the pH is high, then the H is removed and the surface becomes negatively charged. On the contrary, for low pH values, hydrogen is integrated to the OH termination and the surface becomes positively charged [23].

![Figure 8: Coordination Phenomena at Oxide-Water Interface with Acid-Base Reactions](image)

In order to have a good nucleation of cadmium sulfide it is critical to have the oxide surface charge negative. Godes [24] reported that submerging the oxide substrates in potassium hydroxide...
considerably helps to produce uniform films. This was observed in this research because when the surface was treated with the low pH of the piranha cleaning no uniform films could be obtained. On the other hand, the high pH of the RCA treatment consisting of 1:1:10 ammonia/peroxide/water produced uniform films. Thus, the surface charge of the surface oxide must be negative in order to incorporate the positively charged cadmium-ammonia complexes better.

3.5 Cadmium Sulfide Chemical Bath Deposition Mechanisms

![Diagram of Cadmium Sulfide Chemical Bath Deposition Mechanisms](image)

Figure 9: Cadmium Sulfide Chemical Bath Deposition Mechanisms [25]
3.5.1 Dense Cadmium Sulfide Film Growth

In figure 9, ammonia (NH₃) is shown to interact with cadmium to produce cadmium complexes, which are then collected in the surface. Since the oxide surface is negatively charged due to the high pH of the RCA cleaning, cadmium complexes are attracted to it. If the pH of the solution is high enough, then the cadmium complexes change to a cadmium hydroxide (Cd(OH)₂) film. Kitaev et al. [8] mentions that Cd(OH)₂ is very adherent to oxides and it is the main reason for producing uniform cadmium sulfide. Cd(OH)₂ is then ion exchanged to cadmium sulfide by its interaction with thiourea. This process is also known as the ion-by-ion deposition.

3.5.2 Porous Cadmium Sulfide Film Deposition through Homogenous Precipitation

Figure 9 also shows particle deposition, which is known as the cluster-by-cluster deposition. This is a completely different mechanism for making cadmium sulfide films. Here, the substrate is not used as a catalyst for the formation of cadmium sulfide. Cadmium and sulfide ions interact homogenously producing very little particles. The size of the particles allows them to become charged particles and form a colloidal solution. Then, they can stack on any solid surface available and produce a film. The high surface area of these particles makes them very reactive, so they can absorb more cadmium and sulfide ions quickly growing in size to the point that they do not stick to the substrate surface anymore. Large particles produce a homogenous precipitate that is simply stirred around in the solution, and it can be considered wasted material.
CHAPTER 4: MONITORING OF CADMIUM ION MOLARITY

4.1 Cd\(^{2+}\) Ion-Selective-Electrode (ISE)

Thermo Scientific manufactures two models of electrodes that measure cadmium ion concentration: the standard 94-48 cadmium electrode and the 94-48 combination cadmium electrode. A combination electrode is simply an electrode that has an internal voltage reference. The standard model needs to be used with a second electrode for reference, which requires a second meter and more space. Thus, for this work, the more practical combination electrode was chosen.

When the electrode is placed in a solution containing cadmium ions, a voltage develops across the sensing element of the electrode with respect to the voltage reference. The difference between the reference voltage and the sensing element is related to cadmium ion molarity as follows [26]:

\[
V_{\text{sensing}} = V_{\text{reference}} + S \times \log([\text{Cd}^{2+}]) \quad \text{Eq. 11}
\]

\[
[\text{Cd}^{2+}] = 10^{\frac{V_{\text{sensing}} - V_{\text{reference}}}{S}} \quad \text{Eq. 12}
\]

where:

- \(V_{\text{sensing}}\) is the voltage measured by the electrode in mV
- \(V_{\text{reference}}\) is the voltage of the built-in reference potential in mV
- \(S\) is the electrode slope in mV per decade, which is a value approximated to 28mV per decade @ 25°C
- \([\text{Cd}^{2+}]\) is the cadmium ion molarity

Calculating \(V_{\text{reference}}\) and \(S\) is done with the \(V_{\text{sensing}}\) voltages from 89.0mM (10g/L) and 8.9mM (1g/L) commercially available standard solutions of cadmium. While keeping equal temperatures for both standard solutions, \(S\) is calculated by the voltage difference between the standards as:

\[
S = V_{\text{sensing of 89.0mM}} - V_{\text{sensing of 8.9mM \quad Eq. 13}}
\]
Once $S$ is calculated, $V_{\text{reference}}$ is obtained by solving Eq. 11 as follows:

$$V_{\text{reference}} = V_{\text{sensing of 8.9mM}} - S \times \log(8.9 \times 10^{-3}) \quad \text{Eq. 14}$$

Alternatively, $S$ and $V_{\text{reference}}$ can be obtained with fresh custom-made solutions made from the standards. Besides, it is better to find $S$ and $V_{\text{reference}}$ with solutions of lower concentration because the cadmium molarity to be monitored is very small. The method employed is a simple addition of 6mL of the 8.9mM standard solution to a beaker with 450mL of water set to the temperature of the solution. This makes a $1.17 \times 10^{-4}$ molar solution of cadmium ion. Then, 6mL of 89mM standard solution is also added to the same beaker making a $1.16 \times 10^{-3}$ molar solution of cadmium ion. With the measurement of $V_{\text{sensing}}$ from both custom-made solutions, $S$ and $V_{\text{reference}}$ are found with slightly modified Eq. 13 and Eq. 14 equations:

$$S = V_{\text{sensing of 1.16mM}} - V_{\text{sensing of 0.117mM}} \quad \text{Eq. 15}$$

$$V_{\text{reference}} = V_{\text{sensing of 0.117mM}} - S \times \log(1.17 \times 10^{-4}) \quad \text{Eq. 16}$$

At 25°C, typical values of $S$ and $V_{\text{reference}}$ are 28mV/decade and -86mV, and at 60°C, typical values of $S$ and $V_{\text{reference}}$ are 32mV/decade and -61mV. In Figure 10, these values are used to illustrate sensing voltage versus cadmium concentration in a semi-log plot. Typical values of $S$ and $V_{\text{reference}}$ change with time, so $S$ and $V_{\text{reference}}$ should be calculated before any cadmium sulfide CBD deposition.
4.2 Cadmium Sulfide Reactor and Monitoring System

Cadmium sulfide CBD deposition temperatures range from 50°C to 90°C [12] and the cadmium ion ISE can be used from 0°C to 100°C. However, it is recommended to limit its use to a few seconds at temperatures higher than 80°C [26]. Since thiourea reacts slower at lower temperatures, 60°C is selected as the deposition temperature in this work. For example, the reaction rate constant decreases from $17.4 \times 10^{-8}$ at 100°C to $4 \times 10^{-8}$ at 90°C [7]. In addition to protecting the ISE and slowing down thiourea decomposition, 60°C has been used as the deposition temperature to characterize CBD kinetics by Lincot [9] and Voss [10]. Therefore, all experiments in this work are specifically performed at 60°C±0.1 using the reactor in Figure 11.
The temperature of freshly boiled 18MΩ-cm water is always kept at 60°C ± 0.1°C with the help of a J-KEM Model 210 digital temperature controller. The controller adjusts power for the mantel 2048 times per second, so it corrects for exothermic reaction, endothermic reactions, or water evaporation keeping the temperature stable [27].

The stirrer is a motor that holds a 4-blade glass stirring-shaft. The motor is a Model 6000 manufactured by Arrow Engineering. The 4-blade stirring-shaft is manufactured by ChemGlass. Because of the four blades, the temperature in the reactor is kept uniform only using slow stirring speeds.

For pH monitoring, a glass Orion-Ross Combination electrode and an Orion 3-Star plus Portable pH Meter are used. The meter is calibrated with 7.00 and 9.18 buffer solutions at 25°C. The meter is
capable of doing temperature compensation for 60°C, which eliminates the tedious process of heating 2.4L of buffering solution.

The cadmium molarity monitoring system is made of three components: a Cd$^{2+}$ ISE, a multimeter and a real-time data logger. The electrode and multimeter are made manufactured by Thermo Scientific, but the multimeter does not provide a display that logs data and a computer is needed for this propose. In this work, a MATLAB program was developed to process millivolts inputs to molarity, display molarity data in real time and record the data in a CSV file. The program is included in appendix A and its parameters are monitoring-end-time in minutes, $S$, and $V_{\text{reference}}$. A good feature of this program is that it can stay running for many hours and plot thousands of data point without affecting the system memory.

4.3 Determining pH Range for Cadmium Ion Monitoring in CBD

Cadmium ion molarity should be above $10^{-7}$ molar because this is the minimum monitorable concentration by the ISE. In typical CBD, the cadmium ion molarity is below $10^{-7}$ mainly due to the precipitation of cadmium hydroxide at high pH values. The solubility product constant for cadmium hydroxide is $2.2 \times 10^{-14}$ at 25°C [12], and it is the equilibrium constant between cadmium ions and hydroxide ions. Since it is much less than one, cadmium hydroxide is considered an insoluble salt, but in reality a small amount of cadmium hydroxide can be dissolved in water as long as the reaction quotient is less than the equilibrium constant[16]. The reaction quotient is calculated similarly to the equilibrium constant, but it uses the actual concentration of chemicals before they go to equilibrium. If the reaction quotient is larger than the equilibrium constant then the reaction goes to the left, or it goes to right if it is smaller than the equilibrium constant. In this case, if reaction quotient is higher than the equilibrium constant then cadmium hydroxide is formed. Using Eq. 4, the equilibrium constant for cadmium hydroxide is expressed as follows along with its reaction:

$$\text{Cd(OH)}_2(\text{s}) \rightleftharpoons \text{Cd}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq})$$
\[ K_{sp} = [\text{Cd}^{2+}] [\text{OH}^-]^2 = 2.2 \times 10^{-14} \quad \text{Eq. 17} \]

From Eq. 17, a relation can be formed in terms of cadmium molarity and pH with Eq. 8 and pKw = 14.

\[ [\text{Cd}^{2+}] (10^{-14-\text{pH}}) \cdot 2 = 2.2 \times 10^{-14} \quad \text{Eq. 18} \]

Using the negative logarithm, or p, we get:

\[ -\log \{[\text{Cd}^{2+}] (10^{-14-\text{pH}}) \cdot 2\} = \text{p}[\text{Cd}^{2+}] + 2*(14 - \text{pH}) = -\log (2.2 \times 10^{-14}) = 13.66 \quad \text{Eq. 19} \]

Solving for pH, a simple linear correlation is found between pH and p[\text{Cd}^{2+}] as follows:

\[ \text{pH} = \frac{-\text{p}[\text{Cd}^{2+}]}{2} + 7.17 \quad \text{Eq. 20} \]

Figure 12, presents pH values of under-saturated and saturated cadmium hydroxide with respect to cadmium molarity derived from Eq. 20. Under-saturated values of cadmium molarity and pH do not produce cadmium hydroxide precipitate. On the other hand, saturated values produce cadmium hydroxide precipitate because the reaction quotient is bigger than equilibrium forcing the reaction to go to the left. Thus, cadmium molarity can be monitored with pH values from 7.0 to 10.7. However, it is preferred for the deposition parameters to be as far as possible from the precipitation region or saturated region. For example, although 1.16mM of cadmium ion molarity from the custom-made standard solution can be monitored with the ISE between 7 to 8.5 pH values at 25°C, it is better to keep the pH of the solution to 8.0 maximum.
4.4 Attempting to Monitor Cadmium Sulfide CBD under Typical Parameters

Typical cadmium sulfide CBD parameters involve high concentrations of the cadmium salt, ammonia, and thiourea. Cadmium salt molarity is higher than 10mM, and thiourea is at least twice as much the cadmium salt molarity. Ammonia is added to adjust the pH to at least 11.0, which requires the ammonia concentration to be higher than 1.0M [11]. This time cadmium and pH values are in the precipitation region (Figure 12) justifying the need for modified deposition parameters. An experiment was performed using high concentration of regents at 60°C, and as predicted from Figure 12, the ISE monitors the disappearance of cadmium ions by precipitation after addition of ammonia.
Figure 13: Cadmium Hydroxide Formation during Typical CBD at 60°C

Figure 13 shows the experimental result for the limitation of the typical CBD. First, 80mM of cadmium chloride is added producing only 20mM of cadmium ion. The solution pH is 6.0, and it is left 15 min to check for cadmium ion stability. Then, ammonia is added, but only a few drops of concentrated ammonia force cadmium hydroxide precipitation, and after ammonia increases the pH to 7.5, all monitorable cadmium is gone.

From Figure 12, it is theorized that a pH higher than 8.0 forces precipitation of cadmium hydroxide. In theory, cadmium hydroxide should not have precipitated at pH = 7.0, but in reality it did. In Figure 12, it is assumed that cadmium ion is not complexed, but most cadmium precursors form complexes with cadmium ion, particularly cadmium chloride. Since the hydroxide ion can react with complexes and remove the cadmium from them, the actual concentration for Figure 12 is the 20mM of cadmium ion plus the 60mM of complexed ions. Thus, the only way for the ISE to monitor reactive species is by having little complexation in the solution.
4.5 Minimizing the Complexation of Cadmium Ion with Acetate Ions

Chu et al. [12] developed deposition parameters that do not produce cadmium hydroxide at 85°C. The parameters are 1mM of cadmium acetate, 20mM of ammonium acetate, 5mM of thiourea. Cadmium acetate is a very common cadmium precursor used by Kitaev et al. [8] since 1965. The use of ammonium acetate is a later development by Chu et al. [12] in order to buffer pH and ammonia at pH≈9. These two sources of acetate ion can form complexes, and it is important to characterize the complexation. Cadmium coordinates acetate ions forming the complex Cd(CH₃CO₂)₃⁻ that is not sensed by the electrode. Therefore, it is preferable to have more of the cadmium in the form of the cadmium ions for better monitoring.

Cadmium-acetate complexes might interfere with the creation of cadmium-ammonia complexes. In cadmium sulfide CBD, the cadmium precursor is added before ammonia. When dissolved, cadmium acetate may produce cadmium-acetate complexes reducing the amount of cadmium ions available for ammonia. It is important for ammonia to have as much as possible cadmium ions to form complexes with because these complexes transfer the cadmium during heterogeneous growth of cadmium sulfide [25].

In this work, the cadmium ion monitoring system is used to find cadmium and acetate concentrations that minimize complexation. Two experiments at 60°C are performed: one is for measuring the effect of ammonium acetate addition to the custom-made 1.16 mM solution, and the other one is for measuring the actual amount of cadmium ions produced per dissolved cadmium acetate.
In figure 14, ammonium acetate is added to 1.16mM of cadmium nitrate. After the acetate molarity is bigger than 10mM, cadmium ion concentration is reduced, which may be caused by cadmium complexation into $\text{Cd(CH}_3\text{CO}_2\text{)}_3^-$ ions. When the acetate concentration is 20mM, the cadmium concentration is reduced almost by a 50%. In order to avoid cadmium ion complexation into $\text{Cd(CH}_3\text{CO}_2\text{)}_3^-$, the maximum amount of ammonium acetate used in this work for producing cadmium sulfide is 10mM.
In Figure 15, solid cadmium acetate salt is dissolved in a 250mL beaker in steps of approximately 0.015 grams, which produce steps of about 0.25mM in solution. After 7.0% complexation is observed for 4mM of cadmium acetate, the steps are increased to reach higher concentrations in fewer steps. These results show that cadmium acetate produces cadmium-acetate only about 0.1% complexation at cadmium acetate concentrations below 2mM of dissolved. This establishes the maximum concentration of dissolved cadmium acetate to 2mM in cadmium sulfide CBD for this work.

4.6 Determining the Atypical Parameters that allow Cadmium Ion Monitoring during CBD

By combining the atypical parameters developed by Chu et al. [12] that avoid cadmium hydroxide precipitation with the 10mM cadmium acetate that minimize cadmium ion complexation of this work, it is possible to determine the atypical parameters that allow real time monitoring of the changes in cadmium ion molarity during cadmium sulfide CBD.
Table 4: Typical and Atypical Cadmium Sulfide CBD Parameter Comparison

<table>
<thead>
<tr>
<th></th>
<th>Typical Parameters</th>
<th>Chu et al. [12] Atypical Parameters</th>
<th>Atypical Parameters for CBD Cadmium Ion Monitoring</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium Salt</td>
<td>20mM to 0.1M</td>
<td>1mM Cadmium Acetate</td>
<td>1mM Cadmium Acetate</td>
</tr>
<tr>
<td>Thiourea</td>
<td>At least twice the molarity of Cd-Salt</td>
<td>5mM</td>
<td>5mM</td>
</tr>
<tr>
<td>Temperature</td>
<td>50°C to 90°C</td>
<td>85°C</td>
<td>60°C</td>
</tr>
<tr>
<td>pH</td>
<td>At least 11.0</td>
<td>9.1</td>
<td>8.9</td>
</tr>
<tr>
<td>Ammonia</td>
<td>At least 1M</td>
<td>0.4M</td>
<td>0.05M</td>
</tr>
<tr>
<td>Buffering Salt</td>
<td>None</td>
<td>20mM Ammonium Acetate</td>
<td>10mM Ammonium Acetate</td>
</tr>
</tbody>
</table>

Table 4 compares the two different CBD parameters presented so far, and it presents the specific parameters used in the experiment that allows monitoring of cadmium ion molarity during CBD. Chu et al. [12] parameters appear to be applicable for CBD cadmium ion monitoring since they do not produce cadmium hydroxide precipitate. However, 85°C cannot be used due to the cadmium ISE temperature restrictions, and at 60°C, 0.4M of ammonia reduce cadmium ion molarity by complexation below $10^{-7}$ M, which is the detection limit of the ISE.
Figure 16 shows the results of the experiment that measures ammonia concentration vs. cadmium ion concentration under the atypical parameters of this work. It was not possible to determine the cadmium ion molarity for 0.4M of ammonia due to the limitations of the ISE, but 0.3M of ammonia gave about $3 \times 10^{-7}$ M of cadmium ion. Therefore, a smaller molarity of ammonia is required to give the ISE some measurement range, and 0.05M of ammonia is selected as the ammonia parameter because it gives about 2 decades or 60mV of measurable range to the ISE according to the 30mV/decade slope of the ISE.
Figure 17: Ammonia Concentration vs. pH with 10mM Cadmium Acetate and 1mM cadmium acetate at 60°C

Figure 17 presents how pH changes with the increment of ammonia molarity. This experiment is setup simply by making a solution with 10mM cadmium acetate and 1mM cadmium, then different small volumes of concentrated ammonia solutions are added and the pH recorded. With 0.05M of ammonia, the pH produced is about 8.9, which is why the pH value for the monitoring parameters is established as 8.9. In other words, the pH is not a chosen value but an effect of the desired 0.05M ammonia molarity.
4.7 Real-Time Monitoring of Cadmium Ion Molarity during Cadmium Sulfide CBD

Previous experiments dealt with determination of pre-deposition parameters, and no thiourea is introduced. The actual cadmium sulfide Chemical-Bath-Deposition involves setting up pre-deposition parameters, and finally adding thiourea. Thus, in this section, thiourea is finally added to the reactor, and its decomposition effect on cadmium ion molarity is analyzed. It is important to note that the results of this experiment are a breakthrough because no other research on cadmium sulfide CBD to date has ever attempted to change the typical parameters in order to monitor cadmium ion molarity.

Figure 18: Real-Time Cadmium Ion Monitoring of Cadmium Sulfide CBD
4.7.1 Cadmium Residual: t = 0.0 to t = t₁

After the freshly boiled 18MΩ-cm water is placed in the reactor and its temperature stabilized to 60°C, the cadmium ion ISE is placed in the reactor. Then, the MATLAB program is started to record the change in cadmium ion concentration. From t = 0.00 to t = t₁, a residue of cadmium ion is detected in the reactor although it was thoroughly with 18MΩ-cm water. This residue is about 3 x 10⁻⁷ M, and it is slowly decreasing with time at a rate of 0.07 x 10⁻⁷ M/min. Since this residue is very close to the detection limits of the ISE, it can be neglected. Besides, 3 x 10⁻⁷ M is about 3000 smaller than the cadmium ion concentration that is added later. The pH is 6.5 agreeing with the estimated neutral pH of water at 60°C from Figure 3.

4.7.2 10mM Ammonium Acetate Addition and Residual Monitoring: t = t₁ to t = t₂

At t₁, 1.85 grams or 0.024 moles ammonium acetate is added to the reactor with 2.4L of water making a 10mM solution of ammonium acetate. This addition complexes the residue by 50%, and it continues to decrement at about 50% of the previous rate. After the addition, the pH decreases to 6.3 meaning that a little part of the 0.024 moles amount of ammonium acetate salt is in the form of acetic acid.

4.7.3 1mM Cadmium Acetate Addition and Stability Monitoring: t = t₂ to t = t₃

At t₂, 0.64 grams or 0.0024 moles cadmium acetate dehydrated is added to the 2.4L solution increasing the cadmium ion molarity to 1mM. pH changes from 6.3 to 6.0 meaning that the cadmium acetate salt also contains a little of acetic acid. For stability check proposes, the solution is left untouched during 4.4 minutes. From t₂ to t₃, the analyzed data points give an average concentration of 0.95mM with a standard deviation of 0.02mM.
4.7.4 0.05M Ammonia Addition and Cadmium Complexation Monitoring: \( t = t_3 \) to \( t = t_4 \)

From \( t = t_3 \) to \( t = t_4 \), 25mL of 4.9M ammonia is added which increases the concentration of ammonia to 0.05M in with a new solution volume of 2.425mL. The addition is slow in order to prevent any sudden formation of cadmium hydroxide, and to monitor the complexation of cadmium ions into cadmium-ammonia complexes. pH changes from 6.0 to 8.9, and the molarity of cadmium ion changes from 0.95mM to 0.034mM. At \( t = t_4 \), although 96.4% of the original concentration of cadmium is complexed into cadmium-ammonia complexes, there is enough cadmium ion to continue monitoring.

4.7.5 Ammonia Evaporation and Cadmium Decomplexation Monitoring: \( t = t_4 \) to \( t = t_5 \)

From \( t = t_4 \) to \( t = t_5 \), the solution is left undisturbed for 20 minutes to check for cadmium ion stability. Cadmium ion molarity increases from 33µM to 52µM at an approximated rate of 1µM / min. This increment is linked to the amount of ammonia being evaporated from the solution because cadmium ion molarity is dependent of ammonia molarity. From Figure 16, the concentration of ammonia is estimated to change from 0.05M to 0.04M. Moreover, the pH changes from 8.9 to 8.8, and from Figure 17, it can also be estimated that ammonia concentration changes from 0.05M to 0.04M. Thus, ammonia decreases at a rate 0.005M/min.

4.7.6 5mM Thiourea Addition: \( t = t_5 \)

At \( t_5 \), 0.92 grams or 0.012 moles is added to the 2.425mL solution. This makes the thiourea concentration in the solution to be 5mM. Immediately, the cadmium ion molarity decreases from 52 µM to 0.6µM, which represents a decrement of 99% in cadmium ion molarity. Since thiourea does not produce sulfide ions immediately, this decrement should be caused by the interaction of thiourea itself with cadmium ions. In fact, thiourea is known to form cadmium-thiourea complexes by sulfur ligands as \( \text{Cd(CH}_3\text{COO)*2(thiourea)} \) bridged chains similar to the one in Figure 4[21].

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4.7.7 Cadmium Sulfide Chemical Bath Deposition: \( t = t_5 \) to \( t = 52 \) min.

In Figure 19 from \( t = 46 \) to \( t = 46.6 \), cadmium ion molarity increases from 0.6\( \mu \text{M} \) to 1.1\( \mu \text{M} \) at a rate of 0.8 \( \mu \text{M} / \text{min} \), which approximates the rate of 1\( \mu \text{M} / \text{min} \) before the addition of thiourea due to evaporation of ammonia. Therefore, the addition of thiourea has little effect on the rate at which cadmium and ammonia decomplex. From \( t = 46 \) to \( t = 46.6 \), thiourea may be decomposing into sulfide ions and forming cadmium sulfide, but this decomposition is not affecting the cadmium ion molarity. This is indicates that no homogenous precipitation is present during this time because according to Voss et al. [10], in the presence of thiourea, cadmium ion molarity is only affected during homogenous precipitation of cadmium sulfide.

After \( t = 46.6 \), the increment of cadmium ion molarity due to decomplexation of cadmium-ammonia complexes is affected by thiourea. At this point, thiourea has produced enough sulfide ions in solution to affect cadmium ion molarity. Cadmium ion molarity increment is stopped slowly by the reaction reaching homogenous precipitation at \( t = 46.8 \text{min} \). If enough sulfide ions are available in
solution, homogenous precipitation starts and cadmium ions are gradually converted to cadmium sulfide. Once cadmium ions are trapped by homogenous precipitation, they do not redissolved in water, and this reaction continues until all cadmium ions are consumed. Subsequently, homogenous precipitation is represented by a fast and gradual decrease of cadmium ion molarity. Besides, at $t = 48$ minutes, the solution visibly turns cloudy due to scattering of light by the homogenous formation of cadmium sulfide particles. The monitoring of cadmium sulfide is only possible until $t = 52$ min because the cadmium ion concentration reaches the detection limit.

This experiment reached homogenous faster than what is reported on typical cadmium sulfide CBD [9][10]. The other CBD’s have typical parameters with higher pH and thiourea concentration, which decompose thiourea much faster than in this experiment [22]. Therefore, the faster homogenous precipitation is not due to the decomposition rate of thiourea, but to the higher molarity of cadmium ion, which was needed to monitor the reaction.

In order to understand how the higher cadmium ion molarity of this experiment produces homogenous cadmium sulfide faster, an analysis of the equilibrium constant of cadmium sulfide should be used. The reaction that produces cadmium sulfide along with the equilibrium equation is presented as follows [15]:

$$\text{CdS(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Cd}^{2+} (\text{aq}) + \text{HS}^- (\text{aq}) + \text{OH}^- (\text{aq})$$

$$K_{sp} = [\text{Cd}^{2+}] \times [\text{HS}^-] \times [\text{OH}^-] = 8 \times 10^{-28} \quad \text{Eq. 21}$$

Assuming $\text{pH} = 9$ and $[\text{OH}^-] = 10^{-14.9} \text{M} = 10^{-5}$, gives the relation between sulfide ion and cadmium ion that produces precipitation:

$$[\text{Cd}^{2+}] \times [\text{HS}^-] \geq 8 \times 10^{-24} \quad \text{Eq. 22}$$
In Figure 20, the temperature is 25°C, but the plot can be used to illustrate how much sensitive to sulfide ions this experiment is in comparison to other CBD’s with typical parameters. In CBD with typical deposition parameters, the cadmium ion concentration is estimated to be smaller than $10^{-9}$, and at this cadmium ion molarity, the sulfide ion molarity can be as high as $10^{-14}$ and do not precipitate cadmium sulfide. For the atypical parameters of this experiment, the cadmium ion molarity is about $10^{-6}$ after the cadmium-thiourea complexation, and at this cadmium ion molarity, sulfide ion molarity must be below $10^{-17}$M in order to avoid precipitation, which 1000 smaller than the limit of the other CBD’s. Therefore, cadmium sulfide homogenous precipitation for this experiment is much more sensitive to thiourea decomposition into sulfide ions than the other CBD’s due to the high cadmium molarity needed to monitor cadmium ion molarity.
CHAPTER 5: CONTROLLING CADMIUM SULFIDE CBD

Being able to monitor the homogenous precipitation of cadmium sulfide in CBD allows investigation of control techniques that prolong or suppress homogenous precipitation. The atypical parameters develop to monitor this precipitation can be used as baseline for experiments, which objective is to delay the appearance of homogenous precipitation.

5.1 Suppressing Thiourea Decomposition at pH = 7.6

The atypical parameters for monitoring CBD make the reaction extremely sensitive to thiourea decomposition. Fortunately, thiourea decomposition has a threshold pH that can be used to slow its decomposition down and avoid fast formation of cadmium sulfide homogenous precipitation. From Figure 6, at the pH value of 7.6, the reaction rate of thiourea is minimized, and an experiment can be performed at this pH to test how long it takes the reaction to reach homogenous precipitation. In order to obtain this pH value, 0.003M of ammonia should be used. This small molarity of ammonia increases the cadmium ion concentration at the time of thiourea addition, which should make the reaction even more sensitive to thiourea decomposition. Thus, if the experiment produces a very small amount of sulfide ions, then it can be very easily detected by the high molarity of cadmium ions.

<table>
<thead>
<tr>
<th>Table 5: Atypical Parameters for Thiourea Decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atypical Parameters for CBD Cadmium Ion Monitoring BASELINE</strong></td>
</tr>
<tr>
<td>Cadmium Salt</td>
</tr>
<tr>
<td>Thiourea</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Ammonia</td>
</tr>
<tr>
<td>Buffering Salt</td>
</tr>
</tbody>
</table>
5.1.1 Pre-deposition: $t = 0$ to $t = t_1$

At $t = 0$, the solution is formed by 1mM of cadmium acetate, 10mM ammonium acetate, and 0.003M ammonia at pH = 7.6. This solution is monitored for 25 minutes before the thiourea is added. pH changes from 7.6 to 7.5, which corresponds to a reduction of ammonia molarity from 0.003 to 0.0026 in 25 minutes. Thus, the evaporation of ammonia is estimated to be 12µM/min. This evaporation rate is much slower than the one of the baseline meaning better pH buffering, but due to the smaller concentration of ammonia, cadmium ion increases its concentration by 2µM / minute, which is two times faster than in the baseline experiment.
5.1.2 5mM Thiourea addition \( t = t_1 \) to \( t = t_2 \)

At \( t_1 \), cadmium ion molarity decreases almost instantly. This is similar to the baseline experiment during the complexation of cadmium ion and thiourea. This is followed by a fast decrement of 10µM per minute in cadmium ion molarity. This decrement can be attributed to homogenous precipitation of cadmium sulfide, but the solution did not produce any precipitate or change in appearance. Thus, this decrement is more properly attributed to a slower complexation of cadmium and thiourea. Eventually, the decrement stops, and a decomplexation of cadmium ion molarity is observed by an increment in cadmium ion molarity of 1.2µM / min, which can be attributed to evaporation of ammonia. Thus, the thiourea decomposition is effectively suppressed at pH = 7.6.

5.1.2 Addition of Extra Thiourea \( t = t_2 \) to \( t = 140 \) min.

In order to force thiourea decomposition, the concentration of thiourea can be increased. At \( t = t_2 \), \( t = t_3 \), and \( t = t_4 \), thiourea concentration is increased to 10mM, 15mM, and 20mM respectively. After each increment, the cadmium molarity is monitored for about 10 minutes and a clear increment in cadmium concentration is observed, which means that no homogenous precipitation of cadmium sulfide is present. This contributes with the conclusion that at pH = 7.6 thiourea decomposition is suppressed even if the concentration if thiourea is quadrupled. In addition, no heterogeneous film of cadmium sulfide is formed.

5.2 Delaying Homogeneous Precipitation with pH = 8.2

At pH = 7.6, the decomposition of thiourea is suppressed, and at pH = 8.9, the decomposition is so fast that the reaction reaches homogenous precipitation in a minute after thiourea is added. Therefore, thiourea decomposition time can be controlled with pH, and a pH value between 7.6 and 8.9 should decompose thiourea slow enough to delay homogenous precipitation that is caused by fast thiourea
decomposition. An interesting value of pH between 7.6 and 8.9 is 8.2, which corresponds with the pKa of ammonia at 60°C. A practical way of obtaining the pKa of ammonia is by simply making pH = pKa. This happens when the molarity of ammonia and ammonium acetate are the same. In this work, the molarity of ammonium acetate is treated as a constant of 10mM, so when 10mM of ammonia are introduced in the solution, the pH becomes 8.2 that also corresponds to the pKa of ammonia at 60°C.

Figure 22: *Real time* Monitoring of Cadmium Ion Molarity with pH = pKa = 8.2

In this experiment, the evaporation of ammonia produced a decomplexation rate of cadmium ion molarity of 2.8µM / minute, which is three times faster than in the baseline experiment, and 1.35 times faster than at pH = 7.6. Fifteen minutes after the addition of thiourea, at t = 40 minutes, cadmium sulfide film is clearly visible on the walls of the reactor without any signs of homogenously precipitated particles. The solution stays particle free for about 20 minutes. Then at t=58 minute, the solution starts to
produce cadmium sulfide precipitated particles, and the reaction becomes dominated by homogenous precipitation. All monitorable cadmium ion molarity is reduced in only three minutes. The homogenous precipitation dominates the reaction 34 minutes after the addition of the 5mM of thiourea. Since it took 34 times longer than in the baseline experiment to reach homogenous precipitation, at pH = 8.2, thiourea decomposes slowly enough to cause a significant delay in homogenous precipitation.

5.3 Thiourea Titration during CBD at pH = 8.4

From previous experiments, it is found that homogenous precipitation is delayed with reduction of pH, and even thiourea decomposition can be suppressed at pH = 7.6. However, at pH = 8.2, the decomplexation rate of cadmium ion maximizes to 2.8µM / min, and in order to reduce this decomplexation rate, pH is increased slightly to 8.4 with 0.016M of ammonia for this experiment. This new pH represents an increment in hydroxide concentration of 37% from pH = 8.2. Therefore, thiourea is reduced 50% to 2.5mM as a compensation for this higher pH. Besides, thiourea can be added slowly to reduce even further the reaction rate. A slow titration rate of 0.25mM/min allows the concentration to rise to 2.5mM in ten minutes.

For this experiment, seven glass slides are placed in the reactor after being properly cleaned. First, the glass slides are cleaned ultrasonically in a detergent solution made of 0.3g of Alconox® powder solution and 240mL of 18MΩ-cm water for 30 minutes at 40°C, and they are thoroughly rinsed under a stream of 18MΩ-cm water for 5 minutes. Second, the slides are clean ultrasonically using isopropyl alcohol for 10 minutes and again thoroughly rinsed under a stream of 18MΩ-cm water for 5 minutes. A solution with 1:1:7 ratios of ammonia, hydrogen peroxide, and water is used to clean and prepare the surface for cadmium sulfide CBD. The slides are placed in this solution and kept at 70°C for 30 minutes. Then, they are transferred to a storing solution of ammonia with pH = 9 at room temperature and left there overnight in order to saturate the surface with negative charges, which are critical for nucleation sites and formation of uniform films[23] [24]. Before the samples are transferred to the
reactor, the ammonia storage solution is boiled along with the samples for 10 minutes in order to remove ammonia and other gasses. Once the boiled solution has cooled down to about 70°C, the samples are finally transferred inside the reactor.

Figure 23: *Real time Monitoring of Cadmium Ion Molarity with pH = 8.4 and Slowly Titrated Thiourea Molarity of 2.5mM*

5.3.1 Setting up Pre-deposition Parameters: \( t = 0 \) to \( t = t_3 \)

After adding 10mM of ammonium acetate and 1mM of cadmium acetate, the pH is adjusted to 8.4 from \( t = t_2 \) to \( t = t_3 \). Cadmium ion molarity is reduced by complexation to 200\( \mu \)M having 80% of the
cadmium molarity in cadmium-ammonium complexes. In comparison to pH = 8.2, more complexation due to ammonia is observed because amount of ammonia used higher.

5.3.2 Cadmium ion Decomplexation Analysis: t = t_2 to t = t_3

The decomplexation rate is calculated to 1.5µM / min. This is still larger than the decomplexation rate of 1.0µM / min at pH = 8.9, but this decomplexation rate is 46% smaller than the decomplexation of to 2.8µM / min at pH = 8.2. Therefore, the experiment proved that increasing pH from 8.2 to 8.4 does significantly improved the rate of cadmium decomplexation. After measuring the decomplexation rate, a small dose of ammonia is added to keep cadmium ion molarity and pH constant before the addition of the thiourea.

5.3.3 Thiourea Titration: t = t_3 to t = t_4

Thiourea is added slowly at a titration rate of 0.25mM/min during 10 minutes. While thiourea molarity is increased from 0 to 1.4mM, cadmium-thiourea complexes are formed decreasing cadmium ion molarity by about 80%. While increasing the molarity of thiourea from 1.4mM to 2.5mM, cadmium ion molarity stays relatively constant meaning that between 1.4mM to 2.5mM thiourea maximizes it complexation capabilities.

5.3.4 Second Thiourea and Cadmium Complexation Phase: t = t_4 to t = t_5

During this time, no changes in the solution are observed. In cadmium sulfide CBD, cadmium sulfide film deposition is always visible before homogenous precipitation, but no film deposition is visible. Thus, this decrement in cadmium ion molarity is simply a mystery because it does not relate to
cadmium sulfide film deposition or homogenous precipitation. It could be due to a second phase of cadmium ion complexation with thiourea. At $t = t_5$, cadmium ion molarity decrement finally stops.

5.3.5 Cadmium Sulfide Deposition: $t = t_4$ to $t = t_5$

One minute after $t = t_5$, cadmium sulfide film deposition is observable. The yellow cadmium sulfide film coats all the surfaces of the reactor without any homogenous precipitation. At $t = 78$, the first glass slide is removed of the reaction. This slide is covered uniformly with an extremely thin, reflective, and transparent yellow film of cadmium sulfide. In fact, it is as reflective as glass. The film is assumed very thin because it is extremely transparent. It can only be seen with a white background and compared to a new glass slide. After removing it from the reaction, the slide is rinsed under a stream of 18MΩ-cm water and dried with nitrogen. The other six samples are also removed after 27 minutes. It is observed that with the longer deposition the films become a little darker yellow due to thickness increment. All the samples have uniform and transparent films with a very reflective and smooth surface.

After the removal of the first slide, the cadmium ion molarity starts to decrease, and it is the sign of homogenous precipitation occurring. It can be assumed that the removal of the first slide disturbs the supersaturated solution triggering homogenous precipitation. However, this homogenous precipitation is not dominant or suppressed because the solution never shows the light scattering effects or blurring caused by cadmium sulfide particles even after the last cadmium sulfide slide is removed.
CHAPTER 6: CHARACTERIZATION OF CADMIUM SULFIDE FILMS

6.1 Sample Preparation

Both sides of the glass slides are coated with a uniform cadmium sulfide film after CBD, and for optical characterization proposes, one of the sides must be etched. This is achieved by carefully scrubbing for a few seconds one side of the glass slide with a soft polyurethane foam swab dipped in 4M Hydrochloric acid. Since cadmium sulfide reacts with the hydrochloric acid forming soluble cadmium chloride, the scrubbing is mainly used to wet one side of the slide with acid and allow the cadmium chloride formation. It is important to mention that during the etching process the toxic hydrogen sulfide or H₂S gas is formed, so the etching is always performed in a fume hood. Finally, the sample is rinsed with a stream of 18MΩ-cm water and dried with nitrogen gas.

![Figure 24: Glass Slide Surface Regions after Sample Preparation](image)

Additionally, it is required to etch a small area of the side left with cadmium sulfide for surface profiling. In order to have a surface similar to Figure 24, the etching is done by dipping vertically about 0.5cm of the slide in 0.3M hydrochloric acid solution. According to Chu et al [12], the minimum etching rate of cadmium sulfide in 0.3M hydrochloric acid is 5nm/min. Therefore, the samples are left in this
solution for 20 minutes. This is enough time because the etched region of all samples is as clear as new glass. With this etched region, there are two regions on the glass substrate: the cadmium sulfide region covering about 90% of the surface and the cleaned substrate surface covering 10%. Between these two regions, a step is used for thickness measurements.

6.2 Step Height Measurements and Deposition Rate Estimation

From experiment of chapter 5 section 3, seven samples are prepared with a surface similar to that of Figure 24, and their thickness measured using an Alpha-Step surface profiler manufactured by KLA-Tencor Corporation. This instrument uses a stylus that scans the surfaces by physical contact. Ideally, it can measure step heights down to 1nm and up to 2mm.

Figure 25: Surface Profiler Thickness Results for Samples: 7, 6, 5, 4, and 3
The results of all scans of samples: 7, 6, 5, 4, and 3 are presented and summarized in Figure 25. These results are obtained after averaging 10 measurements of each sample in order to reduce the noise influence. The raw data in mm by mm is used in MS Excel to place the step location of all samples at the same point, and illustrate better the thickness difference. Although the instrument has a vertical resolution of 1nm, it was not possible to measure the step height for samples number 1 and 2. Thus, the thickness of these samples is estimated to be below 10 nm.

![Figure 26: Thickness vs. Deposition Time from Surface Profiler Measurements](image)

From Figure 26, the deposition rate in cadmium sulfide CBD with atypical parameters approximates 2nm / min. This is rate is about 15 times slower than 30nm/min in cadmium sulfide CBD with typical parameters [9]. Besides, this deposition rate is known to produce dense films. Films grown with rates of 1 to 2 nm / minutes etch slower than films growth with faster rates with 0.3M hydrochloric acid. Chu et al. [12] explains that films grown with rates higher than 10nm / min etch at more than 20nm / min.
6.3 Transmittance Measurements and Band Gap Estimation

In general, band gap energy is a property that establishes how conductive and transparent materials are to visible light. Conductors have small band gap energy, and they are not transparent to visible light. Insulators have big band gap energy, and they are transparent to visible light. Semiconductors have intermediate band gap energy making them transparent to certain visible light. Colors in light are related to energies in light. Ideally, cadmium sulfide is a semiconductor transparent to light energies below 2.42eV or light wavelengths above than 512nm. Therefore, analyzing transmittance from 400nm to 600nm can be used to find the actual band gap of the cadmium sulfide samples produces in this work.

Cadmium sulfide films are deposited on top of a glass substrate that is almost transparent to light in the 400nm to 600nm range. Since some light is absorbed by the substrate, a double beam spectrophotometer can be used to isolate the transmittance of the cadmium sulfide films using glass in the reference beam of the instrument. In this work, a Cary 5000 double beam spectrophotometer manufactured by Varian Inc. is used to measure the isolated transmittances of the cadmium sulfide films.

![Transmittances of Cadmium Sulfide Films](image)

Figure 27: Transmittances of Cadmium Sulfide Films
Transmittances of samples 3 through 7 together with their thicknesses from Figure 25 are used to calculate the absorption coefficient, \( \alpha \), for each sample using the Lamberts’s Law [28]:

\[
T = e^{-\alpha t}
\]

where: \( T \) is transmittance; \( \alpha \) is the absorption coefficient \( 1 / \text{meter} \); and \( t \) is thickness in meters.

Absorption coefficient is supposed be independent of sample thickness, but thickness is a parameter used for calculated it, and thickness errors are translated in absorption coefficient errors. Thus, each estimated thickness does not match exactly the optical thickness. However, the results give estimations of absorption coefficient that can be used to estimate the band gap of the cadmium sulfide films. The relation between the absorption coefficient and direct band gap is given as follows [29]:

![Figure 28: Absorption Coefficient vs. Wavelength for Samples 3 through 7](image)
\[ E_{\text{photon}} * \alpha = C * (E_{\text{photon}} - Eg)^{1/2} \]  \hspace{1cm} \textbf{Eq. 24}

where: \( E_{\text{photon}} \) is photon (light) energy in eV; \( C \) is a constant in eV\(^2\) / m; \( Eg \) is the band gap.

In order to have \( Eg \) in a straight-line equation in the form of \( y = mx + b \), Eq. 24 must be rewritten as follows:

\[(E_{\text{photon}} * \alpha)^2 = C^2 * E_{\text{photon}} - C^2*Eg \]  \hspace{1cm} \textbf{Eq. 25}

![Figure 29: \( (E_{\text{photon}} * \alpha)^2 \) vs. \( E_{\text{photon}} \)](image)

Eq. 25 can only valid in between photon energies 2.57eV and 2.64eV in Figure 29, where a straight line exists. Therefore, this linear region is analyzed using least-square approximation in order to find \( C^2 \) and \(-C^2*Eg\) and consequently solve for \( Eg \).
Table 6: Band Gap Results by Least-Square Approx. from $E_{\text{photo}} = 2.57\text{eV}$ to $E_{\text{photo}} = 2.64\text{eV}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C^2$ (eV$^4$/m$^2$)</th>
<th>$-C^2 \times E_g$ (eV$^5$/m$^2$)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 7</td>
<td>1.948E+18</td>
<td>-4.658E+18</td>
<td>2.391</td>
</tr>
<tr>
<td>Sample 6</td>
<td>1.842E+18</td>
<td>-4.480E+18</td>
<td>2.433</td>
</tr>
<tr>
<td>Sample 5</td>
<td>2.290E+18</td>
<td>-5.582E+18</td>
<td>2.438</td>
</tr>
<tr>
<td>Sample 4</td>
<td>3.084E+18</td>
<td>-7.574E+18</td>
<td>2.456</td>
</tr>
<tr>
<td>Sample 3</td>
<td>4.425E+18</td>
<td>-1.099E+19</td>
<td>2.485</td>
</tr>
</tbody>
</table>

The average band gap is 2.44eV, and it is in very good agreement with the 2.42eV band gap of single crystal cadmium sulfide. Besides, with the results from Table 6 and points from 2.57eV to 2.64eV, it is possible to plot an extrapolation that shows $E_g$ when $(E_{\text{photon}} \times \alpha)^2 = 0$ as shown in the following figure:

![Figure 30: Extrapolation of $(E_{\text{photon}} \times \alpha)^2$](image)
6.4 Surface Roughness Estimation through Diffusive and Specular Reflectance

Diffusive reflectance is the measurement of reflected light that scatters at a surface, and rough surfaces produce diffusive reflection along with specular. Since diffusive reflectance is due to surface roughness, it is possible to relate them as follows [30] [31]:

\[ R = R_0 e^{-\frac{16\pi^2 \sigma^2}{\lambda^2}} \]

Eq. 25

where: \( R \) is the typical specular reflectance that doesn’t account the scattering at the surface; \( R_0 \) is the highest reflectance that combines both specular and diffusive reflectance taking in account scattering; \( \sigma \) is surface roughness; \( \lambda \) is light wavelength.

Figure 31: Integrating Sphere for Measuring Diffusive and Specular Reflectance

\( R \) is a simple measurement of specular reflectance that only collects the reflected light normal to the surface. However, measuring \( R_0 \) requires the collection of light intensity from all directions not only
normal to the surface because diffusive light can scatter in any direction. Figure 31 illustrates how both diffusive and specular are collected in all directions by a double beam spectrophotometer and an integrating sphere. All collected light is recorded by a light detector inside the sphere that stabilizes the ratio between the reference light beam and all light reflected by the sample. $R_0$ is always greater or equal to $R$ because $R_0$ includes the diffusive light, and if both equal each other, the sample is said to have zero roughness. Therefore, optical roughness of a sample can be determined with the direct measurement of both $R$ and $R_0$.

Figure 32: Roughness vs. Wavelength

Figure 32 presents the results of roughness of all samples. Roughness is then estimated to be around 3nm. Zero roughness would be ideal for any thin film, but most thin films are made of grains that inevitably show some roughness effects in the form diffusive reflectance. Actually, evaporated cadmium sulfide films have typical roughness values between 10nm to 20 nm, so the roughness of the films from this work can be considered to have low roughness.
6.4 Obtaining Index of Refraction and Extinction Coefficients for Cadmium Sulfide Films

6.4.1 Estimating Extinction Coefficients, $k$, from $\alpha$

For samples 3 though 7, abortion coefficient was obtained from transmittance and thickness measurements. Additionally, it is also possible to calculate extinction coefficients, $k$, from absorption coefficients, $\alpha$ using the following equation [28]:

$$k = \frac{\alpha \lambda}{4\pi}$$

Eq. 26

where: $k$ is the extinction coefficient, $\alpha$ is the absorption coefficient, and $\lambda$ is wavelength.

Figure 33: Extinction Coefficient vs. Wavelength
6.4.2 Iterating for Optical Thickness, Refractive Index, and Extinction Coefficient with Specular Reflectance and Roughness

The FILMeasure software included with the thin-film analyzer Filmetrics F20 uses reflectance measurements and optical constant models to iterate for thickness, index of refraction and extinction coefficient. Filmetrics F20 uses a single beam and optic fiber to measure reflectance normal to the surface of a sample. Figure 34 illustrates the reflectance measurements setup of the Filmetrics F20.

![Figure 34: Filmetrics F20 Setup for Reflectance Measurements](image)

The FILMeasure software can iterate for optical constants and optical thickness at the same time with a given reflectance of a sample, but it requires initial values and iteration ranges. Since the optical
constants should be the same for all samples, the iterative analysis of one sample can reveal the optical constants for all the other ones. Subsequently, the optical thickness of all samples can be obtained from these optical constants. As the thickest sample, sample 7 provides the most accurate thickness, and this thickness along with its extinction coefficients can be used to set initial iteration values for the program. For refractive index values, the initial values for the iteration are obtained from the analysis of optical constants on evaporated cadmium sulfide thin films by Khawaja [31].

Table 7: Sample 7 Initial Parameters for FILMeasure Iteration

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectance: 400nm to 600nm</td>
<td>Filmetrics F20 (Figure 34)</td>
</tr>
<tr>
<td>Thickness</td>
<td>47nm ± 10%</td>
</tr>
<tr>
<td>Roughness</td>
<td>3nm</td>
</tr>
<tr>
<td>Extinction Coefficient, k</td>
<td>Figure 33 ± 1.0</td>
</tr>
<tr>
<td>Refractive Index, n</td>
<td>(400nm, 2.55); (500nm, 2.72); (600nm, 2.40); ± 1.0</td>
</tr>
</tbody>
</table>

Figure 35: Extinction Coefficient Iteration Results
Figures 35 and 36 present the results of the iterations. Now, these constants are used by the FILMeasure software to analyze the reflectance and determine the optical thickness of each sample. The only parameter iterated for thickness calculation is the thickness itself, which is set to 50nm ± 100%. The software attempts to find the thickness that converges better with the measured reflectance data. For all samples, the model actually fits the reflectance with a goodness of fit of at least 98%. In Figure 37, all reflectance points are over imposed on the ideal curves generated by the software, and for all samples, the software actually fits the model reflectance and the real reflectance with a goodness of fit of at least 98%. Thus, new thickness values are found for all samples based on the optical constants.
With these new thickness values, deposition rate can be reexamined including samples 1 and 2, and a more precise deposition rate is determined using the linear regression aid from MS Excel on the thickness vs. time data. Figure 38 presents the linear regression line along with the data points including the equation for linear regression, which reestablishes the deposition rate to 1.2nm / min.
Figure 38: Optical Thickness vs. Time

\[ y = 1.2058x + 9.7748 \]
CHAPTER 7: CONCLUSIONS

For the first time, a commercially available cadmium ion selective probe is used to characterize and to monitor in real time the cadmium sulfide Chemical-Bath-Deposition. Initial experiments illustrate that typical parameters make impossible to monitor cadmium ion molarity because cadmium ion molarity goes below detection limits. Experiments reveal that the main limitation of typical parameters is the use of high pH values that precipitate cadmium ion into cadmium hydroxide. This precipitation is assumed critical for the formation of high quality films, but for monitoring cadmium ion molarity, precipitation of cadmium hydroxide is avoided in this work with low pH values. Fortunately, this approach produced high quality cadmium sulfide films with low roughness and highly reflective surfaces. Thus, it is proven that cadmium hydroxide precipitation is not needed for the production of high quality cadmium sulfide thin films.

With the ability to monitor cadmium sulfide CBD, cadmium ion molarity changes due to complexation of substances other than ammonia is minimized. Ammonium acetate is used to buffer pH, but it complexes cadmium ion. It is found that ammonium acetate molarities less than 10mM do not affect significantly the cadmium ion molarity, so the parameter for cadmium sulfide is set to 10mM to minimize complexation. The cadmium precursor in this work, cadmium acetate, is also studied in order to minimize complexation, and for cadmium acetate molarities below 2mM, cadmium ion complexation is minimized. Thus, cadmium acetate molarity parameter is set to 1mM.

Ammonia is the preferred substance to form complexes with cadmium ions, but this complexation can reduce the amount of cadmium ion below the detection limit. A study of cadmium ion molarity and ammonia molarity reveal the ammonia concentration bigger than 0.1M complexes 1mM of cadmium ion to close to the detection limit. The molarity of ammonia that provides a significant complexation is 0.05M, and it leaves detectable levels of cadmium ion. This amount of ammonia
provides enough cadmium ions to monitor the final effect that thiourea has on cadmium ion molarity through complexation and homogenous precipitation of cadmium sulfate.

Furthermore, parameters that suppress and delay thiourea decomposition are developed thorough monitoring of cadmium sulfide CBD. It is found possible to delay the formation of homogenous precipitate of cadmium sulfide with the delay of thiourea decomposition. At a pH value of 8.4, thiourea decomposes slowly enough to favor heterogeneous deposition of cadmium sulfide for more than 30 minutes depositing at a rate between 1 to 2 nanometers per minute.

Optical characterization of the films estimates the band gap to be 2.44eV, which is 0.02eV higher than the bulk crystal value of 2.42eV. With diffusive reflectance from an integrating sphere, the roughness is found to approximate 3nm, which is at least three times smaller than typical cadmium sulfide films. Finally, the optical constants of the films produced in this work are presented and used with the Filmetrics system to provide more precise and simpler thickness measurements than surface profiler measurements.
REFERENCES

APPENDIX A: MATLAB PROGRAM

delete data.csv;
fclose('all');
clear all;
cic;
close all hidden;
disp('Start')
disp('to stop use CTRL+C')

time = 120; %minutes
n = round(time*60/5);

star5 = serial('COM3','Terminator','CR');
fclose(star5);
fopen(star5);

figure(1);
hold on;
y = zeros(1,2);
t = y;
temp = y;
fgetl(star5);
tic
subplot(2,1,1);
plot(t(1),y(1));
subplot(2,1,2);
plot(t(1),temp(1));
data = fopen('data.csv','at');
fprintf(data,'%d,%d,%d
',t(1),y(1),temp(1));

for i = 1:n
    pause(4.7);
    raw = fgetl(star5);
    raw2 = strread(raw,'%s','delimiter',',');
    raw3 = sprintf('%s',raw2{6});
y(2) = str2double(raw3);
    t(2) = i*1/12;
    raw3 = sprintf('%s',raw2{8});
temp(2) = str2double(raw3);
    fprintf(data,'%d,%d,%d
',t(2),y(2),temp(2));

    subplot(2,1,1);
    line(t,y);
    title(['Voltage is ',num2str(y(2)),'mV']);
    subplot(2,1,2);
    line(t,temp);
    title(['Temperature is ',num2str(temp(2)),'°C']);
figure(1);
y(1) = y(2);
t(1) = t(2);
temp(1) = temp(2);
end
toc
fclose(data);
fclose(instrfind);
delete(instrfind);
CURRICULUM VITA

Son of Rafael Ordoñez-Villagran and Edelmira Gonzalez-Marques, Rafael Ordonez was born in Chihuahua, Mexico. He was admitted in the University of Texas in 2002, where he learned about science its many mysteries. Since 2003, he began doing research as a double major student in Chemistry and Electrical Engineering on the field of semiconductor material fabrication with titanium niobates nano-sheets mentored by Dr. Geoffrey Saupe. In 2005, his first journal article, “Evaluation of a new porous titanium-niobium mixed oxide for photocatalytic water decontamination,” was published in the Microchemical Journal. In the academic field since 2003 until 2007, he worked as a chemistry tutor for the Department of Chemistry teaching freshman students the chemistry of basics through team based activities. In 2007, he received his Electrical Engineering Bachelor of Science degree from the University of Texas at El Paso, and he continued doing research as Electrical Engineering Master of Science candidate at the University of Texas mentored by Dr. David Zubia. The research under Dr. Zubia’s mentoring involved improving of fabrication techniques of cadmium sulfide for cadmium telluride solar cells. He also worked as a teaching-assistant developing analog circuits to teach students about rectification, filtering, and amplification concepts.

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